[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Exchange of Methyl for Methanethio Groups on Boron

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The compound $CH_3SB(CH_3)_2$ disproportionates moderately, giving small yields of $B(CH_3)_3$ and the new $(CH_3S)_2BCH_3$ (m.p. −59°; b.p. est. 155°). The recommended preparative sequence is $(CH_3S)_3B + 2B(CH_3)_3 \rightleftarrows 3CH_3SB(CH_3)_2$ and $CH_3SB(CH_3)_2 + (CH_3S)_3B \rightleftarrows 2(CH_3S)_2BCH_3$—reactions requiring heat and a B–H catalyst supplied by diborane. The disproportionation reactions of $(CH_3S)_2BCH_3$ and $CH_3SB(CH_3)_2$ seldom exceed 20%.

The recent discovery of tris-methanethio-borine, $(CH_3S)_3B$,[2,3] and methanethiodimethylborine, $CH_3SB(CH_3)_2$,[3] suggested that the series intermediate bis-methanethio-methylborine, $(CH_3S)_2BCH_3$, also should be found. Furthermore, since compounds of the type BXY_2 often are capable of reversible disproportionation to form BX_3, BY_3 and BX_2Y, there was some interest in the rate and extent of such reactions of $CH_3SB(CH_3)_2$ and $(CH_3S)_2BCH_3$. The present study showed that $(CH_3S)_2BCH_3$ does indeed exist, and can be made from $(CH_3S)_3B$ and $B(CH_3)_3$, as is true also for $CH_3SB(CH_3)_2$. A trace of diborane supplies an effective catalyst for the formation or partial disproportionation of either of these methanethiomethylborines, which become more and more stable with repeated heating and repurification to remove the B–H compounds.

Experimental Part

Disproportionation of Methanethiodimethylborine.—A 21.4-cc.[4] portion of our original sample of $CH_3SB(CH_3)_2$[3] was heated in a sealed tube at 93° for 71 hours. Then it was possible to isolate 0.97 cc. (4.5% yield) of $B(CH_3)_3$, identified by its vapor tension of 31 mm. at −80°, its molecular weight (found 58; calcd. 56) and its formation of a monoammoniate exerting a pressure of 8 mm. at 25°.[5] A trace of less volatile material was observed but not at once identified; however, there could be no doubt of an exchange of CH_3 for CH_3S groups between boron atoms.

It was considered possible that this exchange reaction, like many others of the same type, was catalyzed by a trace of B–H material, since the sample had been derived from the reaction between CH_3SH and $(CH_3)_4B_2H_2$.[3] In order to avoid this effect, a sample of $CH_3SB(CH_3)_2$ was made in a new vacuum system, from $(CH_3)_2BBr$ and CH_3SH. This method proved to be very tedious because the resulting HBr strongly reversed the reaction, and its removal by the use of $(C_2H_5)_3N$ did not help much because of the N–B complexing effect. However, it was at length possible to isolate a sample of hydride-free $CH_3SB(CH_3)_2$, having a vapor tension of 44 mm. at 0° (previous value, 42.8). The 44.8-cc. sample was heated for 48 hours in a sealed tube at 100°, yielding only 0.14 cc. of more volatile material; then after 88 hours at 140° a 29.2-cc. portion yielded 0.6 cc. more of a gas passing a trap at −78° but wholly condensed at −140°. This was not surely identified as $B(CH_3)_3$, but even if it were that substance, it could have resulted from a cleanup of a slight impurity in the sample; and in any case the yield was smaller than that obtained from the old sample under far less drastic conditions.

The catalytic effect of B–H material was more directly demonstrated by heating a 22.4-cc. sample of the hydride-free $CH_3SB(CH_3)_2$ with an added 0.6 cc. of diborane. After 64 hours at 100° it yielded 1.2 cc. (5%) of $B(CH_3)_3$ (32 mm. at −78°).

In none of these experiments was any ethane observed; and as little as 0.05 cc. of it could have been detected as material passing a trap at −140° under high vacuum. Hence the earlier hint of ethane (an observation by the senior author)[3] either was chimaerical or required conditions not here established.

The New Compound Bis-Methanethio-methylborine.—In the above experiments, the production of $B(CH_3)_3$ was accompanied by the formation also of a trace of material definitely less volatile than $CH_3SB(CH_3)_2$ but more so than $(CH_3S)_3B$. Larger samples of the same product, which proved to be the new substance $(CH_3S)_2BCH_3$, were obtained by heating 36.0 cc. each of $(CH_3S)_3B$ and $CH_3SB(CH_3)_2$ with 0.6 cc. of diborane, for 72 hours at 93°.

$$(CH_3S)_3B + CH_3SB(CH_3)_2 \longrightarrow 2(CH_3S)_2BCH_3$$

The new substance was isolated by high-vacuum fractional condensation (through a trap at −15°; condensed completely at −50°); then the recovered reactants were remixed and heated again to bring the yield to 19 cc. (27%). In another such experiment, a considerable sample of $CH_3SB(CH_3)_2$ was made by repeated heating of $(CH_3S)_3B$ with $B(CH_3)_3$ in the presence of a trace of diborane—and then four heatings (each 10 hours at 112°) of a mixture of equivalent portions of $CH_3SB(CH_3)_2$ and $(CH_3S)_3B$ gave a 50% yield of $(CH_3S)_2BCH_3$.

The formula $(CH_3S)_2BCH_3$ was established by hydrolytic analysis, wherein a 24.8-mg. sample (4.63 cc.) yielded 8.9 cc. of CH_3SH and 4.2 cc. of $CH_3B(OH)_2$ (calcd., 9.2 and 4.6); the slightly low values were due in part to an impurity, for it was possible to isolate and identify 0.2 cc. of $(CH_3)_2BOH$. The molecular weight of the first sample was determined as 121 (calcd., 120.0). A more highly purified sample gave the value 120.3 at 117° and 187 mm.

The initial sample of $(CH_3S)_2BCH_3$ seemed fairly unstable, but when attempts were made to determine the extent of disproportionation to $(CH_3)_3B$ and $CH_3SB(CH_3)_2$ (reversal of the formation reaction) the successive heatings in a sealed tube yielded smaller and smaller traces of $CH_3SB(CH_3)_2$ (identified roughly by vapor tensions near 45 mm. at 0°) and less and less of more volatile fractions presumably including the catalyst. Thus the fifth heating of the 30-cc. sample (50 hours at 120°) gave only a 0.3% yield of $CH_3SB(CH_3)_2$. The main sample thus had become essentially stable, and could be purified for dependable measurements of physical properties.

The earliest fairly pure sample of $(CH_3S)_2BCH_3$ melted at −58.2°; the strongly heated and repurified material, at

TABLE I

VAPOR TENSIONS OF LIQUID $(CH_3S)_2BCH_3$

(In order of observations)

t (°C.)	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p (obsd.)	p (calcd.
26.92	5.00	4.98	64.85	35.80	35.90
33.00	6.98	7.10	71.75	48.5	48.7
39.55	10.22	10.23	79.35	67.8	67.2
45.60	14.09	14.09	27.13[a]	5.03	5 03
49.60	17.50	17.29	0.00	0.79	0.88
56.60	24.57	24.43	99.75	146.7	146.3

[a] Observed ten hours later than the preceding datum. The agreement with the calculated value demonstrates the stability of the sample.

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[1] The major part of the experimental work here reported was abstracted from a thesis submitted by Francis M. Graber to the Graduate Faculty of the University of Southern California, in partial fulfillment of the requirements for the degree of Master of Science.

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

[3] A. B. Burg and R. I. Wagner, THIS JOURNAL, **76**, 3310 (1954).

[4] Throughout this note the abbreviation cc. refers to the volume which the substance would occupy as a gas at standard conditions. All reactants and products were manipulated by distillation in the high-vacuum manifold, avoiding interference by extraneous substances.

[5] A. Stock and F. Zeidler, *Ber.*, **54**, 539 (1921).

−59.0°. The latter was used for the determinations of the vapor tensions shown in Table I. These are correlated by the equation $\log_{10}p_{\text{mm}} = -(2553/T) + 1.75 \log_{10}T - 0.004911T + 6.3425$, according to which the normal boiling point would be 154.9° and the Trouton constant approximately 20.9 cal./deg. mole.

The Disproportionation Equilibria.—The determination of true equilibrium states in the formation and disproportionation of $CH_3SB(CH_3)_2$ and $(CH_3S)_2BCH_3$, for the purpose of obtaining free energy–temperature relationships, probably would be quite difficult because the catalyst is destroyed too easily. The evidence so far indicates that neither substance is very extensively converted to the adjacent members of the system by long heating. For example a 20.8-cc. sample of $(CH_3S)_2BCH_3$ with 0.3 cc. of B_2H_6 was heated for 34 days at 84°, after which the recovery of $(CH_3S)_2BCH_3$ was 16.7 cc. (80%). The yield of $(CH_3S)_3B$ was 1.6 cc. and of $CH_3SB(CH_3)_2$, 1.96 cc.; and more volatile material representing the catalyst amounted to 1.1 cc. The question of the existence of substances such as CH_3SBHCH_3 or $(CH_3S)_2BH$, among the catalysts in this system, continues to be interesting.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Phosphorus Trifluoride–Borane and Phosphorus Trifluoride–Borane-d_3[1]

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Phosphorus trifluoride and diborane react under pressure in sealed tubes at room temperature to give the new compound F_3PBH_3.[2] Some physical and chemical properties of the new compound are described. Its properties show a striking resemblance to those of carbon monoxide–borane. NF_3 does not add to the BH_3 group, but under appropriate conditions B_2H_6 is oxidized explosively by NF_3.

The compound $Pt(PF_3)_2Cl_2$ prepared by Chatt and Williams[3] bears a striking resemblance to $Pt(CO)_2Cl_2$, and the complex $Ni(PF_3)_4$ prepared by Irvine and Wilkinson[4] is very similar in properties to $Ni(CO)_4$. This experimental resemblance between the coördinating properties of CO and PF_3 suggested the existence of the compound F_3PBH_3, which would be analogous to the $OCBH_3$ of Burg and Schlesinger.[5] On the other hand Chatt[3] pointed out that PF_3 did not add to $AlCl_3$, $AlBr_3$ or BF_3 and he invoked theoretical arguments as the basis for the prediction that a stable bond was unlikely between the boron in boron acids of the Lewis type and the phosphorus of phosphorus trifluoride. If, as suggested by Chatt, the acid–base type of reaction did not occur, the possibility of an oxidation–reduction reaction between B_2H_6 and PF_3 still merited consideration. In view of these interesting possibilities, an experimental study was conducted on the system B_2H_6–PF_3. The formally analogous system B_2H_6–NF_3 also has been examined.

The Preparation and Physical Properties of Phosphorus Trifluoride–Borane, F_3PBH_3.—The high pressure reaction between diborane and excess phosphorus trifluoride (8 atmospheres) proceeds slowly over the period of several days to yield the compound F_3PBH_3 as the primary product. On prolonged standing secondary reactions involving F_3PBH_3 ensue which give as yet undefined liquid products along with appreciable amounts of hydrogen. The primary phosphorus trifluoride–borane adduct also may be obtained by displacing CO from carbon monoxide–borane using a smaller excess of PF_3 (5 atmospheres).

Phosphorus trifluoride–borane is a colorless gas which is spontaneously inflammable in air. The melting point is −116.1 ± 0.2°. The vapor pressure of F_3PBH_3 over the liquid range can be given by the equation

$$\log_{10} P = -1038.9/T + 7.8061$$

Since the pure material resembles carbon monoxide–borane in that it will dissociate into B_2H_6 and PF_3, it was necessary to purify the compound before each reading and to achieve temperature equilibrium rapidly. The vapor pressure data extrapolate to give a boiling point of −61.8°, a heat of vaporization of 4,760 cal. per mole at the boiling point, and a Trouton constant of 22.5.

The molecular weight by vapor density at 25° was 102.7 as compared to a theoretical value of 101.82.

The Dissociation Constant of Gaseous F_3PBH_3 at 25°.—The equilibrium constant for the reaction

$$2F_3PBH_3(g) \rightleftharpoons 2PF_3(g) + B_2H_6(g)$$

was estimated by analyzing equilibrium mixtures according to the procedures described in the Experimental sections. A value for $K_{(\text{atm.})}$ of 1.0 ± 0.3 was obtained at 25°. The uncertainty in the value can be attributed to three factors. First, a number of experimental difficulties were associated with the separation of the large excess of PF_3 from the product and the unreacted diborane.[6] Secondly, since

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[1] Abstracted in part from a dissertation submitted by Thomas C. Bissot to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The designation of BH_3 as borane is consistent with the system of nomenclature for boron compounds which was presented by G. W. Schaeffer and T. Wartik at the 125th meeting of the American Chemical Society, Kansas City, Missouri.

[3] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951); J. Chatt, *ibid.*, 3340 (1949).

[4] Irvine and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, THIS JOURNAL, **73**, 5501 (1951).

[5] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

[6] The problem is simplified in the case of carbon monoxide–borane since the CO is not condensable with liquid nitrogen whereas the other components are. Since PF_3 boils at −95° and B_2H_6 at −92° chemical procedures had to be employed for analysis.