constant for eq. 6. The term $[Q^+ \ i\text{-}PrO^-]$ can be replaced by an equilibrium constant times the product of the concentrations of free quaternary ammonium ion and isopropoxide ion, but again this would be a mechanism requiring participation by not one, but two, free ions and in $CCl_4$ a mechanism involving an associated species is far more plausible.

Because Allen and Modena[4] had attributed catalysis to chloride ion, an attempt was made to fit the data by replacing the last term of eq. 4 with $kCA\,[Cl^-]$, and because their observed catalytic rate constants were in fact linear in total salt concentration rather than in ion concentration a term $kCAS$ was also tried, but in neither case could an acceptable fit be obtained.

Comparison of our findings with those of Allen and Modena[4] relative to catalysis by HCl in the absence of added salt is impossible, because we find that the rate at very short times is entirely dependent on the small amount of HCl initially present, while Allen and Modena determine rates at zero time and take no account of the possibility of impurity HCl being present. Our observations suggest that such rate constants must be meaningless without knowledge of the initial HCl concentrations.

From our own studies we can conclude with reasonable certainty that there is little or no uncatalyzed reaction in $CCl_4$ between $(C_6H_5)_3SiCl$ and 2-propanol, that the significant HCl catalysis is due to an associated species and not to free ions, and that the apparent catalysis by benzyltriethylammonium chloride results from uncatalyzed attack by an associated quaternary ammonium isopropoxide species on the $(C_6H_5)_3SiCl$.

These conclusions, initially somewhat surprising, are in fact quite reasonable. Failure to observe catalysis by $H^+$ or $Cl^-$ may be attributed simply to the extremely low concentrations of the free ions, while catalysis by HCl, which must be similar in nature to that which might be predicted for $H^+$ or $Cl^-$, is measurable because of the very much greater concentration of HCl. The direct reaction between $(C_6H_5)_3SiCl$ and

the quaternary ammonium isopropoxide, with no equivalent reaction for the alcohol, is explained by the fact that charge separation in $(Q^+ \ i\text{-}PrO^-)$ is very much greater than in $i\text{-}PrOH$. The salt species, even though associated, is then a much stronger nucleophile than the alcohol.

In a case where three species are involved in the rate equation, as in the HCl-catalyzed path described here, it is far more reasonable to accommodate the observation by postulating an intermediate comprising at least two of the species than by requiring a three-body reaction. In the present case the most probable intermediate involves pentacovalent silicon, possibly as shown in structure I.

$$\begin{array}{c} H_5C_6 \qquad C_6H_5 \\ \diagdown \quad \diagup \\ RO-\underset{|}{\overset{|}{Si}}-Cl \\ I \quad H \quad C_6H_5 \end{array}$$
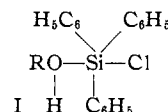
The fact that no reaction is observed in the absence of HCl suggests that the Si–Cl bond is stronger than the Si–O bond in the intermediate. The function of the HCl is then to aid in strengthening the Si–O bond relative to the Si–Cl bond. This may be done through hydrogen-bond formation with either the Cl or the hydroxyl H of I, although the latter possibility is not overly attractive when one considers that the solvent offers far more opportunities for similar interactions and $CCl_4$ is not a sufficient catalyst to effect reaction.

The preliminary formation of an intermediate hydrogen-bonded species $(C_6H_5)_3SiCl. . .HCl$ does not seem nearly as probable as the type represented by **I**, since the great excess of solvent $CCl_4$ competing with $(C_6H_5)_3\,SiCl$ for the limited supply of HCl argues against any significant lifetime for such an intermediate and the mechanism would then not differ significantly from a three-body collision.

In view of these arguments, we conclude that our observations are best rationalized through an intermediate containing pentavalent silicon.

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## The Carborane Series: $B_nC_2H_{n+2}$. II. The Two Isomers of $B_4C_2H_6$

By I. Shapiro,[1] B. Keilin, Robert E. Williams, and C. David Good

Two isomers of carborane-4, $B_4C_2H_6$, have been isolated, and their structures deduced from the nuclear magnetic resonance, infrared, and mass spectral analyses of isotopic variants of the compounds. Some of the physical and chemical properties of the more stable carborane-4, $sym\text{-}B_4C_2H_6$, are given.

The carborane series of compounds have been prepared from the reaction of acetylene with boron hydrides. The simplest member of the series, $B_3C_2H_5$, has already been discussed.[2] The isomers of carborane-4 were prepared from the reaction of pentaborane and acetylene in a silent discharge tube. When these same reactants are confined under pressure at elevated temperatures, the product is another organoboron compound, $B_4C_2H_8$,[3] which differs structurally[4] from the

carboranes. Data on other carboranes and their derivatives will be published later.

### Experimental

**Materials.**—The isotopic variants of acetylene and pentaborane have been described previously.[2]

**Apparatus.**—The apparatus used to prepare and analyze the isomers of carborane-4 are the same as described for carborane-3.[2]

**Procedure.**—Although carborane-4 can be prepared by the high-temperature reaction of acetylene with diborane or pentaborane at low pressures, it was found more convenient to prepare the carboranes by use of the silent discharge apparatus.[2] An equimolar mixture of pentaborane-9 and acetylene (25 mmoles) was circulated through the silent discharge apparatus (15 kv.) for 1 hr. at ambient temperature (the temperature of the reactor increased noticeably during the course of the experiment). During this time, the total pressure of the system gradually decreased, and a light yellow-brown deposit formed on the walls of the reactor. After the high-voltage discharge was discontinued, the condensable products were transferred to a fractionation train in the high vacuum apparatus. Inasmuch as the quantity of volatile product from any one experiment was low, this pro-

(1) Universal Chemical Systems, Inc., Culver City, Calif.

(2) I. Shapiro C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(3) I. Shapiro and H. G. Weiss, experimental work performed 1953–1957, and declassified Nov. 5, 1962; I. Shapiro, paper presented at the XIX Meeting of the International Union of Pure and Applied Chemistry, London, July, 1963.

(4) Attention is called that the structure of $B_4C_2H_8$ cited recently[5] was taken from the previous work[3] without permission or acknowledgment of the senior investigator.

(5) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).
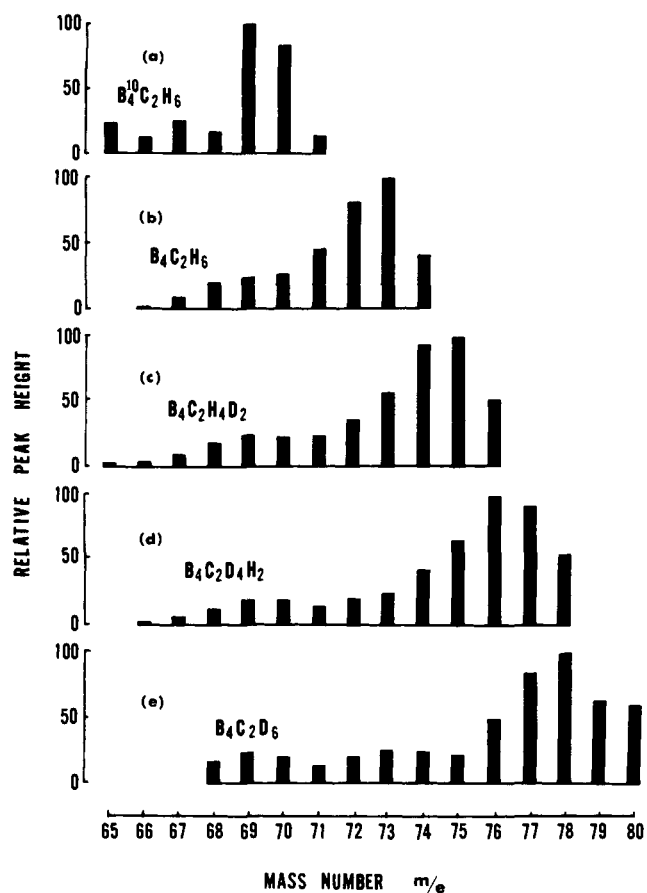
Fig. 1.—Comparison of parent groupings in mass spectra of isotopic variants of sym-carborane-4.

was observed; when a mixture of the two carborane-4 was heated, the sym-carborane-4 appeared to be the more stable form.

## Results

**Spectral Analysis.  Mass Spectra.**—The parent grouping in the mass spectra of the various isotopic species of $B_4C_2H_6$ is illustrated in Fig. 1 and the complete polyisotopic mass spectrum of $sym$-$B_4C_2H_6$ is given in Table I.  The isotopic transformation[6] of the $B^{10}$-enriched spectrum (Fig. 1a) to an isotopically-normal spectrum (Fig. 1b) reveals that the compound contains four boron atoms with a sharp cutoff corresponding to the $B_4C_2H_6{}^+$ species.

TABLE I

POLYISOTOPIC MASS SPECTRUM OF ISOTOPICALLY-NORMAL $sym$-CARBORANE-4 ADJUSTED FOR $m/e$ 73 AT 100 UNITS

| $m/e$ | Peak ht. | $m/e$ | Peak ht. | $m/e$ | Peak ht. |
|---|---|---|---|---|---|
| 12 | 4.8 | 35.5 | 2.8 | 56 | 1.5 |
| 13 | 4.1 | 36 | 15.7 | 57 | 3.6 |
| 14 | 0.5 | 36.5 | 0.5 | 58 | 5.6 |
| .. | ... | 37 | 17.1 | 59 | 5.3 |
| 21 | 0.2 | 38 | 0.4 | 60 | 3.6 |
| 22 | .5 | 39 | 0.3 | 61 | 2.3 |
| 23 | .6 | .. | ... | 62 | 0.6 |
| 24 | 1.1 | 42 | 0.2 | .. | ... |
| 25 | 1.5 | 43 | .4 | 65 | 0.3 |
| 26 | 1.1 | 44 | .5 | 66 | 2.0 |
| 27 | 0.5 | 45 | 1.1 | 67 | 8.6 |
| 28 | 2.3 | 46 | 2.1 | 68 | 19.7 |
| 29 | 0.3 | 47 | 3.0 | 69 | 25.0 |
| .. | ... | 48 | 2.6 | 70 | 25.6 |
| 32 | 0.9 | 49 | 2.8 | 71 | 45.9 |
| 33 | 0.6 | 50 | 5.2 | 72 | 81.3 |
| 34 | 2.3 | 51 | 0.4 | 73 | *100* |
| 34.5 | 0.4 | .. | ... | 74 | 41.7 |
| 35 | 7.0 | 55 | 0.5 | 75 | 1.1 |

cedure was repeated several times in order to accumulate sufficient material for separation and analysis.

Infrared analysis of the reaction mixture indicated the most abundant carborane present was $sym$-carborane-4; the chief component of the mixture was unreacted pentaborane. After removal of $B_3C_2H_5$ and other more volatile materials from the mixture by fractionation at $-126°$,[2] the carboranes were separated from the unreacted pentaborane by complexing the latter with triethylamine and subsequently removing the excess amine with diborane.  Since the volatility of pentaborane is similar to those of the desired products, separation by straight fractionation is difficult; however, complexing the pentaborane with amine (and destroying excess amine with the low boiling diborane) changes the volatility range of the compounds and permits separation of carboranes by low temperature fractionation. An example of this method of separation is given below.

After removal of $B_3C_2H_5$ at $-126°$, the remaining material (consisting chiefly of carboranes and pentaborane-9) was condensed in a tube with a small quantity of triethylamine.  On warming this mixture to $-80°$, a vigorous reaction occurred between the amine and pentaborane, forming a liquid of low volatility.  Upon standing for a short time at room temperature, yellow viscous material of uncharacterized nature appeared. The reaction tube was then immersed in liquid nitrogen and any noncondensable material was removed by evacuation.  The products which were volatile at room temperature (carboranes and triethylamine) were then transferred under vacuum to another tube and condensed at $-196°$ with an excess of diborane. On warming to room temperature, reaction occurred, forming a small quantity of a mobile liquid (triethylamineborane). After fractionation at $-80°$ to remove the less volatile triethylamineborane, and at $-150°$ to remove more volatile diborane, the resulting product was shown by infrared analysis to consist chiefly of $sym$-carborane-4 with small quantities of $unsym$-carborane-4, carborane-5, and traces of unknown materials. The addition of triethylamine (about one-fifth the quantity of carboranes) to this mixture and then fractionation several times at $-105°$ resulted in removal of the $unsym$-carborane-4 and carborane-5 from $sym$-carborane-4.  Traces of triethylamine present with $sym$-carborane-4 were removed by treatment with diborane and fractionation.

In several experiments from the silent discharge apparatus a small quantity of $unsym$-carborane-4 was isolated in relatively pure form.  No interconversion of the two forms of carborane-4

That the compound contains at least six hydrogen atoms can be deduced from the shift in 6 mass units upon complete deuteration (Fig. 1e).  From n.m.r. analysis it is concluded that the compound contains only six hydrogen atoms.  In addition, one can learn the source of hydrogen atoms by partial deuteration. The product given by Fig. 1c was prepared from deuterioacetylene and normal pentaborane, that given by Fig. 1d, from normal acetylene and deuteriopentaborane.  The shift of 2 to 4 mass units higher on carbon deuteration and boron deuteration, respectively, indicates that of the six hydrogen atoms, two of them came from the acetylene and four of them from pentaborane.

Comparison of the monoisotopic spectra of the parent groupings in Fig. 1 indicates a difference in the relative fragmentation of B–H and C–H bonds.  The monoisotopic distribution for the isotopically-normal compound is:  $B_4C_2H_6{}^+$, 67.2;  $B_4C_2H_5{}^+$, 100;  $B_4C_2H_4{}^+$, 11.4;  $B_4C_2H_3{}^+$, 24.1;  $B_4C_2H_2{}^+$, 7.9;  $B_4C_2H^+$, 23.9; and $B_4C_2{}^+$, 4.8.  In the case of the completely deuterated compound, the distribution of ion species follows in the same pattern; in neither case can one distinguish the loss of hydrogen or deuterium specifically from either a boron or carbon atom.  However, in the partially deuterated species with the parent species as a basis, one finds that for the carbon-deuterated compound the relative concentration of $B_4C_2H_3D_2{}^+$ (hydrogen fragmentation from boron) is greater than that of $B_4C_2H_4D^+$ (deuterium fragmentation from carbon), and in the boron-deuterated compound the $B_4C_2D_3H_2{}^+$ (deuterium fragmentation from boron) also is greater than $B_4C_2D_4H^+$ (hydrogen fragmentation from carbon).

(6) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D.C., 1961, p. 127.

An inspection of Table I reveals a low degree of destruction of the basic skeletal structure, with the occurrence of symmetrical cleavage into $B_2CH_3{}^+$ fragments being greater than other B–C combination fragments. This low degree of cleavage of basic structure also had been noted in carborane-3.[2]

**Infrared Spectra.**—The infrared absorption spectra of the two isomers of $B_4C_2H_6$ are given in Table II, and the salient features of isotopic variants of the *sym*-carborane-4, in Table III. The single sharp peak occurring in the 2600–2700 cm.$^{-1}$ region is easily recognized as the B–H asymmetric stretching frequency; and in the 2000 cm.$^{-1}$ region, as the B–D asymmetric stretching frequency. There are no bands for any of the compounds that can be attributed to B–H–B bridge groups.

As in the case of carborane-3[2] there are no frequencies which can be assigned to a C–H (or C–D) stretching vibration, even at a gas pressure of 560 mm. in the cell.

<div align="center">

TABLE II

INFRARED ABSORPTION SPECTRUM OF CARBORANE-4

s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad (cm.$^{-1}$)

*sym*-$B_4C_2H_6$

</div>

| | | | |
|---|---|---|---|
| 4241sh | 1926m | 1332m | 1144sh |
| 4181vw | 1912m | 1327m | 1140sh |
| 4097w | 1859vvw | 1318m | 1134vs |
| 4019sh | 1784vvw | 1301m | 1128vs |
| 3798vw | 1757vvw | 1290m | 1121s |
| 3634w | 1742sh | 1280m | 1115sh |
| 3497w | 1732w | 1269m | 1065vw |
| 3374vw | 1716w | 1265sh | 1058vw |
| 3233vw | 1694w | 1253m | 934sh |
| 3107vw | 1678sh | 1247m | 931m |
| 2962vw | 1586w | 1237m | 927sh |
| 2866vw | 1569w | 1192sh | 923m |
| 2667sh | 1518vwb | 1179sh | 912sh |
| 2657vvs | 1479sh | 1176vvs | 757mb |
| 2310vwb | 1469w | 1165vvs | 743m |
| 2151sh | 1462sh | 1157vvs | 730shb |
| 2128w | 1395w | 1154vvs | 726m |
| 1970w | 1340sh | 1147sh | 708wb |

<div align="center">

*unsym*-$B_4C_2H_6$

</div>

| | | | |
|---|---|---|---|
| 2618vs | 1143s | 1004w | 800wb |
| 1386w | 1133s | 990m | 772mb |
| 1309wb | 1127sh | 977w | 756vw |
| 1256w | 1119sh | 943vw | 750w |
| 1217w | 1073vw | 936vw | 743w |
| 1188sh | 1071vw | 928m | 705wb |
| 1174sh | 1053w | 900w | |
| 1149sh | 1036vw | 867w | |

<div align="center">

TABLE III

SALIENT FEATURES OF INFRARED ABSORPTION SPECTRA OF ISOTOPIC VARIANTS OF *sym*-CARBORANE-4

</div>

| $B_4C_2H_4D_2$, cm.$^{-1}$ | $B_4C_2D_4H_2$, cm.$^{-1}$ | $B_4C_2D_6$, cm.$^{-1}$ |
|---|---|---|
| 2667vs | 2020vs | 2008vs |
| 2632sh | 2008sh | 2000sh |
| 1116s | 2000sh | 1976sh |
| 1103s | 1147s | 1064w |
| 868w | 1140s | 1058sh |
| | 730m | 1055s |

**Nuclear Magnetic Resonance Spectra.**—The H¹ and B¹¹ n.m.r. spectra of isotopically-normal *sym*-$B_4C_2H_6$ are given in Fig. 2. As in the case of carborane-3,[2] the proton spectrum (Fig. 2a) reveals that the protons exist in two distinct environments—some protons connected to identical carbon atoms (single large peak) and others
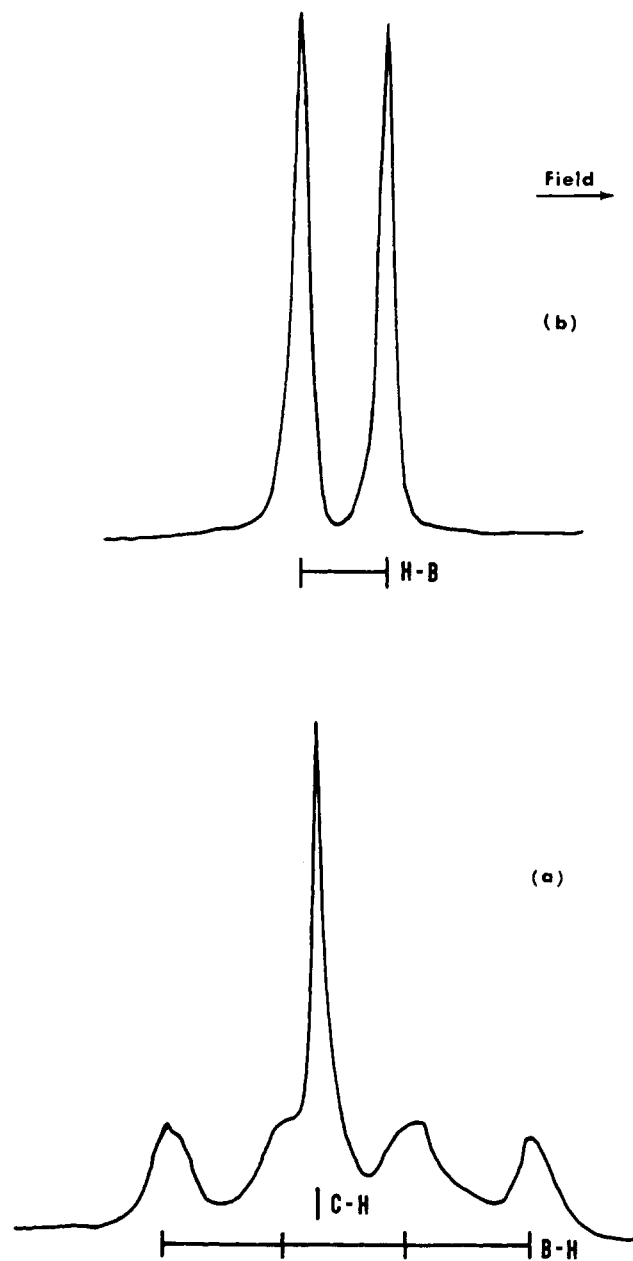




Fig. 2.—N.m.r. spectra of *sym*-carborane-4: (a) H¹ spectrum, 40 Mc.; (b) B¹¹ spectrum, 12.8 Mc.

connected to identical boron atoms (quartet peaks). The proton spectrum also indicates absence of bridge hydrogens.

The doublet of the B¹¹ spectrum (Fig. 2b) demonstrates that all boron atoms are spectroscopically equivalent and that there is only one proton attached to each boron atom. The extreme sharpness of the boron spectrum indicates that the field gradient about each boron atom is nearly zero. The spin-coupling value is 188 c.p.s. and the chemical shift value is approximately 19 based on $BF_3 \cdot O(C_2H_5)_2$ as zero reference.[7] By comparison, the corresponding values for $B_3C_2H_5$ are: $J = 184$ c.p.s. and $\delta \sim -1$.

The H¹ and B¹¹ n.m.r. spectra of the *unsym*-$B_4C_2H_6$ are given in Fig. 3. The proton spectrum (Fig. 3a) shows the familiar characteristics of a single large peak assigned to C–H and a quartet of peaks assigned to B–H. However, in this case, the difference in contour of the quartet peaks leads one to speculate that the quartet actually represents two overlapping quartets

(7) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).
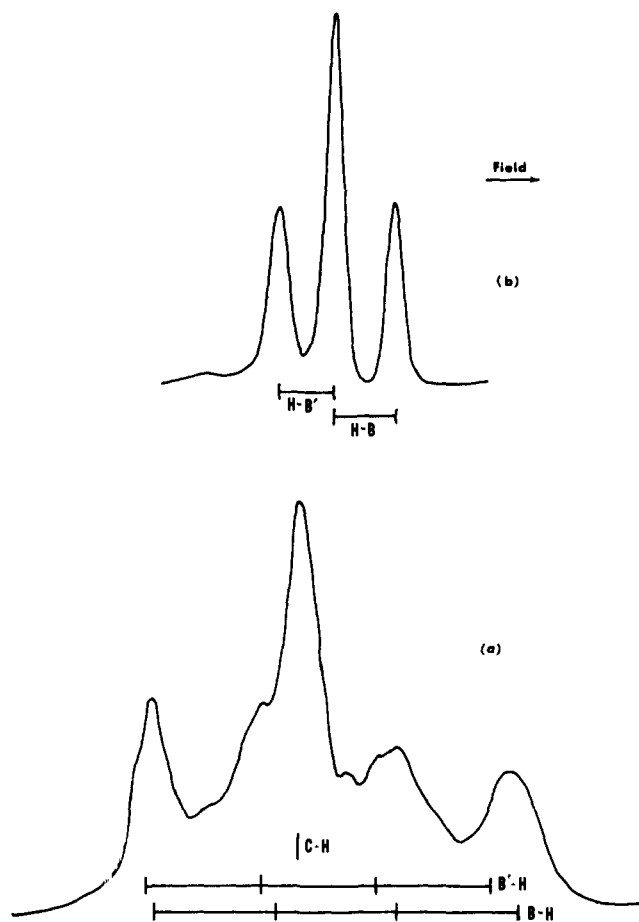
Fig. 3.—N.m.r. spectra of unsym-carborane-4: (a) H$^1$ spectrum, 40 Mc.; (b) B$^{11}$ spectrum, 12.8 Mc.

#### TABLE IV
##### VAPOR PRESSURE OF sym-CARBORANE-4

| Temp., °C. | V.p., mm. | | Dev., mm. |
|---|---|---|---|
| | Obsd. | Calcd. | |
| | Solid | | |
| -82.97 | 1.05 | 1.02 | -0.03 |
| -80.47 | 1.39 | 1.33 | - .06 |
| -64.24 | 6.22 | 6.20 | - .02 |
| -64.23 | 6.17 | 6.21 | + .04 |
| -57.67 | 10.55 | 10.71 | + .16 |
| -46.86 | 24.29 | 24.30 | + .01 |
| -42.51 | 32.95 | 32.93 | - .02 |
| -42.36 | 33.10 | 33.26 | + .16 |
| -40.41 | 38.17 | 37.94 | - .23 |
| -32.63 | 62.52 | 62.53 | + .01 |
| | | Av. dev. | 0.074 |
| | Liquid | | |
| -32.63 | 62.52 | 63.35 | +0.8 |
| -31.65 | 68.00 | 67.07 | - .9 |
| -22.84 | 108.4 | 108.3 | - .1 |
| -17.12 | 146.3 | 144.9 | -1.4 |
| + 0.05 | 316.6 | 318.3 | +1.7 |
| 5.01 | 391.4 | 391.0 | -0.4 |
| 11.13 | 499.3 | 497.8 | -1.5 |
| 14.49 | 564.1 | 565.3 | +1.2 |
| | | Av. dev. | 1.0 |

whose spacings are displaced as shown in Fig. 3a. Such an interpretation would be in agreement with the interpretation of the B$^{11}$ spectrum shown in Fig. 3b. Here the apparent triplet is considered to be the co-incidental overlap of two doublets since there is a slight difference in spacings of the two end peaks from the center peak. The high-field doublet has an apparent value of $J$ of 187 c.p.s.; the low-field doublet, an apparent $J$-value of 174 c.p.s.

**Physical Properties. Vapor Pressure.**—The vapor pressure of sym-carborane-4 was measured over the temperature range of −83 to +15° and is reported in Table IV. The solid has an appreciable vapor pressure which can be expressed by the equation

$$\log P_{mm} = 11.1324 - 1896.94/T - 0.006021T \text{ (solid)}$$

The vapor pressure of the liquid can be expressed by the equation

$$\log P_{mm} = 9.7513 - 1676.40/T - 0.004068T \text{ (liquid)}$$

**Boiling Point.**—Extrapolation of the vapor pressure data to one atmosphere pressure gives a normal boiling point of 22.7°.

**Melting Point.**—Attempts to determine the melting point by means of Stock's ring method were unsuccessful. Visual observation of the melting point gave a value of −32.63 ± 0.05°. Simultaneous solution of the vapor pressure equations for the solid and liquid gives a value of −29.5°. This discrepancy of 3.1° is attributed to the combination of deviations in measurement and the small difference in slopes of the two vapor pressure equations.

**Heat of Vaporization.**—The molar heat of vaporization at the normal boiling point, calculated from the Clausius–Clapeyron equation, is 6042 cal./mole. Trouton's constant is 20.4 cal./deg. mole, a value consistent

with those usually obtained for unassociated compounds.

**Chemical Properties. Stability.**—Storage of pure sym-carborane-4 at room temperature over a period of 6 months resulted in no detectable decomposition.

**Reactivity.**—sym-Carborane-4 has been in contact with acetone, trimethylamine, triethylamine, ammonia, air, and water at room temperature without noticeable reaction.

The hydrogen atoms attached to the boron in sym-carborane-4 will undergo H–D exchange with deuterio-diborane at room temperature, but the rate of exchange is less rapid than in the case of carborane-3.

#### Discussion

Two carborane-4 compounds have been isolated. From the information derived from mass and n.m.r. spectra, the stable compound contains two identical C–H units and four identical B–H units. The mass fragmentation pattern of the compound also point to a symmetrical compound. The most probable structure of the molecule appears to be a tetragonal bipyramid, i.e., four boron atoms and their hydrogens in one plane with one carbon and its hydrogen on each side of the boron plane such that the line joining the two carbon atoms will pass through the center of the square formed by the four boron atoms. Such a structure would indicate high symmetry and stability of the molecule and account for its volatility, which is greater than comparable boranes or straight-chain hydrocarbons. Because of its symmetrical structure, this compound will be referred to as sym-carborane-4.

The exchange of one carbon atom with any one of the four boron atoms in the above structure should result in the formation of an isomer of sym-carborane-4. The n.m.r. spectrum of the second carborane-4 fits such a structure. Each of two boron atoms will be neighboring two carbon atoms and two boron atoms, and each of the other two boron atoms will be neighboring one carbon atom and three boron atoms, thus accounting for two identical C–H units and two pairs of B–H units, each pair differing from the other pair. This compound is less stable than its isomer and is termed "unsym-carborane-4."

In both compounds each carbon atom appears to have five ligands instead of the customary four ligands. To circumvent this anomally, the concept of carbon participating in the so-called "three-centered bonds" with two boron atoms is accepted. In this connection the two carbon atoms can be visualized as substituting for two boron atoms, but with two additional electrons, thus forming the equivalent stable octahedral $B_6H_6^{-2}$ ion.[8] It already has been suggested[9] that carborane-3 ($B_3C_2H_5$) may be isoelectronic with $B_5H_5^{-2}$. The structure postulated for $B_3C_2H_5{}^2$ is indeed that pictured for $B_5H_5^{-2}$.[9]

(8) W. H. Eberhardt, B. Crawford, and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(9) E. B. Moore, L. L. Lohr, and W. N. Lipscomb, *ibid.*, **35**, 1329 (1961).

The apparent lack of hydrogen exchange between boron and carbon hydrogens permit the preparation of specifically labeled isotopic compounds. Although the hydrogens originally attached to the carbon and boron atoms in the parent compounds are retained in their same relative environment in the new compounds, the mechanism of formation of the new compounds must be complex since at least the carbon atoms in acetylene must undergo drastic rearrangement in the $sym$-$B_4C_2H_6$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY, AMES, IOWA]

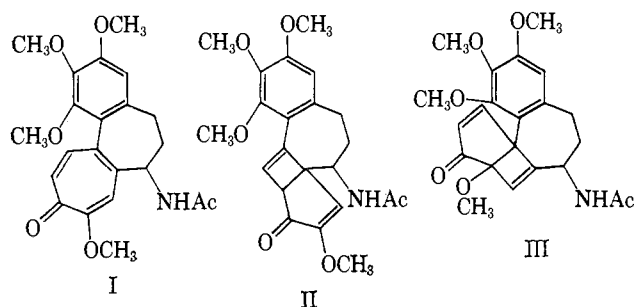# Photoisomerization of Isocolchicine[1]

BY O. L. CHAPMAN, H. G. SMITH, AND P. A. BARKS[2]

Irradiation of isocolchicine in aqueous solution gives a photoisomer which is shown to be II. The mode of photochemical valence tautomerization appears to be controlled by electronic factors. The controlling factor in this case appears to be preservation of a trimethoxystyryl unit.

The difference in mode of photochemical valence tautomerization of colchicine[3–5] and simple tropolone methyl ethers[6,7] can be interpreted as a result of steric control in the colchicine photoisomerization and electronic control in the case of simple tropolone ethers.[8] Isocolchicine (I) poses an interesting problem in this light. There is little steric basis for preference for either gross structure II or III for the valence tautomer; consequently the photoisomerization of isocolchicine should be dominated by electronic factors.



I

II

III

Irradiation of isocolchicine in aqueous solution gives a photoisomer (5.85, 6.01 $\mu$; 218 (4.42) and 260 m$\mu$ (log $\epsilon$ 4.34)) in 40–50% yield. The ultraviolet absorption of the photoisomer is similar to that of $\beta$-lumicolchicine[3,4] and $\gamma$-lumicolchicine,[3,4] suggesting that the molecule contains a trimethoxystyryl chromophore. Structure III does not contain a styryl chromophore, and thus structure II is favored by the ultraviolet absorption. The nuclear magnetic resonance spec-

(1) Part IX of the Photochemical Transformation Series.

(2) Petroleum Research Fund Fellow, 1960–1962. Du Pont Teaching Fellow, 1962–1963.

(3) E. J. Forbes. *J. Chem. Soc.*, 3864 (1955).

(4) P. D. Gardner, R. L. Brandon, and G. R. Haynes, *J. Am. Chem. Soc.*, **79**, 6334 (1957).

(5) O. L. Chapman, H. G. Smith, and R. W. King, *ibid.*, **85**, 803, 806 (1963).

(6) O. L. Chapman and D. J. Pasto, *ibid.*, **82**, 3642 (1960).

(7) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *ibid.*, **83**, 1768 (1961).

(8) O. L. Chapman, Chapter in "Advances in Photochemistry," Vol. 1, edited by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., John Wiley and Sons, Inc., New York, N. Y., in press.

trum (Table I) of the photoisomer is also in accord with structure II. The two olefinic protons overlap giving a two proton signal at 3.65 $\tau$. It can be demonstrated that this two proton singlet arises from chemically nonequivalent protons by use of pyridine as solvent. The nuclear magnetic resonance spectrum of II in pyridine (Table I) shows three singlet absorptions due to the aromatic proton and the two olefinic protons now rendered magnetically nonequivalent by the specific shielding effect of pyridine. The highly specific shifts of the various proton resonance positions in pyridine offers additional support[5] for Slomp's suggestion[9] that the shielding effect of pyridine is due to attachment of solvent molecules at specific sites on the solute rather than a bulk solvent effect. The remaining proton assignments are straightforward and are given in Table I.

Reduction of II with sodium borohydride gives an enol ether alcohol (6.02 $\mu$, amide; 6.09 $\mu$, C=C—OCH$_3$) which proved to be very sensitive. The nuclear magnetic resonance spectrum of IV (Table I) shows the aromatic proton and both olefinic protons clearly separated. The shift of one olefinic proton to high field (5.24 $\tau$) identifies it as the enol ether vinyl proton. The bridgehead proton (6.67 $\tau$) is coupled to both the proton on the carbon bearing the hydroxyl group (5.32 $\tau$, $J = 9.4$ c.p.s.) and to the adjacent cyclobutene proton ($J = 0.86$ c.p.s.). The identity of this latter coupling has been confirmed by a double resonance experiment.[10,11] Irradiation of the bridgehead proton 173 c.p.s. upfield from the cyclobutene proton collapsed the cyclobutene proton to a singlet. The small value for this coupling constant is normal for this system in which the coupling constant falls in the range 0–1 c.p.s.[12] Mild acid hydrolysis of IV gives the keto alcohol V. The infrared carbonyl absorption (5.71 $\mu$) of the keto alcohol confirms the presence of a five-membered ring in the photoisomer II. The keto alcohol shows the expected ultraviolet absorption for

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