values for the collisional efficiency, *b*, for loss of BH_3 would be half of our calculated values. Similar considerations hold for cases where the direct route predominates over the BH_3 route: the values for *b* become smaller as BH_3 becomes less important as an intermediate. We see, however, that by taking the BH_3 route to be the only important one, the values obtained for *b* agree quite well with values obtained in two other independent studies (Figure 2). Therefore we relegate the direct conversion of B_2H_6 to H_2 and boron to a minor role at best.

Hydrogen gas is also a product of the pyrolysis of diborane at higher pressures, lower temperatures, and longer times.[22] There is a temptation to apply the results presented here to an interpretation of the data on the overall pyrolysis under other conditions. For example, Bragg, *et al.*,[23] found that the activation energy for the rate-controlling step leading to the formation of hydrogen is *ca.* 26 kcal, which is the same as our value. In addition their first-order rate constant for the production of H_2 at 353°K, when extrapolated to 530°K, predicts our $B/(1 - B)$ for B_2H_6 at 530°K within a factor of 10. Despite this agreement it is doubtful that BH_3 is a major source of hydrogen during pyrolysis of B_2H_6 under conditions such as those used by Bragg, *et al.* There are two good reasons for this conclusion. First, in the latter study, the major boron-containing products are volatile and nonvolatile (polymer) hydrides. There is no evidence for the formation of elemental boron under conditions such as theirs. Second, in the latter type system there is a large normal isotope effect associated with the production of hydrogen.[24] Therefore, there is no direct connection between the results of this study and the results of the studies under different conditions.[22]

Our major conclusion is that there exists a fruitful area of research on the reactions of BH_3 at lower temperatures where it is less subject to the decomposition to the elements.

Acknowledgments.—This work was supported by a National Science Foundation grant, NSF-GP-6820.

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Rearrangement in Borane Adducts of Trimethylsilylmethylenedimethylsulfurane[1]

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Boron halide, borane, and trimethylboron adducts of the silyl-substituted sulfonium ylide $(CH_3)_3SiCHS(CH_3)_2$ are readily formed. The borane and alkylboron adducts rearrange at low temperature with simultaneous loss of dimethyl sulfide to give *sym*-bis(trimethylsilylmethyl)diborane and 1-(trimethylsilylmethyl)ethyldimethylborane, respectively. These rearranged products were isolated and characterized. A trimethylamine adduct with the dialkyldiborane could be converted into the asymmetrical borane cations $(CH_3)_3SiCH_2BHN(CH_3)_3py^+$ and $(CH_3)_3SiCH_2BHN(CH_3)_3P(CH_3)_3{}^+$.

Rearrangements of alkyl groups from boron to an adjacent carbon are of considerable current interest. In one class of such rearrangements there is a simultaneous migration of a base molecule, base–$CH_2BR_3 \rightarrow$ base–BR_2CH_2R. Tufariello and Lee, for example, reported the migration of an *n*-hexyl group in the reaction of trihexylborane and $(CH_3)_2SCH_2$ in solution.[3] Similar rearrangements are known to occur at higher temperature with borane adducts of phosphorus- and nitrogen-stabilized ylides.[4,5] The isolable sulfonium ylide $(CH_3)_2SCHSi(CH_3)_3$,[6] I, provides novel possibilities for the study of these rearrangements of sulfonium ylides in the absence of reactive solvent, and indeed this ylide does form some boron adducts that readily rearrange. The adduct with diborane is of particular interest in that it leads to a methyl-substituted diborane which would be difficult to prepare otherwise.

Experimental Details

Solvents used were reagent grade; tetrahydrofuran was purified by distillation form lithium aluminum hydride. Boron trichloride (Trona, electronic grade), boron trifluoride (Matheson), and diborane (Callery) were obtained commercially and used without additional purification. Boron trimethyl was prepared from boron trifluoride etherate and methylmagnesium bromide in ether according to standard directions[7] and purified by low-temperature distillation.

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[1] Presented at the 5th Midwest Regional meeting of the American Chemical Society, Kansas City, Mo., Oct 29–31, 1969.

[2] Author to whom inquiries should be addressed.

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Analyses were obtained from Midwest Microlab (Indianapolis, Ind.) and Alfred Bernhardt Microanalytical Laboratory (Mülheim, West Germany).

Many of the manipulations of air-sensitive materials were carried out in a high-vacuum system equipped with Demar-Urry valves and O-ring joints. Extensive use was made of hypodermic syringes in transferring reactive solutions.

Infrared spectra (Table I) were recorded on a Perkin-Elmer 237B instrument, and proton magnetic resonance spectra (Table II) were obtained on a Varian A-60A. Melting points, uncorrected for emergent stem, were taken with a Thomas-Hoover capillary apparatus.

Table I

Infrared Spectra

Compound	Infrared bands,[a] cm^{-1}
$(CH_3)_3SiCH_2SCH_3$	2955 s, 2905 s, 2880 m, 2840 w, 1425 m, 1395 m, 1320 w, 1250 s, 1135 w, 1075 w, 965 m, 850 s, bd, 780 w, 755 w, 700 w, 660 w
$(CH_3)_3SiCHS(CH_3)_2$	2960 s, 2925 m, 1430 m, 1410 m, 1315 w, 1255 m, 1240 s, 1170 m, 1020 m, 980 s, 955 s, 860 s, 835 s, 770 m, bd, 680 m
$(CH_3)_3SiCH(BF_3)S(CH_3)_2$, N	1250 s, 1200 m, 1095 s, 1060 s, 1030 s, 1015 s, 995 s, 970 s, 950 s, 930 m, 845 m, 785 w, 740 w, 700 w
$[(CH_3)_3SiCH_2BH_2]_2$, G	2960 s, 2925 w, 2910 w, 1575 s, bd, 1390 w, bd, 1340 w, 1250 s, 1150 s, bd, 1070 m, 1050 m, 980 w, 940 w, 850 s, bd, 750 w, 700 m
$(CH_3)_3SiCH_2BH_2N(CH_3)_3$, N	2330 s, 2260 s, 1485 s, 1400 w, 1335 w, 1250 s, 1240 s, 1180 m, 1155 s, 1125 w, 1110 m, 1050 w, 990 m, 970 m, 870 s, bd, 835 s, bd, 760 w, 735 w, 685 m
$[(CH_3)_3SiCH_2]_3B$	2960 s, 2900 m, 1410 w, 1380 w, 1300 w, 1250 s, 1210 m, 1180 s, 1070 m, 1025 m, 980 m, 945 w, 850 s, bd, 715 m, 700 m
$(CH_3)_3SiCH_2BHP(CH_3)_3N(CH_3)_3{}^+PF_6{}^-$, N	2360 m, 1485 m, 1415 m, 1325 m, 1305 m, 1260 m, 1240 s, 1140 s, 1115 w, 1100 w, 1055 w, 1020 m, 975 s, 960 s, 925 w, 850 s, bd, 795 m, 760 m, 725 w, 710 w, 630 m
$(CH_3)_3SiCH_2BH(NC_5H_5)N(CH_3)_3{}^+PF_6{}^-$, N	2445 w, bd, 1625 m, 1490 m, 1250 m, 1170 s, 1150 m, 1110 m, 1075 w, 1045 w, 1025 w, 980 m, 955 w, 845 s, bd, 790 w, 770 w, 720 m, 710 m
$(CH_3)_3SiCH(CH_3)B(CH_3)_2$, G	2960 s, 2920 m, 2880 m, 2860 m, 1460 w, 1410 w, 1300 s, 1255 m, 1165 s, 1140 m, 1080 w, 985 m, 900 w, 850 s, bd, 755 w, 695 w
$(CH_3)_3SiCH(CH_3)B(CH_3)_2NH(CH_3)_2$	3285 m, 3030 w, 3000 w, 2950 s, bd, 2890 s, 2855 m, 2830 m, 1470 m, 1430 w, 1400 w, 1295 s, 1275 m, 1245 s, 1140 s, 1085 w, 1030 m, 1000 m, 955 m, 930 w, 900 m, 855 s, 835 s, 755 m, 735 m, 685 m

[a] Infrared data were obtained on a Perkin-Elmer 237B grating spectrometer. The samples were run as neat liquid samples on potassium chloride plates except where indicated: N, the sample was run on a mineral oil mull; G, the sample was run as a gas in a 10-cm gas cell. Very weak absorptions and absorptions masked by mineral oil are not included. Abbreviations: s, strong; m, moderate; w, weak; bd, broad.

Tris(trimethylsilylmethyl)borane was prepared by the Grignard method of Seyferth,[8] from 10 ml of a 1.37 *M* trimethylsilylmethylmagnesium bromide solution in ether and 6.80 ml of 47% boron trifluoride etherate in 7 ml of ether. The product $[(CH_3)_3SiCH_2]_3B$ was purified by distillation, bp 83° (4 mm) [lit.[8] bp 78° (1.6 mm)]; yield 2.43 g (65%).

Trimethylsilylmethyl Methyl Sulfide.—Lithium foil, 2.8 g (0.41 g-atom), 30 ml of tetrahydrofuran (THF), and 38 g (0.35 mol) of trimethylsilyl chloride were placed in a 250-ml three-necked flask under an argon atmosphere. With stirring at −25°, 19.32 g (0.20 mol) of chloromethyl methyl sulfide in 15 ml of THF was added dropwise over a 2.5-hr period. The lithium surface remained shiny throughout this time. When the addition was complete, the mixture was allowed to warm to room temperature, the salt was filtered off, and the filtrate was vaporized through a −40° trap which stopped the product. Further purification was effected by repeated condensations through a −30° trap; 18.8 g was collected (70%). The clear liquid was identified as $(CH_3)_3SiCH_2SCH_3$ by comparison of its infrared spectrum with that of an authentic sample. The proton nmr resonances of a neat sample were singlet peaks at −0.07, −1.74, and −2.08 ppm (assigned to $Si(CH_3)_3$, CH_2, and SCH_3 protons, respectively) downfield from internal tetramethylsilane (TMS) with an intensity ratio 9.0:2.0:3.0.

The sulfide could also be purified by distillation through a Claisen head packed with glass helices; bp 133–136° [lit.[9] bp 70° (93 mm)].

Trimethylsilylmethyldimethylsulfonium Iodide.—Equimolar quantities of trimethylsilylmethyl methyl sulfide and methyl iodide were combined in a reaction flask, whereupon a chalk white precipitate began to form within several minutes. After 2 days the solid formed a reddish yellow cake (the color apparently caused by iodine); this was dissolved in acetonitrile and precipitated by the slow addition of ether, filtered, and washed several times with ether. The white crystalline solid, mp 104–106° (lit.[9] mp 106°), was identified as $(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$ by comparison of its infrared spectrum with that of a known sample. The proton nmr resonances in chloroform were singlet peaks at −0.35, −3.32, and −3.44 ppm (assigned to $Si(CH_3)_3$, CH_2, and ${}^+S(CH_3)_2$ protons, respectively) downfield from TMS, with an intensity ratio 9.0:2.0:5.9, agreeing well with the ratio 9:2:6 expected for first-order effects.

Attempts at metathesis to the hexafluorophosphate salt generally resulted in hydrolytic cleavage of the trimethylsilyl moiety, and only trimethylsulfonium hexafluorophosphate was isolated.

Trimethylsilylmethylenedimethylsulfurane, I.—A slurry of 13.8 g (50 mmol) of trimethylsilylmethyldimethylsulfonium iodide and 20 ml of anhydrous ether was treated slowly under nitrogen with 22.3 ml of 2.26 *M* *n*-butyllithium in hexane at 0°. The mixture was stirred for 0.5–1 hr at 0° and then 15 min at room temperature. After cooling again to 0°, 9.0 g (100 mmol) of 1,2-dimethoxyethane was added, bringing about the precipitation of lithium iodide complex. The mixture was filtered under nitrogen and the filtrate was fractionated through a −40° trap which stopped the product. The contents of this trap were transferred by syringe to a short-path still and distilled, collecting 5.21 g (70%) of clear liquid at 46° (7 mm) [lit.[6] 53° (12 mm)], identified as $(CH_3)_3SiCH^{-+}S(CH_3)_2$ by comparison of its infrared spectra with that of an authentic sample. The proton resonance of a neat sample showed three singlet peaks at +0.07, −0.37, and −2.22 ppm (assigned to $Si(CH_3)_3$, CH, and $S(CH_3)_2$ protons, respectively) relative to added TMS. The integrated intensity ratio was 9.0:1.0:6.0, agreeing with that expected for the first-order spectrum.

Because of the ease of thermal decomposition, the ylide could be more readily purified by fractional condensation than by distillation. The filtered solution is first fractionated, collecting the ylide in a −45° trap as above, and then refractionated, collecting the ylide in a −35° trap. This method generally resulted in 80% yield of essentially pure $(CH_3)SiCHS(CH_3)_2$. The small amount of impurity present was found to be 1,2-dimethoxyethane, always less than 5% as evidenced by proton magnetic resonance analysis.

BF_3 Adduct.—In a 50-ml reflection flask fitted with syringe cap and under a nitrogen atmosphere were added 1.221 g (8.24 mmol) of trimethylsilylmethylenedimethylsulfurane and 20 ml of ether. While stirring at −78°, 4.10 ml of 47% boron trifluoride diethyl etherate was added slowly. A white solid formed immediately, and the resulting slurry was stirred for 2–3 hr and filtered, and the precipitate was washed with ether;

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TABLE II

^{1}H NMR RESONANCES (IN δ, PPM)[a]

	$SiCH_3$	$SiCH_2S$	SCH_3	Other	Solvent	Intensity ratio[b]
$(CH_3)_3SiCH_2SCH_3$	−0.07	−1.74	−2.08			9:2:3
$(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$	−0.35	−3.32	−3.44		$CHCl_3$	9:2:5.9
$(CH_3)_3SiCH^{-+}S(CH_3)_2$	+0.07		−2.22	−0.37, CH^-		9:6:1
$(CH_3)_3SiCH(BF_3)S(CH_3)_2$	−0.21		−2.80		CH_2Cl_2	3:2
$(CH_3)_3SiCH_2BH_2N(CH_3)_3$	+0.08			+0.51, broad, CH_2	CH_2Cl_2	9:2:9
				−2.48, NCH_3	CH_2Cl_2	1:(−)[d]1:1
$(CH_3)_3SiCH_2BHN(CH_3)_3P(CH_3)_3{}^+PF_6{}^-$	−0.04			+0.42, broad, CH_2 −1.52, PCH_3 J_{PCH} = 11 Hz −2.74, NCH_3		
$(CH_3)_3SiCH_2BHN(CH_3)_3NC_5H_5{}^+PF_6{}^-$	+0.27			−2.57, NCH_3 −8.30, m, NC_5H_5	CH_2Cl_2	1:1:(−)[e]
$(CH_3)_3SiCH(CH_3)B(CH_3)_2$	0.00			−0.67, BCH_3 −1.19, broad area, $CHCH_3$	CH_2Cl_2	9:5.8:4.2
$(CH_3)_3SiCH(CH_3)B(CH_3)_2NH(CH_3)_2$	+0.07			+0.33, BCH_3 −0.82, d, 7.5 Hz[c] CCH_3 −2.32, NCH_3		3:2:1:2

[a] Obtained with a Varian A-60A spectrometer. All chemical shifts are reported relative to internal tetramethylsilane (TMS). Abbreviations: d, doublet; m, multiplet. [b] Relative peak areas listed in order of appearance in table. [c] J_{HCCH}. [d] Overlooked on integration. [e] Integration of pyridine multiplet was routinely 50% high.

1.395 g (68%) of gray-white solid was produced. Recrystallization was effected from hot tetrahydrofuran yielding white flakes, mp 118–121°. The infrared and proton magnetic resonance spectra confirmed the structure as the boron trifluoride adduct of the ylide. *Anal.* Calcd for $(CH_3)_3SiCH(BF_3)S(CH_3)_2$: C, 33.4; H, 7.5; S, 14.8. Found: C, 33.3; H, 7.8; S, 14.9.

A 0.4300-g (1.99-mmol) sample of the ylide–boron trifluoride adduct was placed in a 50-ml reaction flask and heated slowly to 140°, initially under 15 mm nitrogen pressure. The solid melted with bubbling at about 120°. After being held at 140° for 3 hr, the nitrogen atmosphere was removed by evacuation through a −40° and a −196° trap. The melt in the reaction flask slowly evolved bubbles of gas and took on a yellow-brown color. The −196° trap contained 0.65 mmol of trimethylfluorosilane; the −40° trap was empty. The pyrolysis was continued to 170° for 2 hr. A total of 1.84 mmol (92%) of trimethylfluorosilane was caught in the −196° trap, and a yellowish uncharacterized powder remained in the reaction flask.

Boron Trichloride Adduct.—In a similar way, an adduct from 0.923 g (6.22 mmol) of trimethylsilylmethylenedimethylsulfurane and 6.22 mmol of boron trichloride was prepared at −78°. After stirring for 1 hr and warming to room temperature, volatiles were removed to leave 1.6915 g (106%) of white tacky material. This was pyrolyzed to 140° for 2–3 hr while evacuating through a −40° and a −196° trap. The residue slowly turned dark brown-black, and $(CH_3)_3SiCl$ was caught in the −196° trap (0.6075 g, 90%; identified by its infrared spectrum).

Borane Adduct.—A solution of 1.1017 g (7.43 mmol) of trimethylsilylmethylenedimethylsulfurane in 20 ml of ether contained in a 50-ml reaction bulb on the vacuum line was cooled to −78°. After evacuation, 3.72 mmol of diborane (measured as a gas) was introduced slowly with stirring. A slurry of white solid formed immediately; it was stirred for 10–15 min at −78° after which excess diborane was removed by evacuation. The remaining mixture was passed through a −50° trap, leaving a white solid in the reaction flask while its temperature was below 0°. The white solid liquefied when most of the ether had been removed and the flask began to warm above 0°. In the −50° trap 0.736 g of slightly volatile liquid was caught. This clear liquid was identified as *sym*-bis(trimethylsilylmethyl)diborane from its infrared spectrum, proton magnetic resonance, and chemical properties. It could not be distilled without decomposition to tris(trimethylsilylmethyl)borane. Some decomposition occurs at room temperature so elemental analyses were not obtained. The liquid is air sensitive, inflaming when placed on a porous surface.

Dimethyl sulfide was detected in the volatiles by odor and reaction with methyl iodide to form trimethylsulfonium iodide.

In subsequent preparations, the white solid was allowed to warm to room temperature before removing solvent. The white solid slowly disappeared and subsequent cooling to −78° did not result in its regeneration, implicating a reaction had occurred. *sym*-Bis(trimethylsilylmethyl)diborane was obtained in excellent yield by fractional condensation.

If no solvent is employed and diborane is condensed onto the ylide at −196° and allowed to warm slowly, the product is a gross mixture of several boron-containing compounds.

A 0.2782-g (1.89-mmol) sample of the rearrangement product was heated 4 hr at 85°. The condensable product was fractionated to give trimethylsilane (0.6 mmol) and diborane (0.07 mmol). The oily residue remaining in the pyrolysis sample is essentially $B[CH_2Si(CH_3)_3]_3$ by infrared analysis.

Reaction of 0.5 Equiv of BH_3 with I.—By the same technique, using 0.5 equiv of BH_3 (2.42 mmol of B_2H_6) and 1.4400 g (9.72 mmol) of trimethylsilylmethylenedimethylsulfurane in 15 ml of dry ether, a white solid was formed at −78°. When allowed to warm to room temperature to permit rearrangement of the adduct in the presence of 1 equiv of trimethylsilylmethylenedimethylsulfurane, the white solid conglomerated into a white, waxy-appearing mass. This solid slowly disappeared while stirring at room temperature for 2–3 hr, and the resulting solution was fractionated through a −50° trap which stopped 0.534 g of liquid. Infrared analysis showed the liquid to be a mixture of two boranes, chiefly *sym*-bis(trimethylsilylmethyl)diborane with some tris(trimethylsilylmethyl)borane, by comparison with known spectra. Remaining in the reaction flask was 0.379 g of tris(trimethylsilylmethyl)borane. A disproportionation of the expected tetrakis(trimethylsilylmethyl)diborane would give $[(CH_3)_3SiCH_2]_3B$ and $[(CH_3)_3SiCH_2BH_2]_2$ in a 2:1 molar ratio which is essentially the ratio observed (1.9).

Trimethylborane Adduct and Its Rearrangement.—Equimolar amounts (5.82 mmol) of the ylide and trimethylborane were combined as with other boron compounds. Reaction was evident within a few minutes by the formation of a considerable amount of white solid. Upon warming to room temperature, the white solid dissolved. Recooling to −78° did not effect the precipitation of the solid. The solution was then fractionally condensed through −45, −78, and −196° U traps. A clear liquid later identified as $(CH_3)_3SiCH(CH_3)B(CH_3)_2$, 0.7161 g (87%), was caught in the −45° trap; it inflamed immediately upon exposure to the atmosphere. Methyl sulfide was detected in the −78 and −196° traps.

A second sample was prepared using trimethylsilylmethylenedimethylsulfurane prepared *in situ* from 3.53 ml of 2.42 *M* *n*-butyllithium and 2.3556 g (8.53 mmol) of $(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$ in 8 ml of ether at 0°. After stirring for 0.5 hr at 0° and 0.5 hr at room temperature, 9 mmol of trimethylborane was added at −78°. The solution was then stirred for 1.5 hr at room temperature and fractionated through −35 and −78° traps, collecting 0.8846 g (73%) of clear liquid (vapor pressure 10 mm (23°)). Infrared and proton magnetic resonance analyses showed it to be $(CH_3)_3SiCH(CH_3)B(CH_3)_2$. *Anal.* Calcd for $(CH_3)_3SiCH(CH_3)B(CH_3)_2$: C, 59.2; H, 13.5; Si, 19.8. Found: C, 59.3; H, 13.6; Si, 22.6.

Dimethylamine and Trimethylamine Adducts of $(CH_3)_3SiCH(CH_3)B(CH_3)_2$.—A mixture of 0.7161 g (5.04 mmol) of $(CH_3)_3SiCH(CH_3)B(CH_3)_2$ and excess dimethylamine at −78° formed a white solid immediately. Excess dimethylamine was removed under vacuum and the slightly volatile liquid adduct was stopped by a −50° trap; yield 0.881 g, 94%. The liquid could not be distilled without decomposition even in a short-path still. A recorded melting point of 7–11° for the adduct is believed to be unreliable for characterization because small amounts of impurities are known to lower melting points of amine–boranes greatly. *Anal.* Calcd for $(CH_3)_3SiCH(CH_3)B(CH_3)_2NH(CH_3)_2$: C, 57.8; H, 14.0; N, 7.5; B, 5.8. Found: C, 57.6; H, 14.3; N, 7.6; B, 5.4.

A mixture of 0.1880 g (1.32 mmol) of $(CH_3)_3SiCH(CH_3)B(CH_3)_2$ and trimethylamine in small excess of 1:1 stoichiometry is solid at −78° suggestive of adduct formation. Distillation through a −35° trap led to the recovery of 0.1255 g of starting borane.

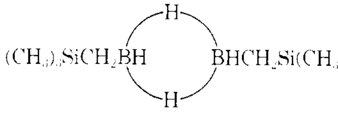
Cation Synthesis.—The trimethylamine adduct of $[(CH_3)_3SiCH_2BH_2]_2$ was prepared from the ylide *in situ*. An ether solution containing 53.6 mmol of ylide (from 22.2 ml of 2.42 *M* n-C_4H_9Li in hexane and 14.8 g of $(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$ in 50 ml of ether) was cooled to −78° and 27 mmol of diborane was added slowly, whereupon a white slurry was produced. The mixture was warmed to room temperature to effect rearrangement and then cooled to −78°, and excess trimethylamine was added. On warming to room temperature and stirring 2 hr, 11.2 ml (108 mmol) of 1,2-dimethoxyethane was added. The mixture was filtered to remove insoluble solvated lithium iodide, and the filtrate was evaporated, leaving the adduct as white needles, mp 53–55°. Recrystallization from pentane gave 6.70 g of product (78%), mp 55–56°. The purified material had to be kept at −78° because of the slow disproportionation that sets in at room temperature. *Anal.* Calcd for $(CH_3)_3SiCH_2BH_2N(CH_3)_3$: C, 52.8; H, 13.9; N, 8.8; B, 6.8. Found: C, 52.5; H, 13.8; N, 8.5; B, 7.1. The highest significant mass spectrum peak for the purified material corresponds to a P − 1 peak at *m/e* 158.

The trimethylamine adduct was monoiodinated in chloroform solution and was then treated with pyridine or trimethylphosphine. Solvent was removed after about 0.5 hr and the white residue (iodide salt) was metathesized to the hexafluorophosphate (in about 80% yield) in acidified water. *Anal.* Calcd for $(CH_3)_3SiCH_2BHN(CH_3)_3P(CH_3)_3{}^+PF_6{}^-$ (mp 113–114°): C, 31.7; H, 8.0; N, 3.7; P, 16.3. Found: C, 31.9; H, 7.9; N, 3.8; P, 16.2. Calcd for $(CH_3)_3SiCH_2BHN(CH_3)_3C_5H_5N^+PF_6{}^-$ (mp 123–124°): C, 37.7; H, 6.8; N, 7.3. Found: C, 37.9; H, 6.7; N, 7.4.

Results and Discussion

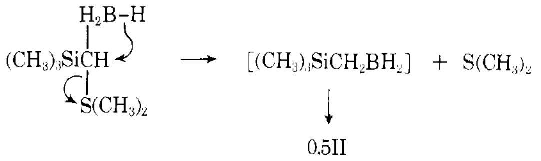
The sulfonium ylide I exhibits a delicate balance of thermal stability and chemical reactivity. It can be isolated and purified by simple vacuum distillation, yet it is extremely reactive to oxygen, water, and Lewis acids. As a neat liquid it slowly decomposes at room temperature—very rapidly in the presence of acids. Catalytic amounts of boron trifluoride bring about vigorous decomposition and formation of a rubbery high polymer. A solution of I in diethyl ether is much more stable toward decomposition. The ether also mediates the vigor of the reaction of I with Lewis acids and permits isolation of simple adducts of boron trifluoride and trichloride. The boron halide adducts decompose on moderate heating with elimination of trimethylsilyl halide and formation of polymeric residue.

Diborane also reacts vigorously with I in the absence of a solvent (producing a mixture of alkylated boranes). In ether or liquid alkanes at −78°, however, a white adduct precipitates. Above 0° the adduct reacts with formation of *sym*-bis(trimethylsilylmethyl)diborane



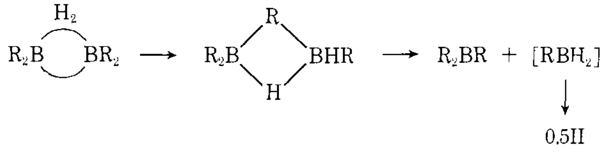
II

This dialkyldiborane, a clear, spontaneously flammable liquid, is isolated by fractional condensation. Its formation can be plausibly explained by a hydride shift with concomitant liberation of dimethyl sulfide



Structure assignment of II was based upon spectral and chemical data. A hydrogen-bridge absorption in the infrared spectrum at 1575 cm^{-1} characteristic of symmetrically substituted diboranes[10] and a singlet B–H stretch at 2510 cm^{-1} support the symmetrically substituted structure proposed. Unsymmetrical substitution is unlikely since the local symmetry about one boron is C_{2v}, and two B–H stretching modes would be expected as observed for $(C_2H_5)_2BHBH_3$.[11] The bulk of the trimethylsilylmethyl groups would be expected to favor the trans configuration in the 1,2-dialkyldiborane.

At room temperature II slowly disproportionates, probably according to $3[(CH_3)_3SiCH_2BH_2]_2 \rightarrow 2[(CH_3)_3SiCH_2]_3B + 2B_2H_6$. This facile migration of hydrogen and alkyl is common for alkylboranes and was also encountered in attempts to prepare tetrakis(trimethylsilylmethyl)diborane from II and sulfurane I. A mixture of 1 mol of ylide and 0.5 mol of BH_3 on warming formed $[(CH_3)_3SiCH_2]_3B$ and $[(CH_3)_3SiCH_2BH_2]_2$ in very nearly 2:1 molar amounts. It is likely that the tetraalkylborane initially formed rearranged to relieve steric strain



sym-Bis(trimethylsilylmethyl)diborane (II) readily

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[10] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, p 178.

[11] I. J. Solomon, M. J. Klein, and K. Hattori, *J. Amer. Chem. Soc.*, **80**, 4520 (1958).

forms an air-stable white solid adduct with trimethylamine

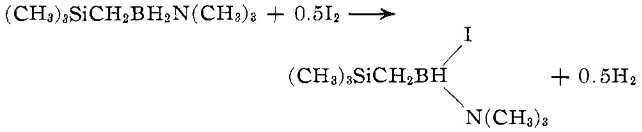
$$[(CH_3)_3SiCH_2BH_2]_2 + 2N(CH_3)_3 \longrightarrow (CH_3)_3SiCH_2BH_2N(CH_3)_3$$

This adduct could be purified by sublimation, but its melting point decreases with time, a behavior characteristic of amine–boranes when small amounts of impurities are present.[12] The proton nmr resonances of the adduct in CH_2Cl_2 showed peaks of equal intensity at +0.08 ($Si-CH_3$) and −2.48 ppm ($N-CH_3$) relative to internal tetramethylsilane. A very broad area at +0.5 ppm is believed due to the methylene protons which are split by the adjacent boron. The relative intensities were 9:9:2 as required by the structure. The high-field position of the trimethylsilyl and methylene groups is evidently a result of their electron-rich nature in the adduct.

Mass spectral analysis[13] of $(CH_3)_3SiCH_2BH_2N(CH_3)_3$ showed a P−1 peak at 158 (calculated molecular weight 159). The absence of a strong parent peak is evidently due to the facile loss of a proton from the parent molecular ion. Fragments of greatest intensity were found at *m/e* 85 ($(CH_3)_3SiCH_2$), 73 ($(CH_3)_3Si$), 59 ($N(CH_3)_3$), 58 ($CH_2N(CH_3)_2$), 43, 42, and 15.

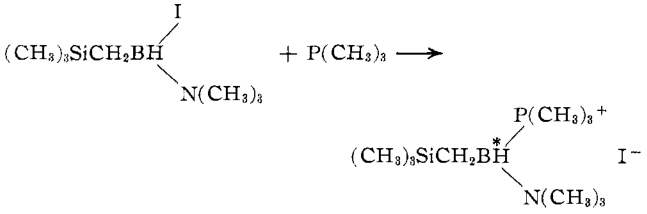
The amine–borane adduct has an odor reminiscent of diborane. It slowly decomposed in several days at room temperature into an oily material that was essentially tris(trimethylsilylmethyl)borane (identified by comparison of its infrared spectrum with that of a known sample). However, the adduct could be stored at −78° without decomposition.

sym-Bis(trimethylsilylmethyl)diborane and its adducts should have derivative chemistries of value. For example, boron-containing cations were prepared from trimethylamine–trimethylsilylmethylborane by use of the Ryschkewitsch modification[12] of the Douglass reaction.[14] Iodine in chloroform solution reacts with the adduct to give hydrogen and iodoborane

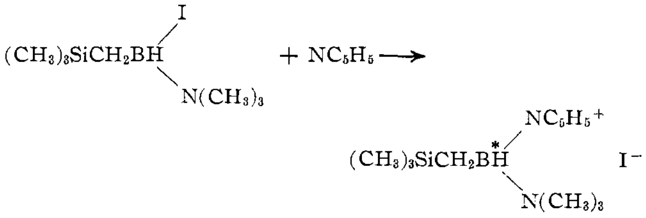


$$(CH_3)_3SiCH_2BH_2N(CH_3)_3 + 0.5I_2 \longrightarrow (CH_3)_3SiCH_2\overset{I}{\underset{N(CH_3)_3}{BH}} + 0.5H_2$$

A small amount of white solid identified as trimethylammonium iodide was also formed. No attempt was made to isolate the iodoborane, but there is little reason to doubt its presence. The addition of trimethylphosphine and pyridine to solutions of the iodoborane gave the corresponding substituted trimethylsilylmethylborane cations as shown below.



$$(CH_3)_3SiCH_2\overset{I}{\underset{N(CH_3)_3}{BH}} + P(CH_3)_3 \longrightarrow (CH_3)_3SiCH_2\overset{P(CH_3)_3^+}{\underset{N(CH_3)_3}{\overset{*}{B}H}}\quad I^-$$



$$(CH_3)_3SiCH_2\overset{I}{\underset{N(CH_3)_3}{BH}} + NC_5H_5 \longrightarrow (CH_3)_3SiCH_2\overset{NC_5H_5^+}{\underset{N(CH_3)_3}{\overset{*}{B}H}}\quad I^-$$

The cations were purified as the hexafluorophosphate salts in water solution. It is apparent from their structure that the boron is an asymmetric center, but no resolution was attempted.

The facile rearrangement of the borane adduct of I encouraged an investigation of alkyl migration. To this end, the interaction of I with trimethylborane was of interest. At −78° it was indeed found that there was a white solid in ether which "dissolved" as did the borane adduct on warming to room temperature. Since the solid could not be reformed immediately when the mixture was cooled to −78°, a rearrangement was inferred. 1-Trimethylsilylethydimethylborane, III, was isolated in 73% yield by fractional condensation. It is clear liquid of low vapor pressure (10 mm at 23°) and enflames in air. Chemical and spectral data support the assigned structure. Proton nmr resonances appearing at 0, 0.67, and 1.19 ppm downfield from internal TMS were assignable to $Si-CH_3$, $B-CH_3$, and $C-CH_3$ groups. The area ratio of the $Si-CH_3$ and $B-CH_3$ peaks was 1.55, very close to that expected if $Si(CH_3)_3$ and $B(CH_3)_2$ moieties were present. Splitting of the methyl protons of the ethyl group by the lone methine hydrogen was not resolved. However, it was seen in the spectrum of the dimethylamine adduct (*vide infra*), so the assignment of the rearranged product seems secure. Rather similar rearrangements have been reported,[3,15] but the boranes were not isolated; their presence was inferred from alcohols produced on oxidative hydrolysis.

The boron acceptor site in III has rather severe steric requirements, as the trimethylamine adduct could be formed only at −78°. A dimethylamine adduct, $(CH_3)_3SiCH_3CHB(CH_3)_2NH(CH_3)_2$, was sufficiently stable to distil (bp 45° (10 mm)). A rather significant vapor-phase dissociation is suspected because this adduct rapidly decomposes to a brown oil in air. The ^1H nmr resonance appears upfield of TMS at 0.33 ppm for $B-CH_3$ and 0.07 ppm for $SiCH_3$, typical for amine–alkylborane adducts.[16]

It is apparent that the rearrangements of borane and alkylborane adducts of I provide a convenient and neat synthesis for a variety of trimethylsilylmethyl-substituted boranes. The synthesis of *sym*-bis(trimethylsilylmethyl)diborane is of particular merit because this diborane would be unattainable by conventional routes of alkylating boron.

Acknowledgment.—Support by a grant from the National Science Foundation is sincerely appreciated. A National Aeronautics and Space Administration fellowship to J. C. M. is also gratefully acknowledged.

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[12] K. N. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Academic Press, New York, N. Y., 1965, p 19.

[13] By Finnigan Instrument Co. on a Model 1015 instrument at the 20th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1969.

[14] J. E. Douglass, *J. Amer. Chem. Soc.*, **86**, 5431 (1964).

[15] J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *ibid.*, **89**, 6804 (1967).

[16] H. Nöth and H. Vahrenkamp, *J. Organometal. Chem.*, **12**, 23 (1968).