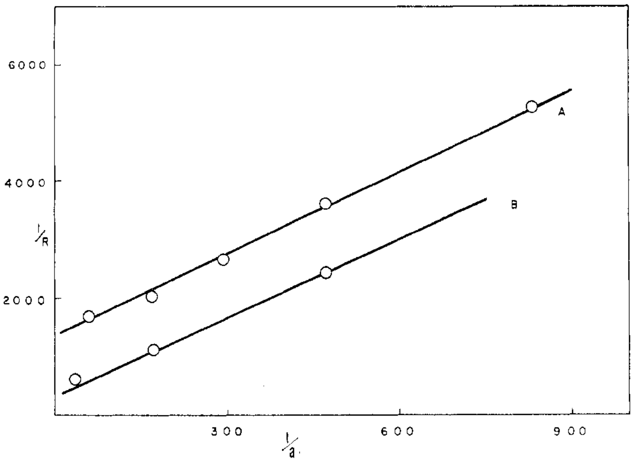

Fig. 5.—Dependence of $1/R$ *vs.* $1/a^{3/2}$ at 20°: curve A, $Al(BH_4)_3 = 2$ cm.; curve B, $Al(BH_4)_3 = 5$ cm.; a = deuteriodiborane concentration

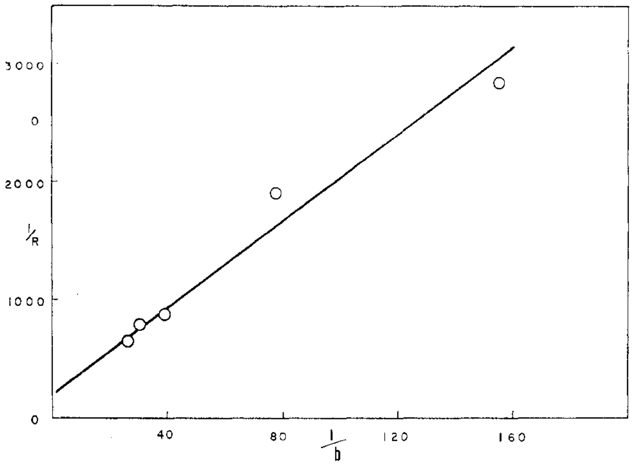

Fig. 6.—Dependence of $1/R$ *vs.* a/b at 20°; b = aluminum borohydride concentration.

would have $k_2(B_2D_6) = k_{-2}(BD_3)^2$. Case II then becomes

$$k_2(B_2D_6) << [(BD_3)^2/6(B_2D_6)]^{1/2}(B_2D_6)^{3/2}$$

$$k_2(B_2D_6) << (k_3/\sqrt{6})(BD_3)(B_2D_6)$$

This suggests that most of the B_2D_6 decomposes by means of reaction 12 rather than 11. This is the result that one would have predicted from our earlier published work. It is also possible to compare the value of $k_3(k_2/6k_{-2})^{1/2}$ obtained in this exchange with the earlier diborane work. The value of $k_3(k_2/6k_{-2})^{1/2}$ obtained from the earlier diborane work is 0.161, which compares favorably with the value 0.216 obtained in this exchange. This comparison serves as an additional test of the mechanism and provides a correlation of the two exchange reactions.

The preceding analysis shows that the usual dependence of R on a and b is consistent with a homogeneous mechanism. The results of the boron-10 exchange studies provide evidence that the boron atoms are undergoing exchange and a comparison of the rates of exchange of H to B^{10} provides evidence for the probable existence of borane (BH_3) as an intermediate in the exchange.

Acknowledgments.—Support of this research by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command Contract AF 18(603)-119 is gratefully acknowledged. The authors are indebted to Dr. Gerald Dudek of Harvard University for assisting us in the mass spectrometric analyses of the boron-10 mixtures and to Dr. Rudy Marcus of Brooklyn Polytechnic Institute for offering helpful suggestions concerning the kinetics. We wish to thank Mr. Edward Fletcher of the National Aeronautics and Space Administration, Cleveland, Ohio, for a sample of aluminum borohydride that was used in this work.

CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY
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Alkylation of Pentaborane-9 Catalyzed by Lewis Acids[1a]

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Substitution of alkyl groups for hydrogen at the apex boron atom of pentaborane-9 was accomplished by the reaction of olefins or alkyl halides in the presence of aluminum chloride, iron(III) chloride, or tin(IV) chloride. The direction of attack and the nature of the substituted alkyl group are consistent with an electrophilic attack on pentaborane-9. The following compounds were prepared and characterized: 1-methyl-, 1-ethyl-, 1-isopropyl-, and 1-*sec*-butylpentaborane-9, as well as 1-methyl-2-*sec*-butylpentaborane-9.

The alkylation of pentaborane-9 with ethylene, using aluminum(III) chloride as a catalyst,[2] has recently been reported. The work reported here confirms this result and also demonstrates that olefin addition to pentaborane-9 may be accomplished with a variety of olefins using anhydrous iron(III) chloride as a catalyst. Alkyl halides may also be used with aluminum(III) chloride to attach alkyl groups to a B_5 skeleton, chlorides and bromides reacting more readily than iodides.

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(1) (a) Abstracted from the Ph.D. Dissertations (Ohio State University) of S. W. H. (1956) and E. J. M. (1957); (b) Department of Chemistry, University of Florida, Gainesville, Florida.

(2) N. J. Blay, I. Dunstan, and R. J. Williams, *J. Chem. Soc.*, 430 (1960). Our work was completed prior to 1957, but publication was delayed by security restrictions.

Both olefins and alkyl halides give substitution at the apex boron atom when Lewis acids are used as catalysts, but polymerization of olefin, or alkyl halide, and rearrangement of the alkyl group may occur in the presence of the catalyst. Yields of alkyl pentaborane ranged from 50 to 85% based on the pentaborane-9 consumed, depending on the compound used and on the reaction conditions.

The 1-alkylpentaboranes prepared all were sensitive to air oxidation and to hydrolysis, the derivatives with smaller alkyl groups resembling pentaborane-9 more closely in this respect. The 1-alkylpentaboranes do not seem to be subject to further alkylation by olefins or alkyl halides in the presence of Lewis acids. 1-Methylpentaborane-9, and presumably the other 1-alkylpentaboranes also, does not react with anhydrous hydrogen halides, but is decomposed by hydrogen halides in the presence of aluminum chloride, as is pentaborane-9.

Experimental

Materials.—Pentaborane-9 was supplied by the Olin Mathieson Chemical Corporation and was quite pure as judged by its vapor pressure and melting point. The olefins used were Matheson C.P. grade products. The alkyl halides used were the best commercial grades available and were used after drying. Reagent grade iron(III) chloride, tin(IV) chloride, and aluminum chloride were used, the aluminum chloride being sublimed before use.

Analytical Methods.—Elemental analyses were made after oxidation of the samples with fuming nitric acid[3] in a sealed bulb. The carbon dioxide produced was purified in a vacuum train and measured as a gas. Boric acid was titrated as the mannitol complex. Hydrolysis by heating in a sealed bulb with air-free water yielded hydrogen, according to the equation

$$B_5H_8R + 14H_2O \longrightarrow 4B(OH)_3 + RB(OH)_2 + 11H_2; \quad R = \text{alkyl}$$

The weight per cent of hydrolyzable hydrogen (the hydrogen attached to boron) was then calculated from the stoichiometry of the equation and the amount of hydrogen gas formed.

Partial oxidation[4] with alkaline hydrogen peroxide yielded the alcohol corresponding to the alkyl group attached to boron. The solution was extracted with chloroform, dried, and the alcohol present was identified by the infrared spectrum of the solution.

1-Methylpentaborane-9.—Pentaborane-9 (38.0 mmoles), methyl iodide (63.3 mmoles), and anhydrous aluminum chloride (6.9 mmoles) were sealed in a 1-l. flask, together with a little mercury (to take up hydrogen iodide), and heated for 40 hr. at 100°. On opening the reaction vessel to the vacuum line, 12.2 mmoles of pentaborane-9 was recovered. The volatile reaction products isolated after repeated fractionations were hydrogen (32 mmoles), boron trichloride (4.6 mmoles), and 1-methylpentaborane-9 (16.7 mmoles). The yield of pentaborane derivative was 78% based on the pentaborane consumed.

The methylpentaborane collected from several runs was purified from pentaborane by heating it with more methyl iodide in the presence of aluminum chloride. Traces of methyl iodide remaining after fractionation were removed by shaking with mercury. No polymethyl derivatives of pentaborane were found.

Methyl bromide and methyl chloride react at much milder conditions than does methyl iodide. For example, 38.8 mmoles of pentaborane-9, 41.5 mmoles of methyl chloride, and 4.1 mmoles of aluminum chloride yielded 19.5 mmoles of 1-methylpentaborane-9 (50% yield) along with hydrogen (11 mmoles), hydrogen chloride, diborane, and methyldichloroborane (7 mmoles).

Anal. Calcd. for $B_5H_8CH_3$: C, 15.57; B, 70.07; H (hydrolyzable), 10.44; mol. wt., 71.20. Found: C, 15.5; B, 70.5; H (hydrolyzable), 10.8; mol. wt., 78.2.

1-Methylpentaborane-9 melts at −56 to −55° and has a normal boiling point of 75.2°. It has a vapor pressure of 144 mm. at 30°. Its vapor pressures in the temperature range −31 to 76° can be expressed by the equation $\log p\ (\text{mm.}) = -1.71 \times 10^3/T + 7.80$. The enthalpy of vaporization calculated from this equation is 7.82 kcal./mole and the entropy of vaporization at the boiling point is 21.5 e.u.[5]

1-Ethylpentaborane-9. A. From Ethylene.—Pentaborane-9 (98.5 mmoles) and ethylene (51.0 mmoles) were placed into a flask attached to a vacuum line containing 3.7 mmoles of anhydrous aluminum chloride which had previously been heated with 0.9 mmole of hydrogen chloride gas, and the mixture was stirred for 6.5 hr. at 27°. On fractionation, 25.8 mmoles of 1-ethylpentaborane was isolated; 30.4 mmoles of pentaborane and 39.9 mmoles of ethylene had been consumed. The yield of ethylpentaborane, based on the pentaborane used, was 85%. With mixtures of ethylene and pentaborane, where iron(III) chloride or tin(IV) chloride were added in the place of aluminum chloride, no reaction occurred at room temperature.

B. From Ethyl Iodide.—Pentaborane-9 (44.6 mmoles), ethyl iodide (29.5 mmoles), and aluminum chloride (3.5 mmoles) were sealed into a 1-l. Pyrex vessel and heated for 15 hr. at 100°. After repeated fractionations in the vacuum line 44 mmoles of hydrogen, 8.6 mmoles of ethane, 3.0 mmoles of hydrogen iodide, 2.0 mmoles of boron trichloride, and 9.1 mmoles of 1-ethylpentaborane-9 were isolated; 13.1 mmoles of unreacted pentaborane-9 was recovered. The yield of ethyl derivative was therefore 29% of the pentaborane used. Nonvolatile tars remained in the reaction flask.

The ethylpentaborane produced was further purified by a method similar to the one used for the purification of 1-methylpentaborane and was identical in all respects with the product obtained from the reaction of pentaborane-9 with ethylene in the presence of aluminum chloride.

C. From Ethyl Chloride.—Pentaborane-9 (48.9 mmoles), ethyl chloride (55.0 mmoles), and aluminum chloride (3.9 mmoles) reacted for 48 hr. at 25° in a 1-l. sealed bulb. The products were hydrogen (25 mmoles), ethane (16.2 mmoles), hydrogen chloride (2.1 mmoles), diborane (1.2 mmoles), and 1-ethylpentaborane-9 (25 mmoles). Ethyldichloroborane and boron trichloride were also found. The yield of ethylpentaborane corresponded to 51% of the pentaborane charged.

Anal. Calcd. for $B_5H_8C_2H_5$: C, 26.4; B, 59.3; H (hydrolyzable), 8.84; mol. wt., 91.22. Found: C, 25.7; B, 59.2; H (hydrolyzable), 8.73; mol. wt., 93.8.

The compound melts at −85 to −84°, boils normally at 106°,[6] and has a vapor pressure of 46.3 mm. at 30°. Its vapor pressure over the temperature interval 0–110° follows the equation $\log p\ (\text{mm.}) = -1.83 \times 10^3/T + 7.42$. Derived from this equation are the enthalpy of vaporization (8.37 kcal./mole) and the entropy of vaporization at the boiling point (21.5 e.u.).

1-Isopropylpentaborane-9.—In the vacuum line 114.8 mmoles of pentaborane-9 and 23.0 mmoles of propene were condensed into a reaction tube containing 1.7 mmoles of anhydrous iron(III) chloride and a trace of anhydrous hydrogen chloride. The mixture was kept at about 50° for 3.5 hr. In that time 20.4 mmoles of the pentaborane and all the olefin were consumed, and 14.9 mmoles of 1-isopropyl pentaborane-9 was isolated, corresponding to a yield of 73%, based on the pentaborane used.

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(3) H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, **57**, 621 (1935).

(4) A. R. Snyder, J. A. Kuck, and J. R. Johnson, *ibid.*, **60**, 106 (1938).

(5) In ref. 9 a compound was isolated in trace quantities and assumed to be 1-methylpentaborane-9, on the basis of infrared and gas chromatographic data. We can confirm this assumption since the reported infrared spectrum perfectly matches the spectrum of the 1-methylpentaborane-9 prepared here in quantity.

(6) N. J. Blay, I. Dunstan, and R. L. Williams, *J. Chem. Soc.*, 430 (1960), report m.p. 85°, b.p. 104°.

The compound melted between −93.5 and −92.5°, and its vapor pressure was 23.2 mm. at 30°. The vapor pressure varies over the temperature interval 0–125° according to the equation $\log p$ (mm.) $= -1.941 \times 10^3/T - 7.764$. This equation leads to a normal boiling point of 124°, an enthalpy of vaporization of 8.880 kcal./mole, and an entropy of vaporization at the boiling point of 22.3 e.u.

When anhydrous tin(IV) chloride was substituted for the iron(III) chloride catalyst, reaction of propene with pentaborane-9 also occurred, but separation of propylpentaborane and the catalyst was extremely difficult to achieve in the vacuum line because of the similarity in the vapor pressures of the two compounds. The use of anhydrous aluminum chloride as a possible catalyst did not produce reaction of propene with pentaborane, but resulted in extensive polymerization of the olefin.

1-*sec*-Butylpentaborane-9.—Pentaborane-9 (128.9 mmoles) and 1-butene (46.5 mmoles) were allowed to react at 50–60° in the presence of 5.5 mmoles of anhydrous iron(III) chloride for 5.5 hr.; 120.5 mmoles of pentaborane-9 and 38.3 mmoles of 1-butene were recovered in the vacuum line and 5.0 mmoles of 1-*sec*-butylpentaborane-9 was isolated. This quantity of product corresponds to a yield of 59% based on the pentaborane-9 consumed.

Anal. Calcd. for $B_5H_8C_4H_9$: C, 40.20; B, 45.36; H (hydrolyzable), 6.76. Found: C, 39.39; B, 44.5; H (hydrolyzable), 6.39; ratio C/B, 3.98/5.00. 2-Butanol was produced on oxidation with hydrogen peroxide.

The compound exhibited a vapor pressure of 6.6 mm. at 30° and a normal boiling point of 148°. In the temperature interval 26–155° its vapor pressure follows the relation $\log p$ (mm.) $= -2.160 \times 10^{-3}/T + 8.006$. From this equation an enthalpy of vaporization of 9.88 kcal./mole and an entropy of vaporization at the boiling point of 23.4 e.u. were calculated.

Tin(IV) chloride, pentaborane-9, and 2-butene did not react at 30° within 0.5 hr.; all of the starting materials were recovered. Aluminum chloride, however, produced rapid polymerization of 2-butene, and butylpentaborane could not be isolated. 1-*sec*-Butylpentaborane was also prepared from *sec*-butyl or *n*-butyl bromide by reaction with a stoichiometric quantity of pentaborane-9 in the presence of aluminum chloride. Yields of butylpentaborane were of the order of 50%, but the product was apparently a mixture of *sec*-butylpentaborane and isobutylpentaborane. This conclusion was reached after examination of the infrared spectra of the chloroform-soluble products from hydrogen peroxide oxidation. *sec*-Butyl alcohol and isobutyl alcohol were found to be present in varying ratios.

sec-Butyl bromide gave predominantly *sec*-butyl derivative (ratio *sec*:iso 30:1) at −11 or 0°. At 20° the ratio of *sec*-butyl derivative to isobutyl derivative was approximately 5:1. *n*-Butyl bromide gave at 0° a *sec*:iso ratio of 3:1 and at 20° a ratio of 3:2. Isobutyl bromide and *tert*-butyl bromide did not yield alkylated pentaboranes under the conditions of our experiment; instead, extensive polymerization of the alkyl groups resulted.

1-Methyl-2-*sec*-butylpentaborane-9.—2-*sec*-Butylpentaborane-9[10] (36.7 mmoles), methyl chloride (92.7 mmoles), and aluminum chloride (4.6 mmoles) were condensed together in a small Pyrex vessel, which was sealed under vacuum and left for 16 hr. at 25°. Hydrogen (19 mmoles) was pumped off and after repeated fractionation of the volatile components the reaction products isolated were: B_2H_6 (2.2 mmoles), HCl (18.6 mmoles), CH_3BCl_2 (5.3 mmoles), and $B_5H_7C_5H_{12}$, 1-methyl-2-*sec*-butylpentaborane-9 (13.4 mmoles). No other methyl derivatives were detected.

Anal. Calcd. for $B_5H_7C_5H_{12}$: C, 45.7; B, 40.6; mol. wt., 133.3. Found: C, 44.7; B, 40.1; ratio C/B, 1.004; mol. wt., 142.

The vapor pressure of the compound is 4.6 mm. at 30°. Vapor pressure data were obtained in the range 28–150° by gradually increasing the temperature of the sample. Decomposition with evolution of noncondensable gas occurred at the higher temperatures. The data are well represented by the equation $\log p$ (mm.) $= -2.14 \times 10^3/T + 7.75$. From this equation there were derived the enthalpy of vaporization, 9.78 kcal./mole, the normal boiling point, 164°, and the entropy of vaporization at the boiling point, 22.3 e.u.

Physical Properties.—Melting points and vapor pressures were determined in the vacuum line in apparatus described by Sanderson.[7] Molecular weights were determined from gas density measurements in apparatus similar to the one used for vapor pressure measurements, but having a bulb calibrated for volume. When the alkylpentaboranes had to be exposed to elevated temperatures great care had to be exercised in thoroughly degassing the equipment, in order to avoid decomposition of the sample with formation of noncondensable gas.

Spectra.—Infrared spectra were recorded with a Perkin-Elmer Model 21 double beam instrument. Spectra of the more volatile compounds (methyl- and ethylpentaborane) were recorded in gas cells suitable for filling in the vacuum line. Other spectra were run on the pure liquids.

All derivatives of pentaborane prepared here showed strong absorption bands in the same regions where pentaborane-9 absorbs (3.95, 5.5, 7.0, 9.7, and 11.3 μ),[8] in addition to absorptions attributable to the presence of the various alkyl groups in the structure. In the 5.5 μ region, two well resolved peaks were observed for all monoalkyl derivatives. In 1-methyl-2-*sec*-butylpentaborane-9 these bands had shifted sufficiently close to each other so that one band appeared only as a shoulder on the other. From a comparison of the infrared spectra of several pentaborane-9 derivatives singly-substituted either at the 1 position (apex)[9] or 2-position (base)[10] it appears that two well separated bands in the 5.5 μ region are a characteristic feature of 1-substituted pentaboranes.

B^{11} magnetic resonance spectra[11] were in agreement with reported observations.[12,13] The high-field absorption, which is a doublet in pentaborane-9 due to spin interaction with hydrogen, was a singlet in the alkyl derivatives prepared here.

Discussion

The compounds prepared here are assigned the structure of 1-pentaborane-9 derivatives. The evidence for this assignment is provided by the molecular weight data, by the elemental analysis and the hydrolysis data for the materials, and by the nature of the infrared and magnetic resonance spectra. Substitution for hydrogen at the apex of the pentaborane pyramid is indicated by the fact that the high-field, low-intensity doublet present in the B^{11} resonance spectrum of the parent compound, pentaborane-9, has coalesced into a singlet absorption. This implies that a proton in the 1 position has been replaced by a carbon atom. A similar change on substitution has been noted elsewhere.[2,12] The successful preparation of 1-methyl-2-*sec*-butylpentaborane-9 indicates that alkyl substitution in itself does not seriously deactivate the pentaborane structure toward further acid-catalyzed alkylation, if deactivation occurs at all. Multiple alkylation, however, was never found in the acid-catalyzed reaction, not even under conditions where polyalkylation products should have been easily detected. This then can be taken as contributing evidence that the acid-catalyzed alkylareaction leads to substitution at a chemically unique boron atom, *i.e.*, the apex boron atom.

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(8) H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

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(10) G. E. Ryschkewitsch, E. J. Mezey, E. R. Altwicker, H. H. Sisler, and A. B. Garrett, *Inorg. Chem.*, **2**, 893 (1963).

(11) J. N. Shoolery, Varian Associates, Palo Alto, California, private communication.

(12) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).

(13) R. Schaeffer, J. N. Shoolery, and R. J. Jones, *ibid.*, **79**, 4606 (1957).

1-Alkypentaboranes are apparently thermodynamically less stable than 2-alkylpentaboranes. This conclusion is based on the recently reported evidence that 1-ethylpentaborane quantitatively isomerizes to 2-ethylpentaborane in the presence of 2,6-lutidine.[12] The heats of combustion of 1-*sec*-butylpentaborane and 2-*sec*-butylpentaborane[10] also indicate that the apex-substituted derivative is less stable than the base-substituted one by at least 3 kcal./mole.[14] Therefore, the position of attachment of carbon on the pentaborane skeleton observed in the products must be controlled by the mechanism of the reaction rather than by the relative thermodynamic stabilities of the possible isomers.

Under the conditions of the reaction strongly electrophilic complexes of the Lewis acid and the olefin or alkyl halide would be expected to form. Indeed the observed reactions involving the alkyl portion of the system (polymerization, rearrangement by proton migration, rearrangement of carbon skeleton) are those typical of such complexes or of the carbonium ions derived from these complexes. Attack of the electrophilic carbon site of a polarized Lewis acid complex or carbonium ion would then occur at that boron atom in the pentaborane which has the highest electron density. According to molecular orbital calculations on pentaborane-9, this atom is the apex boron atom.[15,16] The predictions from the proposed mechanism are thus in full agreement with the observed facts.

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[14] E. A. Hasely, Ph.D. Dissertation, Ohio State University, 1956.

[15] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[16] W. N. Lipscomb, *ibid.*, **25**, 38 (1954).

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A New Synthesis of Alkylpentaboranes[1a]

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The reaction of olefins with pentaborane-9 at 150° was shown to give alkyl derivatives of pentaborane-9, with substitution at a base boron atom. *n*-Butyl-, *sec*-butyl-, isobutyl-, and ethylpentaborane were prepared. The direction of addition on the olefins, the position of substitutions on pentaborane-9, and the reactivity of the olefins are in accord with the expectations of the reaction involving nucleophilic attack of olefin on pentaborane-9.

Derivatives of pentaborane-9 with alkyl-substitution at the base of the B_5H_9 pyramid have been prepared by the isomerization of 1-alkylpentaboranes[2a] and by the pyrolysis of ethylene–diborane mixtures.[2b] In the latter case, ethylpentaboranes of the type $B_5H_{9-n}(C_2H_5)_n$, $n = 1$–5, were reported as minor components in the reaction mixture.[3]

We have prepared a number of pentaborane-9 derivatives in which one alkyl group is attached to the base of the pyramidal boron framework. This was accomplished by the direct reaction of pentaborane-9 with olefins using 1-butene, 2-butene, 2-methylpropene, and ethylene. Pentaborane-9–olefin mixtures were heated for several hours in sealed glass vessels at 150° and the products were separated in a vacuum line. Yields, based on B_5H_9 used, of monoalkyl derivatives ranged from 30 to 80%; between 5 and 10% of the initial B_5H_9 was converted to alkyl derivative under our reaction conditions. Other volatile products included trialkylborane, boron–carbon compounds of low volatility, saturated hydrocarbons, and, in some cases, hydrogen.

The reaction products not easily volatilized at room temperature probably contained more extensively alkylated pentaborane derivatives.

The alkylpentaboranes prepared here in a pure state are colorless, mobile liquids with a characteristic odor. They are very soluble in hydrocarbons, carbon tetrachloride, and ethers. In homogeneous mixture with water in ether solvents hydrolysis proceeds rapidly. In contact with pure water, however, they hydrolyze only slowly, presumably because of their low solubility in this solvent. The bulk liquids are oxidized rapidly in air and, when dispersed on glass wool or filter paper, may ignite spontaneously, even at room temperature. On heating under vacuum at 150° they slowly decompose. The alkylpentaboranes, like pentaborane itself, add aliphatic amines irreversibly. In view of the toxicity of pentaborane the compounds, when inhaled, might be toxic also.

Experimental

Materials.—Pentaborane-9 was kindly supplied by the Olin Mathieson Chemical Corporation and was tensiometrically pure. Olefins were Matheson C.P. grade products. The 2-butene used was the *cis–trans* mixture.

2-Isobutylpentaborane-9.—Pentaborane-9 (54.00 mmoles) and

[1] (a) Abstracted from the Ph.D. Dissertations (Ohio State University) of G. E. R. (1955), E. J. M. (1957), E. R. A. (1957), and the M.S. Thesis of E. J. M. (1954); (b) Department of Chemistry, University of Florida, Gainesville, Florida.

[2] (a) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961); T. P. Onak and F. J. Gerhardt, *Inorg. Chem.*, **1**, 742 (1962); (b) N. J. Blay, J. Williams, and R. G. Williams, *J. Chem. Soc.*, 424 (1960).

[3] This work was completed prior to 1957, but publication was delayed by security restrictions.