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Chemistry of S–B Bonding: Polymeric Thioborines, Methanethiodiborane and Related Substances

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The bond-strengthening effect of methyl groups on sulfur is illustrated by the fair stability of $(CH_3)_2S \cdot BH_3$ (m.p. −38°), the bare existence of $CH_3SH \cdot BH_3$ at −78°, and the non-existence of $H_2S \cdot BH_3$. Loss of H_2 from $CH_3SH \cdot BH_3$ yields the non-volatile and ether-insoluble white solid $(CH_3SBH_2)_x$, which, on heating past its melting range (65–80°) *in vacuo*, distils out a series of CH_3SBH_2 polymers. These are easily hydrolyzed to CH_3SH, $B(OH)_3$ and $2H_2$; or at 140° the approximately dimeric vapor goes over to H_2, B–H polymer and $(CH_3S)_3B$, the last of which was made also from BBr_3 and $NaSCH_3$. The CH_3SBH_2 polymers easily add $(CH_3)_3N$ to form the liquid $(CH_3)_3N \cdot BH_2SCH_3$ (m.p. 14°), the very limited disproportionation of which yields $(CH_3)_3N$, $(CH_3)_3NBH_3$ and $(CH_3S)_3B$. A stream of B_2H_6 at 90° picks up CH_3SBH_2 units from the polymers, or better from $(CH_3)_3N \cdot BH_2SCH_3$, to form the very unstable liquid $CH_3SB_2H_5$ (m.p. −101°, b.p. *ca.* 60°), wherein the S-atom probably bridge-bonds the B atoms. Its decomposition (60% in one hour at 21°) forms B_2H_6 and $(CH_3SBH_2)_x$.

Further studies of S–B bonding include the alternative formation of $(CH_3SBH_2)_x$ from CH_3SSCH_3 and B_2H_6, the preparation of the monomeric $CH_3SB(CH_3)_2$ (m.p. −84°, b.p. 71°, slightly unstable), and an extremely slow reaction between B_2H_6 and H_2S to form a glassy polymer deviating from the formula $(HBS)_x$ in the direction of B–S–B bondings. All present results are consistent with the assumption that methylated sulfur has more electron-donor bonding power than oxygen in similar complexes or polymers, but far less than methylated phosphorus or arsenic.

The recent discovery of the very stable and chemically unreactive phosphinoborine polymers, such as $[(CH_3)_2PBH_2]_3$,[2] and the similar but somewhat less stable and more reactive arsinoborines,[3] made it seem possible that analogous thioborine polymers would exist. Accordingly, methanethiol and diborane were brought together, first forming an adduct which, *in vacuo* at −78°, easily dissociated into its components. On standing, the mixture of adduct and components formed hydrogen and a white solid having the composition CH_3SBH_2. This product was insoluble in the common organic solvents, but upon heating *in vacuo* it yielded slightly volatile, ether-soluble, liquid and solid materials as well as a less volatile glassy liquid. All fractions had the empirical formula CH_3SBH_2, and accordingly were recognized as a series of polymers. The ease with which they could be interconverted, or hydrolyzed to boric acid, hydrogen, and methanethiol, indicated far less stability of polymer bonding than that in the phosphinoborines or arsinoborines. The relative weakness of bonding could be argued also from the average molecular weight value only a little above that of a dimer at 130°, and from the occurrence of a disproportionation reaction at 140°. Furthermore, all of the polymer fractions reacted easily with trimethylamine to form the complex $(CH_3)_3N \cdot BH_2SCH_3$, meaning that the energy requirement for the depolymerization of $(CH_3SBH_2)_x$ is far less than would be needed to break down the phosphinoborine or arsinoborine polymers.

That the CH_3SBH_2 polymers should be more weakly bonded than the phosphinoborines was expected because such polymers depend upon S–B and P–B dative bonding, and in this respect sulfur is always weaker than phosphorus in comparable compounds. A more subtle but also very important argument for the relative weakness of dative bonding in the CH_3SBH_2 polymers is found in the influence of the CH_3 and BH_2 groups. The surprising stability of the phosphinoborine polymers has been ascribed to an enhancement of the dative bonding power of phosphorus by an inductive effect due to the wandering of C–H and B–H bonding electrons into orbitals above the $3sp^3$ octet of phosphorus.[2] A similar effect upon sulfur in the CH_3SBH_2 polymers should be weaker because there are three fewer C–H bonds per S atom. Even so, the effect is important enough to account for much firmer bonding in $(CH_3SBH_2)_x$ than in $(CH_3OBH_2)_x$,[4] wherein oxygen cannot offer any important orbitals above the $2sp^3$ octet.

A more direct indication of the importance of a methyl group on sulfur, in improving the strength of S–B dative bonding, is found in the fair stability of the new compound $(CH_3)_2S \cdot BH_3$ at room temperature—in contrast to the barely demonstrable existence of $CH_3SH \cdot BH_3$ at −78°. The dependence of this effect upon usable sulfur orbitals above the $3sp^3$ octet is shown by comparisons with O–B dative bonded oxygen compounds: $(CH_3)_2O \cdot BH_3$ is far less stable ($p_{\text{diss.}}$ = 18 mm. at −78°)[5] than $(CH_3)_2S \cdot BH_3$, whereas the extreme slowness of the H_2S–B_2H_6 protolysis indicates that H_2S does not hold a BH_3 group nearly so well as H_2O does in the reaction-intermediate $H_2O \cdot BH_3$.[6] The methyl group clearly enhances the dative bonding power of S far more than that of O, just as methylation improves the dative bonding power of phosphine far more than it does for ammonia.

The bond-strengthening effects of the CH_3 and BH_2 groups upon S–B bonding can be overcome by substituting methyl for hydrogen or boron, so that the electron-acceptor bonding power of the boron is sharply decreased.[7] Thus it was found that CH_3SH and $(CH_3)_4B_2H_2$ form no very stable adduct, but they did react protolytically to form the liquid $CH_3SB(CH_3)_2$. This showed no tendency to polymerize, in contrast to the high stability of

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[1] A considerable part of the work here reported was included in a dissertation presented by Ross Irving Wagner to the Faculty of the Department of Chemistry, University of Southern California, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1953. Other parts of the dissertation were published earlier; *cf.* references 2 and 3.

(2) A. B. Burg and R. I. Wagner, THIS JOURNAL, **75**, 3872 (1953).

(3) F. G. A. Stone and A. B. Burg, *ibid.*, **76**, 386 (1954).

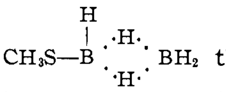
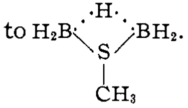
(4) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4020 (1933).

(5) H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 296 (1938).

(6) H. G. Weiss and I. Shapiro, *ibid.*, **75**, 1221 (1953).

(7) H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

the corresponding phosphinoborine polymer, $[(CH_3)_2PB(CH_3)_2]_3$.[2] However, it did slowly decompose to form a solid product worthy of further study.

In view of the evidence for weak polymer-bonding in $(CH_3SBH_2)_x$, it seemed possible that $CH_3SB_2H_5$ might be capable of existence, just as $H_2NB_2H_5$ and $CH_3NHB_2H_5$ exist even though they tend to revert to the corresponding aminoborine polymers and diborane.[8] A sample of $CH_3SB_2H_5$ actually was formed by depolymerizing $(CH_3SBH_2)_x$ in a stream of diborane. It was made more efficiently by forming the monomer-complex $(CH_3)_3N{\cdot}BH_2SCH_3$ and using the diborane stream for the double purpose of removing the amine as $(CH_3)_3NBH_3$ and capturing the CH_3SBH_2 unit as $CH_3SB_2H_5$. This new compound is in the volatility range of the aminodiboranes and as expected, it decomposes very easily to re-form diborane and $(CH_3SBH_2)_x$. The sulfur atom probably bridges the two boron atoms, for if the structure were  $CH_3S{-}\overset{\overset{H}{|}}{B}\overset{\cdot H\cdot}{\underset{\cdot H\cdot}{:\;:}}BH_2$ the sulfur should have enough base-strength to disrupt half of the double-hydrogen bridge, converting the molecule to  $H_2B\overset{\cdot H\cdot}{\underset{\underset{\underset{CH_3}{|}}{S}}{\diagdown\;\diagup}}BH_2$.

Experimental Part

Dimethyl Sulfide–Borine.—Equal gas volumes (10.4 cc. each)[9] of $(CH_3)_2S$ and B_2H_6 were condensed together in an immersible tensimeter[10] and warmed to room temperature; then the mixture was cooled to −78° and the excess B_2H_6 was removed at −78° and measured as 5.1 cc. The formula of the residue thus was very close to $(CH_3)_2S{\cdot}BH_3$. This product, in the gas phase at 53° and 100 mm., had an average molecular weight of 60.0, indicating that the $(CH_3)_2S{\cdot}BH_3$, if monomeric as such, was 63% dissociated into $(CH_3)_2S$ and B_2H_6 under these conditions.

The adduct $(CH_3)_2S{\cdot}BH_3$ melted in the range −40 to −38°. Its vapor tensions, given by Table I, determine the equation $\log p_{mm.} = 9.220 - 2346/T$, from which the normal boiling point would be 97° and the Trouton constant 29.0 cal./deg. mole—a high value consistent with an increase of dissociation during vaporization.

TABLE I

VAPOR TENSIONS OF $(CH_3)_2S{\cdot}BH_3$

t, °C.	0.0	22.2	30.0	40.2
$p_{mm.}$(obsd.)	4.32	19.1	30.3	54.9
$p_{mm.}$(calcd.)	4.31	19.0	30.4	54.2

Methanethiol and Diborane.—The reaction $2CH_3SH + B_2H_6 \rightarrow 2CH_3SH{\cdot}BH_3$ doubtless occurs almost completely at −78°, for the liquid product of mixing the reactants is scarcely one-tenth as volatile as the less volatile reactant, CH_3SH (v.t. 5.2 mm. at −78.5°). However, the exact 2:1 reaction ratio is not easily demonstrated. If excess mercaptan is used, some of the excess remains dissolved in the liquid adduct and its rate of removal *in vacuo* is scarcely greater than that of the dissociation of the adduct. If excess diborane is used, the addition reaction still is incomplete in a period of 20 minutes (during which evolution of hydrogen begins), and removal of the excess diborane at −78° leaves a liquid residue containing more mercaptan than the above equation would require. Two examples illustrate these effects: (1) 49.5 cc. of CH_3SH and 14.15 cc. of B_2H_6 were left together for 20 minutes at −78°, and then a high-vacuum fractional condensation of the immediately available vapors yielded 1.55 cc. of B_2H_6 and 19.3 cc. of CH_3SH, leaving a liquid residue empirically formulated as $BH_3{\cdot}1.2CH_3SH$; (2) 16.0 cc. of CH_3SH and 11.5 cc. of B_2H_6 were left together for 25 minutes in a 60-ml. reaction tube at −78°, and then distilled in high vacuum for eight minutes; next the liquid remaining at −78° was vaporized by slow warming *in vacuo*, and the vapors were separated into 4.25 cc. of B_2H_6 and 9.70 cc. of CH_3SH, indicating the literal formula $BH_3{\cdot}1.14CH_3SH$. In each of these experiments, some 0.2 to 0.3 cc. of H_2 developed during the periods of standing at −78°.

For a full-scale protolysis, 152.9 cc. of CH_3SH and 72.9 cc. of B_2H_6 were maintained together in the high-vacuum system at −78°, yielding 112.0 cc. of H_2 during 108 hours (including 3.4 cc. during the last 12 hours). The reaction mixture now was warmed from −78 to +2° during 24 hours, yielding 32.0 cc. more H_2, with recovery of 3.9 cc. of pure CH_3SH. Then during 55 hours at 23°, a final 1.2 cc. of H_2 came off, along with 5.6 cc. more CH_3SH. No trace of B_2H_6 ever was recovered as such from this experiment. Thus in terms of the equation $2xCH_3SH + xB_2H_6 \rightarrow 2xH_2 + 2(CH_3SBH_2)_x$, the H_2 corresponded exactly to the B_2H_6, while the CH_3SH was estimated 1.6% low—presumably on account of van der Waals effects during the original measurement at 420 mm. and 25°.

It is interesting that some of the mercaptan–borine adduct persisted in the solid product *in vacuo* even up to room temperature, to which the sample had to be warmed to complete the protolysis. The adduct evidently was stabilized by occlusion: apparently neither the protolysis nor the dissociation occurs easily for an adduct molecule which is isolated from others of its own kind within the solid polymer, and the proportion of adduct molecules not thus isolated must decrease rapidly as the protolysis approaches completion.

Although the protolysis experiments here described were carried out largely at −78°, it has been found that the products are essentially the same if the mixture of mercaptan and diborane is warmed at once to room temperature.

The Methanethioborine Polymers.—The white solid product of the protolytic reaction proved to be insoluble in ether, benzene or chloroform, so that a determination of its molecular weight was not feasible. Its vapor tensions were measured as 0.23 mm. at 50°, 0.44 mm. at 55°, and 1.47 mm. at 66.1°, determining the equation $\log p_{mm} = 16.26 - 5460/T$ (calcd. values 0.23, 0.42 and 1.47 mm.). However, these results might be ascribed to polymers more volatile than the main original sample, which melted in the range 65–80° and resolidified only after some hours at room temperature. The evidence of depolymerization became even more definite when the sample was heated *in vacuo* at 100°, for it then yielded colorless liquid and solid products just volatile enough to pass through the high-vacuum manifold at room temperature. These products were slightly soluble in ether, with lowering of the vapor tension, but a molecular weight determination was not attempted because the solid and liquid components of the sample were not separable. Some vapor-tension values for the most volatile fraction were 4.7 mm. at 70.8°, 7.2 mm. at 76.3°, 9.2 mm. at 84.0°, and 15.85 mm. at 99.0°, all well described by the equation $\log p_{mm.} = 7.219 - 2237/T$. However, the low Trouton constant of 19.8 cal./deg. mole argued against uniformity. On standing at room temperature, the original distillate developed a less volatile component, suggesting a process of repolymerization.

Since all fractions of the distillate and residue gave the same result upon hydrolysis—one volume of CH_3SH to two volumes of hydrogen, and boric acid equivalent to one volume of gas—it appeared that they all were mixtures of different polymers of the CH_3SBH_2 unit, to some extent capable of interconversion at moderate temperatures. Two examples of the hydrolysis will suffice: (1) a residue of unknown size was hydrolyzed to yield 0.388 mmole of H_2, 0.190 mmole of CH_3SH and 0.188 mmole of $B(OH)_3$; (2) a distillate of unknown size was hydrolyzed to yield 2.67 mmoles of H_2, 1.30 mmoles of CH_3SH and 1.31 mmoles of $B(OH)_3$.

Further evidence of a series of easily interconvertible polymers came from a study of the least volatile liquid fraction—a brilliantly refractive colorless oil which condensed

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[8] H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 2297 (1938), and A. B. Burg and C. L. Randolph, Jr., *ibid.*, **71**, 3451 (1949).

[9] Throughout this paper the abbreviation cc. refers to the volume which the substance would occupy as a gas at standard conditions.

[10] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 785 (1937).

above the hot zone when the more volatile components were driven off under high vacuum at 80–100°. A portion of this highly viscous liquid was distilled through the all-glass-mercury high-vacuum system into an immersible tensimeter and an attempt was made to remove any more volatile materials which might have formed during the distillation. Then the vapor tensions were observed in the following order: 2.98 mm. at 69.8°, 1.30 mm. at 53.3°, 1.71 mm. at 59.6°, 2.50 mm. at 66.9°, 2.99 mm. at 70.0°, 4.39 mm. at 76.2°, 6.34 mm. at 82.4°, 12.97 mm. at 94.0°, 29.5 mm. at 108.7°, and 54.7 mm. at 120.2°. The graph of log p *vs.* $1/T$ was linear except that the lowest points fell above the curve; neglecting these one would determine the fairly representative equation $\log p_{\text{mm.}} = 10.285 - 3364/T$, from which the normal boiling point would be estimated as 454°K. and the Trouton constant as 33.9 cal./deg. mole. Or it can be argued that the two lowest points showed the presence of 0.40 mm. partial pressure of foreign vapor, subtraction of which would give $\log p_{\text{mm.}} = 10.765 - 3552/T$ (ave. deviation 0.6%), implying that the normal boiling point would be 451°K. and the Trouton constant 36.0 cal./deg. mole. By either interpretation it is clearly indicated that the liquid was some 50 to 60% more highly associated than the vapor.

After these measurements the major part of the sample was bubbled out of the tensimeter at 120° (a process which was so slow as to suggest depolymerization rather than mere evaporation of the liquid), and the residue was vaporized for a volume measurement: 2.043 cc. of standard gas (p = 18.92 mm. at 127°). Hydrolysis of this sample gave 8.60 cc. of H_2 and 4.52 cc. of CH_3SH, implying an average molecular weight 15% higher than that expected for the dimer, $(CH_3SBH_2)_2$. By the Trouton rule, therefore, the liquid would have averaged somewhat more associated than a trimer during the vapor-tension measurements.

Thermal Decomposition of the Methanethioborine Polymers.—A six-hour heating of a sample of $(CH_3SBH_2)_x$ in a closed system at 140° gave, in addition to 22 cc. of H_2 and some typical B–H polymeric material, a 4.5-cc. sample of a liquid substance having a molecular weight of 143 in the gas phase (Me_3S_3B, 152), and hydrolyzing to produce 0.26 cc. of H_2 and 12.7 cc. of CH_3SH. Its vapor tensions corresponded to those of an authentic sample of methyl thioborate, which was prepared by a different method, as described in a later section. Its melting range (2.3–3.3°) was slightly lower than that of the authentic sample, but consistent with that reported by other workers.[11] Thus it appears that the decomposition of $(CH_3SBH_2)_x$ corresponded to the equation $3CH_3SBH_2 \rightarrow (CH_3S)_3B + B_2H_6$, with destruction of the B_2H_6 by its usual thermal decomposition.

An Amine Complex of CH_3SBH_2.—In an attempt to drive the disproportionation to completion without a net loss of B–H bonds, a sample of partially depolymerized $(CH_3SBH_2)_x$ was treated with excess $(CH_3)_3N$, with absorption accurately demonstrating the formula $(CH_3)_3N \cdot BH_2SCH_3$. The reaction was complete within a few minutes at 25° and the product, a liquid having no observable volatility at room temperature, seemed to be only slightly changed by heating at 145°. However, the heated sample, by repeated vacuum refluxing against the cool upper walls of the container, was made to deliver small fractions of mixed solid and liquid, tapering off to no effluent after six repetitions of the process. The first fraction included a trace of $(CH_3)_3N$. The less volatile part of this fraction was exposed to a small amount of water vapor, yielding 0.81 cc. of CH_3SH and 0.27 cc. of $B(OH)_3$ (no H_2)—indicating 0.27 cc. of $(CH_3S)_3B$. The volatile solid now was separated from the remaining trace of water and identified by its vapor tensions and melting point as 0.94 cc. of $(CH_3)_3NBH_3$, a substance which requires acid and elevated temperatures for hydrolysis. The whole set of observations could be explained as a limited disproportionation of the amine complex according to the equation $3(CH_3)_3N \cdot BH_2SCH_3 \rightarrow (CH_3)_3N + 2(CH_3)_3NBH_3 + (CH_3S)_3B$. It is estimated that this process was not more than 10% complete at equilibrium.

The best samples of $(CH_3)_3N \cdot BH_2SCH_3$ melted in the range 13–15°, and seemed to be stable up to 55°, but showed new formation of $(CH_3)_3NBH_3$ during 15 minutes at that temperature. The disproportionation vitiated attempts to determine the vapor tensions of $(CH_3)_3N \cdot BH_2SCH_3$, and the molecular weight of the vapor, although indicative of a monomer, could not be rigorously trusted.

Somewhat more satisfactory molecular weight determinations were done by the tensiometric method in ether. A 10.5-cc. sample of CH_3SH was converted to the insoluble form of $(CH_3SBH_2)_x$ by the action of diborane in excess, and treated with 11.0 cc. of $(CH_3)_3N$ at room temperature. Again the addition reaction was fairly quick, but the recovery of 1.5 cc. of the amine after two days at room temperature showed that only 90% of the thioborine had been converted to the complex. A second sample of $(CH_3SBH_2)_x$, made from 1.03 cc. of B_2H_6, absorbed only 1.85 cc. out of 2.33 cc. of amine—again only 90% of the expected conversion to the complex. Assuming that the partially depolymerized form of the thioborine is metastable relative to the insoluble form at room temperature, it can be suggested that the low polymers of CH_3SBH_2 absorb the amine more completely at equilibrium than do the high polymers. On this basis, the effective size of each sample was taken as equivalent to the absorbed amine, since the high polymer was known to be insoluble in ether. The solutions were made by adding measured volumes of ether, and their vapor tensions were compared with those of pure ether by means of a differential manometer. The results are shown in Table II, which gives the mole fraction as calculated on the basis of purely monomeric $(CH_3)_3N \cdot BH_2SCH_3$, the observed mole fraction from the fractional lowering of the vapor tension of the ether, and the average molecular weight as a multiple of the monomer value.

TABLE II

MOLECULAR WEIGHT STUDIES ON $(CH_3)_3N \cdot BH_2SCH_3$

t, °C.	Mole fraction Calcd.	Mole fraction Obsd.	Mol. wt./monomer
16.1	0.0670	0.0396	1.68
15.3	.0395	.0300	1.32
17.4	.0151	.0130	1.16

The trend toward monomer at low concentrations is fairly clear, and the increase of molecular weight with concentration may be attributed to a dipole association, as expected of such a complex.

Dimethyl Disulfide and Diborane.—Diborane formed a 23 mole per cent. solution in liquid CH_3SSCH_3 at −78° and 74 mm. pressure, but no definite adduct could be recognized. A mixture of 15.2 cc. (64.1 mg.) of CH_3SSCH_3 with 15.4 cc. of B_2H_6 at room temperature gradually liberated 14.1 cc. of H_2 during 33 days, with solidification at 30 days. The solid product was in all respects like the original $(CH_3SBH_2)_x$: vapor tension 1.52 mm. at 65°; slow decomposition at 135°, forming $(CH_3S)_3B$, B–H polymers, and H_2. The initial reaction between CH_3SSCH_3 and B_2H_6 may well have been an S–S bond rupture to form CH_3SBH_2 units and $CH_3SH \cdot BH_3$, followed by the usual protolysis of the latter.

Hydrogen Sulfide with Diborane.—Although no addition reaction between H_2S and B_2H_6 could be observed at any temperature, it was considered that an H_2-producing reaction might well go forward if given enough time. Accordingly 76.3 cc. of H_2S and 25.5 cc. of B_2H_6 were left together in a sealed bulb at room temperature for 137 days. The bulb then showed no change of appearance, but on cooling to −196° a thin, colorless and transparent film peeled off from the inner wall. The volatile components were separated and measured as 77.5 cc. of H_2, 6.35 cc. of B_2H_6 and 33.0 cc. of H_2S. Hydrolysis of a 63.0-mg. sample of the glassy film occurred very easily at room temperature, yielding 26.1 cc. of H_2, 32.6 cc. of H_2S and 29.0 cc. of $B(OH)_3$. The literal formula from synthesis thus would be $H_{0.98}BS_{1.13}$; from analysis, $H_{0.90}BS_{1.12}$. These discrepant indications of the ideal formula $(HBS)_x$ can be explained by supposing that $-\overset{H}{B}-S-$ polymer chains are cross-linked occasionally by B–S–B bonds, and possibly terminated by $H-S-\overset{H}{B}-S\ldots$ units, the H–S part of which would yield no hydrogen on hydrolysis. However, such an interpretation may be far from final.

Preparation and Characterization of $(CH_3S)_3B$.—Although other workers succeeded in making tris-methanethioborine only by the action of BBr_3 on heavy-metal mercaptides, such as $AgSCH_3$ or $Pb(SCH_3)_2$, and could not get it by a reaction of $KSCH_3$ with BF_3 in ether or with BBr_3 in

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[11] J. Goubeau and H. W. Wittmeier, *Z. anorg. allgem. Chem.*, **270**, 16 (1952).

benzene,[11] we found it possible to obtain it by the reaction $3NaSCH_3 + BBr_3 \rightarrow (CH_3S)_3B + 3NaBr$, without a solvent. A 152.4-cc. sample of CH_3SH was treated with an exactly equivalent amount (156.5 mg.) of sodium in liquid ammonia, quantitatively forming H_2 and $NaSCH_3$. After evaporation of the ammonia, the salt was treated with 45.2 cc. of BBr_3, which attacked it vigorously at room temperature. The volatile product contained impurities which were removed by reaction with a further sample of $NaSCH_3$ (54.1 cc.); then the yield of pure $(CH_3S)_3B$, 138.6 mg., represented 45% of the original BBr_3.

The product was identified by hydrolysis, whereby a 5.61-cc. sample (38.1 mg.) yielded 17.04 cc. of CH_3SH and 5.27 cc. of $B(OH)_3$, corresponding to the equation $(CH_3S)_3B + 3HOH \rightarrow 3CH_3SH + B(OH)_3$. A determination of the molecular weight by the vapor density method gave the value 154.9 (calcd. 152.1). The melting range *in vacuo* was 4.1–4.9°. The vapor tensions in the range below 120° (40 mm.) corresponded to the equation $\log p_{\text{mm.}} = 8.464 - 2695/T$. Since this represents a lower range than the literature values,[11] our actual pressure data are given, in Table III.

TABLE III

LOW-RANGE VAPOR TENSIONS OF $(CH_3S)_3B$

t, °C.	$p_{\text{mm.}}$ (obsd.)	$p_{\text{mm.}}$ (calcd.)	t, °C.	$p_{\text{mm.}}$ (obsd.)	$p_{\text{mm.}}$ (calcd.)
30.3	0.37	0.38	80.0	6.94	6.82
40.0	0.69	0.72	90.1	11.3	11.1
50.2	1.36	1.35	100.1	17.7	17.8
60.2	2.39	2.40	109.9	26.7	26.9
70.0	4.11	4.08	120.0	40.1	40.7

Preparation and Properties of $CH_3SB(CH_3)_2$.—A mixture of 53.6 cc. of CH_3SH and 26.4 cc. of $(CH_3)_4B_2H_2$, on warming slowly from −78°, showed a sudden decrease of pressure, indicating an addition reaction—presumably the formation of a very unstable $CH_3SH{\cdot}HB(CH_3)_2$. At 0° the liquid phase contained very little of the mercaptan, but it effervesced at that temperature, developing 43 cc. of H_2 during 40 minutes. When the total H_2 reached 51.3 cc. (97.3% of theory), the main product was purified by means of a microcolumn, refluxing *in vacuo* at −65°. The yield of the pure product was 31.6 cc., or 60%. Confirmation of the formula as $CH_3SB(CH_3)_2$ was obtained by a molecular weight determination (88.2, calcd. 88.0) and by hydrolytic analysis: a 6.46-cc. sample yielded 6.43 cc. of CH_3SH and 6.72 cc. of $(CH_3)_2BOH$ (probably including a trace of water vapor)—all in accord with the equation $CH_3SB(CH_3)_2 + HOH \rightarrow CH_3SH + (CH_3)_2BOH$.

Pure $CH_3SB(CH_3)_2$ melts at $-84.0 \pm 0.2°$. Its vapor tensions, shown in Table IV, determine the equation $\log p_{\text{mm.}} = 7.677 - 1651/T$, according to which the boiling point is 71° and the Trouton constant is 21.9 cal./deg. mole.

TABLE IV

VAPOR TENSIONS OF $CH_3SB(CH_3)_2$

t, °C.	−45.2	−22.9	0.0	20.3	31.0
$p_{\text{mm.}}$obsd.	3.0	12.06	42.8	112.4	177.4
$p_{\text{mm.}}$calcd.	2.7	12.02	42.9	112.5	177.5

The compound $CH_3SB(CH_3)_2$ is not quite stable, for a sample which had been stored for two years at room temperature was 20% converted to more and less volatile materials. During 71 hours in a sealed tube at 93°, a 20-cc. sample developed 0.9 cc. of a gas which seemed to be ethane. A further study of the products of this decomposition would be interesting.

Preparation of Methanethiodiborane.—A sample of $(CH_3SBH_2)_x$ equivalent to 30.3 cc. of the monomer gas was heated to 90° and some 500 cc. of B_2H_6 was allowed to flow across it at pressures between 1 and 1.5 atm. into a trap at −196°. During several such passes the $(CH_3SBH_2)_x$ was largely converted to the glassy-liquid form, which seemed less reactive than the original solid, and there was a small yield of an unstable liquid. On standing, this showed a volume-contraction, forming diborane and a white solid which seemed to be $(CH_3SBH_2)_x$. Further production of the unstable liquid from the glassy $(CH_3SBH_2)_x$ proved to be very tedious, but a great improvement in efficiency resulted from a conversion of this material to $(CH_3)_3N{\cdot}BH_2SCH_3$ by absorption of 10.8 cc. of $(CH_3)_3N$, and treating the product with diborane. Reaction was slight at room temperature, but went very well at 90°, in the B_2H_6-stream as before. The glassy liquid appeared again, and was converted back to the complex by absorption of 5.0 cc. of the amine, for further treatment with diborane. Thus, by the reaction $(CH_3)_3N{\cdot}BH_2SCH_3 + B_2H_6 \rightarrow (CH_3)_3NBH_3 + CH_3SB_2H_5$, most of the thioborine was converted to methanethiodiborane—as demonstrated in the following section.

Proof of Formula of Methanethiodiborane.—The unstable liquid product was purified by distillation very slowly through a trap at −78°, with fractional condensation at −90°. After the physical characterization described in the next section, a sample was very rapidly measured as a gas and then repurified; subtraction of the discarded fraction (0.1 cc. of B_2H_6) then gave the volume as 10.85 cc. This sample was left for 64 minutes in a closed 65-ml. tube at 21°, forming an opaque white scum uniformly over the walls of the tube. The volatile part was fractionally distilled (from −78°, partially through −90° to −196°), yielding 4.33 cc. of the original substance (60% decomp.) and 3.22 cc. of B_2H_6, hydrolysis of 3.18 cc. of which gave 19.02 cc. of H_2 and 6.18 cc. of $B(OH)_3$ (calcd. 19.08 and 6.36). The white solid was hydrolyzed to give 12.86 cc. of H_2, 6.2 cc. of CH_3SH, and 6.45 cc. of $B(OH)_3$ (calcd., 13.04 cc. of H_2 and 6.52 each of CH_3SH and boric acid). These results fully demonstrated the equation $2xCH_3SB_2H_5 \rightarrow 2(CH_3SBH_2)_x + xB_2H_6$.

The major part (4.03 cc.) of the unused $CH_3SB_2H_5$ was hydrolyzed directly, forming 20.2 cc. of H_2, 3.91 cc. of CH_3SH, and 7.88 cc. of $B(OH)_3$ (calcd. values, 20.15, 4.03 and 8.06). The molecular formula $CH_3SB_2H_5$ thus was fully confirmed.

Physical Properties of Methanethiodiborane.—The original purified sample of $CH_3SB_2H_5$ melted in the range −101.5 to −100.7° (Stock magnetic plunger method, with CO_2 vapor tension thermometer). For measurements of its vapor tensions at a series of temperatures, it was maintained in a 2-ml. bulb connected by a 25 cm. long, 3 mm. i.d. tube to a 12 mm. i.d. U-manometer; then as the gas decomposed slightly in the warmer parts of the system, the only effect on the liquid phase would be a slight withdrawal of more gas through the long narrow neck. The values of the vapor tension, taken at successively higher temperatures from −67 to −33°, by an optical system good to 0.02 mm., were averaged in four regions by taking the arithmetic means of $\log p$ and $1/T$ values, with the results 0.94 mm. at −65.0°, 1.86 mm. at −57.4°, 4.10 mm. at −48.3°, and 9.70 mm. at −35.3°. These values determine the equation $\log p_{\text{mm.}} = 7.991 - 1666/T$ (calcd. values, 0.97, 1.86, 3.82 and 9.70 mm.; the third mean point was more influenced by decomposition than the fourth, which was based upon points taken immediately after a pump-off of the gas phase). This would give the normal boiling point as 53° and the Trouton constant as 23.4 cal./deg. mole; the $\log p$ *vs.* $1/T$ curve evidently is concave downward, so that the true boiling point might be as high as 60°. The curve coincides almost exactly with that of $(SiH_3)_2NB_2H_5$, the volatility of which is in the middle of the range of the known aminodiboranes.[12]

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[12] A. B. Burg and E. S. Kuljian, THIS JOURNAL, **72**, 3103 (1950).