170. L. L. Lohr and W. N. Lipscomb, J. Amer. Chem. Soc., 85, 240 (1963).
171. L. L. Lohr and W. N. Lipscomb, in "Noble Gas Compounds" (Edited by H. H. Hyman), University of Chicago Press, Chicago, 1963, p. 347.
172. J. H. Waters and H. B. Gray, J. Amer. Chem. Soc., 85, 825 (1963).
173. G. C. Pimentel and R. D. Spratley, J. Amer. Chem. Soc., 85, 826 (1963).
174. L. C. Allen, Nature, 197, 897 (1963).
175. Y. J. Israéli, Bull. Soc. chim. France, 1336 (1963).
176. Y. J. Israéli, Bull. Soc. chim. France, 649 (1964).
177. R. K. Nesbet, J. Chem. Phys., 38, 1783 (1963).
178. J. Bilham and J. W. Linnett, Nature, 201, 1323 (1964).
179. E. A. Boudreaux, in "Noble Gas Compounds" (Edited by H. H. Hyman), University of Chicago Press, Chicago, 1963, p. 354.
180. D. S. Urch, Nature, 203, 403 (1964).
181. P. Hemmerich, Chimia (Switz.), 17, 289 (1963).
182. R. T. Sanderson, Inorg. Chem., 2, 660 (1963).
183. R. M. Noyes, J. Amer. Chem. Soc., 85, 2202 (1963).
184. S. Yamada, Rev. Phys. Chem. Japan, 33, 39 (1963).
185. C. D. Cornwell and R. S. Yamasaki, J. Chem. Phys., 27, 1060 (1957).
186. W. B. Person, J. Chem. Phys., 35, 908 (1961).
187. D. Lazdine, C. W. Kern, and M. Karplus, J. Chem. Phys., 39, 1611 (1963).
188. C. J. Jameson and H. S. Gutowsky, J. Chem. Phys., 40, 2285 (1964).
189. R. Hoppe, Angew. Chem., 76, 455 (1964).
190. N. Bartlett, Internat. Sci. Technol., No. 33, 56 (1964).
191. G. C. Pimentel, R. D. Spratley, and A. R. Miller, Science, 143, 674 (1964).
192. J. H. Pomeroy, in "Noble Gas Compounds" (Edited by H. H. Hyman), University of Chicago Press, Chicago, 1963, p. 123.

Additional references

193. H. Schwarz, Naturwiss., 51, 397 (1964).
194. H. Selig, J. G. Malm, and H. H. Claassen, Sci. Amer., 210, 66 (1964).
195. K. Enderer and W. Schmid, Laboratoriums-Prax., 16, 81 (1964).
196. T. Tanaka and I. Kavasaki, Chemistry (Japan), 18, 746 (1963).
197. N. Bartlett, Cienc. Nat., 7, 42 (1964).
198. E. Barabas, Revista de Fizica si Chimie, A 1, 211 (1964).
199. O. Ramirez Torres, Rev. Col. quim. Puerto Rico, 21, 14 (1963).
200. A. K. Mukherdjee, J. Sci. Ind. Res., India, 23, 103 (1964).
201. D. P. Mellor, Proc. Roy. Austral. Chem. Inst., 31, 85 (1964).
202. L. Herman and R. Herman, J. Phys. Radium, 24, 73 (1963).
203. J. H. Freeman and R. W. McIllroy, Nature, 201, 69 (1964).
204. P. J. Gellings, Z. phys. Chem. (Frankfurt), 43, 123 (1964).
205. C. G. Wade and J. S. Waugh, J. Chem. Phys., 40, 2063 (1964).
206. H. S. Johnston and R. Woolfolk, J. Chem. Phys., 41, 269 (1964).
207. T. H. Brown, P. H. Kasai, and P. H. Verdier, J. Chem. Phys., 40, 3448 (1964).
208. B. G. Baker and P. G. Fox, Nature, 204, 466 (1964).
209. Shieh Tsu-Chia, N. C. Yang, and C. L. Chernick, J. Amer. Chem. Soc., 86, 5021 (1964).
210. H. H. Claassen and G. Knapp, J. Amer. Chem. Soc., 86, 2341 (1964).

All-Union Institute of Scientific
and Technical Information,
Academy of Sciences of the USSR

U. D. C. 546.271 : 547.244

THE CHEMISTRY OF DECABORANE AND ITS DERIVATIVES

V. I. Stanko, Yu. A. Chapovskii,
V. A. Brattsev, and L. I. Zakharkin

CONTENTS

1. Introduction 424
2. Structure and reactivity of decaborane 425
3. Deuterium exchange in decaborane 427
4. Pyrolysis of decaborane 428
5. Hydrolysis, alcoholysis, and thiolysis 428
6. Decaborane as an acid 429
7. Decaborane Grignard reagents and sodium tridecahydrodecaborate(1^-) 429
8. Nucleophilic substitution in decaborane 430
9. Electrophilic substitutions 432
10. The stable anion $B_{10}H_{10}^{2-}$ 432
11. Carboranes 434

1. INTRODUCTION

Decaborane† is one of the most interesting representatives of the boron hydrides, information about which before the nineteen-fifties was restricted to Stock's unique monograph [1].

After World War II, in connection with the vigorous development of reaction propulsion for aviation there arose the need to devise a more effective aviation fuel than hydrocarbons. The high calorific value of boron hydrides served as an impetus to the intensive investigation of the chemistry of decaborane, the most stable boron hydride. In view of the complex constitution of decaborane the establishment of its structure was the first task.

This problem was solved by the combined forces of a large group of physicists and chemists.

This review surveys all the main literature on the chemistry of decaborane and also that on the structure and reactivity of its stable derivatives — anions of the $B_{10}H_{10}^{2-}$ type, barenes (carboranes), etc.

† Strictly, decaborane(14), according to the nomenclature recommended in the Preliminary Report of the Advisory Committee presented at the 125th Meeting of the American Chemical Society, 25th March, 1954. This nomenclature has been used where possible in this translation (Ed. of Translation).

2. STRUCTURE AND REACTIVITY OF DECABORANE

For long the structure of the boron hydrides was one of the principal unsolved problems of structural chemistry. Although decaborane is a solid crystalline compound and was studied by X-ray diffraction, the few attempts in this direction ended in failure, because of the complexity of the structure [2]. Finally Kasper and coworkers [3] succeeded in solving the problem in 1950, despite a series of difficulties, for example, the absence of heavy atoms from the decaborane molecule.

It was shown that the ordered structure of the unit cell of the crystal consists of eight units (a = 14.45, b = 20.88, c = 5.68 Å). The x, y coordinates of the boron atoms were determined from the initial map obtained for the electron density in the $\rho_z(x', y')$ plane. The z coordinate was then found by trial and error. The use of the electron density method enabled the coordinates of the boron atoms to be defined accurately and the coordinates of the hydrogen atoms to be found. It transpired that ten of these were attached to the ten boron atoms by an ordinary bond and the other four act as bridges between six boron atoms.

Subsequently [4] a more accurate structure was deduced by the method of least squares. It appeared (see Fig. 1) that the skeleton of the molecule consists of two pentagonal pyramids linked by a common edge of the bases.

The molecule has a centre of symmetry and two perpendicular axes of the second order. It can be shown that the boron atoms in the skeleton occupy 10 of the 12 vertices of a slightly deformed icosahedron.

The structure obtained now required explanation from the standpoint of electronic theory, since it did not fit into the framework of the elementary bond theory. The first significant step towards the solution of this problem was the application of the three-centre bond theory to the structure [5]. The starting point for the calculations was two main assumptions: (1) each boron atom gives three electrons and four $2sp^3$ hybridised orbitals, and each hydrogen atom a 1s orbital and one electron; (2) in addition, six boron atoms give one $2sp^3$ orbital and half an electron to each B–H–B bond. As a result it was found that the boron skeleton contains two σ bonds (between atoms 2 and 6, 4 and 9) and six three-centre bonds. Four of these are three-centre central bonds — between the atoms $B_{(10)}-B_{(1)}-B_{(5)}$; $B_{(1)}-B_{(2)}-B_{(3)}$, $B_{(1)}-B_{(4)}-B_{(8)}$, and $B_{(8)}-B_{(3)}-B_{(7)}$ — which are characterised by the direction of three atomic orbitals of boron to the centre of the triangle and the existence of one bonding and two non-bonding orbitals. The other two are open three-centre bonds — between the atoms $B_{(10)}-B_{(4)}-B_{(8)}$ and $B_{(5)}-B_{(2)}-B_{(7)}$ — which are characterised by a special direction of the constituent orbitals of boron and by the presence of bonding, non-bonding, and antibonding orbitals. Despite the undoubted importance of these theoretical concepts, they were insufficiently precise in reflecting the electronic structure of decaborane and led to an incorrect determination of the charges of the boron atoms.

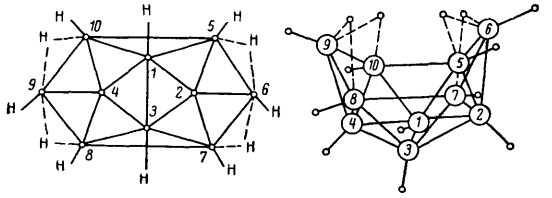


Fig. 1. Structure of the decaborane molecule.

The use of the standard calculation by the LCAO–MO single-electron method, assuming that 16 electrons and 22 atomic orbitals bond the boron skeleton was more fruitful [6]. The following distribution of the formal charge was obtained by calculation of eight wave functions for the given boron skeleton:

B_2, B_4	B_5, B_7	B_8, B_{10}	B_1, B_3	B_6, B_9
$-0.254e$	$-0.031e$		$+0.046e$	$+0.268e$

Starting from the distribution of the formal charge and the structure of the boron skeleton, the dipole moment was found, which agrees well with the value found experimentally [7].

The introduction of a correction with an allowance of $0.2e$ negative charge on the bridging hydrogen atoms leads to the final distribution:

B_2, B_4	B_1, B_3	B_5, B_7, B_8, B_{10}	B_6, B_9
$-0.254e$	$+0.046e$	$+0.069e$	$+0.268e$

Although the calculation of the charges by the LCAO–MO method (even the latest improved values [8]) agrees with the chemical and physical properties of decaborane much better than the method of localised three-centre orbitals, the great difference in charges between the atoms 1, 3 and 2, 4:

B_2, B_4	B_1, B_3	B_5, B_7, B_8, B_{10}	B_6, B_9
$-0.329e$	$-0.102e$	$+0.011e$	$+0.410e$

does not agree with the chemical results and the electronic model [9], which requires further study.

One of the interesting features of decaborane is the presence of four three-centre B–H–B bonds. The nuclear magnetic resonance spectra and theoretical calculations showed [10] that bridge atoms of hydrogen in decaborane are more electropositive than the terminal ones. This is because after departure of the bridge proton the electron pair is employed in the formation of a new B–B bond, instead of the B–H–B bond, so that radical changes in the structure do not take place. As a result of this, decaborane is a strong acid [11] giving various salts with bases.

Furthermore, decaborane participates in interesting exchange reactions with nucleophilic reagents at the $B_{(6)}$ and $B_{(9)}$ atoms, which carry considerable positive charge. For these reactions (for example, with acetonitrile) the liberation of 1 mole hydrogen per 2 moles reacting base with an unshared pair of electrons is remarkable, the compound $B_{10}H_{12}L_2$ being formed with a changed electron balance. Reddy and Lipscomb [12,13], in establishing the structure of the diacetonitrile derivative of decaborane by X-ray diffraction, demonstrated a very small change in the B–B and C–C–N distances compared with the initial decaborane and acetonitrile.

Dickerson and Lipscomb [14] predicted the existence of then unknown stable boron hydrides, and subsequently the existence of stable anions based on boron hydrides was predicted [15]. One of the most interesting anions predicted was $B_{10}H_{14}^{2-}$, the existence of which was confirmed [13] by the preparation of $B_{10}H_{14}Na_2$, since of all the boron hydrides only decaborane is able to add on two electrons, giving a satisfactory valence structure [15].

The bis(acetonitrile) product $B_{10}H_{12}(CNCH_3)_2$ can be considered as a derivative of this anion having two B–H–B bonds between the atoms 7, 8 and 5, 10 and the two BH_2 groups at atoms 6 and 9. The suggested mechanism [13] presupposes the formation of two open three-centre bonds, $B_{(5)}-B_{(6)}-B_{(7)}$ and $B_{(10)}-B_{(9)}-B_{(8)}$ instead of four bridge bonds – with the formation of two new bridge bonds, $B_{(5)}-H-B_{(10)}$ and $B_{(7)}-H-B_{(8)}$ – as a result of which a molecule of hydrogen is detached and at the $B_{(6)}$ and $B_{(9)}$ atoms is released by the orbital occupying the unshared electron pair of the attacking base (Fig. 2).

Furthermore, it is suggested [16] that bis(acetonitrile)-decaborane exists in solution in two tautomeric forms in which the acetonitrile groups are either in the terminal positions, as described above, or occupy the place of two bridge hydrogen atoms. This suggestion was formulated on the basis of the different nuclear magnetic resonance spectra of solutions of $B_{10}H_{12}(CH_3CN)_2$ in acetonitrile and in dimethylformamide.

On the other hand, in view of the presence of negative charges on atoms 2 and 4, in principle decaborane should participate in electrophilic substitution reactions. Stock himself showed [1] that on reaction with halogens decaborane is halogenated. Comparatively recently [17] the structure of an halogeno-derivative was established for the first time, using X-ray diffraction – diiododecaborane. Having found the presence of a second-order axis in the molecule and by using the probable B–I distance (the sum of the covalent radii), the authors calculated the I–I distances for all possible pairs of positions at which the iodine atoms are situated symmetrically relative to the second-order axis (5 pairs) and compared these quantities with the value found experimentally (6.25 Å). Positions 2 and 4 satisfied these requirements, the I–I distance then being 6.21 Å. All this supports the hypothesis of the electrophilic mechanism of iodination of decaborane at the places with maximal electron density.

Due to the non-uniform charge distribution in the molecule, decaborane can also act as a donor of hydride ions. For example, it reduces acetals and ortho-esters to ethers on heating [18].

Although Kasper and coworkers provided sufficient evidence for the structure of decaborane, it has been investigated carefully by many physicochemical methods. The principal merit of these methods, one which they retain unaltered in decaborane chemistry, is the possibility of determining the characteristics of all the types of hydrogen bonds in the molecule. This permits the determination of the mobility of the B–H bonds in different types of reactions and rapid establishment of the structure of the products obtained.

Shoolery made the first interpretation of the proton and ^{11}B nuclear magnetic resonance spectra of decaborane, in 1955 [19]. In this and subsequent investigations [20,21] it was found that the ^{11}B nuclear resonance spectrum (Fig. 3*a*) consists of a high-field doublet and a low-field triplet (ratio of intensities 1 : 4), the latter being, in its turn, the result of the overlap of two doublets of the same intensity.

It was shown that the high-frequency doublet of the spectrum belongs to the vertex atoms $B_{(2)}$ and $B_{(4)}$, the central doublet of the triplet to the equivalent atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$, and the low-field doublet to the atoms $B_{(1)}$, $B_{(3)}$, $B_{(6)}$, and $B_{(9)}$. The last is not completely understood, since these four boron atoms are not equivalent. Actually, the nuclear magnetic resonance spectrum of perdeuterodecaborane [21] (Fig. 3*d*) – in which, because of the weak B–D spin–spin coupling, the number of peaks should equal the number of types of boron atoms in the molecule – showed distinct splitting of the low-field peak into two. Hence the low-field triplet in the nuclear magnetic resonance spectrum of decaborane can be considered as the result of superposition of three doublets with an intensity ratio of 1 : 1 : 2.

The proton spectrum of decaborane (Fig. 3*b*) is a resolved multiplet, with the following interpretation [19]. It is suggested that it consists of two quartets displaced relative to one another, and on these is superimposed a multiplet in the high-field region, which belongs to the bridge protons. The small quartet (shifted to the right) belongs to the two protons bonded with the vertex boron atoms, and the large one to the eight remaining protons. Attempts to interpret this spectrum by saturation of the signal of the proton nuclear magnetic resonance and by excitation of ^{11}B at the frequency 9.6257 MHz (double resonance), that is, by cancelling the B–H spin interaction, led to the spectrum represented in Fig. 3*c*. [20] It was shown that the high-field singlet of the spectrum belongs to the bridge protons, the low-field doublet to all the terminal protons except the "vertex" ones, and the plateau between them to the "vertex" protons. The low-field doublet is the result of the overlap of two peaks of the same intensity [21], in which the high-field singlet of the doublet belongs to four equivalent protons at $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$, and the low-field component may in its turn be a split singlet – protons at $B_{(1)}$, $B_{(3)}$, $B_{(6)}$, and $B_{(9)}$.

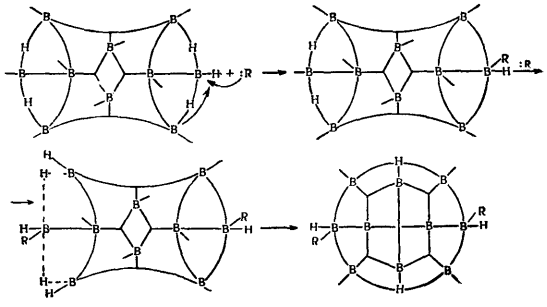


Fig. 2. Mechanism of reaction of decaborane with nucleophilic agents.

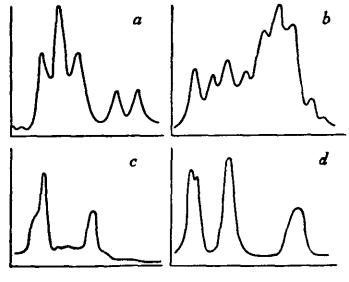


Fig. 3. Nuclear magnetic resonance spectra of decaborane and perdeuterodecaborane.

Hence in the study of the proton and ^{11}B nuclear magnetic resonance spectra of decaborane the hydrogen bridge atoms can easily be distinguished from the terminal ones and the "vertex" terminal hydrogens from the "non-vertex" ones. To distinguish the $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$ hydrogen atoms from $B_{(1)}$, $B_{(3)}$, $B_{(6)}$, and $B_{(9)}$ is more laborious, and the direct establishment of the position of the hydrogen in positions 6 and 9 is almost impossible, compared with 1 and 3.

The use of infrared spectroscopy to study decaborane does not give better results. It was shown [22,23] that the valency vibrations of all the B–H terminal bonds of the molecule (as in the other boron hydrides) produces an absorption band in the spectrum in the region 2350–2630 cm^{-1}, mainly in the form of badly resolved multiplets. The valency vibrations of the B–H–B bridge bonds produce an absorption band in the 1600–2220 cm^{-1} region. However, it seems impossible to distinguish by this method the "non-vertex" from the "vertex" B–H terminal bonds, since the deformation vibrations of the latter produce a band in the 900 cm^{-1} region. The deformation vibrations of the "non-vertex" B–H bonds are difficult to determine, but they are evidently in the 1075–1010 cm^{-1} region.

The mass spectrum of decaborane contains several peaks from unity to one hundred and twenty-four [24]. The theoretically calculated monoisotopic spectrum showed that the maximal mass peak corresponds with the ion of decaborane with *six hydrogen atoms removed.* As this number agrees with the number of terminal hydrogen atoms at the boron atoms which participate in the formation of hydrogen bridges, the authors consider that these hydrogens are the most labile in the molecule (in the sense of ionisation by electrons).

From the near ultraviolet absorption spectrum of decaborane [25] (in the gas phase from 90° to 140°C, in solution at room temperature, and in crystals at 4–4.2°K), the mean value of the minimum energy required for the first electron transition was 3.90 ± 0.1 eV. It is difficult to determine the existence of another electronically excited state of somewhat higher energy, since it is masked by the first transition.

Thermochemical calculations [26] give the following values for the dissociation energies of the various types of bond in decaborane: B–H (σ bond) 93.1 kcal per bond; B–B (σ bond) 83.1 kcal per bond; B–H–B (three-centre bond) 107.2 kcal per bond; B–B–B (three-centre bond) 97.7 kcal per bond.

Decaborane in diamagnetic. Its specific magnetic susceptibility, determined experimentally, is $(-116 \pm 1.5) \times \times 10^{-6}$.

The difference between the measured value and that calculated on the basis of the magnetic susceptibilities of boron and hydrogen (-108×10^{-6}) is obviously due to the presence in the molecule of the bridge atoms of hydrogen.

The dipole moment of decaborane, determined by the Debye and Guggenheim methods, is between 3.17 D (in carbon disulphide solution) and 3.62 D (in benzene solution) [7].

3. DEUTERIUM EXCHANGE IN DECABORANE

Information about the deuteration of decaborane is extremely contradictory. Thus in investigating the nucleophilic reaction of deuterium exchange of decaborane with D_2O and DCl at room temperature in solvents — Lewis bases (dioxan and water) — Hawthorne and Miller [27,28] showed that the hydrogen bridge atoms are exchanged first. The analysis was made using infrared spectra; it was first demonstrated that in what was known synthetically to be perdeuterodecaborane the stretching vibrations of the B–D bonds lie in the 1925 cm^{-1} region and those of the B–D–B bonds in the 1400 cm^{-1} region (in decaborane itself, 2565 and 1800–2140 cm^{-1} respectively). The second stage of the reaction was the slow exchange of deuterium bridges with terminal hydrogen atoms bound to the atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$. In this process, the maximum exchange was eight protons with D_2O and only about six with DCl.

Shapiro and coworkers [29], in studying the kinetics of this reaction, confirmed that the first act is the exchange of the bridge hydrogen atoms, with a subsequent slow migration of deuterium to the atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$. However, there is concurrent deuteration in the $B_{(6)}$ and $B_{(9)}$ terminal positions. If specimens of $B_{10}H_{10}D_4$ are isolated from the reaction medium and dissolved in anhydrous dioxan, then there is only regrouping of D atoms in the $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$ positions.

According to the suggested mechanism, deuterium exchange in decaborane takes place with participation of the Lewis acids and bases. The authors think that the first act is the transfer of the electron pair of the Lewis base to the sixth and ninth boron atoms. In this, the bridge hydrogen atom becomes terminally bound with the neighbouring boron atom ("equatorial") and is rapidly exchanged with deuterium from D_2O. The deuterium subsequently entering into the molecule can be exchanged with the terminal hydrogen atoms at $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$.

The terminal hydrogen atoms at $B_{(6)}$ and $B_{(9)}$ are exchanged intramolecularly in the complex of D_2O with these boron atoms.

The proposed mechanism seems sufficiently satisfactory since it explains why in the case of DCl in dioxan less atoms of deuterium are exchanged than in the case of D_2O [29] — here intramolecular exchange at the $B_{(6)}$ and $B_{(9)}$ terminal positions is impossible. However, Shapiro further maintains that the deuterium exchange with D_2O in aqueous dioxan during prolonged interaction is quantitative, giving in a sense nucleophilic substitution, since the boron atoms 2, 4, 1, and 3 carry a significant negative charge. In methylene dichloride the deuteration of decaborane with D_2O goes only in the bridge positions and the deuteration with DCl does not take place at all [27]. Sodium tridecahydrodecaborate(1^-) exchanges only the bridge hydrogens with DCl. [28] In carrying out electrophilic deuteration of decaborane with DCl in carbon disulphide in the presence of aluminium chloride (at room temperature), Dupont and Hawthorne [30] showed that the reaction proceeds at the terminal hydrogen atoms bonded with the most negative atoms $B_{(2)}$, $B_{(4)}$, $B_{(1)}$, and $B_{(3)}$ and stops at this. The $B_{10}H_{10}D_4$ obtained does not exchange deuterium atoms for hydrogen on interaction with HCl, but reacts with DCl in dioxan almost to complete exchange, giving perdeuterodecaborane. This communication was published in refutation of a previous one [31], where it was maintained that in this reaction there is exchange of six hydrogen atoms in positions 2, 4, 5, 7, 8, and 10.

Apart from the methods described above, partly deuterated decaborane can be obtained by pyrolysis of partly deuterated diborane [32], there then being a statistical distribution of the deuterium in the molecule. A second

method is to heat decaborane with perdeuterodiborane at 100°. As the infrared spectra show, the exchange here is entirely in the terminal positions. Recently[33] an interesting paper reported isotopic exchange of boron atoms between [^{10}B]diborane and ordinary $B_{10}H_{13}Na$, in which all ten boron atoms of the decaborane skeleton participate (62.7% of the ^{10}B is in the recovered diborane). It is suggested that the exchange takes place by formation and splitting of the intermediate anion $B_{11}H_{16}^-$, having the structure of an incomplete icosahedron.

4. PYROLYSIS OF DECABORANE

Stock himself noted[1] the stability of decaborane in the absence of oxygen at elevated temperature (up to 170°C), but a detailed investigation of the pyrolysis of decaborane has been made only recently.

Beachell and Haugh[34] showed that at 170–238° the main product is a polymeric hydride, containing, according to the infrared spectra, decaborane units. Volatile products other than hydrogen were not observed. These results were confirmed by Siegel and Mack[35] who isolated a polymeric product of composition $(BH)_x$ after pyrolysis at 200–250°C. They found that the pyrolysis rate rises sharply with temperature within the limits stated.

Finally, Owen[36] made a complete kinetic investigation of pyrolysis in the gas phase at 220°, 230°, and 250°C and various initial decaborane pressures (from 60 to 600 mmHg) and proposed a complete mechanism for the reaction:

$$B_{10}H_{14} + B_{10}H_{14} \rightleftarrows B_{10}H_{14}^* + B_{10}H_{14}, \quad (1)$$

$$B_{10}H_{14}^* \rightleftarrows B_{10}H_{12} + H_2, \quad (2)$$

$$B_{10}H_{14} + B_{10}H_{12} \rightleftarrows B_{20}H_{24} + H_2, \quad (3)$$

$$B_{20}H_{24}\ (gas) \rightleftarrows B_{20}H_{24}\ (solid), \quad (4)$$

$$2B_{20}H_{24} \rightleftarrows H_2 + \text{involatile solid hydrides}. \quad (5)$$

He showed that the pyrolysis is a first-order reaction with respect to decaborane and Eqn. (2) is the rate-determining stage for the reaction. This dependence is strictly obeyed for the first 60% of the conversion, but as the decaborane concentration falls the rate of reaction (3) approaches the rate of reaction (2) and the overall order becomes greater than first. An attempt was made to isolate the intermediate hydride $B_{20}H_{24}$ from the pyrolysis products at 230°C; a viscous liquid with a very low vapour pressure and an infrared spectrum similar to that of decaborane was obtained. It was shown by deuteration[34] that in the polymerisation of decaborane the terminal, not the bridge, hydrogen atoms are preferentially removed. Moreover, in carrying out the pyrolysis in the presence of ethyl bromide the main product was 2-ethyldecaborane[36]. The authors to suggested that the initial stage of the pyrolysis is the detachment of hydrogen atoms from the "vertex" positions.

The thermal interaction of diborane with decaborane was an interesting reaction. On passing diborane into molten decaborane (100°C), the liberation of hydrogen and the formation of a yellow crystalline product[37] were noted. Diborane itself under these conditions does not change. The following reaction mechanism was proposed on the basis of an analysis of the proton nuclear magnetic resonance spectrum, infrared spectra, and mass-spectra:

$$B_2H_6 + B_{10}H_{14} \rightarrow (BH)_{12} + 4H_2,$$

$$(BH)_{12} \rightarrow B_nH_{n-x} + \frac{x}{2}H_2.$$

The authors think that the $(BH)_{12}$ structure is a complete icosahedron in which the bridge hydrogen bonds are replaced by a B_2H_2 "cap". The polymer consists of chains of icosahedra. This is confirmed by the absence of intermediate boron hydrides between $B_{10}H_{14}$ and B_2H_6 and by the presence of tetraborane and hexaborane — the hydrolysis products of decaborane itself — in the hydrolysis of the polymer.

5. HYDROLYSIS, ALCOHOLYSIS, AND THIOLYSIS

As noted above, Stock[1] found that decaborane is slowly hydrolysed by water on heating. Later this reaction was studied in detail by Atteberry[38], who made a kinetic investigation of the hydrolysis of decaborane by water at 80° and 100°C. It was shown to be a first-order reaction:

$$B_{10}H_{14} + 30H_2O \rightarrow 10B(OH)_3 + 22H_2,$$

the rate constants being:

$$K_{100} = 4.27 \times 10^{-5}\ s^{-1} \quad \text{and} \quad K_{80} = 1.43 \times 10^{-5}\ s^{-1},$$

and the energy of activation E_a = 14.5 kcal mole^{-1}.

On the basis that the activation energy agrees with the quantity found by Guter and Schaeffer[39] for the initial dissociation of decaborane in aqueous dioxan, the author concluded that the most probable mechanism was the ionic-dipolar hydroxylation of boron–hydrogen bonds.

A reaction of interest in this connection is the alcoholysis of decaborane by alcohols, of which there have been several kinetic studies:

$$B_{10}H_{14} + 30ROH \rightarrow 10B(OR)_3 + 22H_2.$$

Beachell and Meeker found[40] that the reaction of decaborane with primary alcohols is second order overall, first order in each of the components. The rate constants and activation energies were determined; there was an increase in the rate constant with the number of carbon atoms in the primary alcohols from 2 to 5. A more detailed study of this reaction with a larger number of alcohols[41] showed that is proceeds through the intermediate donor–aceptor complex $B_{10}H_{14}$.HOR. It appeared that the rate of alcoholysis by halogenated alcohols decreases as the halogen atom approaches along the carbon chain towards the OH group and increases as a CH_3 group approaches. The alcoholysis of decaborane by phenol is much slower than that by cyclopentanol. On the basis of these results and also in connection with the previously observed increase in alcoholysis rate with increase in the number of carbon atoms in the primary alcohol it was concluded that the decisive factor in alcoholysis is the inductive and not the steric effect. The stages determining the reaction rate are the breaking of the O–H bond in the $B_{10}H_{14}$.HOR complex, since there is a strong isotope effect on replacing alcohol by deuteroalcohol. A radical mechanism has been proposed for the breaking of the O–H bond, since in the case of an ionic mechanism:

$$B_{10}H_{14}HOR \rightleftarrows [B_{10}H_{14}OR]^- + H^+,$$

the addition of a base would rapidly shift the equilibrium to the right, that is, the reaction rate would be greatly increased. However, the addition of bases only slightly retards the process, which suggests that the second mechanism is impossible.

Thiols also destroy the decaborane molecule[42]. Thus on boiling in butanethiol for a few days, decaborane is converted quantitatively into tributyl thioborate. The reaction

with lower thiols necessitates heating in a autoclave, since at lower temperatures the reaction is very slow:

$$B_{10}H_{14} + 30RSH \rightarrow 10B(SR)_3 + 22H_2.$$

6. DECABORANE AS AN ACID

It was noted earlier that to a greater extent than the other boron hydrides decaborane is a dual reagent: in some reactions it behaves as a donor of hydride ions and in others as an acid, dissociating to H^+ ions. Guter and Schaeffer[39] found that the curve for the titration of a solution of decaborane in protolytic solvents (alcohol, aqueous alcohol, aqueous dioxan, 0.1 *N* NaOH) is characteristic for a strong monobasic acid. Two possible mechanisms for the formation of the acid are suggested:

$$B_{10}H_{14} + H_2O \rightarrow [B_{10}H_{14}OH]^- + H^+ \text{ (solution)},$$
$$B_{10}H_{14} \rightarrow [B_{10}H_{13}]^- + H^+ \text{ (solution)}.$$

In acetonitrile, decaborane behaves as a weak acid with $pK_a = 3.5$ and in dimethylformamide as a strong acid, the first potential jump being observed at pH 1.2 and the second at pH 6. It is thought that this difference is due to the different electron-donor properties of the solvents, which are stronger in the case of dimethylformamide[43]. However, according to Griffiths and Williams[44] the difference in the titration curves of decaborane in acetonitrile and dimethylformamide is due to the existence in the latter of dimethylamine impurity. In the pure solvents the curves are identical.

The acid properties of decaborane, that is, the presence in it of mobile protonised hydrogen atoms, forms a basis for its reaction with methylenetriphenylphosphorane and trimethylammoniomethylenide, as a result of which substituted phosphonium and ammonium salts with the anion $B_{10}H_{13}^-$ are obtained[45,46]:

$$(C_6H_5)_3P{=}CH_2 + B_{10}H_{14} \rightarrow [(C_6H_5)_3P^+CH_3]\,B_{10}H_{13}^-,$$
$$(CH_3)_3N^+{-}CH_2^- + B_{10}H_{14} \rightarrow [(CH_3)_4N^+]\,B_{10}H_{13}^-.$$

7. DECABORANE GRIGNARD REAGENTS AND SODIUM TRIDECAHYDRODECABORATE(1⁻)

The acidic properties of decaborane explain the ease of formation of its metal derivatives with sodium and magnesium, from which alkyldecaboranes were obtained in turn.

The magnesium derivative was first obtained by Siegel and coworkers[47] in 1958. They studied the reaction of decaborane with methylmagnesium iodide in ether and found that when an excess of decaborane was used a monomangesium derivative was produced:

$$B_{10}H_{14} + CH_3MgI \xrightarrow{\text{ether}} B_{10}H_{13}MgI + CH_4,$$

and when the methylmagnesium iodide was in excess, a dimagnesium derivative, $B_{10}H_{12}(MgI)_2$.

In hydrolysis with moist ether decaborane is regenerated. Benzyldecaborane is obtained by the reaction of decaborane Grignard reagent with benzyl chioride:

$$B_{10}H_{13}MgI + 2C_6H_5CH_2Cl \rightarrow B_{10}H_{13}CH_2C_6H_5 + C_6H_5CH_2I + MgCl_2.$$

The investigation of this compound by infrared spectroscopy and the ^{11}B nuclear magnetic resonance did not allow the authors to discover the precise position of the benzyl group in the decaborane molecule but positions 2 and 4 are excluded because the high-field doublet does not change in intensity compared with that for decaborane.

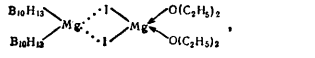
Dunstan and coworkers[48] made a special study of this reaction and found that in the reaction of decaborane with ethylmagnesium iodide a little ethyldecaborane is formed in addition to the magnesium iodide tridecahydrodecaborate(1⁻), and on subsequent addition of dimethyl sulphate to the decaborane Grignard reagent equal amounts of two isometic methyldecaboranes are formed.

In interpreting the ^{11}B nuclear magnetic resonance spectra the authors assigned to the products the structures of 5- and 6-methyldecaboranes. Benzyldecaborane, obtained by the method described above, was also given the structure of the 6-derivative.

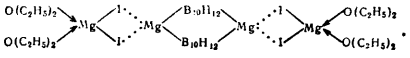
It was shown that of the ordinary alkyl halides only benzyl bromide and chloride[49] and allyl bromide[50] undergo condensation with the decaborane Grignard reagent. In the case of alkyl fluorides and trialkyloxonium salts, various alkyldecaboranes were obtained with good yields[49]:

$$B_{10}H_{13}MgX + RF \rightarrow B_{10}H_{13}R + MgFX,$$
$$B_{10}H_{13}MgX + R_3O^+X^- \quad B_{10}H_{13}R + R_2O + MgX_2.$$

Attempts were made to reveal the structure of the decaborane Grignard reagent by infrared and ultraviolet spectra. It was shown that the infrared spectrum of $B_{10}H_{13}MgI$ is very similar to the spectrum of methylmagnesium iodide; the ultraviolet spectra also showed great similarity. From these results the authors gave magnesium iodide tridecahydrodecaborate(1⁻) the following structure:



and



A convenient reagent for the preparation of alkyldecaboranes is sodium tridecahydrodecaborate(1⁻), which can be obtained by the action of such reagents as sodium, sodium hydride, sodium amide, sodium tetrahydroborate, and dry powdered sodium hydroxide in ether on decaborane[51]:

$$B_{10}H_{14} + NaH \xrightarrow{\text{ether}} B_{10}H_{13}Na + H_2.$$

By carying out this reaction with decaborane with deuterated bridges it was shown that one of the bridge hydrogen atoms is substituted:

$$B_{10}H_{10}D_4 + NaH \xrightarrow{\text{ether}} B_{10}H_{10}D_3Na + HD.$$

The action of benzyl bromide in ether on sodium tridecahydrodecaborate(1⁻) gives benzyldecaborane identical with that obtained from the decaborane Grignard reagent, as described above. The deuteration of benzyldecaborane with D_2O in dioxan showed that four deuterium atoms were rapidly introduced into the molecule, and this is evidence of the rearrangement of the benzyl group from a bridge position to a terminal one. There are only two possibilities for such regrouping: in the 6- or the 5-position. The nuclear magnetic resonance spectrum showed unambigously that the benzyl group is in position 6.

Sodium tridecahydrodecaborate(1⁻) boiled in ether with dimethyl and diethyl sulphate gives the same products as magnesium iodide tridecahydrodecaborate(1⁻), that is, a mixture of the 5- and 6-methyl- or 5- and 6-ethyl-decaboranes[52]. Reaction with iodine in ether at -80°C gave a

mixture of products, consisting of decaborane, ethoxydecaborane, and ethoxyiododecaborane [51]:

$$B_{10}H_{13}Na \xrightarrow[-80^\circ]{\text{ether}} B_{10}H_{13}I + B_{10}H_{14} + B_{10}H_{13}OC_2H_5 + B_{10}H_{12}IOC_2H_5.$$

By using various ethers in this reaction, various alkoxydecaboranes can be obtained [53]. The precise position of the RO group could not be established, but the ^{11}B nuclear magnetic resonance spectrum excludes substitution at boron atoms 2 and 4.

Finally, sodium tridecahydrodecaborate(1$^-$) reacts with chloro(diphenyl)phosphine, forming a phosphorus(III) compound [54]:

$$B_{10}H_{13}Na + (C_6H_5)_2PCl \rightarrow B_{10}H_{13}P(C_6H_5)_2 + NaCl.$$

8. NUCLEOPHILIC SUBSTITUTION IN DECABORANE

It was noted earlier that hydrolysis and alcoholysis of decaborane take place through an intermediate complex, $B_{10}H_{14}.HOR$. This complex is formed because, despite the high degree of symmetry and stability, the decaborane molecule is an electron-deficient system striving to make up the deficiency from molecules having unshared pairs. This property of decaborane appears in many reactions with various nucleophilic reagents.

For example, a solution of decaborane in acetone at low temperatures gives a ^{11}B nuclear magnetic resonance spectrum in which the low-field doublet is degenerate, which indicates the formation of a complex at positions 6 and 9 in the decaborane molecule. On raising the temperature to room temperature or above, the spectrum becomes identical with that in benzene, that is, the complex is decomposed into the initial components [55].

Stock himself noted [1] that decaborane reacts with liquid ammonia, adding up to six molecules of the latter; on heating, the ammonia molecules are split off in stages, and later the decaborane structure is broken down and hydrogen released.

Fitch and Laubengayer [56] studied in detail the reaction of decaborane with dimethylamine at low temperature [56]:

$$B_{10}H_{14} + n(CH_3)_2NH \rightarrow [(CH_3)_2NH]_n.B_{10}H_{14}.$$

By studying the reaction kinetics, the existence of addition compounds with four and five molecules of dimethylamine per molecule of decaborane has been demonstrated. They are very unstable compounds and decompose with formation of dimethylamine and lower addition products even at low temperatures (-60° to 40°C)‡. The addition products with n = 1, 2, or 3 are rather stable and were characterised by X-ray diffraction. Treatment of the addition products with water formed decaborane again. In an excess of dimethylamine at elevated temperatures decaborane undergoes aminolysis with liberation of hydrogen and destruction of the skeleton; in particular, a crystalline product with the ratio B : N = 9 : 1 has been identified.

Interestingly, for most amines at elevated temperature the reaction proceeds with liberation of hydrogen and formation of complexes of the type $B_{10}H_{12}.2L$. The addition products obtained and isolated at low temperatures decompose only by splitting off the amine but without releasing hydrogen. This was confirmed by Burkardt and Fetter [57] for the pyridine derivatives. Under these conditions the addition products $B_{10}H_{14}.2BrC_5H_4N$ and $B_{10}H_{14}.3C_5H_5N$ were obtained, stable on heating to 100°. Investigation of the reaction of decaborane with substituted anilines [32] showed that in every case of the reaction of an amine (*p*-anisidine, *p*-toluidine, *p*-chloroaniline, *N*-methylaniline, *NN*-dimethylaniline) with decaborane at room temperature 1 mole hydrogen is liberated per 1 mole decaborane:

$$B_{10}H_{14} + 2RC_6H_4NH_2 \rightarrow B_{10}H_{12}.(RC_6H_4NH_2)_2 + H_2.$$

Alkylpyridines and alkylquinolines at room temperature dissolve decaborane without releasing hydrogen, giving strongly coloured solutions from which a solid is slowly precipitated. The same reaction in pentane proceeds with evolution of hydrogen. Aliphatic amines give solid products without evolution of hydrogen even in pentane. The reaction with diethylthiourea proceeds with liberation of hydrogen and the formation of a stable crystalline substance, $B_{10}H_{12}[(C_2H_5NH)_2CS]_2$. [58]

A method for the direct colorimetric determination of decaborane has been developed, based on the formation of orange-red solutions with *NN*-diethylnicotinamide with an absorption maximum in the 430–500 mμm region [59]. The value of this method is that neither other boron compounds, nor proteins hinder the determination. The method is applicable to solutions in aqueous systems (for example, blood plasma), and this defines its practical value in view of the considerable toxicity of decaborane.

Nitriles, as substances with very weak basic properties, react with decaborane on heating, hydrogen being liberated [60,61]:

$$B_{10}H_{14} + 2RC{\equiv}N \rightarrow B_{10}H_{12}.(RCN)_2 + H_2,$$

and crystalline products precipitated. The bis(acetonitrile) complex, which is involatile and stable in air, melts with decomposition above 200°C, is diamagnetic, and soluble in acetonitrile. The structure of the substance was determined by X-ray analysis [13]. It was shown that the acetonitrile ligands are in positions 6 and 9. This agrees completely with the fact that these are the most electropositive atoms in the decaborane molecule.

Besides the above nitrogen compounds, amides and cyanamides can enter into reactions analogous to those with nitriles, and so can many Lewis bases not containing nitrogen, such as sulphides, phosphines, phosphites, thiophosphites, ethers, alkylphosphinic acids [alkylphosphonic acids or even alkyl hydrogen phosphonates may be meant (Ed. of Translation)], arsines, and sulphoxides [62–67]. They all have the formula $B_{10}H_{12}L_2$ (where L is the Lewis base) and a structure which is obviously analogous to that of bis(acetonitrile)decaborane.

All the complexes of this type are covalent compounds, as is shown by a study of their infrared and ^{11}B nuclear magnetic resonance spectra, compared with those of the ionic complex $[B_{10}H_{10}]^{2-}.2(C_2H_5)_3\overset{+}{N}H$. [63]

On the basis of complexes of decaborane with phosphines, polymers of the type [67]:

$$[-OP(C_6H_5)_2.B_{10}H_{12}P(C_6H_5)_2-]_x.$$

have been obtained [68].

Kinetic investigation of the reactions of decaborane with various nitriles and sulphides [69] in dioxan at 70–80°C showed that this reaction is first order with respect to each of the reagents and of second order overall. Electron-donor substituents in nitriles and sulphides increase the

‡ These figures appear to be in error; see Fitch and Laubengayer [56] (Ed. of Translation).

reaction rate, electron-acceptor constituents decrease it. The following reaction scheme is proposed:

$$B_{10}H_{14}+L \underset{\text{rapid}}{\rightleftarrows} B_{10}H_{14}L \xrightarrow{\text{slow}} H_2+B_{10}H_{13}L \xrightarrow[\text{rapid}]{L} B_{10}H_{13}L_2.$$

Not only uncharged molecules, but also anions can act as complex-forming agents in this reaction [64-70]. For example, hydrogen is also liberated in the reaction of decaborane in ether with sodium cyanide:

$$NaCN+B_{10}H_{14}R_2 \xrightarrow{25^\circ} [NaB_{10}H_{14}CN] \rightarrow NaB_{10}H_{12}CN+H_2.$$

An ionic compound is formed in which the CN group is obviously situated at one of the boron atoms 6 or 9. The salts $B_{10}H_{11}X^-$, where X = NCO, SCN, OCH_3, and $C(CN)_3$, have also been obtained. ^{11}B nuclear magnetic resonance spectra have shown that all the decaborane complexes of type $B_{10}H_{12}.2L$ and $B_{10}H_{12}.L^-$ are isostructural and are derivatives of the ion $B_{10}H_{14}^{2-}$.

A convenient method has been developed [71] for obtaining the anion $B_{10}H_{14}^{2-}$ by the reaction of decaborane with an aqueous solution of potassium tetrahydroborate:

$$B_{10}H_{14}+H_2O \rightleftarrows B_{10}H_{13}^-+H_3O^+,$$
$$B_{10}H_{13}^-+BH_4^- \rightleftarrows B_{10}H_{14}^{2-}+[BH_3],$$
$$[BH_3]+3H_2O \xrightarrow{\text{rapid}} B(OH)_3+3H_2.$$

$Rb_2B_{10}H_{14}$ and $Cs_2B_{10}H_{14}$ were isolated. The reaction of decaborane with sodium tetrahydroborate in Diglyme [di-(2-methoxyethyl) ether (Ed. of Translation)] at the boiling point is a simple method for preparing [72] the dianion $B_{12}H_{12}^{2-}$. The reaction follows the scheme:

$$B_{10}H_{14}+BH_4^-+R_2O \rightarrow B_{10}H_{13}^-+R_2O\cdot BH_3+H_2;$$
$$B_{10}H_{13}^-+R_2O\cdot BH_3 \rightarrow B_{11}H_{14}^-+H_2+R_2O;$$
$$B_{11}H_{14}^-+BH_4^- \rightarrow B_{12}H_{12}^{2-}+3H_2.$$

The first stage takes place at room temperature, the second at 90°, and the last at the boiling point of Diglyme.

Donor–acceptor complexes including the $B_{10}H_{12}$ unit in their composition undergo characteristic ligand-exchange reactions [10,19,66]:

$$B_{10}H_{12}\cdot 2L'+2L \rightarrow B_{10}H_{12}\cdot 2L+2L',$$

in which the displacement sequence obviously depends on the strength of the base. Thus Hawthorne and Pitochelly [62] found the following displacement order for acetonitrile, diethylcyanamide, and triphenylphosphine:

$$B_{10}H_{12}(CH_3CN)_2 \xrightarrow{2\,(C_2H_5)_2NCN} B_{10}H_{12}[(C_2H_5)_2NCN]_2 \xrightarrow{2P\,(C_6H_5)_3} B_{10}H_{12}[P(C_6H_5)_3]_2.$$

The reverse reactions do not take place.

A series of pyridine complexes of decaborane were obtained by analogous reaction of the dimethyl sulphide complex with substituted pyridines [73]. Since some of these products are coloured the authors suggest the interaction of the pyridine π electron with the three-centre bonds in $B_{10}H_{12}^{2-}$.

Subsequent investigations of the exchange reactions of bis(acetonitrile)decaborane showed that in its reaction with triethylamine in boiling benzene two products with the same overall formula $B_{10}H_{12}.[N(C_2H_5)_3]_2$ should be expected [74]. One of these is a covalent compound of the general type $B_{10}H_{10}.L_2$, and the other the saltlike compound $B_{10}H_{10}^{2-}.2[NH(C_2H_5)_3]^+$. Unlike the first compound, the latter is confirmed by deuterium exchange with D_2O, is insoluble in organic solvents, and soluble in water; in aqueous solutions the $NH(C_2H_5)_3^+$ is exchanged for other cations:

$$B_{10}H_{10}^{2-}\cdot 2NH(C_2H_5)_3^+ + N(CH_3)_4^+Cl^- \rightarrow B_{10}H_{10}^{2-}\cdot N(CH_3)_4^+ + NH^+(C_2H_5)_3Cl^-.$$

It was found [75] that substituted decaboranes also form (like decaborane) complexes with Lewis bases. Thus 2-bromodecaborane reacts with acetonitrile, diethyl sulphide, and triphenylphosphine to give corresponding complexes:

$$2\text{-}B_{10}H_{13}Br \xrightarrow{(C_2H_5)_2S} [(C_2H_5)_2S]_2B_{10}H_{11}Br$$
$$\xrightarrow[CH_3CN]{} (CH_3CN)_2B_{10}H_{11}Br$$
$$\xrightarrow[(C_6H_5)_3P]{} [(C_6H_5)_3P]_2B_{10}H_{11}Br.$$

Monoethyldecaborane, containing 60% 2-ethyl- and 40% 1-ethyl-decaborane, is also readily converted into analogous complexes.

However, it has been noted [75] that boiling 2-iododecaborane with triethylamine in benzene yields not only the salt mentioned, $B_{10}H_{10}[NH(C_2H_5)_3]_2$, but also $B_{12}H_{12}[NH(C_2H_5)_3]_2$, which can also exchange cations, giving, for example, $K_2B_{12}H_{12}$.

2-Bromodecaborane also forms a complex with triethylamine [75], $B_{12}H_{12}[NH(C_2H_5)_3]_2$. However, bis(triethylammonium) nonahydrobromodecaborate is readily obtained by the action of triethylamine in benzene at 20° on $[(C_2H_5)_2S]_2B_{10}H_{11}Br$:

$$[(C_2H_5)_2S]_2B_{10}H_{11}Br+2N(C_2H_5)_3 \rightarrow [(C_2H_5)_3NH]B_{10}H_9Br.$$

A similar product is formed on heating $B_{10}H_{13}Br$ with trimethylamine in boiling toluene. Monoethyldecaborane and triethylamine in toluene give

$$[(C_2H_5)_3NH]_2B_{10}H_9C_2H_5,$$

in high yield.

The symmetry of the stable anion $B_{10}H_{10}^{2-}$ has been demonstrated and an icosahedral structure has been proposed for it.

Hawthorne and coworkers [76] have observed that in the reaction of the disulphide complex of decaborane with ethanol $B_9H_{13}(SR_2)$, a derivative of nonaborane(15) B_9H_{15} is formed. An analogous reaction with the acetonitrile complex takes place thus:

$$B_{10}H_{12}(CH_3CN)_2+2C_2H_5OH \rightarrow B_9H_{12}(CH_3-\underset{\underset{OC_2H_5}{|}}{C}=NH)+CH_3CN+H_2+B(OC_2H_5)_3.$$

Organic sulphide ligands in the last type of compound can be replaced by other ligands:

$$B_9H_{13}(SR_2)+X \rightarrow B_9H_{13}X+SR_2,$$

where X = CH_3CN; R_3N; R_2NH; RNH_2; R_2NCN, $P(C_6H_5)_3$. When a sulphide complex of nonaborane(15) is treated with methylenetriphenylphosphane, a salt of the $B_9H_{12}^-$ anion is formed:

$$B_9H_{13}(SR_2)+(C_6H_5)_3P=CH_2 \rightarrow [(C_6H_5)_3PCH_3]^+[B_9H_{12}]^-+SR_2.$$

The direct alkylation of decaborane by methyllithium and ethyllithium can also be classified as nucleophilic reactions. A mixture of the mono- and di-substituted derivatives is formed [77], which was separated by preparative gas–liquid chromatography and the structure of the

products was established by ^{11}B nuclear magnetic resonance spectra. They are the 5- and 6-alkyl and the 6,9- and 6,5(8)-dialkyl derivatives. These results agree completely with the electron density distribution at the boron atoms of decaborane: 2, 4 > 1, 3 > 5, 7, 8, 10 > 6, 9.

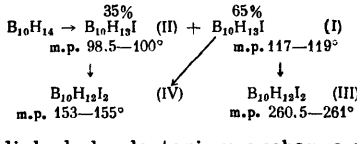
The most electropositive positions, 6 and 9, are the first to undergo nucleophilic attack by alkyllithiums, then 5, 7, 8, and 10; the 2, 4 and 1, 3 positions do not participate in the reaction at all.

9. ELECTROPHILIC SUBSTITUTIONS

As well as nucleophilic substitutions, decaborane is also characterised by electrophilic substitutions. From the electronic non-equivalence of the boron atoms in the decaborane molecule, it is to be expected that electrophilic agents would attack positions 2, 4 and 1, 3.

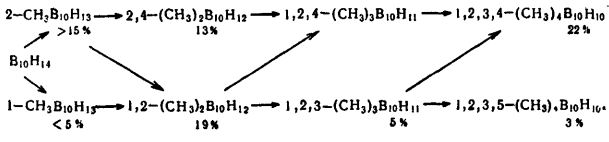
Stock was the first to observe, in 1914, that halogens do not destroy the structure of the decaborane molecule, but only replace from one to three hydrogen atoms by halogen. By heating decaborane with iodine at 100°, diiododecaborane $B_{10}H_{12}I_2$ was obtained and isolated in the pure state. Bromination and iodination under mild conditions gave monobromodecaborane and two monoiododecaboranes[78]. In the ^{11}B nuclear magnetic resonance spectra of the monobromo-derivative and the high-melting monoiodido-derivative a triplet in the low field is unchanged and a doublet in the high field is altered, the intensity of one of the peaks being decreased. This indicates that the halogen atom is in position 2 in both compounds. The spectrum of the low-melting monoiodido-complex shows a decrease in the high-field part of the triplet, belonging to atoms 5, 7, 8, and 10, whereas the low-field doublet is unchanged. Consequently, this substance must be 5-iododecaborane. The formation of this product can be explained by the parallel reaction of radical substitution[78].

Iodination was studied in greater detail by Hillman[79]. He iodinated separately decaborane itself and the monoiododecaboranes which were obtained:



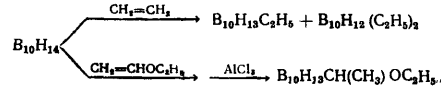
It was established, by deuterium exchange and the earlier X-ray structural analysis of 2,4-diiodo-derivative[17] (III), that compounds (I), (II), and (IV) are respectively 2-iodo-, 5-iodo-, and 2,5-diiodo-decaborane.

Williams and coworkers[80,81] studied the electrophilic alkylation of decaborane under the conditions of the Friedels–Craft reaction. On heating decaborane with methyl bromide in the presence of aluminium chloride in carbon disulphide in a sealed ampoule for 36 h, a mixture of polymethylated decaboranes was obtained:



Alkyldecaboranes, especially ethyldecaboranes, have been obtained by another method, the pyrolysis of ethyldiboranes[82]. 5-Ethyldecaborane (and other products) was isolated from the reaction mixture.

Decaborane adds on to ethyl vinyl ether and the lower alkenes in the presence of aluminium halides[83,84]:



The reaction takes place in a medium of an inert organic solvent. The products are liquids and have been proposed as additives to high-energy rocket fuels.

Finally, decaborane is alkylated by alkyl halides in the presence of metal halides to give a mixture of alkyldecaboranes[85].

10. THE STABLE ANION $B_{10}H_{10}^{2-}$

In 1959 Hawthorne and Pitochelly[74] reported that bis-(acetonitrile)decaborane reacts in two ways with tertiary amines, giving either the covalent compound $B_{10}H_{12}[N(C_2H_5)_3]_2$ or the ionic $B_{10}H_{10}^{2-}[HN^+(C_2H_5)_3]_2$, insoluble in organic solvents. This reacts with tetramethylammonium chloride, giving $B_{10}H_{10}^{2-}[\dot{N}(CH_3)_4]_2$.

The absence of BH_2 groups and hydrogen bridge atoms was shown by infrared spectra[86]. The ^{11}B nuclear magnetic resonance spectrum showed the presence of only two types of boron atom, in the ratio 8 : 2. These results indicate that the system is of high symmetry.

It was suggested[86] that the structure of the $B_{10}H_{10}^{2-}$ anion consists of two B_5H_5 "groups" — tetragonal pyramids, joined to one another by their bases. Hence the molecule contains two "vertex" and eight "equatorial" boron atoms. This structure was confirmed experimentally. Dobrott and Lipscomb[87] made an X-ray diffraction study of the salt $Cu_2B_{10}H_{10}$. The calculations showed that there are three types of B–B distance in the anion (Fig. 4): (1) the distance between the vertex boron atoms and the atoms lying in the base of the pyramid (1.73 ± 0.02 Å); (2) the distance between the atoms lying in the base of each pyramid (1.86 ± 0.03 Å); (3) the distance between atoms lying in the bases of pyramids ("equatorial belt", 1.815 ± ± 0.015 Å).

The calculated bond orders agree well with the data obtained by the LCAO–MO method[88] and are 0.56, 0.40, and 0.51 respectively. The Cu–B distance varies from 2.13, to 2.33 Å, which greatly hinders the calculations. From these results and from the B–Cu–B angle found (46°) the authors think a three-centre bond between the copper atom and the B–B edge the most probable (*sp* hybridisation of copper).

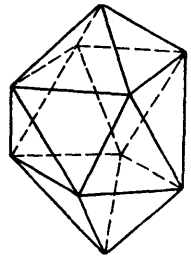


Fig. 4. Structure of the $B_{10}H_{10}^{2-}$ anion.

Calculation of the $B_{10}H_{10}^{2-}$ anion by the LCAO–MO method[88] showed that the vertex atoms are the most electropositive and are the first to be attacked by electrophilic agents.

A mechanism for the formation of the $B_{10}H_{10}^{2-}$ anion from bis(acetonitrile)decaborane has been proposed (Fig. 5).[89] The two bridge hydrogen atoms in bis(acetonitrile)decaborane leave as protons, giving a transition state containing two filled two-centre orbitals between the boron atoms 5 and 10, and 7 and 8. This transition state is stabilised by ejection of the ligands from positions 6 and 9. There is then a general rearrangement of the molecule in which the vertices of the polyhedron formed should be positions 10 and 7 or 5 and 8. This was confirmed by the nuclear magnetic resonance spectra of $B_{10}H_{10}^{2-}$ and $B_{10}H_6D_4^{2-}$, obtained from $B_{10}H_{10}D_4$ with deuterium in positions 1, 2, 3, and 4. The spectra showed the absence of deuterium from the vertex positions of the anion. The infrared spectra confirmed that the anion $B_{10}H_{10}^{2-}$ does not undergo deuterium exchange with D_2O or $(C_2H_5)_3ND$.

Salts of the anion $B_{10}H_{10}^{2-}$ (and also $B_{12}H_{12}^{2-}$) exhibit an astonishing stability with respect to strong acids, bases, and oxidants. They do not react with hot sodium hydroxide, but acids convert them into the acid $B_{10}H_{10}(H_3O)_2 \cdot xH_2O$, which is stronger than sulphuric acid[90]. Many different salts of the anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have been obtained.

In aqueous and or alcoholic solutions, the anion $B_{10}H_{10}^{2-}$ reacts smoothly with chlorine, bromine, and iodine, giving derivatives in which from one to ten hydrogen atoms have been replaced by halogen[91]. It is suggested that such halogenation takes place by radicals. Thus, $B_{10}H_2Cl_8^{2-}$, $B_{10}H_3Br_7^{2-}$, $B_{10}H_7I_3^{2-}$, $B_{10}H_6I_4^{2-}$, $B_{10}H_4I_6^{2-}$, $B_{10}Cl_{10}^{2-}$, $B_{10}Br_{10}^{2-}$, and $B_{10}I_{10}^{2-}$ have been obtained. Halide derivatives of the anion containing other substituents have also been obtained, for example, $B_{10}Cl_9COC_6H_5^{2-}$ and $B_{10}H_2Cl_6[S(CH_3)_2]_2$. The anion $B_{12}H_{12}^{2-}$ undergoes analogous reactions. The halogenated compounds are strong acids, show great stability to acids and bases, and high thermal stability. $Cs_2B_{10}Cl_{10}$ loses only 4% of its weight when heated in a vacuum at 600°C; $B_{10}H_3Br_7^{2-}$ is unchanged after 1 h with CH_3ONa in boiling methanol; $B_{10}H_7I_3^{2-}$ is inert to a solution of KNH_2 in liquid ammonia, but gives $B_{10}H_{10}^{2-}$ by the action of potassium in liquid ammonia. The crystalline acid $(H_3O)_2B_{10}Cl_{10} \cdot .5H_2O$ is reversibly dehydrated in a vacuum at 150°:

$$(H_3O)_2B_{10}Cl_{10} \cdot 5H_2O \rightleftarrows 3H_2O + (H_3O)_2B_{10}Cl_{10} \cdot 2H_2O.$$

Irreversible decomposition starts above 200° and a new compound is formed: octachlorononaborane(9), B_9HCl_8. Its properties have been studied[92], especially its conversion into the anion $B_9Cl_8H^{2-}$.

The caesium salt of the $B_{10}H_{10}^{2-}$ anion is unchanged after heating to 810°C. Some salts of $B_{10}H_{10}^{2-}$ are coloured; thus the pyridinium salt is yellow[93].

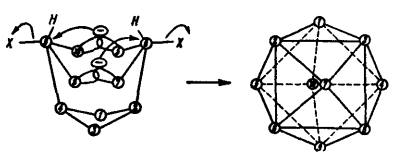
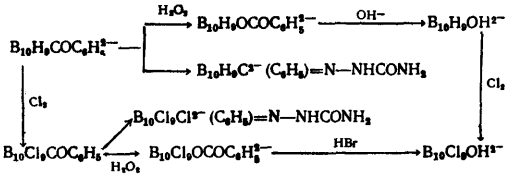


Fig. 5. Mechanism of formation of the $B_{10}H_{10}^{2-}$ anion from bis(acetonitrile)decaborane.

Benzoyl chloride reacts with $B_{10}H_{10}(H_3O)_2$, giving the anion $B_{10}H_9COC_6H_5^{2-}$, which takes part in various reactions[90]:



Amides react with the anion in acid medium, for example:

$$B_{10}H_{10}^{2-} \xrightarrow[[H^+]]{HCON(CH_3)_2} B_{10}H_9^{2-}OCHO + B_{10}H_9N^{2-}.$$

$B_{10}H_{10}^{2-}$ also reacts with donor compounds oxygen- and sulphur-containing compounds. The acid $B_{10}H_{10}(H_3O)_2$ hydroborates styrene. Furthermore the anion reacts with dimethyl sulphoxide:

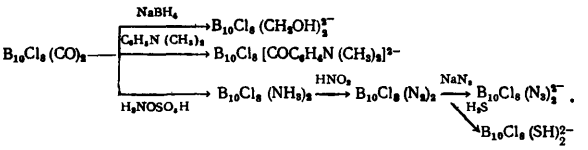
$$B_{10}H_{10}^{2-} + 2(CH_3)_2SO \rightarrow B_{10}H_8[S(CH_3)_2]_2 + H_2O.$$

The mechanism of this reaction is obviously electrophilic under the conditions of an electrophilic reaction; the $S(CH_3)_2$ group occupies the vertex positions (according to the nuclear magnetic resonance spectra). Under these conditions deuteration also takes place at the vertex atoms.

In the treatment of the $B_{10}H_{10}^{2-}$ anion with a large excess of aqueous nitrous acid with subsequent reduction of the precipitate formed, using sodium tetrahydroborate in methanol, a diazonium derivative is formed, $B_{10}H_8(N_2)_2$.[94] The action on this of amines, nitriles, ammonia, and carbon monoxide at 115–140°C releases nitrogen and gives the corresponding $B_{10}H_8L_2$. On carrying out the reaction with carbon monoxide in the presence of cyclohexane, $C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$ are formed. This reaction proceeds by a free radical mechanism. The carbonyl derivative $B_{10}H_8(CO)_2$ exhibits very interesting chemical properties:

$$B_{10}H_8(CO)_2 + \begin{cases} 2CH_3OH \rightleftarrows (H^+)_2B_{10}H_8(COOCH_3)_2^{2-} \\ 4NH_3 \rightarrow (NH_4^+)_2B_{10}H_8(CONH_2)_2^{2-} \\ LiAlH_4 \rightarrow B_{10}H_8(CH_3)_2^{2-} \\ NaN_3 \rightarrow B_{10}H_8(NCO)_2^{2-} \\ H_2O + H_2NOSO_3H \rightarrow B_{10}H_8(NH_3)_2 + 2CO_2. \end{cases}$$

On heating above 300° the caesium salt $Cs_2B_{10}H_8(CONH_2)_2$ is dehydrated to $Cs_2B_{10}H_8(CN)_2$. On halogenating $B_{10}H_8(CO)_2$ in water, $B_{10}Cl_8(CO)_2$ and $B_{10}Br_8(CO)_2$ are obtained. The octachloro-derivatives undergo the following reactions:



In the oxidation of the $B_{10}H_{10}^{2-}$ anion, two new anions of the same composition, but different structure (A and B), ($B_{20}H_{18}^{2-}$) were obtained. The first anion (A) was obtained by oxidation of the triethylammonium salt of $B_{10}H_{10}^{2-}$ by the Fe^{3+} ion in aqueous solution[95]. The second anion (B) was obtained by oxidation of the triethylammonium salt of $B_{10}H_{10}^{2-}$ with a cold aqueous solution of Ce^{4+}.[96] Study of the

nuclear magnetic resonance spectra of the freshly prepared anions showed that they consist of two unchanged polyhedra of the $B_{10}H_{10}^{2-}$ initial ion joined to one another by hydrogen bridge atoms.

Because ion B is quantitatively converted into ion A in an aqueous solution containing catalytic amounts of hydrochloric acid, it is thought that ion B is formed as the result of attack by the Ce^{4+} ion on the more negative vertex atoms of the initial anion. The authors [96] think that the acid catalysis of the isomerisation of B into A takes place without rupture of the bridging bonds by the simple migration of the polyhedra relative to one another.

After passing an ethanol solution of the triethylammonium salt of A through an acid ion-exchange resin, evaporating off the ethanol, and adding water to an ethereal solution of the residue, rapid hydrolysis, accompanied by liberation of hydrogen, is observed [95]. As a result, a new hydride, stable in air was obtained, $B_{18}H_{22}$, acting as a strong acid and containing bridge and terminal hydrogen bonds (according to the infrared spectra).

There is a very interesting reaction between the triethylammonium salt of $B_{10}H_{10}^{2-}$ and nitrogen oxides [97]. By oxidation of the salt with nitrogen dioxide in aqueous acetonitrile or by nitrogen monoxide in the presence of Fe^{3+} the compound $B_{14}H_{12}NO[NH(C_2H_5)_3]_2$ was obtained, and by passing NO_2 into 10% aqueous acetonitrile solution of the initial substance, two other such compounds, $B_{10}H_6(NO)_2N(CH_3)_4$ and $B_{10}H_4(NO)_3N(CH_3)_4$, were isolated. The NO group here is reduced to the NH_2 group by Raney nickel.

It is obvious that the study of the properties of the $B_{10}H_{10}^{2-}$ anion undertaken in recent years — like the study of the properties of decaborane, other higher hydrides, and other anions — is only the start of a larger investigation, judging from the quite interesting and unexpected discoveries in the field of polyhedral molecules having a main skeleton of boron atoms.

11. CARBORANES

In the middle of 1962, Onak and coworkers reported [98] that pentaborane(9) reacts with alkynes (propyne, butyne, and pentyne) in the presence of 2,6-dimethylpyridine, giving compounds with the general formula $B_4C_nH_{2n+4}$:

$$B_5H_9 + R{-}C{\equiv}C{-}R_1 + \text{2,6-dimethylpyridine} \rightarrow$$
$$\rightarrow B_4H_6C_2RR_1 + \text{2,6-dimethylpyridine.}BH_3$$

Side reactions include the cleavage of pentaborane with the formation of two moles of amine.BH_3 complex and $(BH)_x$ polymer.

The proton and ^{11}B spectra of the class of compounds obtained agree with the structure shown in Fig. 6.

The high-field doublet of the ^{11}B nuclear magnetic resonance spectrum is reminiscent of the same doublet, which corresponds to the vertex atom in hexaborane. The low-field doublet corresponds to the boron atoms in hexaborane lying in the base. However, in view of the fact that this doublet is split in the proportion 2 : 1, the non-equivalence of the boron atoms lying at the base of the structure of the compounds obtained is confirmed.

The proton spectrum consists of two overlapping quadruplets in the ratio 3 : 1 (a vertex proton and three lying in the base) and an unresolved multiplet, corresponding to the bridge hydrogens.

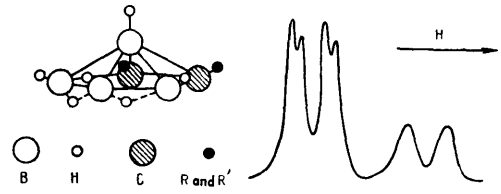


Fig. 6. Structure and ^{11}B nuclear magnetic resonance spectrum of dihydrocarborane(4),

Shapiro and coworkers [99] isolated $B_3C_2H_5$ from the mixture of products obtained by repeated circulation of an equimolecular mixture of pentaborane(9) and acetylene through a silent discharge apparatus (15 kV) at room temperature. The substance obtained (m.p. -126.4°, b.p.-3.7°C) is stable in air and unchanged on contact with acetone, trimethylamine, CO_2, and water at room temperature.

A study of the deuterium exchange of this compound with B_2D_6 showed that only three of the hydrogen atoms bound to boron atoms exchange with deuterium.

The infrared spectrum of $B_3C_2H_5$ shows a highly symmetrical molecule (the band in the 2800–3300 cm^{-1} region, belonging to the C–H bonds, is absent). The spectrum includes bands corresponding to the stretching vibrations of the terminal B–H bonds (but not B–H–B bridges), stretching vibrations of B–B bonds (in the 780 cm^{-1} region) and B–C bonds (in the 1000–1100 cm^{-1} region). The proton nuclear magnetic resonance spectrum suggests the existence in the molecule of two types of proton: those attached to carbon atoms (singlet) and those attached to equivalent boron atoms (quadruplet). The ^{11}B nuclear magnetic resonance spectrum shows a single type of boron atom (single doublet).

The information obtained suggests [98] a trigonal bipyramid as the most probable structure of the $B_3C_2H_5$ molecule, in which all the boron atoms lie in a single plane and the carbon atoms are perpendicular to it.

The compounds of the general formula $B_nC_2H_{2n+2}$ were named carboranes. It was suggested [100] that the polyhedral molecules of the carboranes constitute a superaromatic system, since they satisfy the requirements of the existing theory of aromaticity.

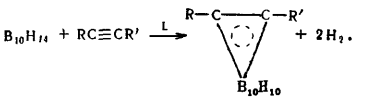
On the basis of the attractive LCAO–MO calculations, great stability was predicted for this class of compound and an ability to participate in electrophilic and nucleophilic substitutions. However, the position of the most electropositive and electronegative atoms could not be found from the calculations.

In view of the stability of the well-known icosahedral ion $B_{12}H_{12}^{2-}$, which is isostructural with the proposed carborane $B_{10}H_{12}C_2$, it was suggested that the latter should exist and might contain three normal σ bonds and ten three-centre bonds in the skeleton, analogous to $B_{12}H_{12}^{2-}$. Possible models for intramolecular migrations of the boron atoms in $B_{10}H_{12}C_2$ through an intermediate cuboctahedral structure were considered [101].

Three groups of investigators recently published communications about the synthesis of $B_{10}H_{12}C_2$ and many of its derivatives (saturated and unsaturated hydrocarbons,

halogenoalkyl compounds, alcohols, acids and their derivatives, amines, ketones, ethers, etc.)[102-106]. The first member of the series $B_{10}H_{10}C_2H_2$, was named barene by Soviet chemists, carborane-10 by the Americans.

Barene and its derivatives were synthesised by the reaction of decaborane with acetylenic compounds in the presence of certain Lewis bases, which form with decaborane the $B_{10}H_{12}L_2$ complexes described above:

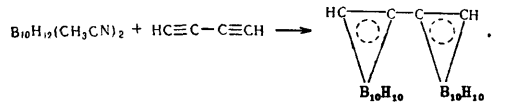


It has been shown[102] that the reaction takes place in two stages: first decaborane and the Lewis base give the complex $B_{10}H_{12}L_2$, which then reacts with the acetylene compound:

$$B_{10}H_{14} + 2L \rightarrow B_{10}H_{12}L_2 + H_2;$$

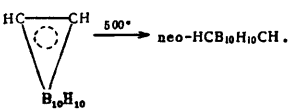
$$B_{10}H_{12}L_2 + RC{\equiv}CR' \rightarrow B_{10}H_{10}C_2RR' + H_2 + 2L.$$

Previously prepared complexes can be introduced into the reaction for the preparation of barenes. CH_3CN, $(C_2H_5)_2S$, $(C_2H_5)_3As$, $HCON(CH_3)_2$, $CH_3CON(CH_3)_2$, and $C_6H_5N(CH_3)_2$ are among the catalysts which have been used. A bisbarenyl compound has also been obtained[107]:



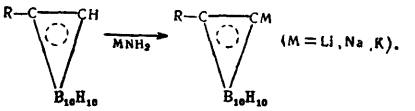
In the formation of a barene (carborane) from $B_{10}H_{12}L_2$ and acetylene a molecule of hydrogen is liberated[103] from the two bridge hydrogen atoms in $B_{10}H_{12}L_2$ – between $B_{(5)}$ and $B_{(10)}$, $B_{(7)}$ and $B_{(8)}$. The structure of the barenes has still not been finally established. A study of their structure using the example of di(bromomethyl)barene by X-ray diffraction showed that the decaborane structure is mainly retained[108]. From X-ray diffraction studies of *B*-octachlorobarene[109], $B_{10}H_2Cl_8C_2H_2$, obtained by chlorinating barene with ultraviolet irradiation, a structure close to icosahedral has been proposed (the isoelectronic structure of a right icosahedron of the dianion $B_{12}H_{12}^{2-}$). The C–C distance is 1.68 ± 0.02 Å and each carbon atom of the nucleus is bound by two three-electron bonds with four neighbouring boron atoms. Isomers of barene were also obtained.

Neocarborane was obtained[110] by heating barene at 465–500°C:

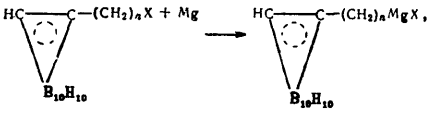


The structure of this isomer has also not been finally established. From studies of the ^{11}B nuclear magnetic resonance spectrum of neo-$B_{10}Cl_{10}C_2H_2$ it was suggested[111] that neocarborane has an icosahedral structure with carbon atoms in a "meta"-position (not bound with one another), as Lipscomb had already proposed[101]. On heating neocarborane at 615°C for 17 h, another isomer was isolated, termed "para"-carborane (it was suggested that the carbon atoms in it are in a "para"-position in the icosahedral structure)[112].

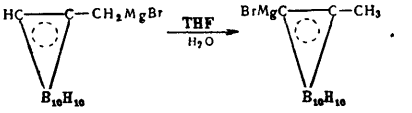
Barene has great thermal stability and is stable to the action of strong acids, several oxidants, and bases. The characteristic property of the barene nucleus is its electron-acceptor behaviour, which has a great effect on the chemical properties of barene compounds. It was shown that the barene nucleus deactivates a double bond towards addition reactions, inhibits nucleophilic substitutions at halogenomethyl derivatives, makes possible metallation at C–H, increases the strength of barenecarboxylic acids, etc.[103,113,114]. Many reactions of barene and its derivatives have been studied. It has been found that barene and its monosubstituted derivatives are metallated at a carbon of the nucleus by the action of alkyllithiums[115,116], sodium amide in boiling toluene[117], and alkali metal amides in liquid ammonia[118]:



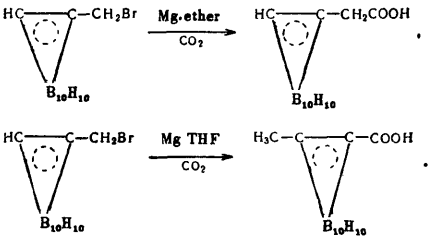
Barene forms both mono- and di-metal derivatives. With magnesium in ether or tetrahydrofuran, the halogenoalkyl derivatives form Grignard reagents[103,104,116]:



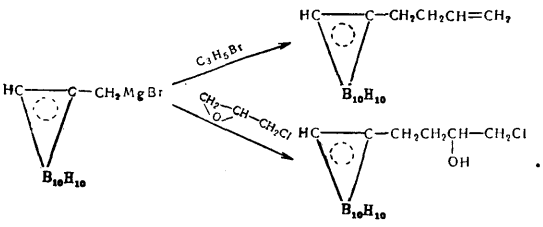
It has been shown that baren-1-ylmethylmagnesium bromide in tetrahydrofuran is isomerised into 1-methylbaren-2-ylmagnesium bromide[114,116]:

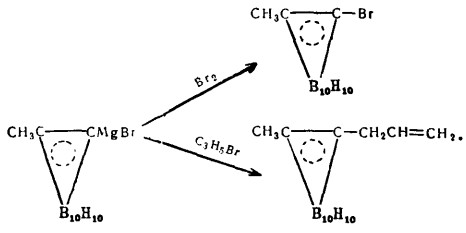


The carbonation of Grignard reagents from barenylmethyl bromide, prepared in either absolute ether or in tetrahydrofuran, has given the difficultly obtainable barenylacetic acid and methylbarenecarboxylic acid, respectively[119]:



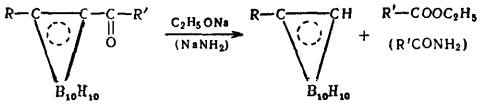
The barene Grignard reagents react with allyl bromide, epichlorhydrin, and bromine in the usual way:





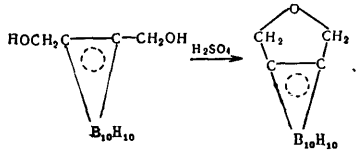
On hydrolysis, these Grignard reagents form alkyl derivatives of barene.

With esters of barenecarboxylic and barenedicarboxylic acids and barenyl phenyl ketones, it was shown that by the action of sodium ethoxide in absolute alcohol and sodium amide in liquid ammonia, rupture of the C–C bond takes place, because of the strong electron acceptor influence of the barene nucleus on the one hand and of the carbonyl group on the other [120,121]:

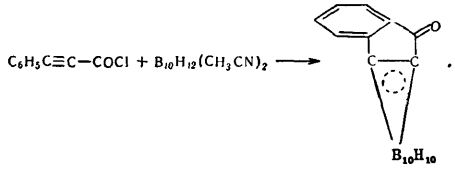


where R = H, CH_3, COOH; R′ = OC_2H_5, C_6H_5, NH_2.

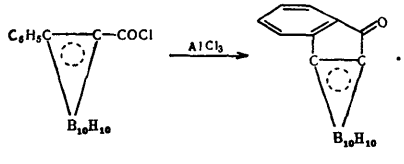
An interesting property of disubstituted barenes is their ease of cyclisation into three-membered exo-rings. When di(hydroxymethyl)barene is heated with sulphuric acid, a cyclic ether is readily formed [114,116]:



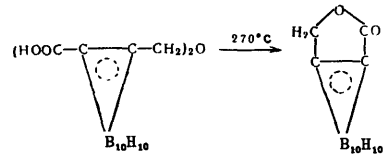
In the reaction of phenylpropynoyl chloride with bis(acetonitrile)decaborane, a cyclic ketone is smoothly formed [122]:



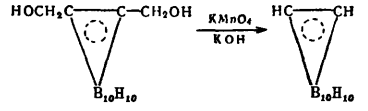
This same ketone is obtained from phenylbarenylcarbonyl chloride by the action of aluminium chloride:



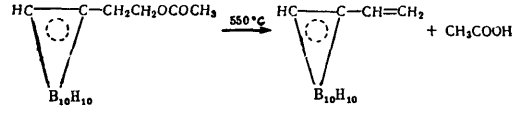
There is an interesting reaction when dicarboxylic acids are heated [123]:



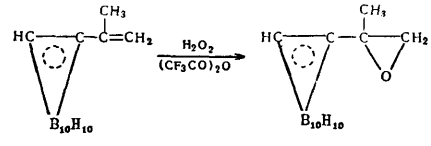
When alcohols of the barene series are oxidised in acid or alkaline media, acids of the barene series are obtained. Di(hydroxymethyl)barene and hydroxymethylbarene are exceptions, which form barene when oxidised by alkaline permanganate [103,114]:



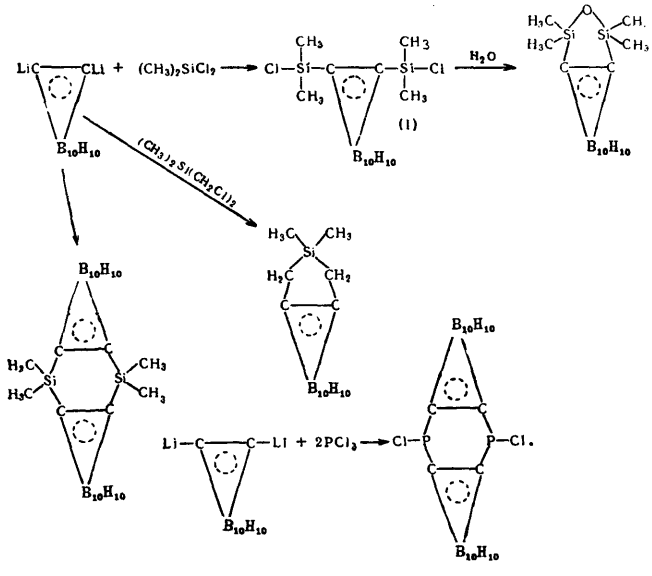
When the acetates of the barene alcohols are heated above 500°C, acetic acid is lost, and unsaturated compounds are obtained [116]:



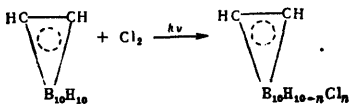
The action of peroxy-acids on the unsaturated compounds yields the corresponding oxides [104,116]:



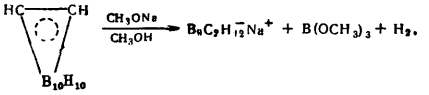
Several organoelemental compounds of the barene series have been prepared from the lithium derivatives: those of phosphorus, silicon, tin, and mercury [116,124,125]. The heterocyclic systems containing silicon and phosphorus are interesting [124,125]:



It has been shown that barene [126,127] and phenylbarene [126] are chlorinated under the action of ultraviolet light at the boron atoms, with formation of *B*-chloroderivatives:



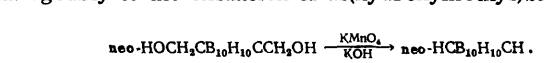
Polyhalogenobarenes from the di- to the decachloro-derivative have been obtained. It is reported [127] that undecachloro-derivative $B_{10}Cl_{10}C_2HCl$ has been made. *B*-Decachlorobarene and phenyl-*B*-decachlorobarene are rather strong acids and dissolve in aqueous alkali solutions [124]. Dodecachlorobarene was obtained by the action of chlorine on the alkali solution of *B*-decachlorobarene [126]. On reaction with alkyl halides in the presence of aluminium chloride, barene compounds are alkylated at boron atoms [128]. The action of strong bases on barenes liberates one mole of hydrogen and forms water-soluble salts of dicarboundecylcarboranes [114,129]:



The chemistry of neocarboranes has been studied little, but in their properties they are close to barenes. Metallation occurs by the action of butyllithium [110]:



The lithium derivatives undergo the usual reactions: carboxylation with CO_2, formation of alcohols with aldehydes, alkylation with alkyl halides. The oxidation of di(hydroxymethyl)neocarborane by alkaline permanganate takes place analogously to the oxidation of di(hydroxymethyl)barene:



neo-$B_{10}Cl_{10}C_2H_2$ was obtained by the chlorination of neocarborane under the action of ultraviolet light [111]. The investigation of barene and its derivatives has opened a new, interesting chapter in the chemistry of the organic compounds of boron.

1. A. Stock, "The Hydrides of Boron and Silicon", Cornell University Press, Ithaca, New York, 1933.
2. A. Stock and E. Pohland, Ber., 62, 90 (1929).
3. J. Kasper, C. Lucht, and D. Harker, Acta Cryst., 3, 436 (1950).
4. E. Moore, R. Dickerson, and W. N. Lipscomb, J. Chem. Phys., 27, 209 (1957).
5. W. Eborhardt, B. Crawford, and W. N. Lipscomb, J. Chem. Phys., 22, 989 (1954).
6. E. Moore, L. Lohr, and W. N. Lipscomb, J. Chem. Phys., 35, 1329 (1961).
7. R. Bottei and A. Laubengayer, J. Phys. Chem., 66, 1449 (1962).
8. E. Moore, J. Chem. Phys., 37, 675 (1962).
9. W. N. Lipscomb, J. Chem. Phys., 25, 38 (1956).
10. W. N. Lipscomb, J. Inorg. Nuclear Chem., 11, 1 (1959).
11. G. Guter and R. Schaeffer, J. Amer. Chem. Soc., 78, 3546 (1956).
12. J. Reddy and W. N. Lipscomb, J. Amer. Chem. Soc., 81, 754 (1959).
13. J. Reddy and W. N. Lipscomb, J. Chem. Phys., 31, 610 (1959).
14. R. Dickerson and W. N. Lipscomb, J. Chem. Phys., 27, 212 (1957).
15. W. N. Lipscomb, J. Phys. Chem., 62, 381 (1958).
16. R. Williams, J. Inorg. Nuclear Chem., 20, 198 (1961).
17. R. Schaeffer, J. Amer. Chem. Soc., 79, 2726 (1957).
18. L. I. Zakharkin, V. I. Stanko, and Yu. A. Chapovskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1118 (1962).
19. J. Shoolery, Discuss. Faraday Soc., No. 19, 215 (1955).
20. R. Schaeffer, J. Shoolery, and R. Jones, J. Amer. Chem. Soc., 79, 4606 (1957).
21. R. Williams and I. Shapiro, J. Chem. Phys., 29, 677 (1958).
22. L. Bellamy and W. Gerrard, J. Chem. Soc., 2412 (1958).
23. I. Shapiro, C. Wilson, and I. Lehman, J. Chem. Phys., 29, 237 (1959).
24. A. Quayle, J. Appl. Chem., 9, 395 (1959).
25. A. Haaland and W. Eberhardt, J. Chem. Phys., 36, 2386 (1962).
26. S. Bauer, J. Amer. Chem. Soc., 80, 294 (1958).
27. M. F. Hawthorne and J. Miller, J. Amer. Chem. Soc., 80, 754 (1958).
28. J. Miller and M. F. Hawthorne, J. Amer. Chem. Soc., 81, 4501 (1959).
29. I. Shapiro, M. Lustig, and R. Williams, J. Amer. Chem. Soc. 81, 838 (1959).
30. J. Dupont and M. F. Hawthorne, J. Amer. Chem. Soc., 84, 1804 (1962).
31. J. Dupont and M. F. Hawthorne, J. Amer. Chem. Soc., 81, 4998 (1959).
32. H. Beachell and B. Dietrich, J. Amer. Chem. Soc., 83, 1347 (1961).
33. R. Schaeffer and F. Tebbe, J. Amer. Chem. Soc., 85, 2020 (1963).
34. H. C. Beachell and J. Haugh, J. Amer. Chem. Soc., 80, 2939 (1958).
35. B. Siegel and J. Mack, J. Phys. Chem., 62, 373 (1958).
36. A. Owen, J. Chem. Soc., 5438 (1961).
37. I. Shapiro and R. Williams, J. Amer. Chem. Soc., 81, 4787 (1959).
38. A. Atteberry, J. Phys. Chem., 62, 1457 (1958).
39. C. Guter and R. Schaeffer, J. Amer. Chem. Soc., 78, 3546 (1956).
40. H. C. Beachell and T. R. Meeker, J. Amer. Chem. Soc., 78, 1796 (1956).
41. H. C. Beachell and W. Schar, J. Amer. Chem. Soc., 80, 2943 (1958).
42. L. I. Zakharkin, V. I. Stanko, and O. Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2083 (1961).
43. A. Atteberry, J. Phys. Chem., 62, 1458 (1958).
44. J. Griffiths and R. Williams, Chem. and Ind., 655 (1959).
45. M. F. Hawthorne, J. Amer. Chem. Soc., 80 3480 (1958).
46. M. F. Hawthorne, A. Pitochelly, J. Miller, and R. Strahm, J. Amer. Chem. Soc., 82, 1825 (1960).
47. B. Siegel, J. Mack, and J. Gallaghan, J. Amer. Chem. Soc., 80, 4523 (1958).
48. I. Dunstan, N. Blay, and R. Williams, J. Chem. Soc., 5016 (1960).
49. J. Gallaghan and B. Siegel, J. Amer. Chem. Soc., 81, 504 (1959).
50. E. Gryszkiewicz-Trochimowski, J. Maurel, and O. Gryszkiewicz-Trochimowski, Bull. Soc. chim. France, 1953 (1959).
51. R. Palchak, J. Norman, and R. Williams, J. Amer. Chem. Soc., 83, 3380 (1961).
52. N. Blay, R. Pace, and R. Williams, J. Chem. Soc., 3416 (1962).
53. M. F. Hawthorne and J. Miller, J. Amer. Chem. Soc., 82, 500 (1960).
54. H. Schroeder, Inorg. Chem., 2, 390 (1963).
55. W. Phillips, H. Miller, and E. Muetterties, J. Amer. Chem.

Soc., 81, 4500 (1959).
56. S. Fitch and A. Laubengayer, J. Amer. Chem. Soc., 80, 5911 (1958).
57. L. Burkardt and N. Fetter, Chem. and Ind., 1191 (1959).
58. H. Beachell and D. Hoffman, J. Amer. Chem. Soc., 84, 180 (1962).
59. D. Hill and E. Gipson, Analyt. Chem., 28, 133 (1956).
60. R. Schaeffer, J. Amer. Chem. Soc., 79, 1006 (1957).
61. J. Dunstan and J. Griffiths, J. Chem. Soc., 1344 (1962).
62. M. F. Hawthorne and A. Pitochelly, J Amer. Chem. Soc., 80, 6685 (1958).
63. R. Pace, J. Williams, and R. Williams, J. Chem. Soc., 2196 (1961).
64. W. Knoth and E. L. Muetterties, J. Inorg. Nuclear Chem., 20, 66 (1961).
65. L. I. Zakharkin and V. I. Stanko, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2078 (1961).
66. V. I. Stanko, A. I. Klimova, and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 919 (1962).
67. H. Schroeder, I. R. Reiner, and T. L. Heying, Inorg Chem., 1, 618 (1962).
68. H. Schroeder, I. R. Reiner, and T. A. Knowles, Inorg. Chem., 2, 393 (1963).
69. M. F. Hawthorne and A. Pitochelly, J. Amer. Chem. Soc., 82, 3228 (1960).
70. V. Aftandilian, H. Miller, and E. L. Muetterties, J. Amer. Chem. Soc., 83, 2471 (1961).
71. E. L. Muetterties, Inorg. Chem., 2, 647 (1963).
72. R. Adams, A. Siedle, and J. Grant, Inorg. Chem., 3, 461 (1964).
73. B. Graybill and M. Hawthorne, J. Amer. Chem. Soc., 83 2673 (1961).
74. M. F. Hawthorne and A. Pitochelly, J. Amer. Chem. Soc., 81, 5519 (1959).
75. T. L. Heying and C. Naar-Colin, Inorg. Chem., 3, 282 (1964).
76. M. Hawthorne, B. Graybill, and A. Pitochelly, Angew. Chem., 73, 79 (1961).
77. I. Dunstan, R. Williams, and N. Blay, J. Chem. Soc., 5012 (1960).
78. R. Schaeffer, J. Shoolery, and R. Jones, J. Amer. Chem. Soc., 80, 2670 (1958).
79. M. Hillman, J. Amer. Chem. Soc., 82, 1096 (1960).
80. R. Williams, I. Dunstan, and N. Blay, J. Chem. Soc., 5006 (1960).
81. N. Blay, I. Dunstan, and R. Williams, J. Chem. Soc., 430 (1960).
82. N. Blay, I. Williams, and R. Williams, J. Chem. Soc., 424 (1960).
83. C. Pearl, U. S. P. 2 977 391; Chem. Abs., 55, 153 499 (1961).
84. I. Neff and E. Wandel, U. S. P. 2 987 552 (1961); Chem. Abs., 56, 14 078a (1962).
85. E. Altwicker, A. Garrett, E. Weilmuckster, and S. Harres, U. S. P. 2 999 117 (1961); Chem. Abs., 56, 1478i (1962).
86. W. N. Lipscomb, A. Pitochelly, and M. F. Hawthorne, J. Amer. Chem. Soc., 81, 5833 (1959).
87. R. Dobrott and W. N. Lipscomb, J. Chem. Phys., 37, 1779 (1962).
88. R. Hoffman and W. N. Lipscomb, J. Chem. Phys., 37, 520 (1962).
89. A. Pitochelly, R. Ettinger, J. Dupont, and M. F. Hawthorne, J. Amer. Chem. Soc., 84, 1057 (1962).
90. W. Knoth, H. Miller, D. England, G. Parshall, and E. L. Muetterties, J. Amer. Chem. Soc., 84, 1056 (1962).
91. W. Knoth, H. Miller, J. Sauer, J. Balthis, and J. Chia, Inorg. Chem., 3, 159 (1964).
92. J. Forstner, T. Haas, and E. L. Muetterties, Inorg. Chem., 3, 155 (1964).
93. E. L. Muetterties, J. Balthis, J. Chia, W. Knoth, and H. Miller, Inorg. Chem., 3, 444 (1964).
94. W. Knoth, J. Sauer, H. Miller, and E. L. Muetterties, J. Amer. Chem. Soc., 86, 115 (1964).
95. A. Pitochelly and M. F. Hawthorne, J. Amer. Chem. Soc., 84, 3218 (1962).
96. A. Pitochelly, W. N. Lipscomb, and M. F. Hawthorne, J. Amer. Chem. Soc., 84, 3026 (1962).
97. R. Wiesboeck, A. Pitochelly, and M. F. Hawthorne, J. Amer. Chem. Soc., 83, 4108 (1961).
98. T. Onak, A. Williams, and H. Weiss, J. Amer. Chem. Soc., 84, 2830 (1962).
99. I. Shapiro, C. D. Good, and R. E. Williams, J. Amer. Chem. Soc., 84, 3837 (1962).
100. R. Hoffman and W. N. Lipscomb, J. Chem. Phys., 36, 3489 (1962).
101. R. Hoffman and W. N. Lipscomb, Inorg. Chem., 2, 231 (1963).
102. L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, and O. Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim., 2238 (1963).
103. L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, A. I. Klimova, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSR, 155, 1119 (1964).
104. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. Cohen, Inorg. Chem., 2, 1111 (1963).
105. M. Fein, D. Grafstein, J. Paustian, J. Bobinski, B. Lichstein, N. Mayes, N. Schwartz, and M. Cohen, Inorg. Chem., 2, 1115 (1963).
106. T. L. Heying, J. W. Ager, S. L. Clark, D. Mangold, H. Goldstein, M. Hillman, R. Polak, and J. Szymarski, Inorg. Chem., 2, 1089 (1963).
107. J. Dupont and M. F. Hawthorne, J. Amer. Chem. Soc., 86, 1643 (1964).
108. L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., 2069 (1963).
109. J. Potenza and W. N. Lipscomb, J. Amer. Chem. Soc., 86, 1874 (1964).
110. D. Grafstein and J. Dvorak, Inorg. Chem., 2, 1128 (1963).
111. H. Schroeder and G. Vickers, Inorg. Chem., 2, 1317 (1963).
112. S. Papetti and T. L. Heying, J. Amer. Chem. Soc., 86, 2295 (1964).
113. L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, and Yu. A. Chapovskii, Dokl. Akad. Nauk SSSR, 157, 1149 (1964).
114. D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. Cohen, and M. Fein, Inorg. Chem., 2, 1120 (1963).
115. L. I. Zakharkin, V. I. Stanko, A. I. Klimova, and Yu. A. Chapovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2236 (1963).
116. T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. Reid, and S. Trotz, Inorg. Chem., 2, 1097 (1963).
117. L. I. Zakharkin, V. I. Stanko, and Yu. A. Chapovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 582 (1964).
118. L. I. Zakharkin, Tetrahedron Letters, 2252 (1964).
119. V. I. Stanko, Zhur. Obshch. Khim., No. 7, 35 (1965).
120. L. I. Zakharkin and Yu. A. Chapovskii, Tetrahedron Letters, 1147 (1964).
121. V. I. Stanko and A. I. Klimova, Zhur. Obshch. Khim., 35 732 (1965).
122. L. I. Zakharkin, V. I. Stanko, and Yu. A. Chapovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 943 (1964).
123. D. Grafstein, J. Bobinski, J. Dvorak, J. Paustian, H. Smith, S. Kaplan, C. Vogel, and M. Fein, Inorg. Chem., 2, 1125 (1963).
124. L. I. Zakharkin, V. I. Bregadze, and O. Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim., 1539 (1964).
125. S. Papetti and T. L. Heying, Inorg. Chem., 2, 1105 (1963); R. Alexander and H. Schroeder, *ibid.*, 2, 771 (1963).

126. L. I. Zakharkin, V. I. Stanko, and A. I. Klimova, Izd. Akad. Nauk SSSR, Ser. Khim., 771 (1964).
127. H. Schroeder, T. L. Heying, and J. Reiner, Inorg. Chem., 2, 1092 (1963).
128. S. Clark and D. Mangold, U. S. P. 3 092 664; Chem. Abs., 57, 11 555h (1963).
129. R. Wiesboeck and M. F. Hawthorne, J. Amer. Chem. Soc., 86, 1642 (1964).

Institute of Organoelemental Compounds, Academy of Sciences of the USSR

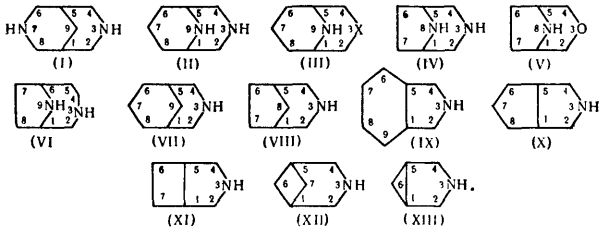
U. D. C. 547.748

SYNTHETIC DIAZA- AND AZA-BICYCLIC SYSTEMS WITH NON-BRIDGEHEAD NITROGEN ATOMS

M. V. Rubtsov and E. S. Nikitskaya

Introduction

Recently a large number of papers have been published on the chemical and biological studies of synthetic diaza- and aza-bicyclic systems with non-bridgehead nitrogen atoms. According to their chemical structure, these bicyclic systems may be divided into the following groups:

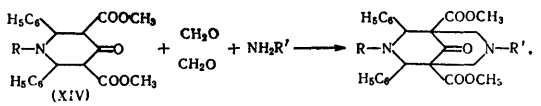


Aza- and diaza-bicyclic compounds are very interesting pharmacologically, since many of them exhibit biological activity and may be used for the investigation and preparation of new drugs. In this connection it appeared useful to give a systematic account of work dealing with the methods of synthesis of the above bicyclic systems, their chemical properties, and pharmacological activity. The present article does not include natural compounds of the tropane series and their synthetic derivatives, since a number of reviews dealing with them already exist[1-4].

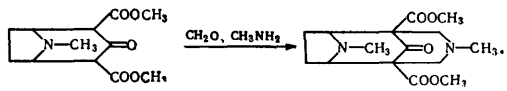
3,7-Diazabicyclo[3,3,1]nonane (I)

The derivatives of 3,7-diazabicyclo[3,3,1] nonane can be divided into two subgroups: 9-oxo-3,7-diazabicyclo[3,3,1]-nonanes or bispidones and the 3,7-diazabicyclo[3,3,1]nonanes themselves or bispidines. The methods available for the preparation of the two subgroups are different; bispidines cannot be obtained from bispidones.

Bispidones. Derivatives of 9-oxo-3,7-diazabicyclo-[3,3,1]nonane were first synthesised by Mannich and Mohs[5] by the condensation of substituted piperidonedicarboxylic ester (XIV) with formaldehyde and primary amines:

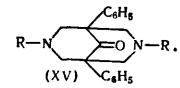


Compound (XIV) was obtained by the reaction of acetonedicarboxylic ester with the appropriate aldehyde and alkylamines[6-8]. The bicyclic system forms very readily at room temperature in aqueous alcoholic medium with a yield of 60–70%. By choosing appropriate derivatives of piperidine and alkylamines, it is possible to obtain easily various bispidones[9]†. Under these conditions the dimethyl ester of tropinonedicarboxylic acid yields a tricyclic system — the dimethyl ester of 6,8-ethylene-3,7-dimethyl-9--oxo-3,7-diazabicyclo[3,3,1]nonane-1,5-dicarboxylic acid:

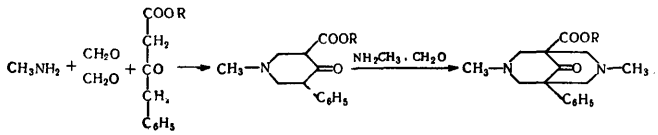


When an attempt was made to prepare a substituted γ-piperidone by the condensation of diphenylacetone, formaldehyde, and ammonia, the sole product isolated was 9-oxo-1,5-diphenyl-3,7-diazabicyclo[3,3,1]nonane[12].

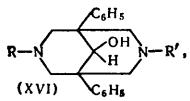
By using various alkylamines in the reaction with diphenylacetone, the authors of these investigations obtained a nunber of bispidone derivatives with the general formula (XV), where R = CH_3CO, CH_3, n-C_2H_7, $C_6H_5CH_2$, $HOCH_2CH_2$, and $ClCH_2CH_2$.



Similar results were obtained also by other workers[13], who allowed γ-phenylacetoacetic ester to react with methylamine and formaldehyde and instead of the expected product (3,5-dialkoxycarbonylphenyl-*N*-methylpiperidone), obtained bispidone derivatives, which are the products of the further interaction of the piperidone with formaldehyde and the amine:



Numerous bispidone derivatives with the general formula (XVI) have been obtained by Chiavarelli and coworkers[14,15] by the condensation of diphenylacetone with formaldehyde and alkylamines followed by reduction of the ketones to alcohols with lithium aluminium hydride:



where R = R′ = C_2H_5, iso-C_3H_7, n-C_4H_9, CH_3, H, $ClCH_2CO$, R_2NCH_2CO, etc.

† A similar reaction[10] has been carried out with pyran derivatives[11]:

