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The Methylstibines and the Monomer Dimethylstibinoborine

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The methylstibines CH_3SbH_2 (b.p. est. 41°; very unstable) and $(CH_3)_2SbH$ (b.p. est. 61°) were obtained by hydridation of $(CH_3)_2SbBr$. Dimethylstibine is a very poor protic acid but has strong hydridic character, reacting with HCl to give H_2 or with B_2H_5Br to give B_2H_6. Its conversion to $H_2 + Sb_2(CH_3)_4$ is strongly catalyzed by B_2H_6, with some formation of $(CH_3)_2SbBH_2$ (b.p. est. 70°), which is better made from $Sb_2(CH_3)_4$ with B_2H_6 at 100° (26% yield). For this purpose $Sb_2(CH_3)_4$ was made in 75% yield from $(CH_3)_2SbBr$ with Na in liquid NH_3. Its thermal decomposition gives $(CH_3)_3Sb$ and Sb; or at room temperature grease converts it to $(CH_3)_3Sb$ and Sb–CH_3 polymeric material. It is cleaved cleanly by HCl or less cleanly by BCl_3. The Sb–CH_3 bond has some mild methylating power. The compound $(CH_3)_2SbBH_2$ is stable up to 200° and fails to exchange H or CH_3 with $B(CH_3)_3$. It also makes no $(CH_3)_3N$ complex nor any stibinodiborane; but on heating, $(CH_3)_3N$ causes its disproportionation, with much formation of $(CH_3)_3NBH_3$. Its monomeric state and relatively unreactive character are attributed to a fairly strong Sb–B pi bond using Sb 5pd and B-2p orbitals.

The interesting results of the reactions of diborane with the methylphosphines[1] and methylarsines[2] led to the expectation that the diborane chemistry of the methylstibines also would be worthy of investigation. Also, since the primary and secondary stibines CH_3SbH_2 and $(CH_3)_2SbH$ were unknown, a study of their properties seemed attractive. Both proved to be unstable in the sense of losing hydrogen to form Sb–Sb bonds, but dimethylstibine was found to be stable enough for extensive study: it showed both methidic and hydridic reaction tendencies but very poor protic-acid character. The little-known bistibine $Sb_2(CH_3)_4$ was easily made from it and also proved worthy of extensive study.

It was expected that the $(CH_3)_2SbBH_2$ unit would be formed by a reaction between dimethylstibine and diborane, but there was no sure basis for predicting whether this unit would be polymeric like $[(CH_3)_2PBH_2]_3$ and $[(CH_3)_2AsBH_2]_3$, or maintain a monomer–polymer equilibrium like that of $(CH_3)_2NBH_2$,[3] or fail to exist on account of easy attainment of some stabler arrangement of the same components. However, we now have made dimethylstibinoborine, $(CH_3)_2SbBH_2$, and found it to exist only as a monomer, stable up to 200°. Unlike $(CH_3)_2NBH_2$,[4] it is inert toward diborane; and unlike some other RBH_2 compounds or units, it fails to form a trimethylamine complex.

The monomeric character of dimethylstibinoborine is not fully understood by a qualitative extrapolation from the strong polymer-bonding in $[(CH_3)_2PBH_2]_3$ and the weaker polymer-bonding in the similar $[(CH_3)_2AsBH_2]_3$. One might indeed recognize that the electron-donor bonding power of the methylated antimony is too weak to sustain the donor–acceptor bonds required for polymerization; for even trimethylstibine forms only a barely recognizable BH_3 complex.[5] However any unit of the type RBH_2 is expected to form a $\mathrm{B}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{H}}\mathrm{B}$ bridged dimer (*i.e.*, a substitution derivative of diborane) unless the R group supplies electrons either for polymer bonding or for an internal pi bond, to satisfy the fourth valence orbital of boron. In the present case, antimony has the lone-pair required for such internal bonding, which would have to be important to account for the failure of trimethylamine to attach itself to boron and also to explain the lack of any easy mechanism for disproportionation. The difficulty is that such a pi bond to boron could not be very effective if based upon interaction of the B-$2p_z$ orbital with any kind of Sb-5sp hybrid. What the situation demands is the directional effect which an antimony 5d orbital could supply; and for an atom as large

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

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

(3) A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 953 (1951).

(4) A. B. Burg and C. L. Randolph, Jr., *ibid.*, **71**, 3451 (1949).

(5) F. Hewitt and A. K. Holliday, *J. Chem. Soc.*, 530 (1953).

as antimony, already forming three covalent bonds, such an orbital would have an energy level deep enough to be important. Thus if we let the Sb–B bonding be directed along the *x*-axis and let the sigma bonds to Sb and to B be based upon sp_xp_y hybrids, the Sb–B pi bond can be formed by overlap between the B-$2p_z$ and a suitable Sb-$5p_z$-d_{x+z} hybrid. Hence the molecule $(CH_3)_2SbBH_2$ is predicted to have a planar configuration, rather than the pyramidal shape of a tertiary stibine. A similar situation for the $(CH_3)_2AsBH_2$ and $(CH_3)_2PBH_2$ units would not be favored because the 4d and 3d orbitals are not sufficiently energetic relative to the 4p and 3p levels; hence the sigma polymer-bonding is a better way for the lone pairs on As or P to bond to the fourth orbital of B.

The Methylstibines

The Reaction of Bromodimethylstibine with Sodium Borohydride.—The compound $(CH_3)_2SbBr$ was made by the dissociation of $(CH_3)_3SbBr_2$[6] and brought to reaction with $NaBH_4$ in the triether known as diglyme, $CH_3O(C_2H_4O)_2CH_3$. A 30-ml. solution containing 2.86 g. (12.3 mmoles) of $(CH_3)_2SbBr$ was mixed *in vacuo* at −78° with a 20-ml. solution containing 0.604 g. (16.0 mmoles) of $NaBH_4$, forming a white precipitate and 4.47 mmoles of hydrogen. As always, the hydrogen was proved by CuO-combustion within the vacuum system. The reaction $(CH_3)_2SbBr + NaBH_4 \rightarrow H_2 + NaBr + (CH_3)_2SbBH_2$ was indicated, but the 7.8 mmole deficiency of H_2 would correspond to a considerably larger formation of $(CH_3)_2SbH$ and a BH_3 complex of the diglyme.

The reaction mixture was filtered through a coarse sintered glass plate at −78° and the volatile products were slowly distilled out under high vacuum, with little increase of temperature. These products were the colorless liquids CH_3SbH_2, $(CH_3)_2SbH$ and $(CH_3)_2SbBH_2$, the last two being so similarly volatile that the $(CH_3)_2SbBH_2$ could be isolated only after the $(CH_3)_2SbH$ had converted itself to $Sb_2(CH_3)_4$ (catalyses described below). Diborane apparently was held back as a BH_3 complex in the diglyme. There was some doubt as to the point of formation of the $(CH_3)_2SbBH_2$: whether it was made by the initial borohydride–bromodimethylstibine reaction, or from $(CH_3)_2SbH$ and the BH_3 complex, or subsequently by a reaction between $(CH_3)_2SbH$ and diborane which had escaped from the diglyme solution could not be decided. The whole experiment was confused by the instability and reactivity of the products, which formed black material both in the original mixture and in the high-vacuum manifold. On this account, the yields could not well be estimated.

Properties of Methylstibine.—A very small sample of the new stibine CH_3SbH_2, adventitiously obtained from the preceding experiment, was purified by high-vacuum fractional condensation, passing a trap at −78° and condensing out at −100°. It proved to be reasonably stable at −78° but at higher temperatures it gave off hydrogen and deposited a black solid. Its vapor tensions obtained by fast measurements on quickly equilibrated small samples, with frequent repurification, are given in Table I. These values determine the equation $\log p_{mm} = 7.438 - 1431/T$, which gives the b.p. as 41° and the Trouton constant as 20.9 cal./deg. mole.

The molecular weight of the vapor at 22° and 118 mm. was determined as 135.6, the deviation from the calculated 138.8 being attributed to decomposition to form hydrogen during the estimation of the gas-volume.

TABLE I

VAPOR TENSIONS OF CH_3SbH_2

t (°C.)	−50.5	−43.7	−35.2	−28.8	−15.5	−8.5	0.0
p_{mm} (obsd.)	10.0	16.0	27.0	39.0	75.2	108.0	158.5
p_{mm} (calcd.)	10.3	15.9	26.6	38.3	76.7	107.6	158.5

The black solid decomposition product proved to be readily soluble in nitric acid or in hot concentrated solutions of HCl or NaOH. It was noticeably reactive toward air. The ideal composition, resulting from simple loss of hydrogen, would be $(CH_3Sb)_x$; however, it probably contained a smaller proportion of methyl groups, for a 47.9 mg. sample, acted upon by concd. HCl for 24 hr. at 70°, gave only 0.13 mmole each of H_2 and CH_4. A low analysis for antimony (33.3 mg.) by the oxine method[7] would indicate that the sample was not completely broken down; however, the conclusion that there were fewer CH_3 groups than Sb atoms seems to remain valid. The decomposition of CH_3SbH_2 might have involved some conversion to more highly methylated volatile stibines, but this question was not explored.

Synthesis of Dimethylstibine.—The by-products of the $NaBH_4$–$(CH_3)_2SbBr$ reaction were avoided in a process wherein the source of hydride was $LiHB(OCH_3)_3$.[8] For example, 1.004 g. (9 mmoles) of $LiHB(OCH_3)_3$ and 1.01 g. (4.3 mmoles) of $(CH_3)_2SbBr$ were allowed to react in solution in 18.4 g. of diglyme below −40°. The gas which came off *in vacuo* between −40 and −20° was collected in a trap at −196° and fractionated to disclose the presence of a small yield of CH_3SbH_2. Dark solid products were observed in the reaction flask. The yield of $(CH_3)_2SbH$ was 228 mg. (1.49 mmoles, or 35%, based upon the bromostibine). The recovery of 2.2 mmoles of $B(OCH_3)_3$ showed that the $LiHB(OCH_3)_3$ had not very seriously disproportionated[8]; but there might have been coprecipitation, limiting the desired reaction.

Physical Properties of Dimethylstibine.—The vapor density of $(CH_3)_2SbH$ at 65 mm. and 26° implied a mol. wt. value of 152.2; calcd., 152.8. The vapor tensions, shown in Table II, determined the equation $\log p_{mm} = 7.605 - 1611/T$, which gives the b.p. as 60.7° and the Trouton constant as 22.1 cal./deg. mole.

TABLE II

VAPOR TENSIONS OF $(CH_3)_2SbH$

t (°C.)	−32.4	−28.6	−17.0	−12.2	−7.1	0.0
p_{mm} (obsd.)	8.1	10.3	20.8	27.0	35.4	50.8
p_{mm} (calcd.)	8.2	10.4	20.7	27.1	35.6	50.7

Catalytic Formation of Tetramethylbistibine.—Of a number of chemical conversions which demonstrate the formula $(CH_3)_2SbH$, the simplest is the quantitative formation of $Sb_2(CH_3)_4$. Although apparently quite stable at −78°, dimethylstibine slowly loses hydrogen during storage in Pyrex glass tubes at room temperature; and if mercury is present the process is noticeably accelerated. An especially effective catalyst for the conversion is diborane, as described in relation to the synthesis of $(CH_3)_2SbBH_2$.

A 95.4-mg. sample (0.624 mmole) of $(CH_3)_2SbH$, after 12 hr. with mercury in a sealed Pyrex tube at room temperature, yielded 0.312 mmole of H_2 (calcd. 0.312) and a slightly volatile yellow oil. A second sample of $(CH_3)_2SbH$ (86 mg., or 0.56 mmole), similarly stored in contact only with Pyrex glass, produced 0.27 mmole of H_2 in four days, again forming the yellow oil. The vapor tensions of this oil were compared with those reported for $Sb_2(CH_3)_4$,[9] as shown in Table III.

The calculated values were based upon the equation $\log p_{mm} = 7.823 - 2450/T$, which conforms well to the rough data of Paneth and Loleit below 100°. This equation would imply a b.p. of 224° and Trouton constant 22.6 cal./deg. mole. Our samples showed none of the reported reactivity toward mercury, but there was no mistaking the characteristic melting from a red solid to a yellow liquid, at

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[6] G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.* (*London*), **110**, 523 (1926).

[7] T. I. Pirtea, *Z. anal. Chem.*, **118**, 26 (1939).

[8] H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, THIS JOURNAL, **75**, 193 (1953).

[9] F. A. Paneth and H. Loleit, *J. Chem. Soc.*, 366 (1935).

TABLE III

COMPARATIVE VAPOR TENSIONS OF $Sb_2(CH_3)_2$

t (°C.)	52.9	64.0	76.0	85.0
p_{mm} (here obsd.)	2.5	4.0	6.4	9.4
p_{mm} (lit.)	..	3.1	6.4	..
p_{mm} (lit. calcd.)	2.0	3.6	6.4	9.6

16–17° (lit. 17.5°).[9] The red solid faded to orange on cooling to −196°.

The Hydridic Behavior of Dimethylstibine.—The Sb–H bond in dimethylstibine has a pronounced hydridic reactivity, as shown by its rapid reaction with HCl to form H_2 and $(CH_3)_2SbCl$ and by its conversion of bromodiborane to diborane. In one experiment 0.630 mmole of $(CH_3)_2SbH$ and 0.689 mmole of HCl were condensed together and allowed to warm to room temperature. Reaction was signalled by a vigorous effervescence, producing 0.627 mmole of H_2 (checked by Cu combustion, as usual) and the colorless liquid $(CH_3)_2SbCl$. The excess HCl was measured as 0.057 mmole (calcd., 0.059). Hence $(CH_3)_2SbH + HCl \rightarrow (CH_3)_2SbCl + H_2$.

Although highly reactive toward HCl, dimethylstibine proved to be entirely inert toward the weak protic acid H_2S, in an experiment running for four days at room temperature.

Another experiment involved a reaction between 0.857 mmole of $(CH_3)_2SbH$ and 0.932 mmole of B_2H_5Br, measured as gases, and so possibly somewhat underestimated. The process was fast at −78°, with frothing and production of a viscous liquid. The yield of diborane was 0.928 mmole (mol. wt. 28.0); 0.064 mmole of H_2 also was obtained. The liquid product had a vapor tension of 2.4 mm. at 22°; known value for $(CH_3)_2SbBr$, 2.2 mm. Its vapor density gave the molecular weight as 232.2; calcd. for $(CH_3)_2SbBr$, 231.7. Hence $(CH_3)_2SbH + B_2H_5Br \rightarrow B_2H_6 + (CH_3)_2SbBr$. Thus it appears that diborane would not have supplied a hydride unit for conversion of $(CH_3)_2SbBr$ to $(CH_3)_2SbH$; however reagents such as $NaBH_4$ or $LiHB(OCH_3)_3$ furnish hydride far more effectively, and so were found suitable for this purpose.

The Methidic Character of Antimony–Methyl Bonds.—The reverse of the preceding reaction was attempted; however, the result was not bromination of diborane, but methylation. The mixture of 0.834 mmole of $(CH_3)_2SbBr$ with 1.040 mmole of B_2H_6 was allowed to react during 24 hr. at 60°, producing 0.964 mmole of H_2. The volatile components included 0.27 mmole of B_2H_6 and 0.549 mmole of material having the same molecular weight and volatility as dimethyldiborane. The non-volatile material was black and inert toward aqueous HCl but was dissolved by nitric acid. The solution contained bromine. It seemed that antimony exchanged methyl for hydrogen, which soon went to H_2, leaving a non-volatile mixture containing $Sb{-}CH_3$ and Sb–Br bonds. No such methylating power toward diborane ever has been observed for $P{-}CH_3$ or $As{-}CH_3$ compounds.

A somewhat similar reaction occurred when 3.580 mmoles of $(CH_3)_3Sb$ and 3.482 mmoles of $(CH_3)_2BBr$ were heated together in a sealed tube for 50 hr. at 60°. The result was a 78.7% yield (2.741 mmoles) of $B(CH_3)_3$ (mol. wt. 56.4; v.t. 34 mm. at −78°). The by-product was a dark-colored semi-fluid material of low volatility, from which the expected $(CH_3)_2SbBr$ could not be isolated.

The methidic character of the $Sb{-}CH_3$ bond was tested more directly in an experiment employing 1.701 mmoles of $(CH_3)_3Sb$ with 4.475 mmoles of HCl. There was little effect at 60°, but the reaction was far advanced after 48 hr. at 100°. The consumption of HCl was 1.298 mmoles, producing a white solid and a mixture of 0.446 mmole of CH_4 and 1.343 mmoles of H_2 (mixture analyzed as usual, by CuO-combustion). Similarly, 0.928 mmole of $(CH_3)_2SbCl$ reacted with 1.637 mmoles of HCl to form the white solid and a mixture of 0.152 mmole of CH_4 with 0.522 mmole of H_2. Evidently the expected formation of methane from $(CH_3)_3Sb$ and HCl was accompanied by another reaction of greater importance: $(CH_3)_3Sb + 2HCl \rightarrow H_2 + (CH_3)_3SbCl_2$. This would be something like the chlorination of trimethylstibine by chloroplatinic acid: $(CH_3)_3Sb + H_2PtCl_6 \rightarrow (CH_3)_3SbCl_2 + H_2PtCl_4$.[10]

Protic Acid Weakness of Dimethylstibine.—The high reactivity of $(CH_3)_3NBH_3$ toward a strong acid such as HCl[11] made it reasonable to employ it as a reagent for testing the protic acid character of dimethylstibine. It was considered that a reaction like that of HCl would place the $(CH_3)_2Sb$ group on boron, forming the $(CH_3)_3N$ complex of $(CH_3)_2SbBH_2$. In one experiment, 2.01 mmoles of $(CH_3)_2SbH$ and 1.99 mmoles of $(CH_3)_3NBH_3$ were left together for 15 hours at room temperature, with no result except a slight conversion of $(CH_3)_2SbH$ to $Sb_2(CH_3)_4$. Continuation for 18 hr. at 60° produced 0.94 mmole of H_2 (calcd., 0.96) and the corresponding yield of $Sb_2(CH_3)_4$.

A more drastic test of protic acid character is the action of sodium in liquid ammonia: any appreciable protic acid action of $(CH_3)_2SbH$ should lead to the salt $NaSb(CH_3)_2$, which in itself would be valuable as a reagent for forming other $(CH_3)_2Sb$ compounds. However, the actual reaction was more like the corresponding dimethylphosphine reaction, wherein the hydridic character of the P–H bond was enhanced by bases from the solvent, leading to aminophosphines and three times the volume of hydrogen which the salt formation would have required.[12] The 1.147 mmole sample of $(CH_3)_2SbH$, reacting with 1.248 mmoles of Na in 0.4 ml. of liquid ammonia, at −50 to −40°, produced 0.625 mmole of H_2 in 30 min.; calcd. for formation of $NaSb(CH_3)_2$, 0.574 mmole of H_2. At this point the sodium-blue had been replaced by an orange color, which soon turned dark red. The evolution of hydrogen continued, in 3.3 hr. reaching a total of 1.089 mmoles, or 190% of that expected for simple formation of the salt $NaSb(CH_3)_2$. It now was found possible to isolate 0.195 mmole of the bistibine $Sb_2(CH_3)_4$, representing 34% of the antimony. Allowing for the formation of this bistibine, an idealized equation for the rest of the process would be (with coefficients in mmoles) $0.757(CH_3)_2SbH + 0.757Na + 1.514NH_3 \rightarrow 0.757(CH_3)_2SbNH_2 + 0.757NaNH_2 + 1.136H_2$. The actual H_2 assignable to this reaction would be 0.894 mmole, indicating that the 0.757 mmole of $(CH_3)_2SbH$ was not all used in this manner, but doubtless mostly so. The black non-volatile residue would account for some other side-reactions, leaving some reducing power which was demonstrated by the action of ammonium bromide in liquid ammonia. This produced 0.071 mmole of H_2, corresponding to 11% of the reducing effect of the original sodium. It could be ascribed to Sb–H or Sb–Sb bonds, or both. The final residue after this reaction was relatively inert, showing neither solubility nor reactivity with methanol, acetone, ether, benzene or water.

A secondary experiment showed that $(CH_3)_2SbH$ is inert toward liquid ammonia alone: the sodium (and its conversion to amide) evidently was quite as necessary to the observed process as in the parallel case with dimethylphosphine.

Dimethylstibinoborine

The original $(CH_3)_2SbBr{-}NaBH_4$ reaction in diglyme had led to a very small yield of the desired $(CH_3)_2SbBH_2$. The process might have been improved but lacked convenience at best; hence other approaches to the synthesis of this compound were sought. Two were moderately successful. The first, in which diborane and dimethylstibine were brought to reaction under advantageous conditions, was unfavorable on account of a considerably larger competing reaction—the catalytic conversion of the stibine to the bistibine. The second, in which diborane attacked the bistibine at considerably higher temperatures, gave a better yield of $(CH_3)_2SbBH_2$ but was complicated by the methidic action of the bistibine, leading to some methylation of the diborane and black solid materials accounting for most of the antimony.

The Diborane–Dimethylstibine Reaction.—It is probable that the complex $(CH_3)_2SbH{\cdot}BH_3$ is formed from $(CH_3)_2SbH$ and B_2H_6 at low temperatures, for 1.263 mmoles of

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[10] G. T. Morgan and V. E. Yarsley, *J. Chem. Soc.*, **127**, 184 (1925).

[11] H. I. Schlesinger, N. W. Flodin and A. B. Burg, THIS JOURNAL, **61**, 1081 (1939).

[12] R. I. Wagner and A. B. Burg, *ibid.*, **75**, 3869 (1953).

B_2H_6 and 1.780 mmoles of $(CH_3)_2SbH$, brought together at $-78°$, formed a white solid. This was wholly dissociated by pumping at $-78°$, with recovery of all the B_2H_6 but not quite all of the $(CH_3)_2SbH$. No $(CH_3)_2SbBH_2$ was obtained from this exploratory experiment, but the formation of 0.047 mole of H_2 would correspond to the formation of a trace of $Sb_2(CH_3)_4$.

In the next experiment the formation of the bistibine was very extensive and almost exclusive: 1.245 mmoles of $(CH_3)_2SbH$ and 4.57 mmoles of B_2H_6, allowed to warm together from -78 to $-10°$ during 12 hr., produced 0.486 mmole of H_2 and 147.8 mg. (0.486 mmole) of $Sb_2(CH_3)_4$. The latter represented 78% of the original $(CH_3)_2SbH$, of which 0.223 mmole (18%) was recovered. The recovery of B_2H_6 was 4.49 mmoles, or 98%. No $(CH_3)_2SbBH_2$ was detected.

In this experiment it seemed that diborane acted only as a catalyst for the formation of the bistibine; and since the reaction did not progress rapidly after the warm-up, the highly unstable complex $(CH_3)_2SbH{\cdot}BH_3$ (existing appreciably only at low temperatures) might be a necessary part of the process. A fairly obvious explanation of the course of events would be that the Sb–H bond in the complex has enough protic acid character to attack the hydridic Sb–H bond in $(CH_3)_2SbH$, thus: $(CH_3)_2Sb^{+}{-}H^{-} + H^{+}{-}Sb^{-}(CH_3)_2{-}BH_3 \rightarrow (CH_3)_2Sb{-}Sb(CH_3)_2 + {}^1/_2B_2H_6 + H_2$. During the slow warm-up there would be plenty of $(CH_3)_2SbH$ from the simple dissociation of the complex. Supposing that the BH_3 part of the complex is less susceptible to protic acid attack than the Sb–H bond in free $(CH_3)_2SbH$, one could account for the failure to form any appreciable yield of $(CH_3)_2SbBH_2$.

On the other hand, when the reactants were warmed together so rapidly as not to permit much complex formation at intermediate temperatures (such as $-78°$), the pattern of reaction mechanisms was sufficiently different to allow some formation of $(CH_3)_2SbBH_2$. Thus 1.330 mmoles of $(CH_3)_2SbH$ and 4.212 mmoles of B_2H_6 were condensed together at $-196°$ and warmed to room temperature by immersion of the reaction tube in water. After 90 min. the mixture had produced 0.598 mmole of H_2; and the recovery of B_2H_6 was 4.100 mmoles (used, 0.112 mmole). The yield of $(CH_3)_2SbBH_2$ was 33.1 mg. (0.201 mmole, representing 90% of the used B_2H_6 and 15% of the stibine); it was identified by its vapor tension, 43 mm. at 0°, and by its mol. wt., 164.6 at 47 mm. and 27° (calcd., 164.7). There was a major yield of $Sb_2(CH_3)_4$, but the exact amount was not determined.

The $(CH_3)_2SbH$–B_2H_6 reaction was tried once with diglyme as the solvent: 4.357 mmoles of $(CH_3)_2SbH$ and 2.151 mmoles of B_2H_6, in 0.5 ml. of diglyme, standing at room temperature for 24 hr., produced 2.290 mmoles of hydrogen (calcd. for formation of bistibine only, 2.18; for the stibinoborine only, 4.302). The recovery of diborane was 1.964 mmoles and the yield of $(CH_3)_2SbBH_2$ 0.268 mmole (mol. wt., 165.0; yield 6.2% based upon the stibine). Evidently the solvent offered no advantage.

The Diborane–Bistibine Reaction.—An initial experiment showed that $Sb_2(CH_3)_4$ and B_2H_6 require temperatures above 60° for the desired reaction, for the chief effect after 8 hr. at that temperature was a 14% decomposition of the diborane. At 100°, a number of experiments employed a total of 8.182 g. of $Sb_2(CH_3)_4$ and gave altogether 1.003 g. of $(CH_3)_2SbBH_2$, an over-all yield of 11.3%. Some methylation of the diborane was noted, and much of the bistibine went to form non-volatile black material. Thus the best success depended upon a search for conditions such as to minimize the large effect of the side reactions. In the best single experiment, 1.762 mmoles of B_2H_6 and 1.726 mmoles of $Sb_2(CH_3)_4$, reacting during 105 min. at 100°, formed 1.865 mmoles of H_2 and a reddish liquid from which it was possible to isolate 0.910 mmole of $(CH_3)_2SbBH_2$ (mol. wt., 164.3; calcd., 164.67), representing 26.4% of the original bistibine. The recovery of B_2H_6 was 0.486 mmole, or 27%. In view of this excess diborane, some formation of the hypothetical $(CH_3)_2SbB_2H_5$ might have been expected if its stability were anything like that of the analogous $(CH_3)_2N$-B_2H_5,[4] but no such stibinodiborane could be recognized.

An attempt to make $(CH_3)_2SbBH_2$ from $Sb_2(CH_3)_4$ and B_2H_5Br did not succeed: a reaction occurred at the m.p. of the bistibine (17°), but the only volatile products were $(CH_3)_2SbBr$ (58%), B_2H_6 (96%) and a trace of methylated diborane.

Analytical Proof of the Stibinoborine Formula.—Exploratory analyses of $(CH_3)_2SbBH_2$ were done by reaction with methanol and HCl, with measurement of the resulting hydrogen and titration of the boric acid. Thus a 77.0-mg. sample (0.48 mmole) gave 0.90 mmole of H_2 and 0.45 mmole of boric acid (calcd., 0.96 and 0.48); these results may have been disturbed by the presence of a little $(CH_3)_2SbH$. In the final experiment, a highly purified sample weighing 74.5 mg. was broken down by 0.4 ml. of a 50% methanol–water solution containing HCl, in a sealed soft-glass tube at 250°. Found: 0.888 mmole of CH_4, 0.447 mmole of Sb(III) by $KBrO_3$ titration, 0.442 mmole of $B(OH)_3$ and 1.361 mmoles of H_2; calcd. values, respectively, 0.906, 0.453, 0.453 and 1.359, according to the equation $(CH_3)_2SbBH_2 + 3HOH + 3HCl \rightarrow 2CH_4 + SbCl_3 + B(OH)_3 + 3H_2$. Taken with numerous molecular weight determinations, all within 0.5% of the calculated value, 164.67, these results demand the formula $(CH_3)_2SbBH_2$.

Physical Properties of the Stibinoborine.—The vapor tensions of a nearly pure sample of $(CH_3)_2SbBH_2$, given by Table IV, determine the equation $\log p_{mm} = 7.777 - 1678/T$, according to which the b.p. would be 70° and the Trouton constant 22.4 cal./deg. mole. Attempts to determine the m.p. were defeated by glass-formation; no distinct crystals could be recognized.

TABLE IV

VAPOR TENSIONS OF $(CH_3)_2SbBH_2$

t (°C.)	-38.8	-29.1	-20.2	-14.0	-10.1	-7.1	0.0
p_{mm} (obsd.)	4.0	7.7	14.1	20.0	25.0	29.4	43.0
p_{mm} (calcd.)	4.1	8.0	14.0	20.0	25.0	29.5	43.0

Chemical Behavior of Dimethylstibinoborine.—The thermal stability of $(CH_3)_2SbBH_2$ was tested with a 195.5-mg. sample, only 17.7% of which was decomposed during 24 hr. at 210°. The chief products were methane and a black solid roughly formulated as SbB. Such resistance to any kind of decomposition is not typical of monomeric or weakly polymerized RBH_2 compounds, all earlier examples of which disproportionate at considerably lower temperatures. Also atypical is the resistance of $(CH_3)_2SbBH_2$ toward methylation by the action of $B(CH_3)_3$: there was no exchange of hydrogen for methyl on B during 67 hr. at 100°. Apparently the boron atom in $(CH_3)_2SbBH_2$ is not in a condition to act as an electron acceptor, for it failed to bond to trimethylamine at $-78°$ or higher temperatures. At 80°, however, trimethylamine promoted a decomposition in which methyl groups moved from one Sb to another, and hydrogen from one B to another, leading to major yields of $(CH_3)_3Sb$ and the very stable $(CH_3)_3NBH_3$. After a preliminary experiment had shown no reaction during an hour at 75°, 0.910 mmole of $(CH_3)_2SbBH_2$ was heated with a larger proportion of $(CH_3)_3N$ for 39 hr. at 80°, forming 0.302 mmole of $(CH_3)_3NBH_3$ and 0.669 mmole of $(CH_3)_3Sb$ (mol. wt. 166.8; v.t. 31 mm. at 0°). The accompanying white solid and yellow oil, neither volatile at 100°, were not studied further. It appeared that the expected $[(CH_3)_2Sb]_2BH$ either had not formed or failed to withstand the heating.

A considerable number of further attempts were made to synthesize $(CH_3)_2SbB_2H_5$ (analogous to the stable dimethylaminodiborane)[4] from $(CH_3)_2SbBH_2$ and B_2H_6 at various temperatures. No evidence for the existence of such a compound could be found.

Further Chemistry of Tetramethylbistibine

Synthesis by the Sodium–Ammonia Method.—A preliminary experiment in which $(CH_3)_2SbBr$ was brought to reaction with sodium in liquid ammonia gave a 15% yield of $Sb_2(CH_3)_4$, the chief difficulty being a loss of solution-contact by the formation of an insoluble complex on the upper walls. In order to minimize this effect, the main experiment was done in a sealed tube which could be shaken. The reactants were 378 mg. (16.4 mmoles) of Na and 3.388 g. (14.62 mmoles) of $(CH_3)_2SbBr$; in 4 ml. of liquid ammonia at -50 to $-40°$ (2 hr.), these produced 1.5725 g. (5.517 mmoles) of $Sb_2(CH_3)_4$, representing a 75% yield. Another experiment, using lithium instead of sodium (on a scale one-fourth as large), gave a 55% yield of the bistibine.

Analysis by the HCl Reaction.—A cleavage of $Sb_2(CH_3)_4$ by HCl occurred easily during a warming of the mixture to room temperature. With HCl in excess, the reaction obeyed the following equation, to which the actual mmole quantities of reactants and products are appended.

$$\begin{array}{cccc} Sb_2(CH_3)_4 + & 2HCl \longrightarrow & 2(CH_3)_2SbCl + & H_2 \\ 0.447 & 0.885 & 0.892 & 0.414 \end{array}$$

The only assumption here was the identity of the colorless liquid $(CH_3)_2SbCl$; its mercury-reactivity made a mol. wt. determination difficult.

Two samples of the bistibine were fully analyzed by carrying on the HCl reaction for 15 hr. at 250°. The HCl requirement was determined by measuring the initial amount and the remainder. The methane–hydrogen mixture was analyzed by CuO-combustion. The $SbCl_3$ was determined by oxidimetric titration, using standard $KBrO_3$ solution. The results are summarized in Table V, listing all products in mmoles.

TABLE V

ANALYSIS OF $Sb_2(CH_3)_4$

Sample	HCl used		H_2		CH_4		$SbCl_3$	
(mg.)	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
182.0	3.598	3.600	0.598	0.600	2.390	2.400	1.201	1.200
242.2	4.786	4.788	0.795	0.798	3.174	3.192	1.595	1.596

This very clean demonstration of the reaction $Sb_2(CH_3)_4 + 6HCl \rightarrow H_2 + 6CH_4 + 2SbCl_3$ dispels any possible doubt of the identity of the bistibine, the formation of which was the most direct evidence of the identity of dimethylstibine.

No such cleavage of $Sb_2(CH_3)_4$ occurred when H_2S was used instead of HCl: there was no reaction during 18 hr. at 100°.

Cleavage by Boron Trichloride.—The fairly clean low-temperature cleavage of $Sb_2(CH_3)_4$ by HCl encouraged the hope of making $(CH_3)_2SbBCl_2$ by the action of BCl_3. However, two experiments at room temperature gave only an adduct empirically formulated as $Sb_2(CH_3)_4 \cdot 0.83BCl_3$. One sample was heated *in vacuo* to 100°, giving a 10% yield of $(CH_3)_2BCl$ (proved by hydrolytic analysis), a black solid, a pale yellow oil and a white sublimate. After destruction of the oil by shaking with mercury, the white sublimate was analyzed, showing two B per Cl. The other sample of the adduct was heated only to 60°, giving a little $(CH_3)_2BCl$, the black solid, and the slightly yellow oil without the sublimate. A chloride analysis on the oil gave 18.61%; calcd. for $(CH_3)_2SbCl$, 18.95%. Thus it seemed that the desired cleavage occurred, but the desired $(CH_3)_2SbBCl_2$ appeared only in the form of its decomposition products, some of which were not intelligible.

In a third experiment on this cleavage the boron trichloride was employed in excess and the mixture was heated for 42 hr. at 60°. In this case the main effect was a methylation of the boron trichloride: 4.696 mmoles of BCl_3, reacting with 3.810 mmoles of $Sb_2(CH_3)_4$, gave 4.318 mmoles of $(CH_3)_2BCl$, representing 95% of the unrecovered BCl_3 (4.541 mmole) and 57% of the methyl groups. Neither the oil nor the sublimate appeared; hence the black solid could contain 0.31 mmole of $SbCl_3$ and a material empirically formulated as $Sb(CH_3)_{1.46}$.

Thermal Decomposition.—A 0.433 mmole sample of $Sb_2(CH_3)_4$ was made by the nearly quantitative conversion of 0.883 mmole of $(CH_3)_2SbH$, and withstood one week of heating in a sealed tube at 100°. Incipient decomposition was observed after 17 hr. at 160°: a trace of metallic mirror had appeared. After 20 hr. at 200°, the mirror had increased and the yellow liquid had become colorless. The yield of $(CH_3)_3Sb$ (mol. wt. 166.8; v.t. 31 mm. at 0°) was 0.571 mmole. The metal weighed 32 mg. (0.263 mg. atom Sb). These results cleanly indicate the equation $3Sb_2(CH_3)_4 \rightarrow 2Sb + 4(CH_3)_3Sb$, which requires 0.289 mg. atom of Sb and 0.578 mmole of $(CH_3)_3Sb$.

Grease-catalyzed Decomposition.—The bistibine proved to be unstable when stored at room temperature with the vapor in contact with a stopcock lubricated with Apiezon T grease. The yellow liquid slowly formed a white solid while the remaining liquid turned bright red. After two days the liquid had turned colorless and the solid was black. The yield of $(CH_3)_3Sb$ now was 0.513 mmole per mole of the original bistibine. Hence the non-volatile black solid had the empirical composition $Sb(CH_3)_{1.65}$.

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LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM VENABLE HALL OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Chemistry of Rhenium and Technetium. II. Magnetic Susceptibilities of $ReCl_5$, $ReCl_3$, $TcCl_4$ and $MoCl_5$

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The magnetic susceptibilities of $ReCl_5$, $ReCl_3$, $TcCl_4$ and $MoCl_5$ have been measured by the Gouy technique from liquid nitrogen at room temperature. The pentachlorides follow the Curie–Weiss relationship with these constants: $ReCl_5$, $\mu_{eff} = 2.21$, $\Delta = 164°$; $MoCl_5$, $\mu_{eff} = 1.52$, $\Delta = -23°$. The $1/\chi$ *vs.* T plots for $ReCl_3$ and $TcCl_4$ are not straight lines. Exchange interaction between the magnetic moments probably is significant for all of these compounds.

Introduction

Magnetic susceptibilities have proven to be useful in inorganic chemistry for interpretations of the electronic structures of compounds, especially those of the first transition series. Not so much is known about the theoretical magnetic behavior of compounds of the heavier transition elements, partly because of a lack of data on a sufficiently wide variety of compounds. We have measured the susceptibilities of several chlorides in order to investigate the magnetic behavior of compounds in this region of the periodic table.

Experimental

The methods described previously[2] were used to prepare $ReCl_5$, $TcCl_4$ and $MoCl_5$. Rhenium trichloride was prepared by (1) the thermal decomposition of $ReCl_5$ at 250° and (2) the reaction between $ReCl_5$ and Re at 450° in a sealed tube. Based on the conversion of $ReCl_5$, (1) gave yields around 50% whereas (2) yields around 85%. After purification by vacuum sublimation at 450°, the products of both reactions were the same. Analysis of several different preparations by essentially the same procedure used previously for $ReCl_5$[2] gave these average results with their standard deviations

% Re (theory 63.66)	% Cl (theory 36.34)	Cl/Re
63.66 ± 0.59	36.25 ± 0.28	3.00 ± 0.04

The compounds were loaded into calibrated Pyrex tubes in the dry box and weighed. The stoppered tubes were sealed off immediately after removal from the dry box.

The magnetic susceptibility measurements were made by the Gouy method in fields of up to 5000 oersted in an apparatus previously described.[3] None of the compounds had a field dependent susceptibility within experimental error. The reproducibility of the results on a single sample

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