CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REACTION MOTORS DIVISION, THIOKOL CHEMICAL CORPORATION, DENVILLE, NEW JERSEY

Carboranes. V. Silicon Derivatives[1,2]

BY NELSON N. SCHWARTZ, EUGENE O'BRIEN, SIDNEY KARLAN, AND MARVIN M. FEIN

Received September 25, 1964

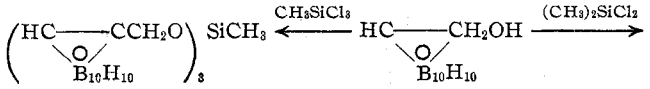
Compounds containing silicon and carborane groups were prepared by (1) reaction of hydroxymethylcarboranes with alkylchlorosilanes, (2) reaction of alkynylsilanes with bis(acetonitrile)decaborane, (3) addition of silanes to alkenyl carboranes, and (4) reaction of carboranyl alkylmagnesium halides with alkoxysilanes. Reaction 1 gave good yields of monomeric products but exocycles were formed when polymers were anticipated. Reaction 2 gave very low yields. Reaction 3 was hindered by increasing proximity of the carborane group. Reaction 4 gave largely carborane–silicon-bonded products due to rearrangement of the Grignard. This rearrangement was found to be favored by increasing basicity of the solvent, increasing temperature, and decreasing length of the alkyl side chain.

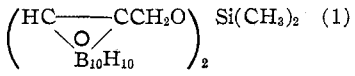
Introduction

In contrast to most other boron hydride derivatives, the carboranes exhibit remarkable hydrolytic, oxidative, and thermal stability.[1,3] This suggests that the polymerization of appropriately constituted carboranyl silanes might afford products with highly desirable characteristics for some specialized applications. The preparation of a series of representative carboranyl silanes was therefore investigated. The results of the synthetic aspects of this investigation are presented in this paper.

Results and Discussion

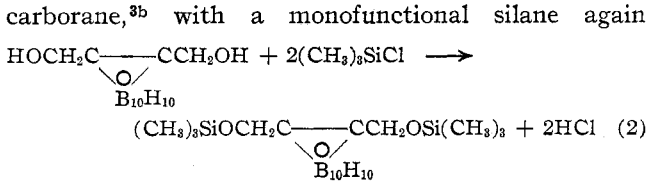
Carboranylalkoxysilanes.—Alkoxysilanes are formed by treatment of an alcohol with a halosilane and extension of this reaction to a carbonyl alcohol results in the formation of the anticipated carboranyl ester. As prototype reactions, 1-hydroxymethylcarborane was treated with dimethyldichlorosilane and methyltrichlorosilane; the anticipated products were obtained in good yield.





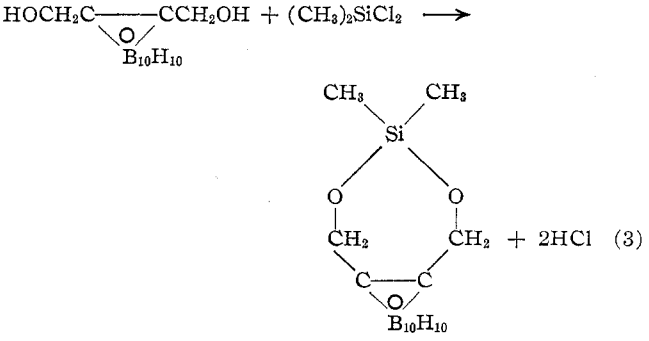
(1)

The reaction of the diol, 1,2-bis(hydroxymethyl)-carborane,[3b] with a monofunctional silane again



(2)

produced the anticipated product. In contrast to the above reactions, the interaction of two difunctional monomers, the carborane diol, and excess dimethyldichlorosilane did not proceed as expected; a seven-membered exocyclic ring was formed. The tendency to produce exocycles containing five, six, and seven ring atoms has been reported previously.[4,5] This formation of a seven-membered exocycle is another example of the tendency of 1,2 difunctional carboranes to cyclize.



(3)

When the analogous reaction was conducted in excess dimethyldiethoxysilane a mixture of products was obtained. The major product (65–70%) was once again the same seven-membered exocycle, although a small amount of a low molecular weight polymeric oil was formed.

Treatment of the cyclic compound with catalytic amounts of acid (*p*-toluenesulfonic acid) or base (KOH) resulted in hydrolysis to the original diol instead of polymerization to a carborane-containing polymer.

The thermal stability of these compounds was determined in a constant volume system by determining the increase in pressure at given temperatures. Those materials derived from the monohydroxycarborane exhibited initial decomposition in the 300–320° range; those prepared from the diol decomposed below 200°.

Carboranylsilanes.—The reaction of ethynyltrimethylsilane with 6,9-bis(acetonitrile)decaborane produced low yields (2.5%) of the desired product,

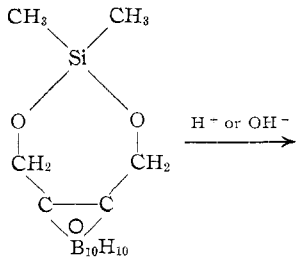
(1) Paper IV: D. Grafstein, J. Bobinski, J. Dvorak, J. Paustian, H. Smith, S. Karlan, C. Vogel, and M. Fein, *Inorg. Chem.*, **2**, 1125 (1963).

(2) All inquiries should be addressed to Mr. Joseph Green at the above address.

(3) (a) M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. Cohen, *Inorg. Chem.*, **2**, 1111 (1963); (b) M. Fein, D. Grafstein, J. Paustian, J. Bobinski, B. Lichstein, N. Mayes, N. Schwartz, and M. Cohen, *ibid.*, **2**, 1115 (1963); (c) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. Cohen, and M. Fein, *ibid.*, **2**, 1120 (1963); (d) T. Heying, J. Ager, S. Clark, D. Mangold, H. Goldstein, M. Hillman, R. Polak, and J. Szymanski, *ibid.*, **2**, 1089 (1963).

(4) T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963); S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963); R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).

(5) J. Green, N. Mayes, A. P. Kotloby, M. M. Fein, E. L. O'Brien, and M. S. Cohen, *Polymer Letters*, **2**, 109 (1964); J. Green, N. Mayes, A. P. Kotloby, and M. S. Cohen, *J. Polymer Sci.*, **2A**, 3135 (1964).



$$HOCH_2C(B_{10}H_{10})CCH_2OH + \left[\begin{matrix}CH_3\\|\\SiO\\|\\CH_3\end{matrix}\right]_n \quad (4)$$

1-carboranyltrimethylsilane (m.p. 80–85°).[6] Pure compounds could not be isolated when propynyltriethoxysilane was treated with the bis(acetonitrile)decaborane.

$$(CH_3CN)_2B_{10}H_{12} + HC{\equiv}CSi(CH_3)_3 \longrightarrow HC(B_{10}H_{10})CSi(CH_3)_3 + 2CH_3CN + H_2 \quad (5)$$

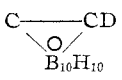
$$(CH_3CN)_2B_{10}H_{12} \xrightarrow{CH_3C{\equiv}CSi(OC_2H_5)_3} \text{trace of carborane compound}$$

An alternate synthesis of compounds having a carboranyl nucleus directly attached to a silicon atom was explored. Condensation reactions of the Grignard reagent, 1-carboranylmethylmagnesium bromide, and its tetrahydrofuran rearrangement isomer, 2-methyl-1-carboranylmagnesium bromide, have been described.[3b,3c] It was now observed that this rearrangement occurred upon addition of the Grignard reagent prepared in ethyl ether to refluxing methyltriethoxysilane. Methyl(2-methyl-1-carboranyl)diethoxysilane was isolated from this reaction.

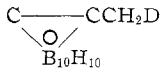
$$HC(B_{10}H_{10})CCH_2MgBr \xrightarrow{CH_3Si(OC_2H_5)_3} CH_3C(B_{10}H_{10})CSi(OC_2H_5)_2(CH_3) \quad (6)$$

Evidence for this rearrangement was found in the infrared spectrum of the product. The characteristic absorption bands at 1017 and 3058–3090 cm.$^{-1}$, which appear in the infrared spectra of all monosubstituted carboranes, were missing in this product.

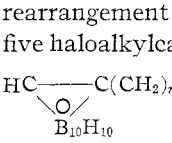
In order to define the conditions for rearrangement of carboranylalkyl Grignard reagents, a number of deuteration experiments were performed. First, after determining that there was no exchange between 1-methylcarborane and deuterium oxide in pure dioxane, samples of 1-deuteriomethylcarborane and 1-methyl-2-deuteriocarborane were prepared from 1-bromomethylcarborane in ether and tetrahydrofuran, respectively, by treatment of the Grignard reagent with deuterium oxide. Infrared spectra showed absorption peaks for

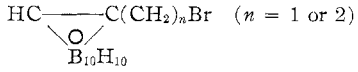


at 2294 cm.$^{-1}$ (calcd. 2270 cm.$^{-1}$), and for



at 2188 cm.$^{-1}$ (calcd. 2160 cm.$^{-1}$). The values for the undeuterated compounds are 3090 and 2940 cm.$^{-1}$, respectively. It was found that rearrangement is general for the Grignard reagents prepared from 1-(ω-haloalkyl)carboranyl compounds. The extent of rearrangement of the Grignard reagents, prepared from five haloalkylcarboranes





could be estimated from the ratios of the CH_2D *vs.* the $B_{10}H_{10}C_2D$ peaks of the products formed when the Grignard reagents were decomposed with D_2O. It was found that the rearrangement occurred at a measurable rate at ambient temperatures and increased with increasing temperatures. As the value of n was decreased, the extent of rearrangement increased. The substitution of bromine for chlorine had little effect on the extent of rearrangement, but the solvent was found to play an important role. The rearrangement at the same temperature is much faster in tetrahydrofuran than in ethyl ether. These observations indicate that the formation of α-(carboranyl)-ω-silanes from the corresponding Grignard reagents would be accompanied by the concomitant formation of the rearranged 1-alkyl-2-silyl carboranes.

Those compounds containing a carborane group bonded directly to a silicon atom were relatively unstable thermally and were difficult to polymerize because the carborane–silicon bond was cleaved by both acids and bases. The treatment of aqueous alcoholic solutions of methyl(1-methyl-2-carboranyl)diethoxysilane with sodium hydroxide, hydrochloric acid, or ammonium chloride resulted in the formation of 1-methylcarborane and a highly cross-linked methylsilicone polymer.

$$CH_3C(B_{10}H_{10})CSi(OC_2H_5)_2CH_3 \xrightarrow[H_2O,\ C_2H_5OH]{H^+ \text{ or } OH^-} CH_3C(B_{10}H_{10})CH + (CH_3SiO_{1.5})_x \quad (7)$$

The analogous acid-catalyzed cleavage of phenylsilanes to form benzene is well known.[7] There are apparently two routes by which carborane–Si cleavage can occur

$$RC(B_{10}H_{10})CSi{\lessdot} + H^+ \longrightarrow RC(B_{10}H_{10})CH + {}^+Si{\lessdot}$$

$${}^+Si{\lessdot} + H_2O \longrightarrow HOSi{\lessdot} + H^+$$

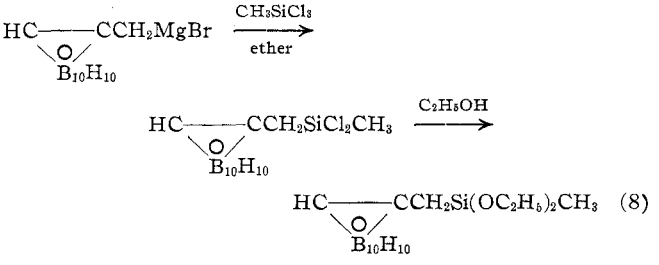
and

$$RC(B_{10}H_{10})CSi{\lessdot} + OH^- \longrightarrow RC(B_{10}H_{10})C^- + HOSi{\lessdot}$$

(6) Also prepared by Papetti and Heying (ref. 4), m.p. 92–94°.

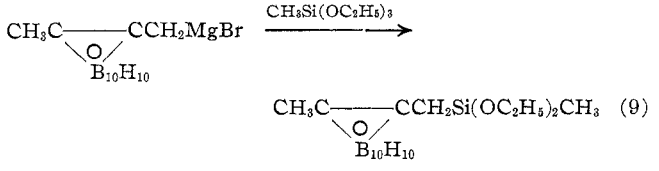
(7) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 25.

Carboranylalkylsilanes.—Compounds containing one methylene group between a silicon atom and a 1-carboranyl group proved difficult to prepare because of the rearrangement described above, and difficult to purify since the crude products were liquids that decomposed upon attempted distillation. The interaction of methyltrichlorosilane in ethyl ether with 1-carboranylmethylmagnesium bromide gave an oil believed to be methyl(1-carboranylmethyl)dichlorosilane. The oil had close to the calculated amount of ionizable chlorine and exhibited the expected infrared spectrum. Treatment of this material with ethyl orthoformate formed what is believed to be methyl(1-carboranylmethyl)diethoxysilane, the isomer of the product obtained in eq. 6. The infrared spectrum of the crude product did show a peak at 3058 cm.$^{-1}$, indicative of a 1-monosubstituted carborane.

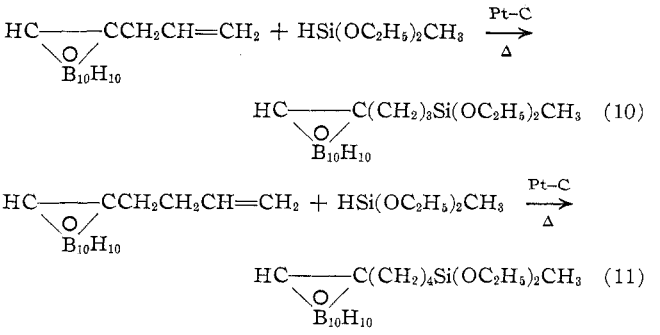


Both of these products decomposed on attempted distillation under reduced pressure.

Another silane, methyl(1-methyl-2-carboranylmethyl)diethoxysilane, was prepared from methyltriethoxysilane and the Grignard reagent from 1-methyl-2-bromomethylcarborane. This preparation was accompanied by the formation of 1,2-dimethylcarborane, presumably due to hydrolysis of unreacted Grignard reagent. This silane also decomposed on attempted distillation.



Organosilanes can be prepared by the addition of –SiH compounds to olefins.[8] We have found that reactions of this type are applicable to alkenylcarboranes. 1-Allylcarborane and 1-(3-butenyl)carborane interacted with methyldiethoxysilane in the presence of platinized charcoal[9] to form 3-(1-carboranyl)propylmethyldiethoxysilane and 4-(1-carboranyl)butylmethyldiethoxysilane, respectively. The reaction to produce the trimethylene product (eq. 10) was significantly slower than that of the next higher homolog.



No product could be obtained from the attempted addition of methyldichlorosilane to 1-vinylcarborane under similar conditions.

Experimental[10]

Dimethyl Bis(1-carboranylmethoxy)silane.—A solution of 0.05 mole of 1-hydroxymethylcarborane[3b] and 0.025 mole of dimethyldichlorosilane in 100 ml. of toluene was heated at reflux for 4 hr. Evaporation of the solvent *in vacuo* left a liquid residue which crystallized after chilling. Fractional crystallization of this residue from petroleum ether gave 6.5 g. (65% yield) of product, m.p. 98–100°. The infrared spectrum of this material was consistent with the proposed structure.

Anal. Calcd. for $C_6H_{32}B_{20}O_2Si$: C, 23.7; H, 8.0; B, 53.5. Found: C, 25.8; H, 8.1; B, 51.5.

Methyl Tris(1-carboranylmethoxy)silane.—A solution of 0.05 mole of 1-hydroxymethylcarborane and 0.017 mole of methyltrichlorosilane in 100 ml. of dry toluene was heated at reflux for 48 hr. during which time evolution of hydrogen chloride ceased. Distillation of the solvent left a sirupy residue. This was crystallized from boiling heptane and yielded the product as clusters of long, white needles, m.p. 220°. The structure was confirmed by infrared analysis.

1,2-Bis(trimethylsiloxymethyl)carborane.—A solution of 0.05 mole of 1,2-bis(hydroxymethyl)carborane,[3b] 0.5 mole trimethylchlorosilane, and 150 ml. of toluene was refluxed for 36 hr. The solution was then filtered and concentrated, and the residue was distilled. A colorless oil, 15.7 g. (90%), boiling at 140–146° (0.05 mm.) was obtained.

Anal. Calcd. for $C_{10}H_{32}B_{10}Si_2O_2$: C, 34.4; H, 9.3; B, 31.0; Si, 16.1. Found: C, 34.2; H, 9.3; B, 30.6; Si, 15.9.

1,1-Dimethyl-1-sila-2,7-dioxa-4,5-(1,2-carborano)cycloheptane.—A solution of 0.36 mole of 1,2-bis(hydroxymethyl)carborane and 0.36 mole of dimethyldichlorosilane in 300 ml. of toluene was refluxed for 24 hr. Concentration of the solution and distillation of the residue at 120° (3 mm.) gave 55 g. (59%) of white crystals, m.p. 98–100°.

Anal. Calcd. for $C_6H_{20}B_{10}SiO_2$: C, 27.7; H, 7.7; Si, 10.8. Found: C, 28.1; H, 8.1; Si, 11.5.

Methyl(1-methyl-2-carboranyl)diethoxysilane.—A Grignard reagent was prepared in the usual way from 0.16 mole of 1-bromomethylcarborane[3b] and 0.16 g.-atom of magnesium in 75 ml. of ether. The reagent was added to 150 ml. of refluxing methyltriethoxysilane, and the ether was removed by distillation, whereon the white, curdy precipitate that formed during the addition dissolved. The solution was refluxed with stirring for 40 hr., during which time a granular precipitate formed. The mixture was filtered and the solution concentrated under reduced pressure. The residue was dissolved in 200 ml. of pentane, and the solution was filtered and again concentrated. 1-Methylcarborane was removed at 110° (0.05 mm.), and the residue distilled at 150–160° (0.05 mm.). The product was a colorless oil weighing 26.3 g. (54% yield).

(8) L. H. Sommers, E. W. Pietruszu, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947); C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947); E. W. Pietrusza, L. H. Sommer, and F. C. Whitmore, *ibid.*, **70**, 484 (1948); D. G. White and E. G. Rochow, *ibid.*, **76**, 3897 (1954); J. L. Speier, J. A. Webster, and G. H. Barnes, *ibid.*, **79**, 974 (1957); R. A. Benkesser and R. A. Hickner, *ibid.*, **80**, 5298 (1958).

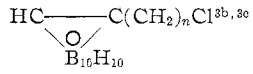
(9) G. H. Wagner, U. S. Patent 2,637,738 (1953).

(10) Melting points are uncorrected. Analyses were performed by F. Hoffman and F. Billovits. Infrared spectra were obtained by L. G. Adlum using a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics. The thermal stability data were determined by R. Crooker and A. Lum. All reactions were carried out in an inert atmosphere and all solvents were dried before use.

Anal. Calcd. for $C_8H_{26}B_{10}SiO_2$: C, 33.06; H, 9.02; B, 37.24; Si, 9.67. Found: C, 33.23; H, 9.05; B, 37.16; Si, 9.20.

1-Deuteriomethylcarborane and 1-Deuterio-2-methylcarborane.—A Grignard reagent was prepared in ether from 1-bromomethylcarborane in the usual way. A portion of the solution was removed shortly after the reaction began and was added to 99+% deuterium oxide. Tetrahydrofuran was added to the remainder of the solution which was then refluxed for 15 min. and treated with deuterium oxide. Each solution was extracted with sodium-dried cyclohexane, and the organic layer was dried with calcium sulfate, filtered, concentrated under reduced pressure, and repeatedly sublimed until no bromine was detected in the products. The infrared spectra of the products showed that the nuclear deuterated material (from the tetrahydrofuran solution) was almost isotopically pure; the methyl deuterated material, however, contained a considerable amount of the other isomer.

Deuteration Experiments.—Grignard reagents were prepared in ether from



(n = 1, 2, and 3). The concentrations were 0.5 M in each case. Aliquots were removed at intervals and hydrolyzed with 99+% deuterium oxide. The alkylcarboranes were extracted with ether and isolated by concentration. The experiments were repeated using the bromo compounds (n = 1 and 2) to evaluate the effect of changing the halogen atom. The Grignard reagent prepared from 1-bromomethylcarborane was treated with benzene and an aliquot refluxed in an effort to determine the temperature dependency and the rearrangement. The use of tetrahydrofuran has been described above.

Methyl(1-carboranylmethyl)dichlorosilane.—A Grignard reagent was prepared as quickly as possible from 0.2 mole of 1-bromomethylcarborane and 0.21 g.-atom of magnesium in 200 ml. of ether. The reagent was filtered and added dropwise with stirring to 0.5 mole of methyltrichlorosilane over a period of 3 hr. After stirring overnight, the mixture was filtered and the solution concentrated under reduced pressure. The residue was extracted with chloroform, filtered, and concentrated under reduced pressure, leaving a clear oil. The infrared spectrum of the product showed a strong peak at 3060 cm.$^{-1}$, indicative of a monosubstituted carborane, and Si–CH_3 and Si–Cl peaks.

Anal. Calcd. for $C_4H_{16}B_{10}SiCl_2$: Hydrolyzable Cl, 26.15. Found: Hydrolyzable Cl, 24.96.

The product decomposed on attempted distillation.

Methyl(1-carboranylmethyl)diethoxysilane.—This compound could not be purified since it could not be distilled without decomposition. Crude material was, however, prepared by treating 0.024 mole of the corresponding chloro compound (above) with 0.05 mole of ethyl orthoformate on a steam bath for 24 hr. Removal of the solvents under reduced pressure left a colorless oil, the infrared spectrum of which showed that the chlorine was replaced by ethoxy and retention of the 3060 cm.$^{-1}$ absorption band.

1-Bromomethyl-2-methylcarborane.—The required 1-bromo-2-butyne was prepared from 2-butyn-1-ol[11] by the method of Petrov and Nikishin.[12] A solution of 0.125 mole of the bromo compound and 0.125 mole of decaborane in 125 ml. of acetonitrile was refluxed for 4 hr. The solvent was removed by distillation and the residue distributed between 500 ml. of 10% sodium hydroxide and 250 ml. of hexane. The hexane solution was dried, and the solvent was removed by distillation under reduced pressure leaving 13.2 g. of a yellow solid which could be purified by sublimation or recrystallization from ethanol–water (5:1). A total of 11.3 g. (36%) of white crystals melting at 125–127° was obtained.

Anal. Calcd. for $C_4H_{15}B_{10}Br$: C, 19.12; H, 6.02; B, 43.07. Found: C, 19.73; H, 6.18; B, 43.93.

Methyl(1-methyl-2-carboranylmethyl)diethoxysilane.—A solution of 0.04 mole of 1-bromomethyl-2-methylcarborane in 30 ml. of ether was added dropwise to 0.045 g.-atom of magnesium in 10 ml. of ether. The reaction started easily, but the magnesium soon became coated; the addition of 20 ml. of tetrahydrofuran allowed the reaction to proceed with the formation of a red oil. After refluxing for 4 hr., a small amount of unreacted magnesium was removed and 25 ml. of methyltriethoxysilane added. After refluxing overnight, a red solid precipitated. The addition of 100 ml. of ethanol resulted in a homogeneous solution which was then concentrated under reduced pressure and extracted with methylene chloride. The solution was concentrated, leaving a clear oil, the infrared spectrum of which showed peaks indicative of a disubstituted carborane, –Si–CH_3, –C–CH_3, and –Si–OC_2H_5. The material decomposed on attempted distillation under reduced pressure.

A small amount of solid, m.p. 260–261°, was obtained during the distillation. This material, insufficient for analysis, had an infrared spectrum consistent with that anticipated for 1,2-dimethylcarborane.

Methyl-3-(1-carboranyl)propyldiethoxysilane.—A solution of 0.14 mole of 1-allylcarborane[4] and 0.22 mole of methyldiethoxysilane containing 1 g. of 5% platinized charcoal was refluxed for 1 week. After filtration and removal of excess methyldiethoxysilane under reduced pressure, the residue was distilled. Unreacted 1-allylcarborane, 8 g., was recovered, and then 8.5 g. (27% conversion) of product boiling at 134–138° (0.2 mm.) was collected.

Anal. Calcd. for $C_{10}H_{30}B_{10}SiO_2$: C, 37.69; H, 9.49; B, 33.96: Si, 8.82. Found: C, 37.40; H, 9.65; B, 34.50; Si, 9.05.

Methyl-4-(1-carboranyl)butyldiethoxysilane.—This compound was prepared from 0.875 mole of 1-(3-butenyl)carborane[3c] and 1.27 moles of methyldiethoxysilane in the presence of 2 g. of 5% platinized charcoal. After refluxing for 4 days, the mixture was filtered, concentrated, and distilled to give 154 g. (53%) of a colorless oil boiling at 160–162° (0.1 mm.).

Anal. Calcd. for $C_{11}H_{32}B_{10}SiO_2$: C, 39.72; H, 9.70; B, 32.52; Si, 8.44. Found: C, 40.11; H, 9.51; B, 32.68; Si, 7.96.

Acknowledgment.—The authors gratefully acknowledge the suggestions of Dr. Murray S. Cohen, Dr. Daniel Grafstein, and Mr. Joseph Green. This work was supported by the United States Air Force under Contracts No. AF 33(616)-5867 and AF 33(616)-6424.

(11) L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 729 (1950).

(12) A. D. Petrov and G. J. Nikishin, *Dokl. Akad. Nauk SSSR*, **93**, 1049 (1953); *Chem. Abstr.*, **49**, 841c (1955).