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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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

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[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.

isobutene (53.8 mmoles) were sealed into a 300-ml. Pyrex vessel fitted with a break-off arm and condensation tip. The mixture was heated for 7.5 hr. at 150°. (A liquid phase was present under these conditions.) The yield of hydrogen (pumped off and collected for measurement in the vacuum line) was 0.3 mmole. The condensable components were repeatedly fractionated in the vacuum line until the vapor pressures of the fractions became constant; 49.3 mmoles of B_5H_9 and 42.5 mmoles of i-C_4H_8 were recovered. In addition, 1.44 mmoles of tributylborane and 2.90 mmoles of 2-isobutylpentaborane-9 were isolated.

Anal. Calcd. for $B_5H_8C_4H_9$: C, 40.25; B (total), 45.30; B (by hydrolysis), 36.29; H (hydrolyzable), 6.75; mol. wt., 119.25. Found: C, 39.3; B (total), 45.20; B (by hydrolysis), 36.9; H (hydrolyzable), 6.54; mol. wt., 119.0.

Hydrogen peroxide oxidation gave isobutyl alcohol and no *tert*-butyl alcohol. Blank experiments with known mixtures of the two alcohols indicated that an impurity of tertiary alcohol greater than 5% of the total alcohol content could have been detected easily.

The compound has a vapor pressure of 5.7 mm. at 30° and a normal boiling point of 152° (extrapolated).

The amount of the alkylpentaborane produced corresponded to a conversion of 5.4% of the pentaborane charged to alkyl derivative with a yield of 61%, based on the pentaborane used up in the reaction. The material remaining in the reaction vessel was a dark yellow viscous liquid of low volatility. The material balance for the reaction indicated a carbon to boron atom ratio of 0.52 in this liquid. The liquid evolved hydrogen on heating with water and had infrared absorption bands similar to the absorption bands of pentaborane-9.

2-*n*-Butylpentaborane-9.—Pentaborane-9 (39.7 mmoles) and 1-butene (46.1 mmoles) reacted in a 300-ml. vessel at 150° for 14.5 hr.; 2.1% of the pentaborane charged was converted to alkyl derivative with a yield of 59%, based on the pentaborane used up. Hydrogen (0.18 mmole), *n*-butane (0.94 mmole), and a small amount of tri-*n*-butylborane were the other volatile products.

Anal. Calcd. for $B_5H_8C_4H_9$: C, 40.25; B, 45.30; H (hydrolyzable), 6.75; mol. wt., 119.25. Found: C, 40.1; B, 44.80; H (hydrolyzable), 6.76; mol. wt., 117.4.

Hydrogen peroxide oxidation gave *n*-butyl alcohol only. The compound has a vapor pressure of 4.1 mm. at 30° and a normal boiling point of 154.5° (extrapolated).

2-*sec*-Butylpentaborane-9.—In the reaction of 99.8 mmoles of pentaborane-9 with 111.9 mmoles of 2-butene in a 300-ml. Pyrex vessel at 150° for 9 hr., 16.8% of the pentaborane charged was converted to alkyl derivative. The yield of alkyl derivative was 57% based on the pentaborane used up. In addition, there were produced 4.9 mmoles of *n*-butane and also tri-*sec*-butylborane.

Anal. Calcd. for $B_5H_8C_4H_9$: C, 40.25; B, 45.30; H (hydrolyzable), 6.75; mol. wt., 119.25. Found: C, 39.62; B, 45.08; H (hydrolyzable), 6.60; mol. wt., 130.

The compound has a vapor pressure of 5.8 mm. at 30° and a normal boiling point of 150° (extrapolated).

Attempted Reaction of Pentaborane-9 with Trimethylborane.—Pentaborane-9 (51.2 mmoles) and trimethylborane (42.3 mmoles) were heated in a 1-l. Pyrex bulb at 150° for 48 hr. On opening to the vacuum line 99% of the pentaborane and the trimethylborane were recovered pure and a trace of a material with a vapor pressure of 5 mm. at −80° was isolated.

Reaction of Pentaborane-9 with Ethylene.—In a representative experiment 35.8 mmoles of pentaborane-9 and 38.5 mmoles of ethylene were heated in a 200-ml. stainless steel bomb at 150° for 66 hr.; 31.9 mmoles of pentaborane-9 and 32.4 mmoles of ethylene were recovered on fractionation in the vacuum line. After repeated vacuum line fractionation the volatile reaction products were separated into three fractions, designated A (0.044 g.), B (0.286 g.), and C (0.057 g.); 20 mg. of less volatile material remained in the bomb.

Fraction A, with a vapor pressure of 6.0 mm. at 0°, proved to be predominantly ethylpentaborane.

Anal. Calcd. for $B_5H_8C_2H_5$: C, 26.4; B, 59.3. Found: C, 39.3; B, 54.4. A similar fraction from another experiment gave: C, 30.8; B, 50.8.

The infrared spectrum of fraction A indicated the presence of pentaborane derivative with triethylborane as impurity. The ethylpentaborane content calculated from the elemental analysis and assuming triethylborane as the only other impurity was about 85 mole %. Fraction C (vapor pressure 13.0 mm., 0°) proved to be impure triethylborane. Triethylborane has a vapor pressure of 12.5 mm. at 0°. Fraction B (vapor pressure 10 mm., 0°) was a mixture of fractions A and C. Further attempts at purification of the ethylpentaborane sample in the vacuum line proved to be fruitless since the vapor pressures of the components were too close together.

Analytical Methods. Oxidation.—Weighed samples were condensed into bomb tubes containing a few ml. of fuming nitric acid at −196° and the tubes were sealed and slowly warmed. Contact with liquid nitric acid near room temperature produced, on occasion, violent explosion. The samples were heated for about 24 hr. at 250°. The carbon dioxide produced in the oxidation was purified in a vacuum train and measured as a gas.[4] The boric acid remaining in the bomb tube was titrated as the mannitol complex.

Hydrolysis.—Weighed samples were heated with water for 20 hr. at 150° in sealed tubes. The hydrogen evolved was pumped off at −196° and measured as gas. Weight per cents of hydrolyzable hydrogen in the samples were then calculated according to the equation

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

Boric acid in the hydrolyzed mixture was titrated with standard NaOH in the presence of mannitol to the end point of the mannitol complex. The alkylboric acids which are also present in the mixture do not interfere with this titration.

Oxidation with Hydrogen Peroxide.—Partial oxidation[5] of the alkylpentaboranes, leaving the carbon skeleton of the alkyl groups intact, was accomplished by treating samples with 10% hydrogen peroxide in alkaline solution. The alcohol thus produced was extracted with chloroform and identified by the infrared spectrum of the solution. In each instance only one alcohol was found to be present.

Vapor Pressure and Molecular Weight.—Vapor pressures were determined statically in a tensimeter similar to the one described by Sanderson.[6] Molecular weights were determined by gas density in an apparatus similar to the tensimeter. During these measurements reaction to form products with high volatility occurred in several instances. Reproducible results were obtained only after the apparatus was degassed for several days at elevated temperature. Even then, prolonged heating of the samples at 150° led to slow decomposition. Table I lists the values of the constants derived by fitting the equation $\log p$ (mm.) $= -A/T + B$ to the vapor pressure data. The enthalpies of vaporization and the entropies of vaporization at the boiling point were calculated from the vapor pressure equation and are also listed.

Spectra.—Infrared spectra were determined from the pure liquids with a Perkin-Elmer Model 21 double beam instrument.

TABLE I

CONSTANTS IN VAPOR PRESSURE EQUATION $\log p = -A/T + B$, HEAT OF VAPORIZATION, AND ENTROPY OF VAPORIZATION FOR SOME BUTYLPENTABORANES

Alkyl group	$A \times 10^{-3}$	B	ΔH_v	ΔS_v
n-C_4H_9	2.34	8.34	10.71	25.0
sec-C_4H_9	2.26	8.23	10.35	24.5
i-C_4H_9	2.25	8.17	10.29	24.2

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

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

(6) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 84.

All compounds had absorption bands in the same region where pentaborane-9 absorbs (3.95, 5.5, 7.0, and 11.3 μ). Superimposed on these bands were the absorptions characteristic of the alkyl groups. In the 5.5 μ region only a single strong band was observed. In contrast, a number of pentaborane derivatives substituted at the apex boron atom show two strong bands in this region.[7,8]

The B^{11} nuclear magnetic resonance spectra of the compounds[9] showed two doublet peaks, as in pentaborane-9.[2a,10] The high field peak, associated with the apex boron atom, was of lowest intensity.

Discussion

The experiments reported here leave little doubt of the structure of the derivatives. Elemental analysis, hydrolysis data, molecular weight, and the characteristics of the infrared spectra indicate the presence of a singly-substituted pentaborane-9. The production, on peroxide oxidation, of alcohol with only one OH function shows the presence of only one boron–carbon per alkyl unit and the position of the OH group on the carbon skeleton indicates the place of original attachment of a pentaborane unit.[5] The fact that the B^{11} magnetic resonance spectrum contains a doublet, with a chemical shift and intensity appropriate to the unique boron atom in pentaborane-9 (the apex boron position), shows that the apex boron atom is still bonded to hydrogen and that, therefore, the alkyl group must be attached at one of the boron atoms at the base of the molecule (position 2). This conclusion is supported by the observation that the *sec*-butylpentaborane from the reaction of 2-butene with pentaborane-9 reported here differs from the isomeric *sec*-butyl derivative which has been prepared by the $AlCl_3$-catalyzed addition of 1-butene to pentaborane-9. The latter reaction has been shown to lead to substitution at the 1 position in pentaborane, the apex atom.[8,11] Lastly, the existence of polyalkylated derivatives implies that at least one position on the base of the B_5 pyramid must be alkylated. The over-all reaction must then be capable of effecting substitution at the 2-position of pentaborane-9.

Trimethylborane does not react with pentaborane-9 under conditions where alkylation with olefins occurred. This leads one to believe that the alkylboranes found as reaction products are not the important alkylating agents but are produced subsequent to alkylation of the pentaborane structure. Instead, consideration of the electronic structure of pentaborane-9 suggests that direct attack of olefin on pentaborane occurs.

A simple molecular orbital treatment of pentaborane-9 in terms of three-center bonds predicts a small positive formal charge on each of the boron atoms and a small negative formal charge on the apex boron atom.[12,13] Nucleophilic attack by the olefinic system would be expected to occur at the point of lowest electron density in the boron framework, that is, at a base boron atom. In harmony with this view, only one alkyl isomer was produced from either 1-butene or 2-methylpropene, where two different alkyl isomers could have been formed by addition to either side of the double bond. Since in the reaction with 2-butene no *n*-butyl derivative was found, isomerization, which changes the point of attachment of boron on the carbon skeleton, and which occurs in alkylboranes at elevated temperatures,[14] must be ruled out. The position of the observed attachment of boron on the carbon skeleton in the pentaborane derivative which was finally isolated thus represents the position of initial attack and this position is indeed the one with highest electron density in the olefin. The relative reactivities of the various olefins toward reaction with pentaborane, as judged by the amounts of pentaborane-9 consumed, also are in accord with a mechanism of nucleophilic attack by the olefin. Ethylene is the least reactive one and, as alkyl groups are substituted for hydrogen adjacent to the double bond, reactivity increases in the series ethylene, 1-butene, 2-butene or 2-methylpropene. (The latter two olefins are quite similar in reactivity.)

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