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Organoboranes. II. The Preparation and Properties of Alkyldiboranes Containing Bulky Alkyl Substituents[1]

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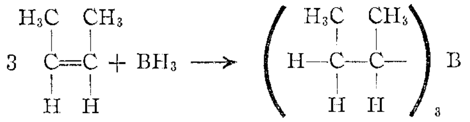
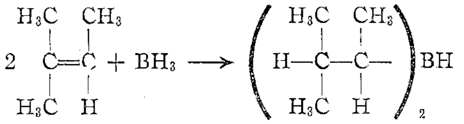
The reaction of a number of representative hindered olefins with diborane was investigated as a possible route to the preparation of monoalkyl- and dialkylboranes. The hydroboration of 2-methyl-2-butene yields bis-3-methyl-2-butylborane (disiamylborane) in 99% yield. Molecular weight determinations and the infrared spectrum identify the products as a dimer, *sym*-tetrasiamyldiborane. The dimer reacts at 0° with diborane in diglyme solution to form the unsymmetrical dimer, 1,1-disiamyldiborane, in equilibrium with the reactants. The trimethylamine addition compound of disiamylborane is relatively unstable; it is partially dissociated into its components at room temperature. Tetrasiamyldiborane undergoes rapid methanolysis, being converted into methyl disiamylborinate which is slowly oxidized by dry air. The hydroboration of 2,3-dimethyl-2-butene yields 2,3-dimethyl-2-butylborane (thexylborane), while 2,4,4-trimethyl-2-pentene yields 2,4,4-trimethyl-3-pentylborane, both in quantitative yields. Molecular weight determinations and infrared spectra reveal that these compounds are the symmetrical dimers, $RHBH_2BHR$. The infrared spectra indicate that the compounds are quite stable toward disproportionation. *sym*-Dithexyldiborane reacts with diborane in diglyme at 0° to form the monothexyldiborane. *sym*-Dithexyldiborane reacts with trimethylamine to form the addition compound, trimethylamine-thexylborane, stable at room temperature. The methanolysis of *sym*-dithexyldiborane is rapid, yielding dimethyl thexylboronate, which is stable in dry air. The hydroboration of cyclohexene and 1-methylcyclohexene, under controlled conditions in the stoichiometric ratios, yields the corresponding *sym*-tetraalkyldiboranes in quantitative yield. However, under the same conditions *d*-α-pinene reacts with diborane (tetrahydrofuran solution) to form an equilibrium mixture of triisopinocampheyldiborane and tetraisopinocampheyldiborane. The equilibrium can be shifted to the quantitative formation of the tetraalkyl derivative by addition of excess α-pinene. Tetraisopinocampheyldiborane reacts readily with methanol to form methyl diisopinocampheylborinate, an optically active borinate ester. The addition of cyclohexene or *d*-α-pinene to a solution of diborane in tetrahydrofuran, in a ratio of 1 olefin to 1 BH_3, yields the unsymmetrical dimer, $R_2BH_2BH_2$, in equilibrium with relatively small quantities of the symmetrical dimer, $R_2BH_2BR_2$, and tetrahydrofuran-borane. Finally, infrared examination of the reaction products produced in the hydroboration of 2-methylpropene, 2 methyl-1-butene, 2,4,4-trimethyl-1-pentene, and β-pinene (2 olefin/BH_3) confirmed the conclusion that the reaction proceeds primarily to the formation of the tetraalkyldiboranes, $R_2BH_2BR_2$, in equilibrium with small amounts of the unsymmetrical dialkyldiboranes, $R_2BH_2BH_2$, and unreacted tetrahydrofuran-borane.

The rapid reaction of diborane with olefins in the presence of ethers provides a convenient synthetic route to the organoboranes.[3] In the case of the large majority of olefins examined, the reaction proceeds quantitatively to the formation of the trialkylboranes



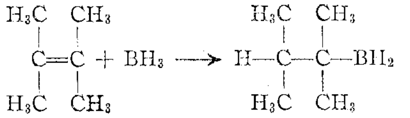
$$3\ \underset{H}{\overset{H_3C}{C}}=\underset{H}{\overset{CH_3}{C}} + BH_3 \longrightarrow \left(H-\underset{H}{\overset{H_3C}{C}}-\underset{H}{\overset{CH_3}{C}}-\right)_3 B \quad (1)$$

However, in the case of more hindered olefins, such as 2-methyl-2-butene, it was observed that hydroboration occurred rapidly only to the dialkylborane stage



$$2\ \underset{H_3C}{\overset{H_3C}{C}}=\underset{H}{\overset{CH_3}{C}} + BH_3 \longrightarrow \left(H-\underset{H_3C}{\overset{H_3C}{C}}-\underset{H}{\overset{CH_3}{C}}-\right)_2 BH \quad (2)$$

With a more hindered olefin, such as 2,3-dimethyl-2-butene, the reaction proceeded rapidly only to the monoalkylborane stage



$$\underset{H_3C}{\overset{H_3C}{C}}=\underset{CH_3}{\overset{CH_3}{C}} + BH_3 \longrightarrow H-\underset{H_3C}{\overset{H_3C}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-BH_2 \quad (3)$$

Some of these intermediates have proven to be of considerable value as selective hydroborating[4,5] and reducing agents.[6] Consequently, it appeared desirable to initiate a study of the reaction of diborane with a number of representative hindered

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[1] Based upon a thesis submitted by Gerald J. Klender in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Research assistant, 1957–1961, on Contract AT(11-1)-170 supported by the Atomic Energy Commission.

[3] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).

[4] H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961); G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183, 190 (1962).

[5] H. C. Brown and A. Moerikofer, *ibid.*, **83**, 3417 (1961).

[6] H. C. Brown and D. B. Bigley, *ibid.*, **83**, 486 (1961).

olefins in order to establish conditions for the ready synthesis of mono- and dialkylboranes of this kind.[7]

Although the data clearly indicate that a number of such substances containing bulky alkyl groups can be readily obtained *via* the hydroboration reaction, almost nothing is known about the pure, individual products. Their formation has been deduced from the stoichiometry of the reaction and the rates of olefin utilization.[3,7] They have been synthesized in solution and utilized in that form.[4–7] Accordingly, it appeared desirable to undertake the isolation and characterization of a number of such monoalkyl- and dialkylboranes containing bulky alkyl groups.[8]

It should be pointed out that the preparation of partially alkylated diboranes has been achieved previously by Schlesinger and his co-workers through the equilibration of trimethylborane, triethylborane, and tri-*n*-propylborane with diborane.[9] However, this procedure generally yields a mixture of derivatives[10] and the reaction products must be subjected to tedious fractionation to obtain pure components.[9]

It appeared that the controlled hydroboration of relatively hindered olefins offered a simple route to the quantitative synthesis of pure mono- and dialkylboranes with relatively bulky alkyl groups.[7] Accordingly, this study was restricted to products readily available through this new synthesis. A particularly detailed study was made of the dialkylborane from 2-methyl-2-butene (disiamylborane) and of the monoalkylborane from 2,3-dimethyl-2-butene (thexylborane), as typical representatives of the derivatives available *via* hydroboration.

These alkylboranes are highly sensitive to oxygen and moisture. Consequently, their isolation and characterization were largely carried out in the high vacuum apparatus, utilizing techniques common in the study of diborane chemistry.

The investigations of Shapiro and his co-workers on the infrared spectra of the methyl and ethyl derivatives of diborane have made available a powerful tool for the study of alkyl substituted diboranes.[11] It appeared desirable to subject the individual products to infrared examination as an aid in attaining an understanding of their structures and of the intermediates involved in their formation.

Results

Tri-*n*-pentylborane.—In order to test the experimental procedures, 1-pentene was treated with the theoretical quantity of diborane (6 1-pentene/B_2H_6) in the presence of ethyl ether at 0°. After several hours, the volatile materials were removed. Analysis indicated that the reaction was 98% complete. Ethyl ether was added and the molecular weight determined at 0° from the lowering of the vapor pressure. The observed value, 226 ± 3, agreed very well with the theoretical value of 224. In tetrahydrofuran, a less volatile solvent, the experimental uncertainty is somewhat greater. However, the value obtained, 237, was considered satisfactory.

The product was a liquid with no detectable vapor pressure at 0°, solid at −78°. The infrared spectrum was observed in carbon tetrachloride, cyclohexane, and tetrahydrofuran. The band at 1125 cm.$^{-1}$ (8.16 μ) was assigned to the boron–carbon stretching vibration, in excellent agreement with the reported[12] value of 1127 cm.$^{-1}$.

***sym*-Tetrasiamyldiborane.**—The reaction between 2-methyl-2-butene and diborane in ethyl ether at 0° in the ratio 2 olefin/BH_3 proceeded to 99% completion after 12 hr. The molecular weight in ethyl ether, from vapor pressure lowering, was 315, corresponding to the dimeric structure (calculated value: 308). In tetrahydrofuran the product was also dimeric, with an observed molecular weight of 297.

The product, a white solid with a vapor pressure of less than 0.1 mm. at 0°, was isolated by volatilization of the solvent. At room temperature the vapor pressure was less than 0.5 mm., but the product could be sublimed easily at room temperature in the high vacuum apparatus.

The product exhibited somewhat unusual behavior on melting, indicative of irreversible changes. Thus a sample which had been prepared and maintained for 24 hr. at 0° began to soften at 38.2° and melted from 40.6 to 44.5°, whereas an-

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(7) H. C. Brown and A. Moerikofer, *J. Am. Chem. Soc.*, **84**, 1478 (1962).

(8) This investigation has demonstrated that these substances exist as the dimers, even in ether solvents. Thus they are alkyldiboranes. However, it is often convenient to discuss them in terms of the monomeric formulation, and to consider them as diborane derivatives only in cases where the diborane structure is of significance in the chemistry of the product.

(9) H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, **57**, 621 (1935); H. I. Schlesinger, L. Horovitz, and A. B. Burg, *ibid.*, **58**, 407 (1936); H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *ibid.*, **61**, 1078 (1939).

(10) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, **82**, 4703 (1960).

(11) I. Shapiro, C. O. Wilson, Jr., and W. J. Lehman, *J. Chem. Phys.*, **29**, 237 (1958); W. J. Lehman, C. O. Wilson, Jr., and I. Shapiro, *ibid.*, **32**, 1088 (1960); *ibid.*, **32**, 1786 (1960); *ibid.*, **33**, 590 (1960).

(12) W. J. Lehman, C. O. Wilson, Jr., and I. Shapiro, *ibid.*, **28**, 777 (1958); *ibid.*, **28**, 781 (1958).

other sample prepared and maintained for 36 hr. at 0° began to melt at 35°, with most of the sample melting from 40.9 to 43.3°. Samples which were permitted to stand at room temperature for any length of time, or which had been sublimed, melted as low as 27°. Once a sample had been melted, it remained partially liquid at room temperature or lower. Eventually the entire sample liquified. One sample, placed in a sealed ampoule under vacuum, became liquid after six days at room temperature.

The infrared spectrum of tetrasiamyldiborane in cyclohexane solution exhibits a strong absorption at 1565 cm.$^{-1}$ (6.39 μ), characteristic of the bridge hydrogen absorption in diborane derivatives.[11] The spectrum in tetrahydrofuran solution is similar, with the boron–hydrogen bridge absorption undergoing a slight shift to 1551 cm.$^{-1}$ (6.41 μ).

A solution of tetrasiamyldiborane in diglyme rapidly absorbs diborane at 0°. When the theoretical quantity of diborane was introduced, the pressure dropped rapidly from 131 mm. to a residual value of 16 mm. at 0°. The drop in pressure corresponded to the equilibrium formation of a 1:1 reaction product which had proceeded 83% toward completion.

$$(\mathrm{Sia_2BH})_2 + \mathrm{B_2H_6} \underset{0^\circ}{\overset{\text{Diglyme}}{\rightleftharpoons}} 2\mathrm{Sia_2BH_2BH_2} \quad (4)$$

The rapid reaction at 0° indicates that we are not dealing with an exchange of alkyl groups and hydrogen.[8] The formation of the unsymmetrical disiamyldiborane, indicated in equation 4, was supported by the infrared spectrum. This revealed a strong doublet at 2571 cm.$^{-1}$ (3.89 μ) and 2500 cm.$^{-1}$ (4.0 μ) of equal intensity, characteristic of 1,1-dialkyldiboranes.[11] Moreover, there is present a very strong absorption, in the bridge-hydrogen region, at 1517 cm.$^{-1}$ (6.59 μ), shifted somewhat from the normal bridge band observed in tetrasiamyldiborane. This latter band is just barely visible as a shoulder at 1565 cm.$^{-1}$ (6.39 μ).

Trimethylamine reacts with tetrasiamyldiborane to form an unstable 1:1 addition compound

$$(\mathrm{Sia_2BH})_2 + 2(\mathrm{CH_3})_3\mathrm{N} \overset{0^\circ}{\rightleftharpoons} 2(\mathrm{CH_3})_3\mathrm{N{:}BHSia_2} \quad (5)$$

The product is a liquid at −78.7°, but melts at a slightly lower temperature, −86 to −82°. The product exhibited a dissociation pressure of trimethylamine above the addition compound of 1.6 mm. at −78.7°, 3.4 mm. at −63.6°, 8.1 mm. at −45.4°, 12.4 mm. at −36.8°, and 35.2 mm. at 0°. These values lead to a heat of dissociation of 6.7 kcal./mole, on the basis of the reaction

$$2(\mathrm{CH_3})_3\mathrm{N{:}BHSia_{2(l)}} \rightleftharpoons 2(\mathrm{CH_3})_3\mathrm{N_{(g)}} + (\mathrm{Sia_2BH})_{2(s)} \quad (6)$$

The addition compound in cyclohexane solution exhibited a very broad, rather weak absorption at 2366 cm.$^{-1}$ (4.3 μ) and a bridge absorption of reduced intensity at 1546 cm.$^{-1}$ (6.47 μ), indicating considerable dissociation in the solution at 25°.

Tetrasiamyldiborane reacts rapidly with the stoichiometric quantity of methanol in tetrahydrofuran solution at 0°, the reaction being 93% complete in 30 min. The product, a water white liquid, exhibited complete loss of the hydride absorption bands, with the appearance of new strong bands at 1330–1350 cm.$^{-1}$ (7.4–7.6 μ) for the boron–oxygen stretching frequency.

The pure ester was treated with dry air at 1 atm. pressure. Oxygen was absorbed—70% of the available oxygen in 2 hr.

***sym*-Dithexyldiborane.**—2,3-Dimethyl-2-butene was placed in contact with the theoretical quantity of diborane to form monothexylborane[7] in diethyl ether at 0°. After 1 hr., the volatile components were removed and examined—96% completion of the reaction was indicated. After 10 hr., the procedure indicated the complete absence of either diborane or the olefin in the volatile fraction, confirming the conclusion that a reaction mixture containing stoichiometric amounts of 2,3-dimethyl-2-butene and borane would react cleanly in a 1:1 ratio (eq. 3).[7]

The product was a water-white liquid with a vapor pressure of less than 0.5 mm. at 0°. However, it was sufficiently volatile to be distilled in the high vacuum apparatus. The compound melted from −34.7 to −32.3° and, in contrast to the behavior of tetrasiamyldiborane, the melting point was easily reproducible.

The molecular weight in ethyl ether solution (0.25 M) was 196. The calculated value for dimeric thexylborane is 197. In tetrahydrofuran solution (0.7 M), a molecular weight of 193 was observed.

The infrared spectra in cyclohexane and in tetrahydrofuran were identical. The bridge-hydrogen band was observed at 1565 cm.$^{-1}$ (6.39 μ), together with a single sharp band at 2540 cm.$^{-1}$ (3.98 μ) characteristic of the terminal BHR structure.[11]

The data are therefore consistent with the formation of thexylborane as the simple dimer, *sym*-dithexyldiborane.

Treatment of dithexyldiborane in diglyme solution at 0° with an equimolar quantity of diborane led to a rapid absorption of the gas, the pressure dropping from 137 to 72 mm. within 30 min. This absorption corresponds to 43% reaction to form monothexyldiborane.

$$(t\text{-HexBH}_2)_2 + \mathrm{B_2H_6} \rightleftharpoons 2t\text{-HexHBH}_2\mathrm{BH}_2 \quad (7)$$

The addition of another equal portion of diborane led to additional absorption, corresponding to 65% conversion to monothexyldiborane. By reducing the pressure it was possible to remove the diborane quantitatively.

The equilibrium was approached from the opposite direction. At −64° treatment of the *sym*-dithexyldiborane with an excess of diborane resulted in the quantitative absorption of diborane for formation of monothexyldiborane. The excess was removed and the temperature raised to 0°. Dissociation was observed and the reaction mixture came to equilibrium with the formation of 49% of the addition compound indicated. (This compares with the 43% value observed in approaching the equilibrium from the opposite direction.)

The ready dissociation of the addition compound created a problem for observation of the infrared spectrum. However, the 1:1 reaction mixture was examined at room temperature by utilizing an atmosphere of nitrogen above the solution to assist in repressing the escape of diborane. The bridge band was evident at 1565 cm.$^{-1}$ (6.39 μ) and diborane could not be detected in the spectrum. Besides the terminal boron–hydrogen band at 2500 cm.$^{-1}$ (4.0 μ), which would arise from a terminal BHR structure common to both *sym*-dithexyldiborane and monothexyldiborane, an asymmetric boron–hydrogen band was observed at 2571 cm.$^{-1}$ (3.89 μ). This could arise only from the terminal $\mathrm{BH_2}$ structure of the monothexylborane species.

sym-Dithexylborane reacted with excess trimethylamine at 0° to form a stable 1:1 addition compound

$$(t\text{-HexBH}_2)_2 + 2(\mathrm{CH_3})_3\mathrm{N} \xrightarrow{0°} 2(\mathrm{CH_3})_3\mathrm{N{:}BH_2}t\text{-Hex} \quad (8)$$

The product is a white solid at low temperatures, melting at −3 to −2° to a water-white liquid which exhibits no tendency to undergo dissociation at room temperature. The vapor pressure was approximately 0.2 mm. at 0° and under 1 mm. at 25°. It could be distilled about the high vacuum apparatus with no evidence for loss of trimethylamine.[13]

The infrared spectrum shows the characteristic absorption band at 2381 cm.$^{-1}$ (4.2 μ) and 2326 cm.$^{-1}$ (4.3 μ) for the symmetrical and asymmetrical boron–hydrogen stretching modes of a borane addition compound. The overtone band observed in trimethylamine-borane, ascribed to a $\mathrm{BH_3}$ deformation,[14] is absent in the spectrum of trimethylamine-thexylborane.

Methanol reacts rapidly at 0° with dithexylborane in tetrahydrofuran to convert both boron–hydrogen bonds to hydrogen[15]

$$(t\text{-HexBH}_2)_2 + 4\mathrm{CH_3OH} \xrightarrow{0°} 2t\text{-HexB(OCH}_3)_2 + 4\mathrm{H_2} \quad (9)$$

The product is a colorless liquid which exhibited no absorption of oxygen in contact with dry air over a period of 16 hr.

The infrared spectrum of the product, dimethyl thexylboronate, shows a strong absorption band at 1350–1290 cm.$^{-1}$ (7.4–7.7 μ), characteristic of the boron–oxygen band.

***sym*-Bis-(2,4,4-trimethyl-3-pentyl)-diborane.**—The study of the hydroboration of 2,4,4-trimethyl-2-pentene in diglyme indicated that the reaction proceeds rapidly to the monoalkylborane stage at 0°, and then relatively slowly to the dialkylborane stage.[7] It was confirmed that the reaction of 2,4,4-trimethyl-2-pentene with diborane in stoichiometric amounts provides a convenient route to the corresponding monoalkyl borane. Thus treatment of two moles of the olefin with one mole of diborane in diethyl ether at 0° led to the complete utilization of both olefin and diborane in 2 hr.

It had been demonstrated previously that the hydroboration of 2,4,4-trimethyl-2-pentene proceeds to place the boron atom on the secondary position.[16]

The product was a white solid which exhibited indefinite melting characteristics reminiscent of the behavior of tetrasiamyldiborane. Thus a freshly prepared sample was solid at 0°, but began

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(13) A related substance, trimethylamine-*t*-butylborane, has been synthesized *via* the Grignard reaction, followed by reduction of the *t*-butylboronic anhydride with lithium aluminum hydride in the presence of trimethylamine: M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

(14) B. Rice, R. J. Galiano, and W. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

(15) Under the same conditions only two of the three hydrogen atoms of borane react. The third comes off only after many hours, or by raising the temperature. Research in progress with Dr. David B. Bigley.

(16) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

melting somewhat over that temperature, becoming completely liquid at 33°. Once melted, the product did not completely solidify again at 0°. The product was sufficiently volatile to be sublimed slowly in the high vacuum apparatus at room temperature.

The molecular weight in ethyl ether (0.25 *M*) was 248, and in tetrahydrofuran (0.25 *M*), 250. The dimeric formulation requires a molecular weight of 252.

The infrared spectra exhibited boron–hydrogen bands at 2500 cm.$^{-1}$ (4.0 μ), a singlet, and at 1580 cm.$^{-1}$ (6.32 μ), characteristic of a symmetrical dimer, $(RBH_2)_2$.[11] No change in the spectrum was observed for a solution in cyclohexane which had been maintained under vacuum for four days at room temperature.

Thus the reaction product is to be formulated as bis-(2,4,4-trimethyl-3-pentyl)-diborane.

***sym*-Tetracyclohexyldiborane.**—Cyclohexene and diborane, in a 4/1 molar ratio, were permitted to react in the presence of diethyl ether at 0° for 14 hr. The reaction was complete, as shown by the absence of either of the two reactants in the volatile material removed from the reaction mixture. The reaction product was a white solid with no detectable vapor pressure at 0°. It could be sublimed at 80° under high vacuum. A sharp, reproducible melting point of 103–105° was observed.

The product was only slightly soluble in diethyl ether and tetrahydrofuran at 0°. From the lowering in vapor pressure, the solubilities were estimated to be 0.05 *M* in diethyl ether and 0.15 *M* in tetrahydrofuran. Because of these low solubilities, primary reliance was placed on the infrared spectrum to establish the dimeric nature of the product.

The product could be dissolved in cyclohexane and in tetrahydrofuran at 40–50°, with the solution separating only slowly at room temperature. These solutions exhibited a strong bridge hydride band at 1550 cm.$^{-1}$ (6.46 μ) with no absorption in the terminal boron–hydrogen region.[11] Consequently, the spectrum points to the formulation as the symmetrical dimer, tetracyclohexyldiborane.

***sym*-Tetrakis-(*trans*-2-methylcyclohexyl)-diborane.**—The reaction of diborane and 1-methylcyclohexene in diethyl ether at 0° proceeds without complication to the formation of the dialkylborane.[7] The product is a white solid, practically insoluble in ethyl ether, tetrahydrofuran, and cyclohexane. It melted in a sealed ampoule (under vacuum) at 116–119°. Once melted and resolidified, the material tended to melt at lower temperatures over a wide range.

The infrared spectrum was observed as a suspension of the product in cyclohexane and in tetrahydrofuran. A bridge-hydrogen band was evident at 1540 cm.$^{-1}$ (6.48 μ), indicating the existence of the product as a dimer.

***sym*-Tetraisopinocampheyldiborane.**—In preliminary experiments, α-pinene was treated with diborane (2 α-pinene per BH_3) in the presence of tetrahydrofuran at 0°. A solid precipitated, presumably diisopinocampheylborane (or its dimer), but free α-pinene was identified in the volatile products. Since the precipitation of an intermediate might have caused the incomplete reaction, the preparation was repeated, and the reaction was permitted to remain for 24 hr. at room temperature. Infrared examination showed the usual bridge band, but there also was present a distinct sharp singlet at 4.0 μ, characteristic of the terminal BHR structure. No change was observed after the mixture was permitted to stand for another two days. Methanol was added to convert residual boron–hydrogen bonds to hydrogen gas. The hydrogen collected was 20% greater (0.20 mmole) than calculated for the formation of tetraisopinocampheyldiborane. Gas chromatographic analysis of the solution revealed the presence of an equivalent quantity (0.20 mmole) of free α-pinene.

When the reaction was repeated with an excess of α-pinene, 3 α-pinene/BH_3, only the bridge band at 1522 cm.$^{-1}$ (6.57 μ) was evident in the infrared spectrum after 24 hr. Methanolysis of residual hydride and gas chromatographic analysis for residual α-pinene indicated that the reaction had proceeded 97% toward the formation of tetraisopinocampheyldiborane.

However, when the residual α-pinene and tetrahydrofuran were pumped from the product, re-examination in fresh tetrahydrofuran showed the reappearance of the boron–hydrogen terminal band at 2500 cm.$^{-1}$ (4.0 μ) and the slight shift of the bridge band to 1555 cm.$^{-1}$ (6.43 μ).

It is evident that the product, tetraisopinocampheyldiborane, is stable only in the presence of excess α-pinene; otherwise it exists as an equilibrium mixture of the tetra- and triisopinocampheyldiboranes.

In the presence of excess α-pinene (1.25 *M*), the product exhibited a solubility of approximately 0.1 *M* in tetrahydrofuran at 25°.

The derivative melted over a considerable range, 74.5–79°, with slow evolution of a material, presumably α-pinene.

Tetraisopinocampheyldiborane reacts readily with water and with methanol to liberate the theoretical quantity of hydrogen. The products, presumably diisopinocampheylborinic acid and its methyl ester, are much more soluble than the original diborane derivative.

It was of interest to examine the optical activity of this interesting hydroborating and reducing agent.[17,18] Accordingly, *d*-α-pinene ($[\alpha]^{20}\mathrm{D}$ + 47.5°; lit.[19] +51.5°) was hydroborated (3 olefin/BH_3) in sufficient tetrahydrofuran to give a clear solution (0.143 *M* in tetraisopinocampheyldiborane and 0.286 *M* in α-pinene). The optical rotation of this solution was measured and corrected for the optical contribution of the excess α-pinene. In this way the specific optical rotation of tetraisopinocampheyldiborane, $[\alpha]^{20}\mathrm{D}$, is −37.1°, and the molecular optical rotation, $[M]^{20}\mathrm{D}$ is −212.7°. The solution was treated with the calculated quantity of methanol to form the methyl ester of diisopinocampheylborinic acid: $[\alpha]^{20}\mathrm{D}$ −53.6°, $[M]^{20}\mathrm{D}$ −169.3°.

The Reaction of Cyclohexene and α-Pinene with Borane in a 1:1 Ratio—Tetracyclohexyldiborane possesses only very limited solubility in tetrahydrofuran at 0°. However, it was observed that no precipitate was obtained in adding cyclohexene to a solution of borane in tetrahydrofuran until the olefin/borane ratio exceeded one. This suggested the desirability of exploring the nature of the initial reaction product in the reaction of cyclohexene and α-pinene with borane in tetrahydrofuran.

Accordingly, cyclohexene was added slowly to an equimolar quantity of borane in tetrahydrofuran at 0°. The infrared spectrum of the solution was observed after one-half of the cyclohexene had been added, after complete addition, and 1 hr. after addition was complete. These spectra show that the unsymmetrical dimer, 1,1-dicyclohexyldiborane, is the major product of the reaction, with a strong doublet of equivalent intensities in the 2600–2500 cm.$^{-1}$ (3.85 and 3.96 μ) region and a strong bridge absorption at 1525 cm.$^{-1}$ (6.55 μ) showing the normal bridge absorption as a strong shoulder at 1563 cm.$^{-1}$ (6.40 μ). The spectra showed the presence of some free tetrahydrofuran-borane, even 1 hr. after the addition had been completed. However, no cyclohexene was present. The solution was clear at first, but became cloudy 1 hr. after complete addition of the olefin.

The reaction product was treated with methanol. Distillation at atmospheric pressure yielded methyl borate, corresponding to 45% of the borane used. Distillation at reduced pressure showed no dimethyl cyclohexaneboronate present. However, on attempting to distill the borinic ester at higher temperatures disproportionation into dimethylcyclohexaneboronate and tricyclohexylborane occurred.

These results point to the formation of the 1,1-dicyclohexylborane as the preferred product of the 1:1 reaction.

$$2C_6H_{10} + 2BH_3 \xrightarrow[\mathrm{THF}]{0°} (C_6H_{11})_2BH_2BH_2 \tag{9}$$

$$(C_6H_{11})_2BH_2BH_2 + 4CH_3OH \longrightarrow (C_6H_{11})_2BOCH_3 + (CH_3O)_3B + 4H_2 \tag{10}$$

In the same way, α-pinene was treated with an equimolar amount of borane in tetrahydrofuran. The spectrum of the reaction mixture, after 1 hr., exhibited a doublet of equal intensities at 2597 cm.$^{-1}$ (3.85 μ) and 2518 cm.$^{-1}$ (3.98 μ), and the shifted bridge band at 1513 cm.$^{-1}$ (6.61 μ). This spectrum established the formation of 1,1-diisopinocampheyldiborane as the major product. A band at 2200 cm.$^{-1}$ (4.15 μ) characteristic of tetrahydrofuran-borane and the normal bridge band, visible as a shoulder at 1550 cm.$^{-1}$ (6.42 μ), indicate the existence of an equilibrium mixture (eq. 11), estimated to be 90% to the left.

$$2R_2BH_2BH_2 \underset{\mathrm{THF}}{\overset{0°}{\rightleftharpoons}} R_2BH_2BR_2 + 2\mathrm{THF}:BH_3 \tag{11}$$

Removal of the tetrahydrofuran yielded a water-white liquid of negligible vapor pressure.

Hydroboration of Disubstituted Terminal Olefins.—The hydroboration of 2-methylpropene, 2-methyl-1-butene, 2,4,4-trimethyl-1-pentene, and β-pinene had been examined earlier in an effort to achieve the synthesis of dialkylboranes containing alkyl groups of only moderate steric requirements.[7] The earlier study utilized methanolysis of the reaction products, followed by distillation, to follow the course of the reaction. The data indicated that the addition of two moles of olefin to one mole of borane in tetrahydrofuran resulted in the formation of 10–13% unreacted borane,

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(17) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

(18) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 3166 (1961).

(19) F. H. Thurber and R. C. Thielke, *ibid.*, **53**, 1030 (1931).

20–26% of the trialkylborane, with 61–70% of the desired dialkylborane.

With the utility of the infrared tool demonstrated, it appeared desirable to re-study these reactions, applying infrared spectroscopy to examine the initial reaction products. Since the results merely confirm the previous conclusions, the experiments need not be reported in detail. One experiment will be described to illustrate the approach.

β-Pinene, 100 mmoles, was added to 50 mmoles of borane in 100 ml. of tetrahydrofuran. The spectrum, after 2 hr., showed a strong bridge-hydrogen absorption band at 1565 cm.$^{-1}$ (6.39 μ) and a weak doublet of roughly equal intensities at 2577 cm.$^{-1}$ (3.88 μ) and 2518 cm.$^{-1}$ (3.98 μ). A tetrahydrofuran-borane band of approximately twice the intensity of the doublet was observed at 4.13 μ. After 6 hr. there was no observable change in spectrum.

The observation that the two bands of the doublet are of equal intensity confirms the earlier conclusion that there is no significant quantity of monoalkylborane derivatives present. The di-β-pinylborane is largely present as tetra-β-pinyldiborane, accompanied by a small amount of 1,1-di-β-pinyldiborane.

The β-pinene used was material of 94% optical purity, with $[\alpha]^{20}\text{D}$ $-21.3°$ (lit.[19] $-22.7°$). Hydroboration to yield tri-β-pinylborane provided a product with $[\alpha]^{20}\text{D}$ $-27.4°$, $[M]^{20}\text{D}$ $-116°$. On the basis of the analysis of the 2 β-pinene/1 BH_3 reaction mixture, 13% tetrahydrofuran, 61% tetra-β-pinyldiborane, 26% tri-β-pinylborane, optical rotations were calculated for tetra-β-pinyldiborane: $[\alpha]^{20}\text{D}$ $-34.7°$, $[M]^{20}\text{D}$ $-197°$. The product was treated with methanol, producing the methyl ester of di-β-pinylborinic acid: $[\alpha]^{20}\text{D}$ $-27.0°$, $[M]^{20}\text{D}$ $-85.5°$.

Discussion

The present study has confirmed the conclusion that the hydroboration of a number of relatively hindered olefins provides a convenient route for the synthesis of the corresponding mono- and dialkylboranes in high purity.

Thus 2,3-dimethyl-2-butene is readily converted into 2,3-dimethyl-2-butylborane (thexylborane) and 2,4,4-trimethyl-2-pentene is converted into 2,4,4-trimethyl-3-pentylborane. In the case of less hindered olefins the reaction proceeds to the dialkylborane stage. In this way, 2-methyl-2-butene is converted into bis-(3-methyl-2-butyl)-borane (disiamylborane), and both cyclohexene and 1-methylcyclohexene are cleanly converted into the corresponding derivatives. α-Pinene can be converted into diisopinocampheylborane, but the product exhibits some tendency to lose α-pinene reversibly.

The individual reaction products have been isolated and characterized. Molecular weight determinations and infrared spectra reveal that these derivatives are uniformly dimeric, even in tetrahydrofuran, a solvent which readily dissociates diborane itself.[20] Consequently, the reaction products are more properly considered as alkyldiboranes, related to the simple derivatives previously synthesized by H. I. Schlesinger and his co-workers.[9]

The failure of tetrahydrofuran to dissociate *sym*-dithexyldiborane and related derivatives, as it does diborane itself[20] presumably is due to the combined polar and steric influences of the alkyl substituent which reduce the acceptor ability of the boron atom. This causes a decrease in the stability of the alkylborane addition compound relative to that formed by borane itself. On the other hand, the formation of a diborane bridge involves both the acceptor abilities of boron and the donor properties of the hydrogen. Although the alkyl substituent weakens the acceptor properties of the boron atom, it must simultaneously increase the donor properties of the hydrogen atom. The two effects should tend to compensate for each other, so that the bridge structure in the alkyl-substituted diboranes may possess stabilities comparable to that of diborane itself.

Certain of the products, such as *sym*-dithexyldiborane and *sym*-tetracyclohexyldiborane, exhibit relatively sharp, easily reproducible melting points. Others such as *sym*-tetrasiamyldiborane and *sym*-bis-(2,4,4-trimethyl-3-pentyl)-diborane, exhibit indefinite melting points which vary somewhat with the previous history of the sample. In part this behavior would appear to arise from formation of isomeric derivatives.

In the case of *sym*-diethexyldiborane, the boron atom becomes attached to the tertiary carbon atom. If we ignore the possibility for the existence of *cis–trans* isomers involving restricted rotation about the bridge-hydrogens,[21] the product

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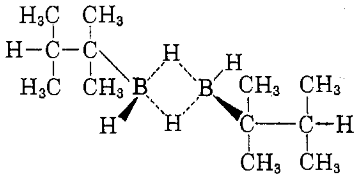
(20) (a) J. R. Elliott, W. L. Roth, G. T. Roedel, and E. M. Boldebuck, *J. Am. Chem. Soc.*, **74**, 5211 (1952); (b) B. Rice, J. A. Livasy, and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955).

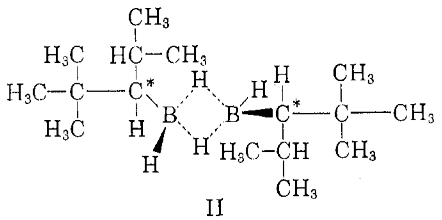
(21) Such isomerism has not been reported for diborane derivatives. In the present cases, the large steric requirements of the bulky alkyl substituents would favor strongly the formation of the *trans* derivative shown.



I

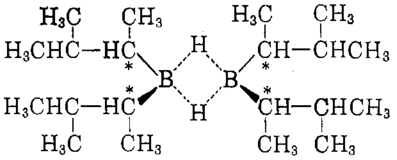
would exist only in one isomeric form (I). Similarly, only one isomer would be anticipated for *sym*-tetracyclohexyldiborane.

However, the attachment of the boron atom to the 3-position of 2,4,4-trimethyl-2-pentene creates a center of asymmetry. In this case the product should exist as a pair of diastereoisomers (*meso*, *dl*) (II).



II

The same argument leads to the conclusion that tetrasiamylborane contains four asymmetric centers and should form five different diastereoisomers (3 *meso*, 2 *dl*) (III).



III

Presumably hydroboration produces a mixture of diastereoisomers which interconvert relatively easily and cause the observed melting point to be both indefinite and dependent on the history of the sample.

sym-Dithexyldiborane and *sym*-tetrasiamyldiborane were selected for more detailed study, as representative "mono- and dialkylboranes."

Both substances absorb diborane readily at 0°, resulting in a reversible equilibrium distribution between the original symmetrical compounds and the corresponding unsymmetrical diboranes. This appears to be a general reaction of these alkyldiboranes.

$$(RBH_2)_2 + (BH_3)_2 \rightleftharpoons 2RHBH_2BH_2 \quad (12)$$

$$(R_2BH)_2 + (BH_3)_2 \rightleftharpoons 2R_2BH_2BH_2 \quad (13)$$

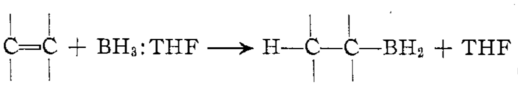
The equilibrium lies farther to the right with the siamyl, than with the thexyl derivative. This might be the result of the larger steric requirements of the four siamyl groups in tetrasiamyldiborane, as compared to the smaller steric requirements of the two thexyl groups in *sym*-dithexyldiborane. The presence of large strains in the tetraalkyldiborane molecule would be considerably relieved in the formation of the 1,1-dialkyldiborane. This could provide a potent driving force for the formation of the unsymmetrical derivative. Although a quantitative study was not attempted, some of the observations on the formation of 1,1-dicyclohexyldiborane and 1,1-diisopinocampheyldiborane by the controlled hydroboration of the olefins point to the existence in these systems of an equilibrium which lies strongly away from the *sym*-tetraalkyldiboranes.

sym-Dithexyldiborane forms a relatively stable addition compound with trimethylamine. On the other hand, *sym*-tetrasiamylborane forms an addition compound which is highly dissociated at room temperature. The heat of dissociation, 6.7 kcal./mole, is only a little greater than the heat of vaporization of trimethylamine, 5.5 kcal./mole. This behavior is presumably also a reflection of the very large steric requirements of the two siamyl groups.[22]

At 0°, in tetrahydrofuran solution, only two of the three hydrogen atoms of borane react readily with methanol. However, all of the mono- and dialkylboranes here prepared react readily and quantitatively with methanol to produce the corresponding boronic and borinic esters. Consequently, the hydroboration of these olefins also provides a convenient route for the quantitative synthesis of the corresponding borinic and boronic acids and esters.

The observation that the addition of cyclohexene or α-pinene to an equimolar quantity of borane (0°, tetrahydrofuran solution) leads predominantly to the formation of the 1,1-dialkyldiborane is important to an understanding of the reaction course.

In tetrahydrofuran solution, diborane exists as the monomeric species, tetrahydrofuran-borane. Presumably, the first step in the reaction must involve the addition of this component to the olefin to give the corresponding monoalkylborane



$$\overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + BH_3{:}THF \longrightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}BH_2 + THF \qquad (14)$$

In the case of highly hindered olefins, such as 2,4,4-trimethyl-2-pentene and 2,3-dimethyl-2-bu-

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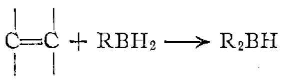
[22] The related addition compound, trimethylamine-dimethylborane, is quite stable at room temperature (ref. 9).

tene, the reaction to place an additional alkyl group upon the boron becomes relatively slow, and the monoalkylborane particles dimerize to form the *sym*-dialkyldiboranes which are identified in the reaction solution and isolated therefrom.

On the other hand, it appears that the reaction of a less hindered olefin with the monoalkylborane intermediate is faster than the reaction with tetrahydrofuran-borane. As a result, with these olefins the monoalkylborane intermediates are converted into dialkylborane derivatives in spite of the presence of considerable quantities of tetrahydrofuran-borane (eq. 15). The dialkylboranes apparently are able to compete successfully with tetrahydrofuran for the borane groups (eq. 16).



$$\mathrm{C{=}C + RBH_2 \longrightarrow R_2BH} \qquad (15)$$

$$\mathrm{R_2BH + BH_3{:}THF \rightleftharpoons R_2BH_2BH_2 + THF} \qquad (16)$$

The further addition of olefin converts the 1,1-dialkyldiborane derivative into the corresponding tetraalkyldiborane, and in the case of less hindered derivatives, into trialkylboranes.

In the case of the disubstituted terminal olefins (2-methylpropene, 2-methyl-1-butene, 2,4,4-trimethyl-2-pentene, and β-pinene), the reaction of the olefin with the tetraalkyldiborane appears to proceed at a rate competitive with the reaction of the olefin with tetrahydrofuran-borane. As a result, the reaction contains both the borane and trialkylborane in addition to the 60–70% of the desired tetraalkyldiborane.

Finally, it is of interest that the highly hindered olefin, α-pinene, undergoes conversion to the tetraisopinocampheyldiborane in tetrahydrofuran only in the presence of excess α-pinene.[23] There appears to be a reversible formation of a triisopinocampheyldiborane

$$\mathrm{R_2BH_2BR_2 \rightleftharpoons R_2BH_2BHR} + \alpha\text{-pinene} \qquad (17)$$

In spite of this difficulty, the ready formation of an optically active dialkylborane and its derivatives offers major promise as a useful synthetic tool.

Experimental Part

Materials.—Diborane was generated on the vacuum line by the slow addition of sodium borohydride solution in diglyme to a slight excess of boron trifluoride in diglyme.[24] It then was passed through successive −78 and −111.8° traps to obtain tensiometrically homogeneous material (v.p. 225 mm. at −111.8°). Sodium borohydride, a sample from Metal Hydrides of 98+ % purity, was used without further purification.

Diglyme (from the Ansul Chemical Co.) was treated with a small quantity of lithium aluminum hydride and distilled under reduced pressure. Boron trifluoride diglymate was prepared by adding freshly distilled boron trifluoride etherate to excess diglyme, followed by removing the ethyl ether under vacuum.

Diethyl ether (Mallinckrodt Analytical Reagent) was freed from inhibitor by distillation from lithium aluminum hydride into the vacuum apparatus. The central fraction, with a constant vapor pressure of 186.39 ± 0.08 mm. at ice temperature, was stored.

Tetrahydrofuran (Baker Analytical Grade) was distilled at atmospheric pressure under nitrogen from lithium aluminum hydride. The distillate was treated with fresh hydride into the vacuum apparatus. The central fraction exhibited a constant vapor pressure of 48.59 ± 0.10 mm. at 0°.

Trimethylamine (Eastman, anhydrous) was condensed on phosphorus pentoxide at 0°. The product then was fractionated from −80°. The material used exhibited a vapor pressure of 680 mm. at 0°.

Methanol (Baker Analytical Grade, 99.9%) was used without further treatment.

The olefins used were largely Phillips Petroleum Co. products, certified to be at least 99% pure. They have been characterized adequately in earlier publications. 2,3-Dimethyl-2-butene was a sample kindly provided by Dr. Kenneth Greenlee of A.P.I. Project 45 at Ohio State University. The material was distilled from calcium hydride directly into the vacuum apparatus. The sample exhibited the following properties: vapor pressure, 36.4 mm. at 0°, 107 mm. at 23°; $n^{20}\mathrm{D}$ 1.4125 (lit. $n^{20}\mathrm{D}$ 1.4122). α- and β-Pinene were samples of high optical activity from the Hercules Powder Company.

Apparatus and General Procedures.—The experiments were for the most part carried out on a high vacuum line using the general techniques described by Sanderson.[25]

All of the reactants were gases or volatile liquids, with the exception of diglyme. They were measured manometrically as gases, at less than 50% of the room temperature saturation pressure. Diglyme was measured by difference using a transfer tube, which was weighed before and after transfer.

Hydrogen evolved was measured manometrically by use of a Urry model Töpler pump.

Infrared Measurements.—A Perkin-Elmer Model 137 Infracord with sodium chloride optics was used for the spectra. Sealed sodium chloride cells, 0.05 mm., were used for the solutions and the solvent was compensated for in the reference cell either by use of a matched cell or by use of a variable thickness cell.

Because of the high sensitivity of these compounds to air, special sampling techniques were required. One ml. of solvent was measured by volume and condensed onto the isolated compound in a small flat-bottomed flask connected to the apparatus by a ground-joint, and containing a small Teflon covered magnetic stirring bar. Dry nitrogen was introduced and the cold flask separated under positive ni-

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[23] The insolubility of the product in diglyme appears to drive the reaction to essential completion (ref. 7).

[24] H. C. Brown and P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

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

trogen pressure and quickly closed with a rubber serum cap. The flask then was brought to room temperature and the excess pressure developed in the flask relieved by removing aliquots of nitrogen through the serum cap with a dry 1-cc. hypodermic syringe and a 3/8 in. No. 27 needle. At room temperature, the flask was stirred magnetically to assure uniform solution. The syringe needle again was inserted into the serum cap so that it protruded about 6 mm. into the flask. The flask then was tilted so that the solution ran down to the cap and a sample of about 0.2 ml. was withdrawn from the solution not in direct contact with the cap. The flask was tilted back, the syringe withdrawn and quickly transferred into a 0.05 mm. cell which had been completely flushed with nitrogen. The first portion of the solution entering the cell was forced through and absorbed on cotton. When the cell was filled, it was quickly capped with Teflon plugs and the spectrum taken. Solutions in the cell give reproducible spectra for at least 1 hr. Moreover, a second sample removed from the flask within 1 or 2 hr. exhibits no observable change from the spectrum taken with the original sample.

The infrared spectra are reported in the Ph.D. thesis of G. J. Klender, Purdue University Libraries.

Preparation of Tetrasiamyldiborane.—The following procedure is representative.

The reagents, 0.543 mmole of diborane and 2.172 mmoles of 2-methyl-2-butene (ratio of olefin/B_2H_6 = 4.01/1.00), were condensed onto 15.33 mmoles of diethyl ether and the mixture permitted to remain at 0° for 12 hr. The volatile products, 15.33 mmoles, were condensed away from the flask maintained at 0°. The product, tetrasiamyldiborane, remained in the flask as a white solid.

Ethyl ether, 14.88 mmoles, was introduced to give a clear solution at 0°. From the observed vapor pressure, 179.90 mm., a decrease in vapor pressure of 6.49 mm. was indicated. Correcting for the small amount of solvent in the gas phase, 0.09 mmole, we arrive at a molecular weight of 315. In a similar experiment 141.3 mg. of product (calculated on the basis of a quantitative synthesis from the diborane and 2-methyl-2-butene used) in 6.50 mmoles of tetrahydrofuran gave a vapor pressure lowering of 3.25 mm. The data lead to a molecular weight of 311.

Reaction of Tetrasiamyldiborane with Diborane.—Tetrasiamyldiborane, 0.500 mmole, formed a clear solution with 7.49 mmoles of diglyme at 0°. Diborane, 0.484 mmole, was added. The pressure initially was 131 mm. and dropped to 16 mm. in 8 min., remaining constant thereafter. From the amount of diborane in the gas phase and Henry's law constant, the amount of diborane reacting was estimated to be 0.402 mmole of the 0.484 mmole introduced.

Reaction of Tetrasiamyldiborane with Trimethylamine.—Trimethylamine, 9.69 mmoles, was condensed onto 0.485 mmole of tetrasiamyldiborane dimer and warmed to 0°. A clear water-white solution was observed. Excess trimethylamine, 8.71 mmoles, was removed at −78°, leaving the product (trimethylamine/tetrasiamyldiborane = 2.02/1.00) as a colorless liquid at −78°. The melting point was observed to be −86 to −82°. The sample was maintained at various temperatures and the dissociation pressures were observed. Trmiethylamine could be pumped off completely at 0°, leaving a white solid.

Reaction of Tetrasiamyldiborane with Methanol.—Methanol, 1.11 mmoles, was condensed on a solution of 0.528 mmole of tetrasiamyldiborane in 12.36 mmoles of tetrahydrofuran. The solution was brought to 0°. Hydrogen was evolved rapidly: 0.986 mmole (93%) in 30 min., 1.00 mmole in 1 hr., 1.01 mmoles (96%) in 16 hr. The borinate was a water-white liquid at 0°.

The ester, 0.30 mmole, was treated with 1.05 mmoles of dry air (0.21 mmole of oxygen). The drop in pressure was moderately slow. After 2 hr., the decrease in pressure corresponded to the absorption of 0.14 mmole of oxygen. Thus the product is reasonably sensitive to air oxidation.

Preparation of *sym*-Dithexyldiborane.—2,3-Dimethyl-2-butene, 1.22 mmoles, was reacted with 0.606 mmole of diborane in 11.21 mmoles of diethyl ether at 0°. After 10 hr., 11.21 mmoles of volatile products was removed, leaving a water-white liquid.

The product, 118.8 mg. (from the reactants used, assuming 100% conversion to product) in 10.68 mmoles of diethyl ether lowered the pressure to 176.41 mm., a vapor pressure lowering of 9.98 mm. This leads to a calculated molecular weight of 187.

Reaction of *sym*-Dithexyldiborane with Diborane.—Diborane, 0.488 mmole, was added to a clear solution of 0.472 mmole of dithexyldiborane in 6.90 mmoles of diglyme at 0°. The pressure dropped from an initial value of 137 mm. to a value of 72 mm. in 30 min. A second addition of diborane, 0.483 mmole, brought the pressure up to 192 mm., from whence it dropped to 177 mm. in 30 min. The first absorption of diborane amounted to 0.199 mmole (43% of the dithexyldiborane); the second to 0.306 mmole (65% of the dithexyldiborane). At −64° additional diborane reacted. Removal of excess diborane left a 1:1 product, *t*-Hex-HBH_2BH_2. At 0°, diborane was evolved from this product, demonstrating the reversibility of the reaction.

Reaction of *sym*-Dithexyldiborane with Trimethylamine.—The trimethylamine, 11.22 mmoles, was condensed on 0.535 mmole of dithexyldiborane at 0°. After 20 min., 10.12 mmoles of the amine was removed at −78°. The white solid which remained melted from −3 to −2°. It was stable at room temperature and could be distilled about the vacuum apparatus without loss of amine.

Reaction of *sym*-Dithexyldiborane with Methanol.—Methanol, 2.04 mmoles, was condensed on 0.509 mmole of thexylborane dimer in 12.8 mmoles of tetrahydrofuran. After 20 min., 2.00 mmoles of hydrogen was evolved, 2.05 mmoles after 12 hr. The product was stable to dry air under the same conditions as those utilized for the corresponding ester from tetrasiamyldiborane.

Preparation of *sym*-Bis-(2,4,4-trimethyl-3-pentyl)-diborane.—2,4,4-Trimethyl-2-pentene, 1.042 mmoles, and 0.521 mmole of diborane were allowed to react in 10.84 mmoles of diethyl ether at 0° for 2 hr. There was recovered 10.88 mmoles of volatiles which contained no diborane, and less than 0.1% of the original sample of olefin (gas chromatographic examination).

Preparation of *sym*-Tetracyclohexyldiborane and *sym*-Tetrakis-(*trans*-2-methylcyclohexyl)-diborane.—The procedures were similar to those described for the preparation of *sym*-tetrasiamyldiborane.

Preparation of *sym*-Tetraisopinocampheyldiborane.—*d*-α-Pinene, 0.27899 g. (2.047 mmoles) and diborane, 0.505 mmole, were condensed together in 9.26 mmoles of tetrahydrofuran. After 24 hr. at room temperature, infrared examination showed a singlet at 4.0 μ, indicating the presence of a terminal BHR structure. After three additional days, the infrared spectrum was the same. The volatile components of the system were removed and treated with ethylene glycol—the absence of hydrogen indicated the absence of residual diborane. In a duplicate experiment the total reaction mixture was treated with methanol. There was obtained 1.21 mmoles of hydrogen, whereas complete formation of diisopinocampheylborane would have resulted in 1.01 mmoles. The volatile products were separated and 0.229 mmole of α-pinene was found by gas chromatography. This corresponds to the excess hydride found. Therefore the reaction mixture contains 0.21 mmole of isopinocampheylborane and 0.81 mmole of diisopinocampheylborane. However, since the compounds exist as dimeric species, the products are 0.30 mmole of tetraisopinocampheyldiborane and 0.21 mmole of triisopinocampheyldiborane.

Excess α-pinene drives the reaction to completion, as shown by the following experiment. *d*-α-Pinene, 0.3731 g. (2.74 mmoles) and 0.455 mmole of diborane were condensed in 9.60 mmoles of tetrahydrofuran. After 24 hr. at room temperature, the infrared spectrum showed no terminal boron–hydrogen band. Methanolysis yielded 0.939 mmole of hydrogen (expected 0.910 mmole) and gas chromatography showed 0.961 mmole of α-pinene (expected 0.948). Oxidation of the methanolysis product, the methyl ester of diisopinocampheylborinic acid, with alkaline hydrogen peroxide yielded 0.94 mmole of boric acid (expected 0.91 mmole). The evidence is that the reaction had proceeded 97% to the formation of tetraisopinocampheyldiborane (0.44 mmole).

The infrared spectra for this system were determined at about 0.5 *M* in dimer. The products were only partially soluble in the tetrahydrofuran. It was noted that the suspension appeared to decrease or even disappear while the infrared spectra were measured.

Reaction of Cyclohexene and Borane in a 1:1 Ratio.—The reaction was carried out in the usual large scale hydroboration flask fitted with a dropping funnel, condenser, stirrer, and side-tube for removing samples with a hypodermic syringe. The system was flushed with nitrogen and a static nitrogen atmosphere was maintained throughout the reaction. In the flask was placed 247 ml. of a 1.39 *M* solution of borane in tetrahydrofuran, a total of 343 mmoles. The reaction mixture was cooled to 0°. Then 28.2 g. (343 mmoles) of cyclohexene was added through the pressure-equalized dropping funnel over 1 hr. followed by 65 ml. of tetrahydrofuran. Samples were removed for infrared examination after one-half of the cyclohexene had been added, after complete addition, and 1 hr. afterwards. The spectra indicated that the reaction had proceeded largely to the formation of 1,1-dicyclohexyldiborane.

After 2 hr., the reaction mixture at 0° was treated with 60 ml. (1.48 moles) of methanol, added slowly through the dropping funnel. There were evolved 12.64 l. of hydrogen (0.501 mole) in 0.5 hr., and 15.8 l. (0.629 mole) after 12 hr.[15] Material volatile at 60–65° (738 mm.) was distilled to recover methyl borate. Titration of an aliquot of the distillate in the presence of mannitol indicated the presence of 153 mmoles of methyl borate (171 mmoles expected for the formation of 1,1-dicyclohexylborane).

The pressure was reduced to 21 mm. and the temperature of the flask raised. A few drops distilled at 72°, but then distillation ceased as the pot temperature was raised from 120 to 200°. At this temperature material came over at 104°, but then came over too slowly to maintain a fixed temperature on the thermometer. The system behaved not as a simple distillation, but as a change of a less volatile material into a more volatile one. The residue solidified into a white solid, m.p. 96.5–99.5°, identified as tricyclohexylborane (lit. m.p. 98–100°).[26] There was obtained 19.4 g., 73 mmoles. The distillate, 15.9 g., was redistilled: 12.9 g. (82 mmoles) of dimethyl cyclohexylboronate, b.p. 67–68° at 14 mm., $n^{20}\text{D}$ 1.4375.

Anal. Calcd. for $C_8H_{17}O_2B$: C, 60.79; H, 10.84; B, 6.83. Found: C, 61.25; H, 11.23; B, 6.82.

Thus, the hydroboration to produce 1,1-dicyclohexylborane, followed by methanolysis and disproportionation, should yield 171 mmoles of methyl borate, 686 mmoles of hydrogen, 85 mmoles of dimethyl cyclohexylboronate, and 85 mmoles of tricyclohexylborane. In fact, there were obtained 153 mmoles of methyl borate, 629 mmoles of hydrogen, 82 mmoles of the boronate, and 73 mmoles of the borane.

The evidence is that the reaction proceeds almost quantitatively as indicated.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Dr. A. W. Moerikofer with several of the experiments here reported, especially those dealing with the determination of the optical rotations of boron derivatives of α- and β-pinene.

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(26) E. Krause and H. Pollack, *Ber.*, **61**, 271 (1928).