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REACTIONS OF BORANES AND CARBORANES WITH SILANES, ORGANOSILANES, AND RELATED COMPOUNDS

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SUMMARY

Gas-phase thermal and electric discharge interactions of SiH_4, Si_2H_6, and $(CH_3)_2SiH_2$ with B_4H_{10}, B_5H_9, and 2,3-$C_2B_4H_8$ were studied, as well as the reactions of $(CH_3)_2GeH_2$ and $(CH_3)_2SnH_2$ with 2,3-$C_2B_4H_8$. In addition, several silyl-substituted derivatives of 2,3-$C_2B_4H_8$ were prepared from silylacetylenes and boron hydrides, and their conversion to *closo*-carborane silyl derivatives was examined. All silylcarboranes obtained were C-substituted, and no volatile products containing Si–B bonds were obtained in any reaction studied. Evidence for methyl derivatives of a $GeC_2B_5H_7$ polyhedral cage system was obtained.

INTRODUCTION

Although boron hydride and silicon hydride chemistry have developed separately into areas of considerable scope, direct interactions between silanes and cage boranes have received little attention**.

In this investigation, gas phase and solution reactions of silane, disilane, dimethylsilane, and three alkynylsilanes with several boron cage species were examined. The boron reactants chosen included the unstable hydride tetraborane(10), the relatively stable pentaborane(9), and 2,3-dicarbahexaborane(8), an open-cage carborane. For comparative purposes, a few experiments involving germanium and tin hydrides were also conducted.

RESULTS AND DISCUSSION

Gas-phase reactions of silane and disilane with small boranes

Mixtures of B_4H_{10} with SiH_4 or Si_2H_6 in sealed bulbs at 25° produced only nonvolatile polymeric solids, small boranes, and hydrogen (the experiments with

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** Stock[3] has reported the reduction of disilane to silane by tetraborane (10); Thompson and Schaeffer[4] have studied deuterium exchange between SiD_4 and B_5H_9.

Si_2H_6 also produced some SiH_4, as reported many years ago by Stock[3].

The reaction of SiH_4 with B_5H_9 at 210° produced yellow-brown amorphous solids and decaborane(14), but virtually no other volatile products. While the solid products have not been structurally characterized, these reactions appear to be dominated by the tendency of unsubstituted silanes to catenate and form polymeric chains.

Reactions of tetraborane–acetylene–silane mixtures

Previous work[5-7] has shown that the reaction of B_4H_{10} and C_2H_2 in the gas phase at 25° yields open-cage carborane species, while the same reactants at 100° interact violently to form polyhedral carboranes. To determine whether SiH_4 reacts with intermediate species in the carborane-forming process, equimolar mixtures of SiH_4, B_4H_{10}, and C_2H_2 were allowed to stand at 25° and at 100°. Surprisingly, the low-temperature reaction yielded no carborane species whatsoever, indicating that SiH_4 intercepts one or more important intermediates, as yet unidentified, which normally lead to carborane products in C_2H_2/B_4H_{10} gas phase reactions. Direct SiH_4/B_4H_{10} interaction cannot, in itself, account for the absence of carborane products, since the normal decomposition products of B_4H_{10} decomposition (*e.g.*, B_2H_6 and B_5H_{11}) were formed in abundance.

In contrast to the 25° reaction, the presence of SiH_4 has little apparent effect on the 100° C_2H_2/B_4H_{10} flash reaction. The volatile products (primarily small *closo*-carboranes) were essentially the same as those known to form[7] in the absence of SiH_4, except for small quantities of alkylsilanes.

Reaction of dimethylsilane with pentaborane

Steric considerations suggested that polymer formation from dimethylsilane would be inhibited in comparison with reactions of unsubstituted silanes, thus increasing the yield of volatile silicon-containing products. Such an effect was observed in the gas-phase reactions of $(CH_3)_2SiH_2$ and B_5H_9 at 170–200°. At 170° the volatile products (Table 1) unexpectedly included the polyhedral carborane 1,5-$C_2B_3H_5$, representing an unusual example of insertion of alkyl carbon atoms into a borane cage. The products obtained from the same reactants at 200° did not include $C_2B_3H_5$, undoubtedly due to the instability of this carborane above 150° [8].

The formation of carboranes at temperatures as low as 170° from $(CH_3)_2SiH_2$ and B_5H_9 contrasts with the gas-phase reaction of C_2H_2 with B_5H_9, which does not occur at an appreciable rate below about 215° [8]*.

Copyrolysis of 2,3-*dicarbahexaborane*(8) *with disilane and with dimethylsilane*

Several studies have shown that 2,3-$C_2B_4H_8$ is converted into polyhedral carboranes, primarily 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$, when heated above 290° [8,10] or subjected to an electric discharge[8]. In this work, the copyrolysis of 2,3-$C_2B_4H_8$ and Si_2H_6 at 195° resulted in the complete disappearance of the carborane;

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* It seemed possible that 2-$CH_3B_5H_8$, the main volatile product of the $(CH_3)_2SiH_2/B_5H_9$ reaction, might be an intermediate in the formation of 1,5-$C_2B_3H_5$, particularly since Onak, *et al.*[9], have obtained small carboranes from 2-$CH_3B_5H_8$ in a fast-flow system at 520°. In this work, the pyrolysis of 2-$CH_3B_5H_8$ at 200° gave only small amounts of solids and hydrogen, making it unlikely as a carborane precursor at that temperature.

TABLE 1

DATA FROM SELECTED THERMAL REACTIONS OF ORGANOSILANES AND ORGANOGERMANES WITH BORON CAGE COMPOUNDS[a]

Reagents	(mmoles)	Temp. (°C)	Time (h)	Reactor Vol. (ml)	Volatile products	Yield[b]
$(CH_3)_2SiH_2$	5.78	170	43	500	$2\text{-}CH_3B_5H_8$	3.4
B_5H_9	1.15				$1,5\text{-}C_2B_3H_5$	1.4
					$(CH_3)_3SiH$	Trace
					CH_3SiH_3	Trace
$(CH_3)_2SiH_2$	5.78	200	12	500	$2\text{-}CH_3B_5H_8$	1.1
B_5H_9	1.15				$2,3\text{-}(CH_3)_2B_5H_7$	0.5
					$(CH_3)_5Si_2H$	Trace
$(CH_3)_2SiH_2$	0.94	320	19	10	$2,4\text{-}C_2B_5H_7$	28
$2,3\text{-}C_2B_4H_8$	0.73				$3\text{-}CH_3\text{-}C_2B_5H_6$	4
					$1,7\text{-}(CH_3)_2\text{-}C_2B_5H_5$	4
					$2\text{-}(CH_3)_2SiHC_2B_5H_6$	1
					$2\text{-}CH_3SiH_2\text{-}C_2B_5H_6$	1
$(CH_3)_3SiC{\equiv}CH$	3.80	186	68	500	$2\text{-}(CH_3)_3Si\text{-}2,3\text{-}C_2B_4H_7$	49
B_5H_9	3.87				$2\text{-}CH_3B_5H_8$	Trace
					$(CH_3)_3SiH$	Trace
$SiH_3C{\equiv}CH$	3.08	185	12	500	$2\text{-}SiH_3\text{-}2,3\text{-}C_2B_4H_7$	12
B_5H_9	4.36					
$(SiH_3)_2C_2$	3.40	184	13	500	$2,3\text{-}(SiH_3)_2\text{-}2,3\text{-}C_2B_4H_6$	2
B_5H_9	3.90					
$2\text{-}(CH_3)_3Si\text{-}2,3\text{-}C_2B_4H_7$	3.3[c]	280	19	10	$2\text{-}(CH_3)_3Si\text{-}2,4\text{-}C_2B_5H_6$	16
$(CH_3)_2GeH_2$	4.6	300	1	100	$2,4\text{-}C_2B_5H_7$	4
$2,3\text{-}C_2B_4H_8$	2.7				$1\text{-}CH_3\text{-}C_2B_5H_6$	12
					$3\text{-}CH_3\text{-}C_2B_5H_6$	23
					$5\text{-}CH_3\text{-}C_2B_5H_6$	12
					$(CH_3)_2C_2B_5H_5$	15[d]
					$(CH_3)_3C_2B_5H_4$	3
					$(CH_3)_4C_2B_5H_3$	3
					$(CH_3)_5C_2B_5H_2$	Trace
					$(CH_3)_3C_2B_3H_2$	9
					$(CH_3)_nGeC_2B_5H_{7-n}$[e]	10[f]

[a] Gas phase unless otherwise indicated. [b] % Based on boron consumed. [c] Diphenyl ether solution. [d] Total yield of 2 isomers. [e] $n = 2\text{–}6$. [f] Estimated total yield of 5 compounds.

since $C_2B_4H_8$ is thermally stable at this temperature, silane–borane interactions leading to nonvolatile solid products are clearly present.

Not unexpectedly, the reaction of $2,3\text{-}C_2B_4H_8$ with $(CH_3)_2SiH_2$ gave much higher yields of volatile products than did the $Si_2H_6/C_2B_4H_8$ system, producing both B–methyl and C–silyl carboranes (Table 1).

Electric discharge reactions of 2,3-*dicarbahexaborane*(8) *with silane and dimethylsilane*

The volatile products obtained from mixtures of $2,3\text{-}C_2B_4H_8$ with SiH_4 or $(CH_3)_2SiH_2$ in an ozonizer-type discharge are given in Table 2. The unusual formation of B_2H_6 and B_5H_9 from the more thermodynamically stable carborane suggests that the carbon atoms of $C_2B_4H_8$ are attacked by methylsilyl or methylsilene radicals, with extensive formation of nonvolatile Si–C bonded products (SiH_2 radicals have been postulated[11] to form in the electric discharge of SiH_4). This is consistent with the fact that volatile silicon-containing products were absent in reactions in which boranes were obtained, and *vice versa* (Table 2).

TABLE 2

ELECTRIC DISCHARGE REACTIONS OF SILANES WITH 2,3-$C_2B_4H_8$

Silane reactant	Mole ratio (Silane/$C_2B_4H_8$)	Voltage (kV)	Time (h)	Volatile products[a]	Yield
SiH_4	1.0	5.0	2	B_2H_6	0.4
SiH_4	1.0	3.0	2	B_2H_6	11
				1,5-$C_2B_3H_5$	4
				1,2-$C_2B_4H_6$	7
				1,6-$C_2B_4H_6$	9
$(CH_3)_2SiH_2$	1.0	3.0	3.3	B_2H_6	10
				B_5H_9	4
				1,5-$C_2B_3H_5$	8
				1,2-$C_2B_4H_6$	18
				1,6-$C_2B_4H_6$	18
$(CH_3)_2SiH_2$	2.7	2.0	2.0	1,5-$C_2B_3H_5$	9
				$(CH_3)_3SiH$	1
				$(CH_3)_2Si_2H_4$	11
				CH_3SiH_3	10

[a] Excluding CH_4 and H_2. Yields as % of boron or silicon consumed.

Reactions of silylacetylenes with tetraborane(10) *and pentaborane*(9)

The reaction of $(CH_3)_3SiC{\equiv}CH$ with B_4H_{10} either in the gas phase at 25°, or in diphenyl ether solution at 50°, yielded no volatile products other than boranes (in contrast to the $CH_3C{\equiv}CH/B_4H_{10}$ reaction[6], which forms numerous carborane products), but the separate gas-phase reactions of B_5H_9 with trimethylsilyl-, silyl-, and disilylacetylene produced the corresponding C-substituted derivatives of 2,3-$C_2B_4H_8$ (Table 1). Since B_5H_9 and C_2H_2 ordinarily require temperatures of 215° or higher for reaction[8], it is apparent that silyl substituents, like alkyl groups[8], enhance the reactivity of the acetylenic carbon–carbon bond toward B_5H_9. The tendency of Si–H bonds to lead to polymeric products is also evident in the yield data for the three reactions studied. It is noteworthy that the reaction of B_5H_9 with $(CH_3)_3SiC{\equiv}CH$ in diphenyl ether gave only a 12% yield of 2-$(CH_3)_3Si$–$C_2B_4H_7$, in contrast to a 49% yield in the gas phase reaction.

Pyrolysis of 2-(*trimethylsilyl*)-2,3-*dicarbahexaborane*(8)

The decomposition of 2-$(CH_3)_3Si$–2,3-$C_2B_4H_7$ at 225° in the gas phase produced mostly solids, hydrogen, and a trace of $CH_3C_2B_4H_7$. However, in diphenyl ether at 280° the same reactant yielded the *C*-trimethylsilyl derivative of the polyhedral carborane 2,4-$C_2B_5H_7$ (Table 1). Relatively high thermal stability of the silicon–cage carbon bond is evident in this conversion, which requires extensive rearrangement from a four-boron cage in which the carbon atoms are adjacent, to a five-boron polyhedral system containing nonadjacent carbons.

Reactions of dimethylgermane and dimethylstannane with 2,3-dicarbahexaborane(8)

The gas-phase reaction of $(CH_3)_2GeH_2$ with 2,3-$C_2B_4H_8$ yielded the volatile products shown in Table 1, as well as a dark reddish-brown polymeric solid whose composition corresponds to $[GeCH_3]_n$. The pronounced tendency of dimethylgermane to lose methyl groups, which has been noted in studies of its thermal decomposition[12], is evident in the large number and yield of methylcarboranes obtained. In addition to the carborane products, material of lower volatility was obtained which was shown from mass spectroscopic analysis to consist of a series of five carborane-like compounds having molecular weights up to 246. These products have been tentatively identified (see Experimental Section) as polymethyl derivatives of a $GeC_2B_5H_7$ cage system* which is isoelectronic with the known polyhedral carborane $C_2B_6H_8$ of idealized D_{2d} symmetry[13].

The copyrolysis of $(CH_3)_2SnH_2$ and 2,3-$C_2B_4H_8$ for 21 h at 175° resulted only in the decomposition of the tin compound, and all of the original carborane was recovered.

GENERAL OBSERVATIONS

The variety of reactions examined in this work was sufficiently broad to identify some clear trends in the product distribution. The greater reactivity of Si–H in comparison with Si–C bonds is obvious in the reactions of silanes, silylacetylenes, and dimethylsilane with borane cage molecules. Also, from the products listed in Table 1 it is apparent that the Ge–CH_3 bond cleaves more readily than the Si–CH_3 bond in reactions of dimethylgermane and dimethylsilane with 2,3-dicarbahexaborane(8). Both observations are consistent with recent studies[12] of the pyrolysis of methylsilane and methylgermane.

The relative stability of Si–C bonds (including both silicon–methyl and silicon–carborane links) may partially explain the failure to detect products containing silicon–boron bonds. Thus, while electrophilic silyl attack at boron cage atoms may well occur in $(CH_3)_2SiH_2/C_2B_4H_8$ reactions, subsequent migration of the silyl ligands to the carborane carbon atoms would account for the fact that only *C*–silyl and *B*–methyl derivatives of 2,4-$C_2B_5H_7$ were observed. Evidence for direct silane–borane and dimethylsilane–borane interactions was mentioned earlier.

Although these results in no way preclude the possible existence of stable silacarboranes containing cage silicon atoms, they do suggest that such compounds are unlikely to be obtained in reactions of the type described here. One possible route to such species involves the interaction of carborane anions (*e.g.*, $C_2B_4H_7^-$ and $C_3B_3H_6^-$)[14,15] with silyl halides; these reactions are currently under study and will be the subject of a future paper.

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* The possibility that these derivatives were formed by insertion of germanium into the polyhedral $C_2B_5H_7$ system was examined by copyrolysis of $C_2B_5H_7$ and $(CH_3)_2GeH_2$, which gave only methylgermanes, $(CH_3)_3B$, and solids.

EXPERIMENTAL SECTION

Spectra

The instruments used in this work included a Beckman IR-8 grating spectrophotometer, a Perkin–Elmer–Hitachi RMU-6D mass spectrometer, a Varian A60 NMR spectrometer (for ^1H resonance), and a Varian HA100 NMR spectrometer (for ^1H and ^{11}B resonance). Gas infrared spectra were obtained in Pyrex cells of 3.5 and 7.0 ml fitted with NaCl windows.

Materials

Dimethyldichlorosilane and trimethylchlorosilane (both from Matheson, Coleman and Bell), sodium acetylide (20% suspension in xylene, K and K), aluminum iodide, iodine (both reagent grade from Mallinckrodt), dimethyldichlorogermane and dimethyldichlorostannane (both from Alfa) were used as received.

Dioxane, tetrahydrofuran, and n-butyl ether were dried over $LiAlH_4$ and distilled before use. Diphenyl ether (Eastman) was used as received. Silane and acetylene (both from Matheson) were distilled through −135° and −128° traps, respectively, before use. Tetraborane(10) was prepared from diborane (K and K) as described elsewhere[6]. Pentaborane(9) (Olin) was purified by fractionation through a −63° trap followed by condensation at −95°. 2,3-Dicarbahexaborane(8) was prepared from pentaborane(9) and acetylene in the gas phase by the method of Onak, et *al.*[8]. Disilane was produced by circulating silane through an ozonizer-type electric discharge as described by Spanier and MacDiarmid[16]. Dimethylsilane was prepared from dimethyldichlorosilane and lithium aluminum hydride in dioxane under vacuum, using the general procedure described by Finholt, *et al.*[17], for the synthesis of alkylsilanes. The product was purified by fractionation through traps at −95°, −128°, and −148°; the dimethylsilane was collected at −128° and its purity checked by GLC and infrared[18] analysis.

Dimethylgermane was prepared by the reaction of lithium aluminum hydride and dimethyldichlorogermane at 40° in n-butyl ether under nitrogen. The product was distilled through a −95° trap (which removed solvent and unreacted reagent), collected at −196°, and checked by infrared and mass spectroscopy. The infrared spectrum displayed the expected C–H and Ge–H stretching bands at 2970 and 2040 cm^{-1}, respectively, and the mass spectrum contained a cutoff at *m/e* 107, corresponding to the $(^{12}CH_3)_2{}^{76}GeH^+$ ion. Dimethylstannane was obtained from dimethyldichlorostannane at room temperature by an analogous procedure. The product was purified by fractionation through a −78° trap, collected at −95°, and its identity and purity established by IR and mass spectrometry. The mass spectrum contains a cutoff at *m/e* 156, corresponding to the $(^{12}CH_3)_2{}^{124}SnH_2^+$ parent ion.

(Trimethylsilyl)acetylene was prepared as described by Davidsohn and Henry[19], utilizing the reaction of sodium acetylide and trimethylchlorosilane in refluxing n-butyl ether under nitrogen. The crude product was distilled through a −63° trap and collected at −128°; final purification was achieved via GLC on a column of 30% Apiezon-L on Chromosorb-W at 50°. The IR spectrum was identical to that given in the literature[20].

Silylacetylene and disilylacetylene were obtained in the reaction of iodosilane (prepared as described below) and sodium acetylide in n-butyl ether. In a typical reaction, 52 mmoles of NaC_2H and 15.1 mmoles of iodosilane were stirred under vacuum at $-52°$ for 1 h, and then at room temperature for 1.5 h. The reactor was cooled in liquid nitrogen and noncondensibles were pumped off, after which the remaining volatile material was distilled through $-95°$ and $-135°$ traps to remove silane and acetylene, which passed through. The fraction condensing at $-135°$ was silylacetylene, identified from its infrared spectrum[21]. The material condensing at $-95°$ was distilled through a $-63°$ trap and collected at $-95°$, this fraction being pure disilylacetylene. The latter compound was characterized by comparison of its infrared spectrum with that of silylacetylene, and from its mass spectrum, which contained an intense parent peak at m/e 86, corresponding to $(^{28}SiH_3)_2{}^{12}C_2^+$, and a cutoff at m/e 90, assigned to $(^{30}SiH_3)_2{}^{12}C_2^+$.

Iodosilane was prepared by the gas-phase reaction of iodine with silane in a sealed Pyrex bulb in the absence of a catalyst (the same reactants in the presence of anhydrous AlI_3 gave polysubstituted iodosilanes as major products). Typically, 29 mmoles of silane were condensed at $-196°$ into an evacuated reactor containing 12.2 mmoles of powdered iodine crystals. The flask was sealed and placed in an oven at 170° for 2 to 3 days, after which it was opened on the vacuum line. Silane was removed by fractionation of the volatiles through a $-135°$ trap, following which the material condensing at $-135°$ was distilled through $-63°$ and $-95°$ traps. Iodosilane (5.2 mmoles) was collected at $-95°$, while hydrogen iodide passed through this trap. Polyiodo silanes, also produced in the reaction, were trapped at $-63°$. The iodosilane was identified from its infrared[22] and mass spectra.

General procedures

Standard high vacuum techniques were used throughout. Unless otherwise indicated, all reactions were carried out in the gas phase in sealed Pyrex bulbs equipped either with breakoff tips or greaseless stopcocks containing Viton o-rings (Ace Scientific Co.) which could be attached to the vacuum line. Gas-liquid chromatography was conducted on columns constructed of 0.25 in. × 12 ft. copper tubing and sealed into the vacuum system. The liquid phases employed were Apiezon-L and Kel-F greases, each 30% by weight on Chromosorb-W. Yields indicated were calculated from calibrated chromatogram peak areas or from pressure/volume measurements in the vacuum line.

Known silanes, boranes, carboranes, and methyl carboranes were identified from their infrared and/or mass spectra by comparison with literature spectra.

Reaction of SiH_4 with B_4H_{10}

Silane (3.1 mmoles) and tetraborane (0.84 mmole) were condensed in an evacuated 250 ml flask at $-196°$. The reactor was sealed and allowed to stand at room temperature for 2 days, during which a brown oily acetone-soluble polymer formed on the walls. After 7 days the volatiles were removed and fractionated through $-95°$ and $-128°$ traps. The $-128°$ fraction consisted of a 3.5 mmole mixture of SiH_4 and B_2H_6, which were not separated; the material condensing at $-95°$ was pentaborane(9) (0.35 mmole).

Reaction of Si_2H_6 with B_4H_{10}

The procedure was identical to that used in the preceding reaction. In 17 days at room temperature, B_4H_{10} (0.23 mmole) and Si_2H_6 (0.18 mmole) formed a polymer which was insoluble in acetone or CCl_4 but soluble in water, and a total of 0.30 mmole of SiH_4, B_2H_6, and B_5H_9, which were identified by infrared and mass spectra but were not separated.

Reactions of B_4H_{10}, C_2H_2, and SiH_4

(*a*). *Room temperature reaction.* A mixture of 3.1 mmoles of each reagent in a 250 ml reactor was allowed to stand for 7 days. Subsequent fractionation of the volatiles through a $-95°$ trap gave 0.14 mmole of B_5H_{11}, which condensed at $-95°$, while the remainder consisted of a mixture of B_2H_6 and SiH_4 totalling 0.86 mmole. No other volatile products were found, and no C_2H_2 was recovered.

(*b*). *Flash reaction.* A mixture containing 1.9 mmoles of each reagent was condensed into a 250 ml reactor, sealed, and after reaching room temperature, was placed in an oven at 100°. After 2–3 min the mixture flashed, and the volatiles were separated by GLC and identified from their IR and mass spectra. The products consisted of 2,4-$C_2B_5H_7$, 1,6-$C_2B_4H_6$, monomethyl derivatives of these, methylsilanes, and traces of hydrocarbons. As the total yield of volatile products was only 0.1 mmole, no attempt was made to measure individual yields.

Reaction of $(CH_3)_2SiH_2$ with B_5H_9

The gas phase reactions of dimethylsilane and pentaborane(9) in sealed bulbs were conducted in several different mole ratios at 170° and 200°; data for two typical experiments are presented in Table 1. In each case the reactor walls became coated with a yellow-brown solid which was not investigated. Volatile products were distilled from the reactor at 80° and separated by preparative-scale GLC. The chromatography was facilitated by prior fractionation through a $-95°$ trap. The IR spectra of 2-$CH_3B_5H_8$[23], 2,3-$(CH_3)_2B_5H_7$[24], 1,5-$C_2B_3H_5$[25], $(CH_3)_3SiH$[18], and CH_3SiH_3[18] were in agreement with the literature, and confirmed by their mass spectra; $(CH_3)_5Si_2H$ was identified from its mass spectrum, which contained a cutoff at *m/e* 134 corresponding to the $(^{12}CH_3)_5{}^{30}Si^{28}SiH^+$ ion, and its gas IR spectrum, which displayed strong absorptions in the CH_3 and SiH stretching regions.

Pyrolysis of 2-$CH_3B_5H_8$

A sample of 2-$CH_3B_5H_8$ (0.10 mmole) was distilled into an evacuated 50 ml reactor which was sealed and maintained at 200° for 18 h. Most of the reactant was recovered, and the only products found were H_2 and a small quantity of nonvolatile solids.

Reactions of 2,3-$C_2B_4H_8$ with Si_2H_6 and $(CH_3)_2SiH_2$

Si_2H_6 (0.85 mmole) and $C_2B_4H_8$ (0.43 mmole) in a 125 ml reactor gave no evidence of reaction in 2 days at room temperature. The reactor was placed in an oven and the temperature gradually raised until solid formation was observed at 195°. After 30 min at 195°, the reaction was quenched in liquid nitrogen and the volatile products examined. Only Si_3H_8 (0.02 mmole, identified from its IR spectrum[16]) and traces of higher silanes were found.

$(CH_3)_2SiH_2$ and $C_2B_4H_8$ did not react in 2 days at 280°. At 320° reaction did occur as indicated in Table 1 to give the products listed, accompanied by a yellow-brown amorphous solid. The carboranes, methyl carboranes, and methylsilanes were identified from their IR spectra. The *C*-monomethylsilyl and *C*-dimethylsilyl derivatives of $2,4\text{-}C_2B_5H_7$ were characterized from IR and mass spectra of the pure compounds, and by comparison with the *C*-trimethylsilyl derivative (described below). The mass spectra display cutoffs at *m/e* 132 and 146, respectively, corresponding to the parent ions $^{12}CH_3{}^{30}SiH_2{}^{12}C_2{}^{11}B_5H_6^+$ and $(^{12}CH_3)_2{}^{30}SiH^{12}C_2{}^{11}B_5H_6^+$. The fragmentation patterns in both spectra are typical of polyhedral carboranes and are consistent with the calculated polyisotopic spectra for species containing 1 Si and 5 B atoms. Intense peaks at *m/e* 59 and 45 are assigned to $(^{12}CH_3)_2{}^{28}SiH^+$ and $^{12}CH_3\text{-}{}^{28}SiH_2^+$ fragments, respectively. The IR spectrum of $2\text{-}(CH_3)_2SiH\text{–}2,4\text{-}C_2B_5H_6$ in the gas phase contains absorptions at 2960 s, 2910 m, 2610 vs, 2140 s, 1230 m, 1260 s, 1205 s, 1155 m, 1030 m(br), 880 vs, and 840 m cm^{-1}. The gas phase IR spectrum of $2\text{-}CH_3SiH_2\text{–}2,4\text{-}C_2B_5H_6$ contains absorptions at 2960 m, 2910 m, 2615 vs, 2155 s, 1340 m(br), 1260 m, 1210 m, 1160 m(br), 1040 m, 950 m, 895 vs, 865 m, and 760 m(br) cm^{-1}.

Electric discharge reactions of $2,3\text{-}C_2B_4H_8$ *with* SiH_4 *and* $(CH_3)_2SiH_2$

The apparatus consisted of a Pyrex ozonizer in which an a.c. potential was maintained between a central tube filled with $CuSO_4$ solution and an outer covering of Al foil, separated by 1 cm. A 500 ml-capacity Toepler pump circulated gases through the system, which contained a U-trap around which cold baths were placed in some experiments. The entire apparatus was connected to a high vacuum system and was evacuated before each use. Typically, 0.5 mmole of each reagent was condensed into the U-trap at −196°, helium was introduced to a total pressure of 10 mm, the reagents were warmed to room temperature, and the mixture was circulated for 15 min at a pumping rate of 660 ml/min. After 15 min the discharge was switched on and the voltage maintained as indicated in Table 2. Following the discharge period the U-trap was cooled to −196° and circulation was continued for several minutes to collect most of the condensible material. The noncondensibles were pumped out of the system through another −196° trap. The condensibles were separated by GLC and identified (Table 2) from IR and mass spectra.

Reaction of $(CH_3)_3SiC{\equiv}CH$ *with* B_4H_{10}

(*a*). *Gas phase.* A 1.0 mmole sample of each reactant was condensed at −196° into an evacuated 125 ml reactor, which was sealed and allowed to stand at room temperature. After 12 h a yellow solid covered the bottom surface. Following 3.5 days at room temperature the volatile products consisted of B_2H_6 and B_5H_9, which were not measured. The yellow solid displayed Si–H stretching bands in the IR spectrum, and the presence of a strong O–H band indicated that rapid hydrolysis occurred on exposure to air.

(*b*). *Diphenyl ether solution.* A 1.0 mmole sample of each reactant was condensed into an evacuated 10 ml reactor containing 3 ml of diphenyl ether at −196°. After shaking the mixture at room temperature the reactor was heated to 50° for 35 min, following which the volatiles were distilled through a trap at 0°, which removed most of the solvent, and were collected at −196°. The volatile products again consisted only B_2H_6 and B_5H_9.

Reactions of B_5H_9 with $(CH_3)_3SiC{\equiv}CH$, $SiH_3C{\equiv}CH$, and $(SiH_3)_2C_2$

The three reactions were conducted in the gas phase under conditions indicated in Table 1. The 2-$(CH_3)_3Si$–2,3-$C_2B_4H_7$ was characterized from its ^{11}B NMR, ^{1}H NMR, IR, and mass spectra. The ^{11}B NMR spectrum (neat liquid) contains a low-field multiplet of area 3 [δ +3.0 ppm relative to $BF_3 \cdot (C_2H_5)_2O$], assigned to the basal boron atoms, and a high-field doublet of area 1 (δ +57 ppm, J 185 Hz) assigned to the apex boron. The ^{1}H NMR spectrum (neat liquid) contains a strong absorption [δ +0.5 ppm relative to $(CH_3)_4Si$] assigned to the 9 equivalent methyl protons, a weak band at −6.1 ppm assigned to the cage C–H group, and weak, broad absorptions arising from B–H groups. The IR spectrum contains bands at 3000 m, 2960 vs, 2890 m, 2590 vvs, 1930 m, 1870 w, 1510 s, 1480 (sh), 1400 m, 1330 m, 1250 vs, 1095 s, 970 w, 910 m, 830 vvs, 740 m, 700 w, and 640 w cm^{-1}. The mass spectrum displays a cutoff at *m/e* 150, corresponding to the $(^{12}CH_3)_3{}^{30}Si^{12}C_2{}^{11}B_4H_7^+$ parent ion, and intense peaks at *m/e* 73, 59, and 45, assigned to the $(^{12}CH_3)_n{}^{28}SiH_{3-n}^+$ fragments (where n = 1, 2, 3).

The structures of 2-SiH_3–2,3-$C_2B_4H_7$ and 2,3-$(SiH_3)_2$–2,3-$C_2B_4H_6$ were assigned from their IR and mass spectra. The mass spectra contain the expected parent peaks, and the fragmentation patterns are consistent with the presence of 1 Si and 4 B atoms. The gas phase IR spectrum of the monosilyl derivative contains absorptions at 3010 m, 2970 w, 2600 vvs, 2220 vs, 2170 vvs, 2120 (sh), 1935 s, 1880 s, 1600 (sh), 1520 vs, 1495 (sh), 1340 s, 1240 s, 1100 vs, 1045 w, 975 w, 920 vvs (br), 870 s, 835 s, 760 (sh), 730 (sh), 705 vs, and 640 vs cm^{-1}. The gas phase IR spectrum of the disilyl derivative absorbs at 2600 vs, 2160 vs, 1940 (sh), 1920 m, 1540 (sh), 1530 s, 1500 s (br), 1270 m, 1090 s, 1030 w, 990 w, 930 vs, 900 vs, 830 m, 790 w, 740 m, 710 s, 670 m, and 620 s cm^{-1}.

Pyrolysis of 2-$(CH_3)_3Si$–2,3-$C_2B_4H_7$

(*a*). *Gas phase.* A 4.2 mmole sample of the compound was condensed into an evacuated 500 ml reactor, to which helium was added to a pressure of 35 mm. The reactor was sealed and heated at 225° for 19 h, during which gray solids formed. On removal of the volatiles in the usual manner, only a small fraction of the starting material and a trace of $CH_3C_2B_4H_7$ (identified in the mass spectrum) were detected.

(*b*). *Diphenyl ether solution.* A 3.3 mmole sample of the compound was condensed with 0.5 ml of the solvent into a 10 ml reactor, which was sealed, shaken, and heated to 280°C for 19 h. The solution became dark brown during this period. Other than traces of methylsilanes (identified from IR and mass spectra) the only volatile product was 2-$(CH_3)_3Si$–2,4-$C_2B_5H_6$, whose IR and mass spectra are identical to those of an authentic sample prepared[26] from $(CH_3)_3SiCl$ and 2-$LiC_2B_5H_6$. The mass spectrum of 2-$(CH_3)_3SiC_2B_5H_6$ contains the expected parent peak as well as intense peaks corresponding to $(CH_3)_3Si^+$ and $(CH_3)_2SiH^+$ fragments. The IR spectrum displays bands at 2960 s, 2900 m, 2600 vs, 1410 w, 1330 w (br), 1255 vs, 1200 s, 1150 m (br), 1100 w, 1030 m, 905 w (br), 830 vs, 760 m, and 690 w cm^{-1}.

Reaction of $(CH_3)_2GeH_2$ with 2,3-$C_2B_4H_8$

Preliminary experiments gave no indication of reaction in the gas phase below 280°. The reaction at 300° in a Pyrex bulb, under conditions given in Table 1, produced a dark metallic film on the reactor walls and a red-brown powdery solid which contained C, 13.0; H, 3.5; B, < 1 and Ge, 83.1% (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.). After 1 h the volatiles were distilled from the reactor, which was heated to 100° in the final stages of distillation. The volatile products were fractionated through traps at −23°, −35°, −45°, and −63° on the vacuum line. All fractions condensing in the three coldest traps were separated into individual compounds by GLC using the Kel-F and Apiezon columns described above. The $C_2B_5H_7$ and its monomethyl derivatives (Table 1) were identified from IR spectra and GLC retention times by comparison with the data from known compounds[27]. The polymethyl carborane derivatives were characterized from their IR and mass spectra; positions of cage substitution could not be assigned, but the presence of $B{-}CH_3$ stretching bands near 1320 cm^{-1} and the absence of $C{-}CH_3$ absorptions in the 1450 cm^{-1} region identify these as primarily *B*-methylated products.

The material condensing at −23° proved insufficiently volatile for GLC handling, but was separated into several fractions during vacuum distillation from a trap at 70°. Mass spectra of the separate fractions disclosed a series of compounds with cutoffs at *m/e* 246, 232, 218, 204, and 190, corresponding to parent ions of composition $^{76}Ge^{12}C_2{}^{11}B_5(^{12}CH_3)_nH_{7-n}^+$ in which n has values of 2 through 6, respectively. The fragmentation pattern in each case is typical of a polyhedral boron cage and is consistent with the presence of 1 germanium and 5 boron atoms in their normal isotopic distributions. The mass spectra and volatilities of these compounds do not appear reconcilable with known carborane systems or their alkyl derivatives, and the presence of exopolyhedral germanium-containing groups may be ruled out by the absence of significant peaks corresponding to $(CH_3)_xGe^+$-type fragments in the mass spectra.

Reaction of $(CH_3)_2SnH_2$ *with* 2,3-$C_2B_4H_8$

Dimethylstannane (5.0 mmoles) and 2,3-dicarbahexaborane(8) (1.9 mmoles) were heated to 175° in a sealed 500 ml reactor, which became coated with a metallic deposit within 20 min. After 21 h the volatile products were removed and found to contain all of the original carborane reactant plus decomposition products of dimethylstannane [including $(CH_3)_3SnH$ and CH_3SnH_3] which were identified from their mass spectra.

Reaction of $(CH_3)_2GeH_2$ *with* 2,4-$C_2B_5H_7$

A 6.6 mmole sample of dimethylgermane and 3.1 mmoles of the carborane were condensed into a 100 ml reactor which was sealed and heated to 270° for 2 h. Dark solids formed within the first 20 min of reaction. Chromatography of the volatile materials gave 1.3 mmoles of trimethyl boron, $(CH_3)_3GeH$, $(CH_3)_4Ge$ (identified from mass spectra) and unidentified products, and starting materials. A total of 2.7 mmoles $C_2B_5H_7$ and 1.3 mmole $(CH_3)_2GeH_2$ were recovered.

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REFERENCES

1 W. A. LEDOUX, Thesis University of Virginia 1970.
2 W. A. LEDOUX AND R. N. GRIMES, *158th National Meeting of the Amer. Chem. Soc.*, New York, September 1969. *Abstr. INOR*-101.

3 A. Stock, *Ber.*, 56 (1923) 789.
4 M. L. Thompson and R. Schaeffer, *Inorg. Chem.*, 7 (1968) 1677.
5 R. N. Grimes and C. L. Bramlett, *J. Amer. Chem. Soc.*, 89 (1967) 2557.
6 R. N. Grimes, C. L. Bramlett and R. L. Vance, *Inorg. Chem.*, 7 (1968) 1066.
7 R. N. Grimes, C. L. Bramlett and R. L. Vance, *Inorg. Chem.*, 8 (1969) 55.
8 T. P. Onak, R. P. Drake and G. B. Dunks, *Inorg. Chem.*, 3 (1964) 1686.
9 T. Onak, P. Mattschei and E. Groszek, *J. Chem. Soc. A*, (1969) 1990.
10 T. P. Onak, F. J. Gerhart and R. E. Williams, *J. Amer. Chem. Soc.*, 85 (1963) 3378.
11 M. A. Ring, G. D. Beverly, F. H. Koester and R. P. Hollingsworth, *Inorg. Chem.*, 8 (1969) 2033.
12 J. J. Kohanek, P. Estacio and M. A. Ring, *Inorg. Chem.*, 8 (1969) 2516.
13 H. Hart and W. N. Lipscomb, *Inorg. Chem.*, 7 (1968) 1070.
14 T. Onak and G. B. Dunks, *Inorg. Chem.*, 5 (1966) 439.
15 D. A. Franz, J. W. Howard and R. N. Grimes, *J. Amer. Chem. Soc.*, 91 (1969) 4010.
16 E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, 1 (1962) 432.
17 A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 69 (1947) 2693.
18 S. Kaye and S. Tannenbaum, *J. Org. Chem.*, 18 (1953) 1750.
19 W. E. Davidsohn and M. C. Henry, *Chem. Rev.*, 67 (1967) 73.
20 H. Buchert and W. Zeil, *Z. Phys. Chem. (Frankfurt am Main)*, 29 (1961) 317.
21 R. B. Reeves, R. E. Wilde and D. W. Robinson, *J. Chem. Phys.*, 40 (1964) 125.
22 R. N. Dixon and N. Sheppard, *Trans. Faraday Soc.*, 53 (1957) 282.
23 A. B. Burg and J. S. Sandhu, *J. Amer. Chem. Soc.*, 87 (1965) 3787.
24 T. Onak, G. B. Dunks, I. W. Searcy and J. Spielman, *Inorg. Chem.*, 6 (1967) 1465.
25 I. Shapiro, C. D. Good and R. E. Williams, *J. Amer. Chem. Soc.*, 84 (1962) 3837.
26 R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, 92 (1970) 5072.
27 R. N. Grimes, *J. Amer. Chem. Soc.*, 88 (1966) 1895.