

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIFORNIA

The Synthesis of Nonaborane, B_9H_{15}

BY ANTON B. BURG AND REINHOLD KRATZER

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The nonaborane B_9H_{15} has been obtained in yields near 13% by the interaction of B_5H_{11} with a surface of hexamethylenetetramine, $(CH_2)_6N_4$. Purification by high-vacuum distillation methods and by low-temperature crystallization raised the m.p. to $+2.6^\circ$; vapor tension 0.8 mm. at 28° . The formula was proved by quantitative decomposition to H_2 and B and by a molecular weight determination involving flash evaporation. The mass spectrum suggests the same substance as the B_9H_{15} used for the X-ray determination of structure. The infrared and B^{11} magnetic resonance spectra are presented. Further experience with the synthesis of other polyboranes from B_5H_{11} also is described.

The very unstable nonaborane B_9H_{15} has been known only as a very minor by-product of polyborane interconversion processes¹; and its formula has been assured only by an X-ray crystallographic determination of its molecular structure, supplemented by its mass spectrum.² Experiments on the catalytic conversion of B_5H_{11} ³ always had yielded hexaborane fractions containing small amounts of an oily liquid having the volatility of B_9H_{15} ; and the same was true when we sought new catalysts for improvement of the yield of hexaborane. But when the catalyst was the crystalline four-way tertiary amine $(CH_2)_6N_4$ (urotropine) the yields of B_6H_{10} were relatively low, while the conversion of B_5H_{11} to B_9H_{15} was in the range 11–15%. Thus we have found a dependable method for the synthesis of B_9H_{15} , leading to a pure sample for which the molecular formula could be demonstrated by evidence more conventional than the X-ray pattern. Its properties are such as to indicate that the previously con-

jectured " B_8H_x "⁴ actually was the same B_9H_{15} .

Synthesis and Proof of Formula

Procedure for Synthesis.—A 300-ml. erlenmeyer flask was sealed to the high-vacuum manifold and $(CH_2)_6N_4$ was vacuum-sublimed rapidly to the inside wall of the flat bottom, to form a microcrystalline surface. Then nearly pure B_5H_{11} (20.365 mmoles; 53.2 mm. at 0° ; purest samples, 52.8 mm. vs. 66 mm. for B_5H_9) was left in contact with that surface for 2 hr. at 0° . Roughly 1 mmole of hydrogen was pumped off and the other volatile components were roughly separated by a high-vacuum fractional condensation using U-traps at -63 , -96 , and -196° ; then the -96° condensate (mostly B_5H_{11}) was returned for 3 hr. further contact with the resublimed $(CH_2)_6N_4$ at 0° . It is worthy of mention that the resublimation of the $(CH_2)_6N_4$ yielded a yellow oil which collected in the nearest cold point, but then could not be further distilled *in vacuo*; it proved to be soluble in ether.

The second recovered B_5H_{11} fraction was exposed again to $(CH_2)_6N_4$ (not resublimed), this time for 4 hr. at 0° . Now the pentaborane fraction was isolated again and purified as well as possible, with removal of a top fraction for analysis by hydrolysis at 0° ; thus it was possible to isolate the B_5H_9 and so determine the unused B_5H_{11} .⁵ The experiment consumed 12.65 mmoles of B_5H_{11} , forming the products listed in Table I.

These products account for 55% of the boron in the consumed B_5H_{11} . Not on the list is a fraction having a

(1) V. W. Kotlensky and R. Schaeffer, *J. Am. Chem. Soc.*, **80**, 4517 (1958).

(2) (a) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957); (b) P. G. Simpson and W. N. Lipscomb, *ibid.*, **35**, 1340 (1961).

(3) J. L. Boone and A. B. Burg, *J. Am. Chem. Soc.*, **81**, 1766 (1959).

(4) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4015 (1933).

(5) J. L. Boone and A. B. Burg, *ibid.*, **80**, 1519 (1958).

TABLE I
PRODUCTS OF CONVERSION OF 12.65 MMOLES OF B_9H_{11}

Substance	Identification	mmoles yield	% yield
B_2H_6	225.2 mm. at -111.8°	7.523	23.8
B_4H_{10}	3.1 mm. at -78.5°	1.588	10.1
B_5H_9	66.0 mm. at 0°	0.48	3.8
B_8H_{10}	7.5 mm. at 0°	.064	0.6
B_9H_{15}	0.8 mm. at 28°	.954	13.6
$B_{10}H_{14}$	M.p. 97-98°	.186	2.9 ₃

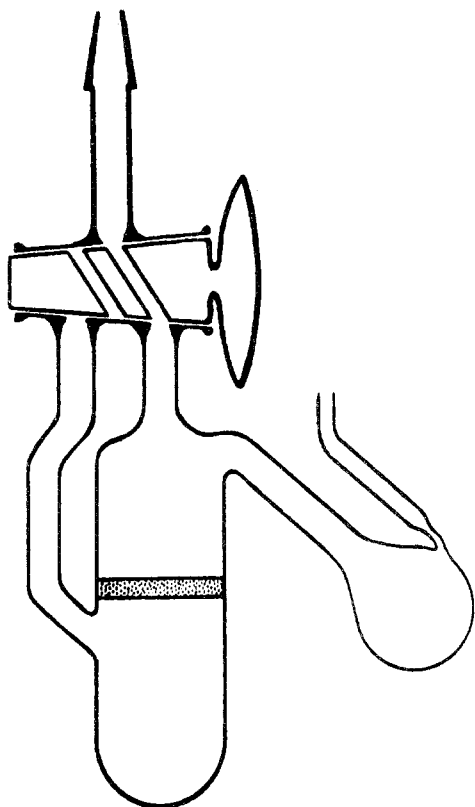


Fig. 1.—Device for the low-temperature crystallization. The sample and solvent are condensed in the side arm, the outlet of which assists complete transfer by leading off any trace of non-condensable gas into the high-vacuum system. After the outlet has been sealed off, the side arm serves as the crystallization chamber.

vapor tension near 3 mm. at 27° and requiring further investigation. This might be a polyborane intermediate between B_8H_{10} and B_9H_{15} , but a break-down product of $(CH_2)_6N_4$ cannot yet be excluded.

Purification of Nonaborane.—A fraction containing the major part of the B_9H_{15} was obtained by high-vacuum distillation through a trap at -13° , with fractional condensation at -24° . Separation from $B_{10}H_{14}$ was roughly accomplished by a quick distillation *in vacuo* from a tube at 0° , stopping when the appearance of solid $B_{10}H_{14}$ indicated a saturated solution. Final purification then was accomplished by low-temperature crystallization. The solvent was a mixture of 2- and 3-methylpentanes, previously freed of sulfur compounds and olefins by treatment with bromine, followed by $Na_2S_2O_3$ and vacuum distillation from $LiAlH_4$ at -78° . The solution was

cooled to -78° in the side arm of an apparatus like that shown in Fig. 1, and the crystals were collected on the sintered plate. Then the apparatus was warmed to -13° for high-vacuum sublimation of the crystals into the main vacuum system. This method is not effective unless the $B_{10}H_{14}$ content has been minimized; but once the B_9H_{15} has been purified, high-vacuum fractional condensation is adequate for its repurification after partial decomposition. Very pure B_9H_{15} , melting in the range $+2.5$ - 2.7° , could be kept at 0° for 1 hr. without appreciable change. The most dependable vapor tension measurement was 0.80 mm. at 28.2° .

The Elementary Analysis.—A pure sample of B_9H_{15} (19.8 mg.) was entirely decomposed in a weighed Vycor spiral, heated to a bright glow by a methane-oxygen flame. The weight of boron was 17.1₅ mg., or 1.58₅ mg.-atom. The hydrogen was measured as 29.50 cc. of standard gas, or 2.632 mg.-atom. Thus the ratio of H to B was 1.661; calcd. for B_9H_{15} , 1.667.

The Molecular Weight.—It was necessary to employ a vapor-phase method for the molecular weight determination, for attempts to work in solution (vapor tension lowering of pure *n*-butane) gave results in the range 129-135 (calcd. 112.5) at feasible concentrations. For the vapor-phase method, however, it would be necessary to work at temperatures over 70° in order to have enough vapor for accurate determinations of the pressure and sample weight. Hence very rapid equilibration and observation would be required to minimize decomposition during measurement.

For this purpose the immersible tensimeter shown in Fig. 2 proved suitable. The sample was delivered from a

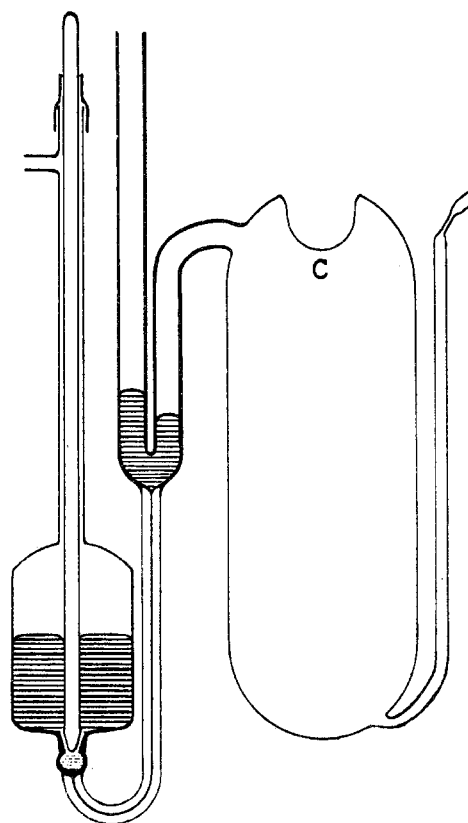


Figure 2.

weighed stopcock tube (with no other contact with greases, which strongly absorb B_9H_{15} vapors) and entered through the empty U-manometer tube, for condensation by solid carbon dioxide at C. Any part of the sample passing C, or any non-condensable gas, would have been carried back to the vacuum system through the small sealable outlet tube; actually such loss was negligible. With the sample at C and the outlet sealed, mercury was admitted to the arms of the U-manometer and the system was immersed in a motor-stirred hot water bath, almost up to the lip of the cold-cup C. Now a Leica Model 11-f camera (with fine-grain film) was focused upon the manometer and adjacent calibrated scale, using a close-up lens for a picture about 10% larger than the actual object. For a flash-evaporation of the sample, the solid carbon dioxide was blown out of the cold-cup, which then was submerged by pouring in hot water. The manometer and scale were photographed at 5-sec. intervals, with temperature readings between. Then the negatives could be measured by a micrometer microscope to determine pressures within 0.01 mm. Pressure constancy usually was attained within 15–20 sec.

This method was tested by means of a sodium-dried sample of acetic anhydride, giving the molecular weight value as 103.7, or 1.6% higher than the calculated value, 102.2. This test showed also that the evaporation of mercury was not fast enough to affect the total pressure within the 40 sec. of photographic observation.

For the actual determination, a 13.2-mg. sample of B_9H_{15} , flash-evaporated in a 638-ml. volume, showed an average pressure of 3.89 mm. (corr. to 0°) at 74.9°, during the time interval 20–40 sec. Thus the observed molecular weight was 115.4, or 2.6% above the calculated 112.5. This deviation is reasonable in view of the 1.6%-high result for the somewhat more volatile acetic anhydride under similar conditions.

After the 40-sec. exposure of the vaporized sample to the 74.9° temperature, the vapors were delivered to a trap at -196° and the H_2 was pumped off for measurement as 0.00192 mmole, or 0.016 H_2 per B_9H_{15} . The recovered sample melted in the range -0.6 to 0° , still far above the literature sample (-21°).¹ Thus the decomposition at 3.89 mm. and 74.9° had not gone far enough, even after 40 sec., for any serious effect upon the molecular weight determination.

Instrumental Characterization

Our pure sample of B_9H_{15} melted at least 23° higher than that described by Kotlensky and Schaeffer¹; hence one might question whether our product was an isomer of the B_9H_{15} for which the structure determination was performed.² However, the mass spectrum correlates very well with the X-ray sample^{2a} and the B^{11} magnetic resonance spectrum is the same as for a sample obtained by decomposing diborane in a silent electric discharge—the method which produced the X-ray sample.¹ Thus it appears that our product was a more highly purified sample of the same B_9H_{15} . Correlation of the mass spectrum with the still earlier sample reported by Norton also is good.⁶

As a further aid to identification, the relatively complex infrared spectrum of pure liquid B_9H_{15} also is presented.

The Mass Spectrum.—Dr. J. F. Ditter employed a CEC Model 21-620 mass spectrograph (operating at 70 v.) at the Pasadena laboratory of National Engineering Science Co. to obtain the record shown in Fig. 3 for our B_9H_{15} . Comparison

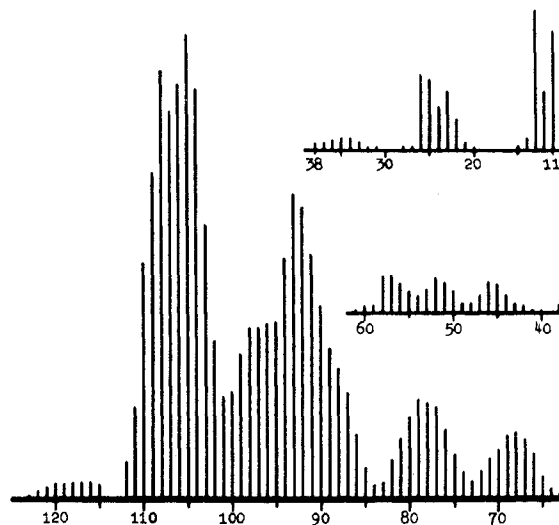


Fig. 3.—The mass spectrum of B_9H_{15} .

of the pattern with that reported for the crystallographic sample^{2a} shows a virtually perfect agreement in the important region around the maximum at mass number 105, and only minor deviations elsewhere—attributable to impurities in the earlier sample.

The Nuclear Magnetic Resonance Spectrum.—Dr. R. E. Williams (then also at the National Engineering Science Co. laboratory) used the Varian High Resolution nuclear magnetic resonance spectrometer (operating at 12.8 Mc.) to record the B^{11} spectrum of our highly purified B_9H_{15} . The resulting pattern, shown in Fig. 4

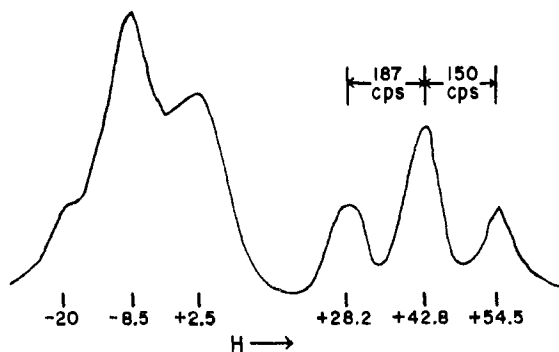


Fig. 4.—The B^{11} n.m.r. spectrum of B_9H_{15} .

(6) F. J. Norton, *J. Am. Chem. Soc.*, **72**, 1899 (1950).

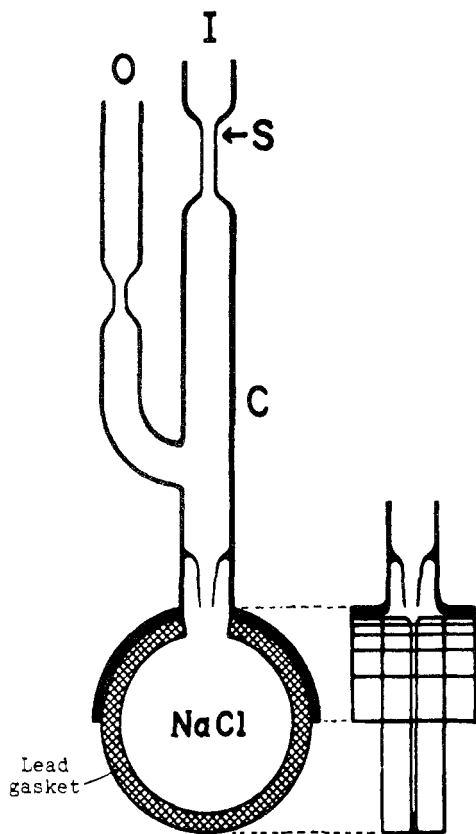
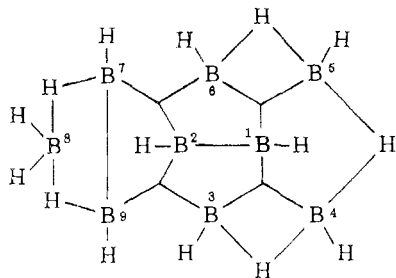


Fig. 5.—Infrared cell for pure liquids.

with chemical shifts based upon $\delta = 0$ for $(C_2H_5)_2OBF_3$, proved to be the same as one which had been recorded earlier under the same conditions for a slightly volatile product of the silent electric discharge through diborane.

Dr. Williams points out that the interpretation of this spectrum is necessarily complex, for it must account for boron in six different electronic environments. Thus the high-field pattern, appearing like a 1:2:1 triplet, actually lacks symmetry and probably is composed of two doublets. These can be compared with the B^{11} n.m.r. spectra of other polyboranes, and thus seem to represent the boron atoms numbered 1 and 7,9 in the following structural formula.²



Then the still more irregular low-field pattern

would represent the four kinds of boron in the remaining six positions. Final assignments represent a difficult problem for the future.

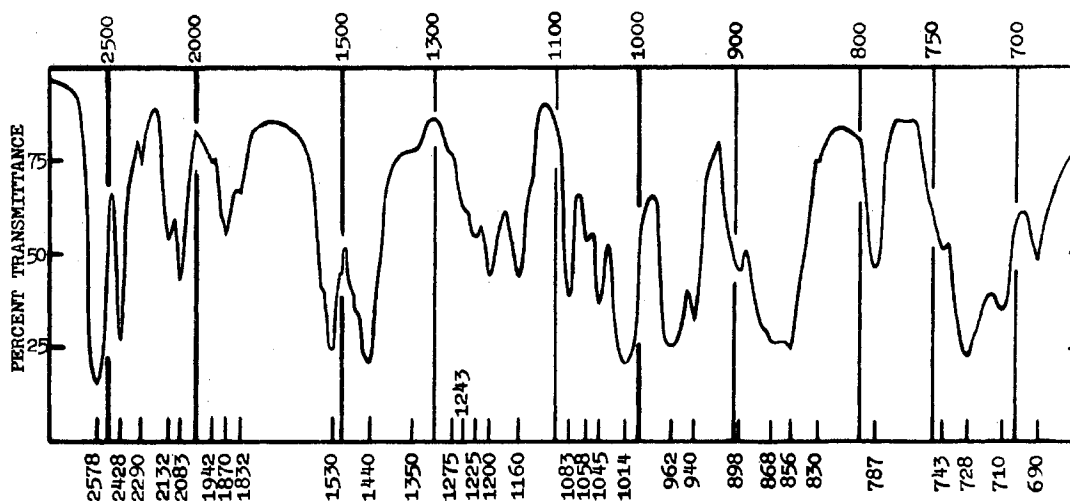
The Infrared Spectrum.—For adequate intensity of infrared absorption it was necessary to work with the liquid phase, for the required pressure of B_9H_{15} vapor could not develop except at temperatures too high for stability. The cell employed for pure liquid B_9H_{15} is shown in Fig. 5. Two 35-mm. NaCl disks, polished optically flat and separated by a circular lead gasket 0.05 mm. thick, were mounted in a T-connected hemicylindrical socket made by longitudinal bisection of a short piece of 35 mm. i.d. Pyrex tubing. Glyptal resin (baked on at 100°) was used to bond the disk-edges together and to the glass hemicylinder, rendering the system air-tight. The B_9H_{15} vapor entered at I and condensed at C, where the tube was cooled by cotton soaked in liquid nitrogen. The outlet O (to another part of the vacuum system) led off H_2 , a trace of which would hinder arrival of the vapor at C. The outlet and inlet were sealed off (the latter at S to leave a tip for a vacuum tube-opener) and the melted sample dripped through the small in-sealed nozzle into the space between the NaCl disks. The sample was scanned as soon as possible by the Perkin-Elmer Infracord instrument; then the most interesting or uncertain features of the spectrum were checked by short-range scans by the Beckman IR7 instrument.

The resulting spectrum, shown in Fig. 6, has all of the complexity which might be expected of the B_9H_{15} structure. The bands from 1440 to 2578 cm.^{-1} seem adequate to account for three kinds of B-H-B bridging, five kinds of simple B-H stretching, and the symmetric and asymmetric BH_2 stretchings; and the lower frequencies would relate mostly to various B-H bending modes and to B-B stretching. The pattern probably was not affected by decomposition, for the formation of H_2 was slight.

Other Catalytic Conversions of B_5H_{11}

During the search for a practical catalytic synthesis of B_9H_{15} , a number of catalysts other than $(CH_2)_6N_4$ were tried, leading to further new knowledge of B_5H_{11} conversions and products.

Hexaborane by the Diglyme Method.—The previously reported synthesis of B_6H_{10} by passage of a low-pressure stream of B_5H_{11} vapor over a large surface of diglyme³ was repeated on a larger scale and with a wider variation of flow and sur-

Fig. 6.—The infrared spectrum of B_9H_{15} (frequencies given in cm^{-1}).TABLE II
LIQUID-VAPOR EQUILIBRIA OF B_6H_{10}

$$(\log P_{mm} = 6.4529 + 1.75 \log T - 0.00561T - 2270/T)$$

t ($^{\circ}C.$)	-20.6	-13.9	-7.45	0.00	5.0	11.7	18.4
P_{mm} (obsd.)	1.78	2.93	4.60	7.47	10.21	15.21	22.11
P_{mm} (calcd.)	1.79	2.93	4.59	7.48	10.21	15.19	22.12

face conditions. Also tried was tetraglyme, $CH_3O(C_2H_4O)_4CH_3$ (for a sample of which we are glad to acknowledge the generosity of Ansul Chemical Co.), but it gave no better yields, and the C-O-C bond cleavage (leading to volatile C-H impurities) was more pronounced than when diglyme was used. The best yields by the diglyme method were only 65% as high as previously indicated.³ It now appears that the earlier "hexaborane" fractions included considerable proportions of B_9H_{15} , and probably intermediate polyboranes not yet identified—all of which would have been difficult to isolate and measure on such a small scale. The present syntheses led to highly purified samples of B_6H_{10} , permitting correction of its physical properties.

The m.p. of B_6H_{10} was redetermined as -62.3° ; cf. earlier -63.5° ⁷ and -65.1° .⁸ The liquid-vapor equilibrium pressures are presented in Table II, with an equation which estimates the normal b.p. as 108° and the Trouton constant as 21.0 cal./deg. mole.

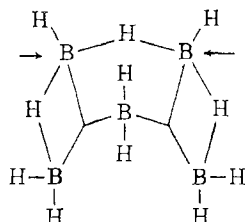
These results nearly confirm Stock's original 7.2 mm. at 0° and sharply contradict the data of Gibbins and Shapiro.⁷ Their graph of $\log P$ vs. $1/T$ would show a line concave upward, proving the presence of a more volatile impurity.

The infrared spectrum of B_6H_{10} was recorded for two samples: one made by the diglyme method and the other obtained as a by-product of the flow synthesis of B_5H_{11} ⁹; the latter B_6H_{10} sample could be guaranteed free of C-H impurities. The spectrum was recorded by the Beckman IR7 instrument, using a 10-cm. cell and pressures of B_6H_{10} vapor as high as 16 mm. The results for both samples were essentially the same, showing absorption at the following frequencies (in cm^{-1}): 2610 vs, 1940 s (broad), 1567 wsh, 1547 s, 1492 sh, 1487 sh, 1484 vs, 1481 sh, 1477 sh, 1027 sh, 1020 w, 1020 sh, 884 s, 777 sh, 760 s, 752 sh, 698 sh, 690 w, and 668 sh (v = very; s = strong; w = weak; sh = shoulder). Except for minor differences of intensity of some bands, these results agree reasonably well with an earlier spectrum⁷; however, the original record, kindly shown to us by Dr. Gibbins, includes a doubtful peak at 1625 cm^{-1} and a spurious one at 1351 cm^{-1} , which he ascribes to a trace of some higher polyborane.

The Dimethyl Ether Reaction.—The previously mentioned adduct of empirical composition $B_5H_{11} \cdot 1.56(CH_3)_2O$ was made again at -78° (using B_5H_{11} having a volatility of 52.8 mm. at 0°), with an apparent combining ratio of 1.50 $(CH_3)_2O$ per B_5H_{11} . However, a 3-hr. pumping at -78° led to

(7) S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).(8) A. Stock and E. Kusz, *Ber.*, **56**, 803 (1923).(9) A. B. Burg and F. G. A. Stone, *J. Am. Chem. Soc.*, **75**, 228 (1953).

the recovery of 4.8% of the ether and 1.1% of the pentaborane as B_5H_9 —presumably an original impurity, for no H_2 was observed. Thus the remaining adduct had the composition $B_5H_{11} \cdot 1.45 (CH_3)_2O$, suggesting solid-solution effects in the retention of $(CH_3)_2O$ beyond the 1:1 ratio. The experiment showed that the adduct was not a mixture of $(CH_3)_2OBH_3$ with some kind of etherated B_4H_8 , for the pumping at -78° gave no diborane, as by the reaction $2(CH_3)_2OBH_3 \rightarrow 2(CH_3)_2O + B_2H_6$.¹⁰ Most probably the main adduct formation was due to the maximum Lewis acid character of two boron atoms which participate triply in three-center bonding, namely those marked with arrows in the following structural pattern.¹¹



Attachment of $(CH_3)_2O$ to one marked B would suppress H-bridging to the other, which then would be a weaker Lewis acid than before.

It is just the unusual Lewis acid strength of the marked boron atoms which would most readily account for the hydrolysis of B_5H_{11} at 0° to give equimolar yields of B_4H_{10} :⁵ when water connects through O to one of the triply three-center bonded B atoms, it easily removes a neutral BH unit, leaving a pattern which can become ordinary B_4H_{10} by a minimal and localized readjustment of three-center bonds. Also the $(CH_2)_6N_4 \cdot B_5H_{11}$ reaction may well begin by an electron-dative attack at one of these especially electron-deficient boron atoms. It seems that $(CH_2)_6N_4$ in solid form cannot attach itself to boron in the $=BH_2$ situation (where $=$ means two three-center bonds); for it failed to absorb any liquid diborane at -78° or any gaseous diborane (at 3 atm.) up to 25° .

The adduct $B_5H_{11} \cdot 1.45(CH_3)_2O$ was treated with $1.24B_2H_6$ per B_5H_{11} (195 min. at -47° and 15 min. at -23°), with recovery of $1.51B_2H_6$ (net

(10) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 296 (1938).

(11) L. R. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 615 (1954).

gain, 0.27), $0.352B_5H_{11}$, and $0.003H_2$ per B_5H_{11} in the adduct. Evidently the initial presence of diborane did not much affect the yield of B_6H_{10} , which was estimated as 21% of the unrecovered B_5H_{11} . The other products were not measured.

Trimethylamine Borane as a Catalyst.—If B_5H_{11} really is a stronger Lewis acid than diborane (as indicated above), one might expect it to displace BH_3 (as diborane) from the decidedly stable complex $(CH_3)_3NBH_3$. The result then should be equivalent to the $(CH_3)_3N \cdot B_5H_{11}$ reaction⁸ in the presence of diborane. This hypothesis is supported by the results of an experiment in which 4.58 mmoles of $(CH_3)_3NBH_3$ (high-vacuum sublimed to form a wooly mass in a U-tube) and 1.61 mmoles of B_5H_{11} reacted only slightly during slow warming to -20° , but extensively during 2 hr. at 0° . The liquid and solid both turned yellow and the B_5H_{11} was 96% consumed. The yields of volatile products were 32% B_2H_6 , 6.5% B_4H_{10} , 13% B_6H_{10} , and approximately 10% B_5H_9 , all based upon boron not recovered as B_5H_{11} . There was a slight yield of a fraction corresponding to B_9H_{15} , and non-volatile solids accounted for some 30% of the boron. There was only a trace of decaborane. The recovery of $(CH_3)_3NBH_3$ was 4.169 mmoles; thus only 0.413 mmole of this had been consumed. Its function must have been primarily catalytic, perhaps in the postulated manner.

The borohydride ion might be construed as the stable complex $(H^-) \cdot BH_3$ and accordingly eligible for the same kind of catalytic reaction with B_5H_{11} as that just demonstrated for $(CH_3)_3NBH_3$. However, the reaction of solid $NaBH_4$ with B_5H_{11} during 2 hr. at 0° was no more than slight—possibly for lack of a large surface. There is no known B_5H_{11} -inert solvent for $NaBH_4$; thus the reaction could not be tried in the liquid phase.

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