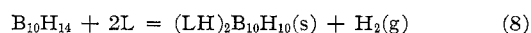


The direct closure of decaborane is promoted by bases, such as amines<sup>3</sup> and sulfides<sup>1</sup> in nonaqueous media



The standard free energy change for such cage closure depends on the nature of the base and the solvent used. From the free energy data for decaborane and the decahydrodecaborate ion we can derive a general expression for the free energy change accompanying cage closure

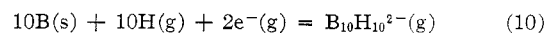
$$\Delta G^\circ_{298} = 24 - 1.36(2pK_a + pK_{sp}) \quad (9)$$

where  $pK_a$  takes into account the base strength of the closing agent and  $pK_{sp}$  is the solubility product of the resulting salt in a given solvent. It would appear that, were it not for interference from side reactions such as hydrolysis, any moderate to strong base could be used to close the decaborane cage in water and in a wide range of polar organic solvents. For example, even though  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{10}\text{H}_{10}$  is quite soluble in water ( $pK_{sp} \approx 0$ ), triethylamine ( $pK_a = 10.8$ ) should be capable of closing the cage in water. Use of weakly polar or nonpolar solvents, such as toluene and benzene, in which salts of the polyhedral ion are only sparingly soluble, provides extra advantage by making the  $pK_{sp}$  very large.

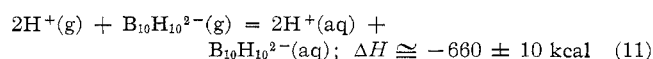
Even though none of the reactions described by eq 5-8 can be carried out in water, the calculated free energy decrease is in each case large enough to assure that the processes would be favorable in any medium; in other words, free energy changes involving solubilities or changes of solvent will not be large enough to vitiate qualitative conclusions based on our calculations. It may also be remarked that our qualitative conclusions could be changed only by very large alterations in the accepted thermodynamic properties of the sub-

stances taking part in reaction 1. For example, the most recent and reliable figure for the enthalpy of formation of the permanganate ion<sup>8</sup> differs from the NBS value<sup>4</sup> by 6 kcal mol<sup>-1</sup>, which corresponds to a difference of no less than 84 kcal mol<sup>-1</sup> in the enthalpy of formation of  $\text{B}_{10}\text{H}_{10}^{2-}(\text{aq})$ , but the resulting shift of about 0.09 V in the related oxidation potentials would not alter the order of stability of the boron hydrides involved.

Finally, it is interesting to estimate the hydration enthalpy of the decahydrodecaborate ion. With the aid of the semiempirical bond-energy additive scheme used earlier,<sup>11-13</sup> the enthalpy change for the reaction



is found to be -1924 kcal, while the theoretical<sup>10</sup> electronic energy referred to decaborane gives  $(-2078.7)(636.1/681.5) = -1940$  kcal. Using our experimental value for the enthalpy of formation of  $\text{B}_{10}\text{H}_{10}^{2-}(\text{aq})$ , we then obtain



so that the single-ion enthalpy of hydration on the usual basis<sup>26</sup> is about -140 kcal mol<sup>-1</sup> for the decahydrodecaborate ion. In the Born equation, which should be useful for such a large ion, this corresponds to an effective ion radius of about 4.5 Å, in pleasant accord with the figure we used earlier in estimating the ionic entropy.

**Acknowledgment.**—We wish to thank the Air Force Office of Scientific Research for the support of this project. We are also indebted to Professor Loren Heppler for information regarding the best current thermodynamic data for manganese compounds.

(26) See, for example, C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. 1, Oxford University Press, London, 1965, pp 160-162.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
ST. LOUIS UNIVERSITY, ST. LOUIS, MISSOURI 63103

## The Synthesis and Reactions of 1,2-(2'-Substituted 1',3',2'-Dithiabora)-*o*-carboranes<sup>1</sup>

BY HAMPTON D. SMITH, JR., AND LEO F. HOHNSTEDT

Received August 30, 1967

1,2-Bis(mercapto)-*o*-carborane reacts with a variety of boranes including diborane and alkyl-, aryl-, chloro-, and aminoboranes to produce 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes. Reaction with trichloroborane in a 1:1 mole ratio gives a good yield of 1,2-(2'-chloro-1',3',2'-dithiabora)-*o*-carborane, some reactions of which are reported. Reaction of 1,2-bis(mercapto)-*o*-carborane with trichloroborane in a 2:1 mole ratio gives what appears to be a novel ring system in which boron is tetracoordinated by sulfur.

### Introduction

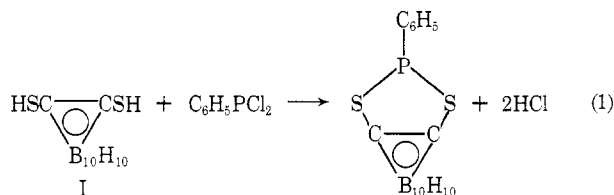
The derivative chemistry of dicarbaclovododecaborane(12) has recently been extended to include mer-

capto derivatives of both the *ortho* and *meta* isomers.<sup>2</sup> The divalent sulfur atoms are bonded to the carbon atoms of the carborane nucleus. The lability of the

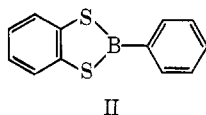
(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; (b) taken in part from the M.S. Thesis of H. D. Smith, Jr., St. Louis University, 1966.

(2) H. D. Smith, Jr., C. O. Obenland, and S. Papetti, *Inorg. Chem.*, **5**, 1013 (1966).

sulfur-bonded protons in the *o*-carborane<sup>3</sup> derivative is demonstrated in the reactions of 1,2-bis(mercapto)-*o*-carborane, I, with a number of reagents to give five-membered cyclic systems<sup>2,4</sup> as illustrated in eq 1.

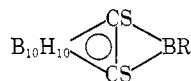


Relatively little work has been done in the area of boron-sulfur chemistry, probably owing to the inherent instability or sensitivity of most known boron-sulfur systems. In 1958 Dewar, *et al.*,<sup>5</sup> prepared an organo-sulfur derivative of boron by treating thiocatechol with phenyldichloroborane. The compound, 2-phenyl-1,3,2-dithianaphthene, II, was reported to be thermally stable



but sensitive to moisture. It is expected that hetero-aromatic systems of this type could provide systems with relatively stable B-S linkages because the boron-containing rings can conceivably be resonance stabilized. The apparent instability of the B-S bond in a variety of noncyclic compounds and cyclic compounds in which only B and S atoms form the ring system may be explicable in terms of ineffective overlap of boron and sulfur orbitals as a result of the large difference in size and energy of the respective orbitals. Alteration of the electronic environment of the sulfur atom by either inductive or conjugative effects should affect the B-S linkage.

In 1,2-bis(mercapto)-*o*-carborane the sulfur atoms are not only attached to a highly electronegative moiety but also constrained in a system of rigid geometry. It was of interest to us to determine what effect these factors would have on the B-S bond in cyclic systems of the type<sup>6</sup>

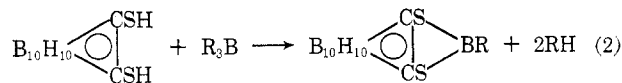


if they could be prepared. This paper discusses the reaction of 1,2-bis(mercapto)-*o*-carborane with a variety of boranes to produce a number of 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes and reports some of the reactions of these new compounds.

### Results and Discussion

Triphenyl- and tributylborane reacted readily with 1,2-bis(mercapto)-*o*-carborane, in the absence of sol-

vents, at temperatures in the neighborhood of 250° to form the cyclic compounds 1,2-(2'-phenyl-1',3',2'-dithiabora)-*o*-carborane, III, and 1,2-(2'-butyl-1',3',2'-dithiabora)-*o*-carborane, IV, respectively, according to



Exposure of these new boron-sulfur heterocycles to the atmosphere resulted in the immediate cleavage of the B-S bonds with the formation of phenyl- or butylboronic anhydride and 1,2-bis(mercapto)-*o*-carborane.

When triethylborane was heated with 1,2-bis(mercapto)-*o*-carborane for up to 24 hr, no reaction occurred until a few drops of acetonitrile were added, at which time a vigorous evolution of ethane occurred. The desired product, 1,2-(2'-ethyl-1',3',2'-dithiabora)-*o*-carborane, V, was obtained in approximately 40% yield on vacuum distillation of the reaction mixture.

When the reaction between triethylborane and 1,2-bis(mercapto)-*o*-carborane was run using nitrobenzene as the solvent, a vigorous reaction occurred when the temperature of the reaction mixture reached 150°. The reaction was immediately quenched using a -80° bath and after removal of the nitrobenzene at 80° (0.6 mm), the desired product was obtained as a colorless liquid boiling at 60° (0.1 mm). On standing at room temperature under vacuum, the liquid solidified forming colorless, well-defined crystals.

It seemed probable that the reaction of I with boranes should proceed *via* a two-step process and that the monosubstituted intermediate should be isolable. It was noticed that in the case of triphenyl- and tributylborane, approximately half the theoretical amount of hydrocarbon was evolved over a short temperature range after the initial reaction temperature had been reached. In order to complete the reaction, it was necessary to raise the temperature approximately 20°. However, we were unable to isolate the suspected intermediates. Even when I reacted with di-*n*-butylchloroborane at relatively low temperatures, the gas evolved at the very beginning of the reaction consisted of a mixture of hydrocarbons and HCl. Separation of the mixture in the reaction vessel after stopping the reaction gave di-*n*-butylchloroborane, 1,2-(2'-butyl-1',3',2'-dithiabora)-*o*-carborane, and I. The 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes appear to be thermally stable on distillation or sublimation and on standing at room temperature. However, the postulated intermediates, if formed, apparently are unstable with respect to formation of exocyclic ring systems under the reaction conditions employed in the studies which form the basis of this report, except perhaps in the case of the ethyl derivative. The ease of formation of the exocyclic system from reaction of the corresponding triborane and 1,2-bis(mercapto)-*o*-carborane in the case of the phenyl- and butylboranes as opposed to the ethyl compound is believed to be due to the higher temperatures obtainable by refluxing the phenyl- and butylboranes. Although no attempt was made to determine

(3) For brevity the term *o*-carborane is used throughout this paper for 1,2-dicarbacyclododecaborane(12).

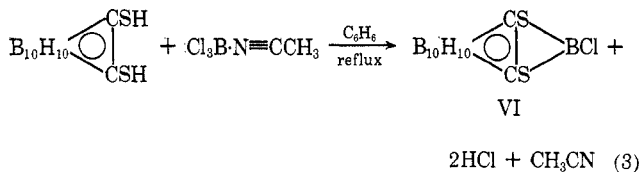
(4) H. D. Smith, Jr., M. A. Robinson, and S. Papetti, *Inorg. Chem.*, **6**, 1014 (1967).

(5) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(6) Following the accepted nomenclature usage of *o*-carborane to represent 1,2-dicarbacyclododecaborane(12), we propose that compounds of such structure be named as 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes.

the exact nature of the catalytic effect of acetonitrile or nitrobenzene on the reaction of triethylborane and 1,2-bis(mercapto)-*o*-carborane, coordination of the boron in the borane by these basic reagents could result in a weakening of the B-C bonds and thereby facilitate electrophilic attack at the carbon atom by the acidic hydrogen atoms attached to the sulfur atoms of the mercaptoborane.

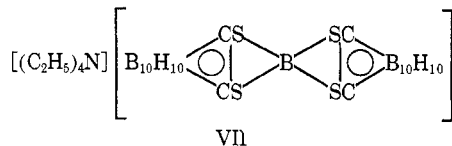
Although no reaction was observed when boron trichloride was bubbled through a hot benzene solution of I, reaction was effected when the acetonitrile complex of boron trichloride was heated with I in benzene



The effect of acetonitrile on the reaction of trichloroborane with the mercaptocarborane may be catalytic but may also be the result of the effective retention of the chloroborane in the hot reaction solvent by complexation with acetonitrile. The acetonitrile complex of trichloroborane can be employed to synthesize B-trichloroborazine under conditions similar to those at which trichloroborane in the absence of acetonitrile will react to form the borazine, but at a much slower effective rate than is achieved using the acetonitrile complex.<sup>7</sup>

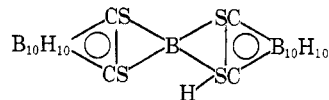
Exposure of VI, 1,2-(2'-chloro-1',3',2'-dithiabora)-*o*-carborane, to the atmosphere resulted in the rapid and complete conversion to the parent mercaptocarborane, boric acid, and HCl. Compound VI reacted with a number of reagents, including silver thiocyanate, primary amines, butyllithium, and phenyl isocyanate.

When the ratio of I to the complex was 2:1 and the reaction conditions were the same as shown by eq 3, a measurement of the HCl evolved indicated 100% elimination of chlorine atoms as HCl. Addition of tetraethylammonium bromide after reaction caused vigorous evolution of hydrogen bromide and precipitation of a compound, the analysis of which corresponded to that expected for the tetraethylammonium salt VII.



Compound VII was not affected by prolonged exposure to air or by contact with boiling water. We are unaware of any other proposed  $\text{BS}_4^-$  systems and, although positive structural proof (X-ray data) has not yet been obtained, in light of the existence of  $\text{BCl}_4^-$  and  $\text{BBr}_4^-$  in salts of heavy cations, it does not seem unlikely that such a compound should exist. Preliminary experiments have shown that 1,2-bis(mercapto)-*o*-carborane and tetraethylammonium bromide do not react un-

der conditions analogous to those employed in the synthesis of VII, and molecular models indicate that four sulfur atoms can accommodate around a boron atom without steric hindrance. The observations and data available suggest that the product, not yet isolated, which reacts as an acid with tetraethylammonium bromide is



in which coordination to boron of the one remaining mercapto sulfur atom weakens the S-H bond sufficiently to account for the observed acidic behavior not exhibited by bis(mercapto)-*o*-carborane.

The  $\text{B}^{11}$  nmr spectra of IV and VII were obtained.<sup>8</sup> The observed chemical shift for VII was  $-4.9$  ppm relative to trimethyl borate while that of IV was  $-54.1$  ppm, in the range reported for other  $\text{B}(\text{SR})_2$  and  $\text{B}(\text{SR})_3$  systems (Table I).

TABLE I  
CHEMICAL SHIFTS OF SOME COMPOUNDS  
CONTAINING B-S BONDS

| Compound                                                                                                                                                                                | Chem shifts, ppm,<br>relative to $\text{B}(\text{OCH}_3)_3$ |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|
| $i\text{-C}_4\text{H}_9\text{B} \begin{array}{c} \text{SCH}_2 \\   \\ \text{SCH}_2 \end{array}$                                                                                         | $-51.9^a$                                                   |
| $n\text{-C}_4\text{H}_9\text{B} \cdot \text{S} \cdot n\text{-C}_4\text{H}_9$                                                                                                            | $-51.3^a$                                                   |
| $\text{B}(\text{S} \cdot n\text{-C}_4\text{H}_9)_3$                                                                                                                                     | $-47.9^a$                                                   |
| $n\text{-C}_4\text{H}_9\text{B} \begin{array}{c} \text{SC} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{SC} \end{array} \text{B}_{10}\text{H}_{10}$<br>IV | $-54.1^b$                                                   |
| VII                                                                                                                                                                                     | $-4.9^b$                                                    |

<sup>a</sup> M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 1345 (1961). <sup>b</sup> Reference 8.

As shown in Table II the trend of shifting upfield in going from  $\text{BX}_3$  to  $\text{BX}_4^-$  is a consistent one. Also, the data suggest that the magnitude of the chemical shift difference between  $\text{B}(\text{SR})_3$  and  $\text{B}(\text{SR}_4)^-$  should be

TABLE II  
CHEMICAL SHIFT DATA FOR  $\text{BX}_3$  vs.  $\text{BX}_4^-$  SYSTEMS

| X              | $\delta\text{BX}_3^a$ | $\delta\text{BX}_4^-^b$ | $\Delta(\delta\text{BX}_4^- - \delta\text{BX}_3)$ |
|----------------|-----------------------|-------------------------|---------------------------------------------------|
| F              | +6.6                  | +19.9                   | 13.3                                              |
| Cl             | -29.2                 | +11.5                   | 40.7                                              |
| Br             | -22.7                 | +42.0                   | 64.7                                              |
| I              | +23.3                 | +146.1                  | 122.8                                             |
| $\text{OCH}_3$ | 0.0                   | +15.2                   | 15.2                                              |

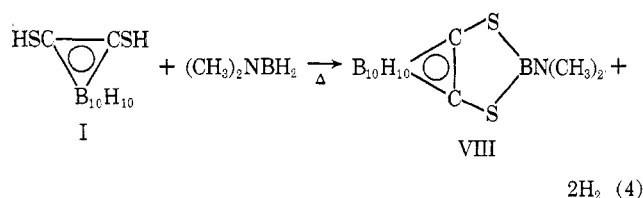
<sup>a</sup> W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). <sup>b</sup> R. J. Thompson and J. C. Davis, Jr., *Inorg. Chem.*, **4**, 1465 (1965).

greater than 15.2 ppm, the difference between  $\text{B}(\text{OCH}_3)_3$  and  $\text{B}(\text{OCH}_3)_4^-$ . As shown in Table II, the magnitude of the differences in chemical shifts increases in the halogen series with increasing size of the atom.

The reactions of two representative aminoboranes with I were investigated. Dimethylaminoborane was

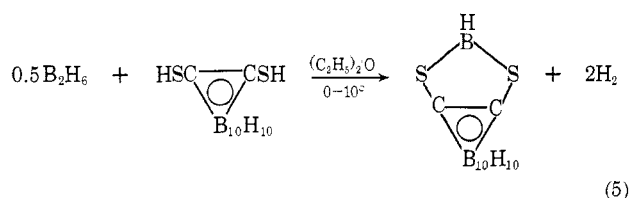
(8) We wish to thank Mr. D. Vickers of the Olin Chemical Corp. for measurement of these  $\text{B}^{11}$  nmr spectra.

chosen to represent aminoboranes with hydrogen on boron while aminodibutylboron represented similar compounds with hydrogen on nitrogen. The dimethylaminoborane reaction (eq 4) quantitatively yielded 1,2-(2'-dimethylamino-1',3',2'-dithiabora)-*o*-carborane, VIII, with elimination of the stoichiometric amount of hydrogen.



Aminodibutylboron reacted with I to form the 2-butyl derivative IV and a red-brown solid residue. An examination of the infrared spectrum of the residue suggested the presence of an ammonium salt of I (bands at 3100 and 1400  $\text{cm}^{-1}$  characteristic of  $\text{NH}_4^+$ ).

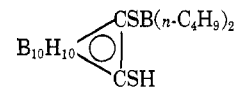
Compound I reacted with diborane in diethyl ether, liberating hydrogen and forming an etherate which evolved ether on warming to 40°. The white product obtained was very sensitive to both air and moisture. Attempts to purify the compound by sublimation and recrystallization resulted in extensive decomposition. From the fact that the expected amount of hydrogen was evolved and an interpretation of the infrared spectrum of the product, it is suggested that the reaction proceeded as in



The infrared spectrum shows the normal B-H stretching and deformation modes of the *o*-carborane nucleus at 2600 and 730  $\text{cm}^{-1}$ , the expected B-H stretch of the single exocycle B-H at 2495  $\text{cm}^{-1}$ , and a strong absorption near 795  $\text{cm}^{-1}$ , characteristic of all of the heterocyclic compounds prepared in this research.

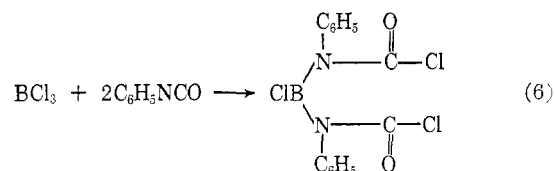
The exocyclic ring structures proposed for the reported 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes are based on the methods of synthesis, analytical data, molecular weight data, and ir spectra. The latter were not analyzed in detail but present no obvious inconsistency with the assigned structures. Molecular weights determined by the vapor pressure depression technique were lower than calculated values, which we attribute to the extreme sensitivity of the compounds to hydrolysis. Mass spectral data substantiated assigned structures for each compound for which such data were obtained. Further support is provided by the synthesis of 1,2-(2'-*n*-butyl-1',3',2'-dithiabora)-*o*-carborane by three methods: the reaction of 1,2-bis(mercapto)-*o*-carborane with tri-*n*-butylborane and with di-*n*-butylchloroborane and the reaction of *n*-butyllithium with 1,2-(2'-chloro-1',3',2'-dithiabora)-*o*-carborane to re-

place the chlorine atom by an *n*-butyl group. The products of the three syntheses differed only in that the product recovered from the butylborane reaction appeared to be contaminated by a slight amount of impurity; ir spectra led us to speculate that the impurity might be the postulated monosubstituted intermediate



but as discussed above, efforts to isolate this or similar intermediates have been unsuccessful so far.

As mentioned previously, VI reacts with phenyl isocyanate. According to Lappert and co-workers<sup>9</sup> phenyldichloroborane and related compounds containing the B-Cl linkage react with isocyanates to form B-N systems as shown in the example



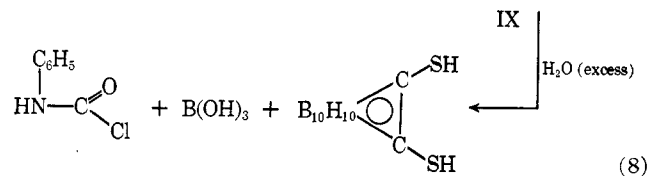
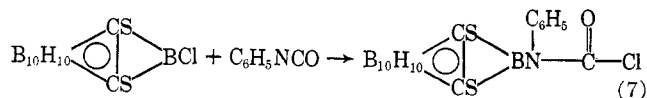
The mechanism by which this reaction proceeds is not known with certainty but is presumed to involve an initial nucleophilic attack on boron by either the oxygen or the nitrogen atoms followed by a rearrangement. Attack by oxygen seems most likely from both steric and electronic considerations.

When equimolar quantities of phenyl isocyanate and VI were mixed in hexane or heptane at room temperature, a white precipitate formed, the infrared spectrum of which indicated that addition to the N=C rather than the C=O bond had occurred. The infrared spectrum also suggested that the cyclic S-B-S system had been altered since the strong band which appears as a doublet between 795 and 775  $\text{cm}^{-1}$  in all of the cyclic compounds reported herein had disappeared.

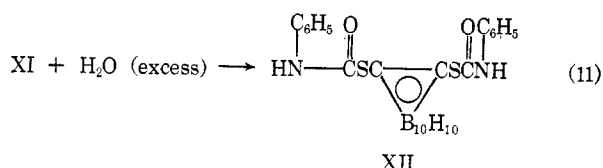
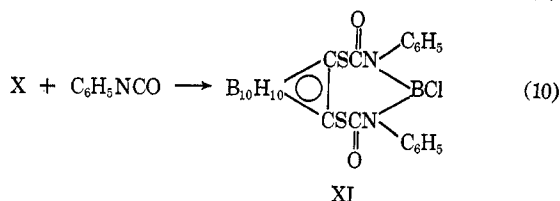
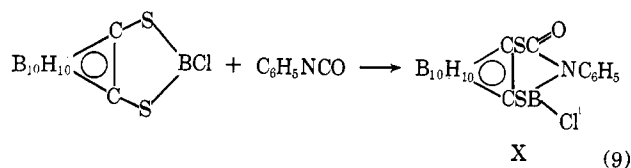
In refluxing hexane or heptane the product obtained exhibited a similar but not identical infrared spectrum. When the reaction was run in refluxing carbon tetrachloride, a clear solution persisted until the system was allowed to cool at which time a crystalline white product precipitated. On reheating the mixture to reflux, it was observed that most of the precipitate would not redissolve, even when additional carbon tetrachloride was added. This product was sensitive to moisture and therefore readily reacted with excess water, yielding a product which melted at 131-132° after one recrystallization from a benzene-hexane mixture. The infrared spectrum of the hydrolysis product indicated the presence of C=O and NH functionalities as well as the normal BH stretching and deformation modes of *o*-carborane. The elemental analysis was in accord with the empirical formula  $\text{C}_8\text{H}_{11}\text{B}_5\text{NSO}$ .

Had the initial reaction between phenyl isocyanate and 1,2-(2'-chloro-1',3',2'-dithiabora)-*o*-carborane proceeded *via* cleavage of the B-Cl bond the resulting com-

pound should have been one which on hydrolysis would yield 1,2-bis(mercapto)-*o*-carborane as indicated by the reactions



Based on the evidence reported above, the suggested reaction sequence is



Note that XII has the molecular formula  $\text{C}_{16}\text{H}_{22}\text{B}_{10}\text{N}_2\text{S}_2\text{O}_2$ , or twice the experimental empirical formula. A subsequent molecular weight determination was in accord with the molecular formula indicated for XII.

These results suggested that other 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes should react in an analogous fashion with phenyl isocyanate. Therefore 1,2-(2'-butyl-1',3',2'-dithiabora)-*o*-carborane was mixed with excess phenyl isocyanate in carbon tetrachloride at room temperature. Hydrolysis of the resulting mixture and recrystallization of the water-insoluble precipitate from a benzene-hexane mixture afforded XII as anticipated.

### Experimental Section

**Materials.**—All solvents used in this research were purified and dried according to standard methods as outlined by Vogel.<sup>10</sup>

All other reagents were used as received from the various commercial sources unless otherwise specified. *o*-Carborane was obtained from the Olin Mathieson Chemical Corp.

**Molecular Weights.**—Molecular weights were obtained cryoscopically in methyl ethyl ketone or benzene by use of a Mechrolab osmometer, Model 302, or by mass spectrometry.

**Infrared Spectra.**—Infrared spectra were recorded with a Perkin-Elmer Infracord spectrophotometer. Solids were run as Nujol or Fluorolube mulls while liquids were run as thin films.

**Analyses.**—The elemental analyses were by Galbraith Laboratories, Inc., and Schwarzkopf Microanalytical Laboratory, Inc. Mass spectral analyses were by the Olin Mathieson Chemical Corp.<sup>11</sup>

**Syntheses.**—In general, reactions and distillations were carried out using a dry nitrogen atmosphere to preclude hydrolysis and possible reactions with oxygen. Materials were handled in a nitrogen atmosphere drybox or glove bag when necessary.

**1,2-Bis(mercapto)-*o*-carborane.**—This compound was prepared by the method of Smith, *et al.*<sup>2</sup>

**Triphenylboron.**—Trichloroborane (11.43 g, 0.094 mol) was condensed into a three-necked, 500-ml flask fitted with a dropping funnel and water condenser. Diethyl ether (250 ml) was added to the borane at  $-80^\circ$  and the mixture warmed to  $0^\circ$ . A solution of phenyllithium (25.2 g) in a benzene-ether mixture (75:25 ml) was added dropwise over a 2-hr period. The temperature was held at  $5^\circ$  during the first hour of addition and  $30^\circ$  during the last hour. The ether was removed by distillation at atmospheric pressure and 150 ml of benzene, followed by 150 ml of water, was added to the residue. To this mixture was added an aqueous solution of trimethylamine hydrochloride ( $\sim 0.15$  mol in 100 ml). The resulting precipitate was collected, washed with water, and finally dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$ .

When dry the salt was transferred to a 50-ml flask and heated in a stream of nitrogen to  $250^\circ$ , the triphenylboron distilled out of the flask and was redistilled at  $205^\circ$  (0.5 mm); mp  $137^\circ$ ; yield 6.0 g (24.8% over-all based on trichloroborane used).

**1,2-(2'-*n*-Butyl-1',3',2'-dithiabora)-*o*-carborane.**—Equimolar quantities of tri-*n*-butylborane and 1,2-bis(mercapto)-*o*-carborane were mixed in a single-neck flask and connected to a standard vacuum line through a water condenser. The system was blanketed with a nitrogen pressure of 500 mm and the reaction flask was heated in an oil bath to  $200^\circ$ . The pressure was maintained between 500 and 700 mm, by bleeding the overhead gases through a series of  $-196^\circ$  traps intermittently. When there was no further pressure change in the system, the tan liquid product in the flask was vacuum distilled at  $120^\circ$  (0.2 mm). The clear, colorless distillate was redistilled at  $91^\circ$  (0.15 mm).

The butane obtained as the by-product was identified by its infrared spectrum and vapor density. Within experimental error, the yield was 100%.

**Anal.** Calcd for  $\text{C}_8\text{H}_{18}\text{B}_{10}\text{S}_2$ : C, 26.25; H, 6.98; S, 23.32; mol wt, 274. Found: C, 26.24; H, 6.51; S, 23.24; mol wt, 232. This compound was also identified by its mass spectrum, major mass peak at 274.

**1,2-(2'-Phenyl-1',3',2'-dithiabora)-*o*-carborane.**—The procedure was similar to that employed for the 2-butyl derivative. The benzene formed was removed from the pot at regular intervals, measured, and identified by its infrared spectrum and vapor density.

The tan, waxlike reaction product on sublimation at  $80^\circ$  (0.25 mm) gave a white, waxy solid which melted between  $90$  and  $100^\circ$ .

**Anal.** Calcd for  $\text{C}_8\text{H}_{15}\text{B}_{10}\text{S}_2$ : C, 32.65; H, 5.20; mol wt, 294.23. Found: C, 32.60; H, 5.50. The major mass peak from the mass spectrum was at 294.

**1,2-(2'-Ethyl-1',3',2'-dithiabora)-*o*-carborane.**—Equimolar quantities of 1,2-bis(mercapto)-*o*-carborane and triethylboron were mixed as described for the 2-butyl and 2-phenyl derivatives. After 12 hr at 500 mm of nitrogen pressure and a bath temperature of  $290^\circ$ , the reaction flask was cooled to  $30^\circ$  and a 2 molar excess of acetonitrile was added. On reheating to reflux, gas evolution began. When the reaction was complete, the flask contained two layers, a clear liquid top layer and a tan, opaque but fluid bottom layer. On heating this mixture to  $50^\circ$  (1 mm) the acetonitrile was recovered along with a small amount of unreacted triethylboron. The residue was distilled at  $100^\circ$  (0.5 mm). The distillate was a light yellow volatile liquid which on redistillation at  $78^\circ$  (0.25 mm) gave a colorless liquid which solidified on standing for 48 hr; mp  $44-47^\circ$ .

(10) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956.

(11) The authors wish to thank Mr. Herman Hobrecht for obtaining and interpreting the mass spectral data.

*Anal.* Calcd for  $C_4H_{15}B_{11}S_2$ : C, 19.5; H, 6.1. Found: C, 19.31; H, 6.1.

**1,2-(2'-Chloro-1',3',2'-dithiabora)-o-carborane.**—The acetonitrile-trichloroborane complex was formed by condensing 7.0 g (0.06 mol) of trichloroborane onto a solution of 3.0 g of acetonitrile in 50 ml of dry benzene at  $-80^\circ$  and slowly warming the solution to room temperature. An additional 50 ml of benzene was added and the resulting slurry was heated to reflux. A solution of 1,2-bis(mercapto)-o-carborane in benzene (10.4 g in 25 ml) was added to the hot mixture and the reaction mixture was refluxed for 2 hr. The hydrogen chloride formed was collected as the triethylamine salt.

When the yellow reaction solution cooled to room temperature, excess  $CH_3CN \cdot BCl_3$  precipitated. The clear solution was filtered away from the crystals with the aid of a fritted stick. (The entire experiment was conducted under  $N_2$  atmosphere.) The solvent was removed under reduced pressure and the yellow residue was transferred to a sublimator in a nitrogen-filled dry-box. Sublimation at  $90^\circ$  (0.25 mm) gave 12.5 g of a white crystalline material; mp  $62.4-64.2^\circ$ .

*Anal.* Calcd for  $C_2H_{10}B_{11}S_2Cl$ : C, 9.50; H, 3.96; B, 47.20; S, 25.40; Cl, 14.10. Found: C, 9.52; H, 4.19; B, 44.53; S, 25.00; Cl, 13.62.

**Compound VII.**—The acetonitrile-trichloroborane complex was prepared from 1.2 g (0.01 mol) of trichloroborane and 1.0 g (0.024 mol) of acetonitrile according to the procedure described above. A solution of 1,2-bis(mercapto)-o-carborane in benzene (0.029 mol in 50 ml) was added to the complex and the mixture was refluxed for 6 hr. Tetraethylammonium bromide (2.0 g, 0.0095 mol) in 10 ml of acetonitrile was added to the hot solution. A white precipitate formed when the solution cooled to room temperature. The product was recrystallized from a benzene-ethyl acetate mixture, washed with petroleum ether (bp  $30-60^\circ$ ), and vacuum dried over  $P_2O_5$ ; mp  $320^\circ$ .

*Anal.* Calcd for  $C_{12}H_{40}B_{21}S_4N$ : C, 26.05; H, 7.27; N, 2.53; B, 41.00; S, 23.20. Found: C, 25.81; H, 7.60; N, 2.64; B, 40.75; S, 21.30.

**1,2(2'-Dimethylamino-1',3',2'-dithiabora)-o-carborane.**—A tensimeter apparatus was charged with 0.57 g of dimethylaminoborane and 2.08 g (0.01 mol) of 1,2-bis(mercapto)-o-carborane

and connected to the vacuum line. The entire system was evaluated and the stopcock was closed. The apparatus was submerged to the stopcock in an oil bath and the temperature was raised to  $210^\circ$ . An external source of nitrogen pressure was required to maintain equal mercury levels in the tensimeter. A measure of this pressure, corrected for temperature, was used to calculate the amount of hydrogen evolved in the reaction. The total volume of hydrogen evolved was 448 ml (STP) or 100% of theoretical maximum yield.

The white residue in the reaction tube was removed and the product was purified by sublimation at  $140^\circ$  (0.4–0.2 mm), mp  $137-139^\circ$ .

*Anal.* Calcd for  $C_4H_{16}B_{11}S_2N$ : C, 18.35; H, 6.13; N, 5.36. Found: C, 17.78; H, 6.12; N, 5.24.

**Reaction of Diborane with 1,2-Bis(mercapto)-o-carborane.**—A 50-ml reaction flask was charged with 2.35 g (0.01 mol) of 1,2-bis(mercapto)-o-carborane and 15 ml of dry diethyl ether. The flask was cooled to  $-196^\circ$  and evacuated. Diborane (0.3 ml, 0.134 g) was condensed on the mixture and the flask was allowed to warm to  $-80^\circ$ . After the cessation of hydrogen evolution (total hydrogen evolved amounted to approximately 0.02 mol) the ether was distilled from the white crystalline product. On warming the reaction flask to  $50^\circ$ , additional ether was evolved. The resulting product was insoluble in diethyl ether but soluble in petroleum ether; mp  $42-50^\circ$ . The infrared spectrum was in agreement with that expected for 1,2-(2'-hydro-1',3',2'-dithiabora)-o-carborane.

**Carborane 1,2-Bis(phenylthiocarbamate).**—Phenyl isocyanate, 0.707 g, was dissolved in 10–15 ml of carbon tetrachloride and added to a solution of 1.5 g of 1,2-(2'-chloro-1',3',2'-dithiabora)-o-carborane in carbon tetrachloride. The mixture was refluxed for 30 min and cooled to  $20^\circ$ , and the resulting precipitate was collected, washed with petroleum ether (bp  $30-60^\circ$ ), and dried in a nitrogen stream. A portion of this product was hydrolyzed and the water-insoluble fraction of the resulting materials was dried over  $P_2O_5$ . Recrystallization of this fraction from a benzene-hexane mixture (10:1) yielded white crystals; mp  $131.0-132.5^\circ$ .

*Anal.* Calcd for  $C_{16}H_{22}B_{10}N_2S_2O_2$ : C, 43.09; H, 4.94; B, 24.20; N, 6.28; S, 14.35. Found: C, 44.40; H, 5.30; B, 23.88; N, 6.28; S, 13.98.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA 22903

## Carborane Formation in Alkyne-Borane Gas-Phase Systems. II. Slow Reactions of Tetraborane(10) and Pentaborane(11) with Acetylene, Methylacetylene, and Dimethylacetylene<sup>1</sup>

By RUSSELL N. GRIMES, CHRISTOPHER L. BRAMLETT,<sup>2</sup> AND R. LEONARD VANCE

Received January 9, 1968

The reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene, and dimethylacetylene have been examined in the vapor phase at  $25-50^\circ$  and the volatile products have been isolated and characterized. Alkyl derivatives of the *nido*-carboranes  $CB_3H_9$ ,  $C_2B_4H_8$ , and  $C_3B_5H_7$  are produced together with alkylboranes, hydrocarbons, and organoboron polymers, but the products and yields vary considerably with choice of reactants. In the  $B_4H_{10}$  reactions, carboranes account for all organoboron products, but  $B_5H_{11}$  gives alkylboranes plus small yields of carboranes. With either  $B_4H_{10}$  or  $B_5H_{11}$ , acetylene tends to give  $C_3B_3$  rather than  $C_2B_4$  carboranes, while the reverse is true in reactions with higher alkynes. Derivatives of  $CB_3H_9$  are formed from  $B_4H_{10}$  but not from  $B_5H_{11}$ . Diboration of the alkyne triple bond is postulated to account for the carbon-carbon cleavage which is evidenced by reaction products of both boranes.

### Introduction

The gas-phase interaction between tetraborane(10) and acetylene has been reported in an earlier paper<sup>3</sup> to

(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

take place explosively at  $100^\circ$  giving volatile *closo*-carboranes and to proceed slowly at  $25-50^\circ$  forming methyl

(2) Philip Francis du Pont Predoctoral Fellow, 1965–1967.

(3) R. N. Grimes and C. L. Bramlett, *J. Am. Chem. Soc.*, **89**, 2557 (1967).