rates of the individual steps are mainly determined by the statistical distribution of the halogen on the rings and possible changes in activation energies would be slight. However, a definite answer to this problem could be had only from more detailed data than are reported here.

We interpret our inability to isolate pure derivatives containing both B-ethyl and B-chloro substitution as due to a fairly rapid redistribution equilibrium that is disturbed during the separation. Comparing this to the apparent resistance to redistribution of the corresponding butyl derivatives, one can rationalize the difficulties that previous workers have encountered in attempts to prepare the analogous methyl derivatives.[9] If one proposes a bridged dimer transition state[10] for the redistribution reaction and recalls the decrease of stability of aluminum trialkyl dimers with increase in the length of alkyl groups, it is reasonable to suppose that a *n*-butyl group functions less efficiently in the formation of alkyl bridges than ethyl. More detailed and exact data on redistribution reactions in this system and of boranes in general would be required to give a definite answer.

**Acknowledgment.**—The support of this work by the Koppers Company through a research contract with the University of Florida is gratefully acknowledged.

[9] *Chem. Eng. News*, **45**, 67 (Sept. 16, 1957).

[10] T. D. Parsons, M. B. Silverman and D. M. Ritter, THIS JOURNAL, **79**, 5091 (1957); P. A. McCusker, G. F. Hennion and E. C. Ashby, *ibid.*, **79**, 5192 (1957).

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# Decomposition of Diborane in a Silent Discharge. Isolation of $B_6H_{10}$ and $B_9H_{15}$

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The decomposition of diborane in a silent discharge in the presence of an inert gas produces $B_4H_{10}$ in 40% yield, $B_5H_9$ in 20% yield, $B_5H_{11}$ in 30% yield and small amounts of $B_6H_{10}$ and a previously unidentified hydride, $B_9H_{15}$. This is the first new borane isolated since the work of Stock more than thirty years ago. A partial mass spectrum of $B_6H_{10}$ is presented.

The early efforts of Jones and Taylor[1,2] and others[3-5] to prepare a boron hydride by the acid hydrolysis of magnesium boride were unsuccessful. Development by Stock[6] of adequate methods for handling volatile materials in the absence of air or moisture enabled him to isolate and identify a series of highly reactive boron hydrides as the products of this hydrolysis. Despite the difficult and thorough examination by Stock of the effect of experimental conditions, the yield of boron hydride by hydrolysis methods never exceeded one per cent. of the theoretically obtainable amount. In one experiment, decomposition of 4200 g. of magnesium boride produced only 6 g. of $B_4H_{10}$, and lesser amounts of other boron and silicon hydrides. In another experiment, decomposition of 2000 g. of the boride produced a mixture from which he isolated 60 mg. of $B_5H_9$ and one gram of $B_6H_{10}$. Investigation of the reactions of higher boron hydrides has been limited by the difficulties met in their preparation.

Tetraborane is always the major product of the boride hydrolysis and was used by Stock to prepare the other boranes. Decomposition of $B_4H_{10}$ at elevated temperatures produced $B_5H_9$, $B_{10}H_{14}$ and $B_2H_6$; $B_5H_{11}$ was prepared by thermal decomposition of $B_2H_6$. No measurable amount of $B_6H_{10}$ was observed as a product of the thermal decomposition of either $B_2H_6$ or $B_4H_{10}$.

In 1930, Schlesinger and Burg[7] reported that diborane could be prepared by passing boron trichloride and hydrogen through a high voltage discharge. Schlesinger and co-workers[8,9] later developed several methods for preparing diborane in nearly quantitative yield from readily available materials; consequently efforts to prepare the higher hydrides of boron have been largely concentrated on the elucidation of the mechanism of thermal decomposition of diborane and the effects of catalysts and other experimental conditions on the yields of various boranes.[10-12]

The most difficult boron hydride to prepare is $B_6H_{10}$ although several methods for preparing it have been described in the literature. Stock[6] obtained comparatively small yields of $B_6H_{10}$ in his tedious boride hydrolysis method. Wiberg and Stecher[13] claimed to have isolated very small quantities of $B_6H_{10}$ from the products of the reaction between trimethylamine and $B_5H_{11}$. Mass spectral evidence of the formation of hexaborane by decomposition of $B_5H_{11}$ at −80° over a period of several months has been reported by Norton.[14] Stock and Mathing[15] have reported that $B_6H_{10}$ could be obtained by decomposing the brown solid formed when diborane was decomposed in a silent discharge. On slowly heating 30 mg. of this solid to 1000°, 0.4 cc. of $B_6H_{10}$ was formed.

This investigation was undertaken to develop

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[1] F. Jones and R. Taylor, *Chem. News*, **38**, 262 (1878).

[2] F. Jones and R. Taylor, *J. Chem. Soc.*, **39**, 213 (1881).

[3] H. Buff and F. Wohler, *Chem. Cent.*, **28**, 775 (1857).

[4] P. Sabatier, *Compt. rend.*, **112**, 866 (1891).

[5] W. Ramsay and H. Hatfield, *Proc. Chem. Soc.*, **17**, 152 (1901).

[6] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[7] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 432 (1931).

[8] H. I. Schlesinger and H. C. Brown, *ibid.*, **75**, 195 (1953).

[9] A. E. Finholt, A. C. Bond and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

[10] R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951).

[11] J. K. Bragg, L. W. McCarty and F. J. Norton, *ibid.*, **73**, 2137 (1951).

[12] H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

[13] W. Klemm, "Anorganische Chemie," Teil I, Dieterich'sche Verlagsbuchhandlung Inh. W. Klemm, Wiesbaden (April, 1949), E. Wiberg and O. Stecher, p. 129.

[14] F. J. Norton, THIS JOURNAL, **72**, 1849 (1950).

[15] A. Stock and W. Mathing, *Ber.*, **69B**, 1469 (1936).

the method of Stock and Mathing into a procedure satisfactory for preparing samples of hexaborane sufficient for chemical studies. According to these workers, only a brown solid was obtained when diborane mixed with hydrogen or argon was passed through an electric discharge of 15 kv., although about 11% of a mixture of $B_5H_9$ and $B_5H_{11}$ in addition to the brown solid was obtained when only $B_2H_6$ was passed through the discharge. In contrast to their results, it was discovered in this study that $B_6H_{10}$ could be prepared directly by the discharge decomposition of diborane, although in poor yield. Large yields of $B_4H_{10}$ and both pentaboranes, and traces of slightly volatile higher hydrides also were obtained. A hitherto unknown hydride, $B_9H_{15}$, was isolated from the latter mixture and there were indications that still other new hydrides might be present in this mixture.

## Experimental

The apparatus and methods employed in the purification, isolation and identification of volatile products have been adequately described by Sanderson.[16] All pressures are given in millimeters of mercury and all gas volumes, unless otherwise stated, are given in cubic centimeters of gas at 0° and 760 mm. pressure. The diborane employed in this investigation was made by the reaction of the freshly prepared ethyl etherate of boron trifloride with either lithium hydride or lithium aluminohydride using the methods described by Schlesinger and co-workers.[8,9] Each sample of diborane was purified before use, if necessary, and the purity established by comparison of its vapor pressure at −112° with the known vapor pressure of diborane (225 mm.) at that temperature.

The discharge system used for this investigation consisted of a diborane reservoir connected to the gas inlet by a spiral tube (which permitted an inert sweep gas to reach bath temperature before reaching the diborane), a discharge tube made from a Pyrex condenser, and three traps maintained at −80, −196 and −196°, respectively. A glow discharge was maintained between the central tube of the condenser which was filled with dilute sulfuric acid and a tin foil wrapper on its outer surface by application of a voltage of up to 15 kv. from a gas tube transformer.[17] Products of the reaction and unchanged diborane were recovered in cold traps at −80 and −196°, and gas flow was estimated by passing the hydride-free gas to a gasometer. A vapor pressure thermometer built into the diborane reservoir was used to measure the actual temperature of the liquid diborane and thus establish roughly its partial pressure in the gas stream.

**Procedure.**—A measured amount of diborane was condensed at −196° in the diborane reservoir, cooling baths were placed around the traps and the reservoir warmed to -135°. An inert gas then was passed through the liquid diborane to sweep it through the discharge tube, the stopcock to the gas-measuring device opened, the rate of flow adjusted as desired, and the discharge started. About 45 minutes was required for one complete pass. To recharge the diborane reservoir, the discharge tube was turned off, the inert gas inlet and the outlet to the gasometer closed, and the system evacuated completely. After closing the three-way stopcock, the nitrogen baths were removed and a liquid nitrogen bath placed around the reservoir, thus allowing the hydrides volatile at −80° to condense in the reservoir for additional passes through the discharge tube; three to six passes were made per run. After the run was completed, all the volatile hydrides were collected in the fractionating system and fractionated according to usual high vacuum methods.[17]

Most satisfactory results are obtained by using a number of successive passes (or better still, a cyclic system) and helium as the inert sweep gas. Between 20 and 50% of the diborane taken was decomposed after three passes through the discharge. Rate of flow of the inert gas did not markedly affect the amount of diborane decomposed.

**Isolation and Identification of $B_6H_{10}$ and $B_9H_{15}$.**—The hydrides obtained from the discharge reaction were separated into seven distinct fractions. Undecomposed $B_2H_6$ was recovered by fractionating the crude mixture through two traps maintained at −112 and −135°, and collected in one at −196°. The material retained in the −112 and −135° traps was fractionated further by passage through a −95° trap. The material passing this trap was stopped in one at −196° and shown to be $B_4H_{10}$ by comparison of its vapor pressure at 0° of 386 mm. and its molecular weight by gas density of 53.7 with those of $B_4H_{10}$ (386 and 53.3 mm., respectively).

The two pentaboranes were separated from the material retained at −95° by several quick distillations through a −63° trap. Distillations were not allowed to continue after all liquid had distilled from the first tube since $B_6H_{10}$ was carried through the −63° trap on long pumping. This process was repeated until the hydride retained in the −63° trap showed a 0° vapor tension between 7 and 8 mm. The pentaborane mixture was split into two components by numerous fractionations through a −80° trap with pumping of one-half to one hour on each pass. One borane came through the −80° trap and final identification as $B_5H_9$ was achieved by measurement of its zero vapor pressure of 64 mm. ($B_5H_9$ = 65 mm.) and its molecular weight by gas density as 63.5 (calculated 63.2). The material retained in the −80° trap was purified further by several quick passes through a −63° trap and was identified as $B_5H_{11}$ by its vapor pressure at 0° of 53 mm. ($B_5H_{11}$ = 52.8 mm.) and its molecular weight by gas density of 65.7 (calculated 65.19).

The material coming through a −30.6° trap, but stopped by the −63° trap, was always present in relatively small quantities. Its zero vapor tension in various samples was between 6.8 and 7.2 mm. compared with the value of 7.2 mm. for $B_6H_{10}$ reported by Stock.[6]

The material stopped by a −30.6° trap had a vapor pressure of about 1.3 mm. at room temperature (27°) and a vapor pressure at 0° of 0.8 mm. This material crystallized as small rectangular, flat plates and melted at about −21°. Burg and Schlesinger[18] reported a vapor pressure of 1.2 mm. at room temperature for a material they isolated from the products of the decomposition of $B_2H_6$ at room temperature and suggested that it was an octaborane. Evidence concerning the nature of the material isolated in the present experiments is given below.

The least volatile fraction was stopped by a −11° trap and was identified as $B_{10}H_{14}$ by its physical appearance and by comparison of its infrared spectrum with that of $B_{10}H_{14}$.

In addition to the volatile boron hydrides, non-volatile white and yellow solids were deposited in the discharge tube. However, little work was done with these solids and their nature was not established.

A small sample of the material presumed to be $B_6H_{10}$ was used for mass spectrometric analysis.[19] Maximum peak heights were observed at mass numbers 35, 48, 59 and 71, with sharp breaks between successive groups. One disturbing feature of the observed spectrum was the fact that the peaks near 59 mass numbers are significantly larger than those near 71 mass numbers. This was in distinct contrast to the known mass spectra of other boron hydrides[20-22] and suggested that the sample was contaminated with hydrides of lower molecular weight, presumably either $B_5H_9$, $B_5H_{11}$ or both.

To test this possibility, successive samples were introduced for analysis by warming the original sample until the pressure at the leak rose to about 100 $\mu$, then freezing the remaining sample until a new portion was needed. A fractionation to give first the most volatile components is implicit in this method and the peak heights due to the more

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[16] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[17] Cat. No. R 1560 supplied by the Sola Electric Company, Chicago, Illinois.

[18] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4009 (1933).

[19] Mass spectra of $B_6H_{10}$ and $B_9H_{15}$ were otained by Mr. Bailey Donnelly in Professor Nier's laboratory at the University of Minnesota. Professor William Lipscomb made arrangements for the determinations and assisted in the analysis. We wish to express our appreciation to both individuals for their willing assistance and advice.

[20] I. Shapiro and B. Keilin, THIS JOURNAL, **76**, 3864 (1954).

[21] V. H. Dibeler and F. L. Mohler, *ibid.*, **70**, 987 (1948).

[22] V. H. Dibeler, F. L. Mohler, L. Williamson and R. M. Reese, *J. Research Nat. Bur. Standards*, **43**, 97 (1949).

volatile hydrides, if they are present as impurities, should consequently diminish in relation to the peak at 71 in successive samples. The fact that lower mass peaks actually did diminish in successive samples as shown in Fig. 1 offers strong support for the presence of more volatile hydride impurities in the original sample. The lower peaks did not disappear entirely, of course, since a compound containing six boron atoms would give fragments of these masses.

The highest mass number which should be observed for $B_6H_{10}$ is 76 and the peak of maximum intensity should fall four or five mass numbers lower if the spectrum is similar to that of other boron hydrides.[12,14,20–22] The maximum peak height occurred at mass number 71; the peak at mass number 77 was less than 2% of the one at 76 and, furthermore, no peak above mass 77 was more than 2% of the one at 71. The observed mass spectrum and measured vapor tension thus serve to identify the material as $B_6H_{10}$.[23] The last fraction illustrated in Fig. 1 should be essentially pure $B_6H_{10}$ and the observed spectrum should be a close approximation to the mass spectrum of hexaborance since negligible changes took place in the last three samples. The mass spectral data for the higher peaks of the sample are listed in Table I. No previous observations of the mass spectrum of $B_6H_{10}$ have been made.

TABLE I

PARTIAL MASS SPECTRUM OF HEXABORANE

| Mass number *m/e* | Relative intensity | Mass number *m/e* | Relative intensity |
|---|---|---|---|
| 77 | 2.9 | 61 | 37.2 |
| 76 | 25.4 | 60 | 57.8 |
| 75 | 36.2 | 59 | 70.0 |
| 74 | 55.6 | 58 | 59.0 |
| 73 | 59.4 | 57 | 47.0 |
| 72 | 91.2 | 56 | 37.0 |
| 71 | 100 | 55 | 29.2 |
| 70 | 78.2 | 54 | 17.4 |
| 69 | 56.6 | 53 | 7.2 |
| 68 | 42.7 | 52 | 6.6 |
| 67 | 37.4 | 51 | 7.6 |
| 66 | 29.2 | 50 | 19.5 |
| 65 | 15.7 | 49 | 23.5 |
| 64 | 23.5 | 48 | 36.2 |
| 63 | 24.2 | 47 | 3.92 |
| 62 | 37.4 | 46 | 8.0 |

A sample of the material retained in the −30° trap was also subjected to mass spectral analysis.[19] When four successive samples were introduced, fractionation occurred as in the $B_6H_{10}$ spectrum. Comparison of the four samples showed that the most intense peaks occurred first at about 80 mass numbers, then at *e/m* = 93, and finally at *e/m* = 105. The simplest and most probable interpretation of this effect is that the sample contained hydrides made up of seven, eight and nine boron atoms per molecule. That the latter predominated is evidenced by the fact that after only a small fraction of the material was removed the peaks near 105 were the most intense. The shape of the high mass peak (near 110) resembles those attributed by Norton to $B_9H_{13}$.[14] On cooling, a substantial fraction of the sample was converted to well-formed, rectangular crystals melting at about −23°. A complete structural determination utilizing the method of Holmes showed the crystalline material to be $B_9H_{15}$.[24] Other definite molecular hydrides may have been present, but were not obtained in crystalline form. It is interesting to note that $B_9H_{15}$ is the only borane isolated and characterized since the early work of Stock.

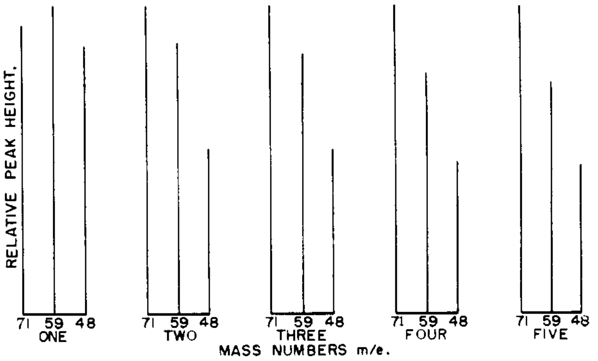

Fig. 1.—Mass spectra of successive samples of impure hexaborane.

The approximate yields of boranes observed in a typical experiment are shown in Table II.

TABLE II

YIELDS OF BORANES BASED ON $B_2H_6$ CONVERTED

| Borane | Approximate yields, % of the theor. amt. obtainable |
|---|---|
| $B_4H_{10}$ | 40 |
| $B_5H_9$ | 20 |
| $B_5H_{11}$ | 30 |
| $B_6H_{10}$ | 1.5 |
| $B_9H_{15}$ | |
| $B_{10}H_{15}$ | |

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[23] Further conclusive proof of the identity of the material with Stock's $B_6H_{10}$ is provided by the structural determination by Professor Lipscomb, F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).

[24] R. E. Dickerson, P. J. Wheatley, P. A. Howell and W. N. Lipscomb, *ibid.*, **27**, 200 (1957).