

**$\mu$ -Mercaptodiborane**

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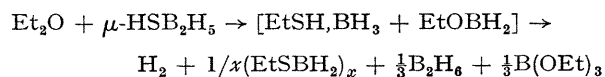
COTTON AND WADDINGTON reported that solutions of tetraalkylammonium hydrogen sulphide in liquid hydrogen sulphide absorbed diborane at  $-78^\circ$  to form an unstable product of composition  $R_4NSH, B_2H_6$ ;<sup>1</sup> they suggested that the compound might be  $R_4NHS(BH_3)_2$ . An  $^{11}B$  n.m.r. spectrum<sup>†</sup> at  $-75^\circ$  of a liquid hydrogen sulphide solution of  $Et_4NSH$  in the presence of an excess of diborane confirms this assignment, showing a large quartet with  $\delta +23.9$  p.p.m. and  $J$  102 Hz. in addition to the triplet-of-triplets signal characteristic of diborane. The  $HS(BH_3)_2^-$  ion is structurally related to the  $H_2P(BH_3)_2^-$  ion.<sup>2,3</sup>

Evaporation of the hydrogen sulphide solvent under reduced pressure at  $-78^\circ$  from a solution of  $Et_4NHS(BH_3)_2$ , and treatment of the residue with an excess of anhydrous hydrogen chloride at the same temperature gave hydrogen and the new compound  $\mu$ -mercaptodiborane. The volatiles were distilled from the reaction vessel as it warmed to room temperature, and the product was separated from residual hydrogen sulphide and the excess of hydrogen chloride by distillation into a trap maintained at  $-126^\circ$ ; traces of less volatile organic impurities, derived from cleavage of the tetraethylammonium cation, were removed by fractionation through a trap at  $-95^\circ$ .

The  $\mu$ - $HSB_2H_5$  has an extrapolated b.p. of  $27^\circ$ . The  $^{11}B$  n.m.r. spectrum of the pure liquid at  $-10^\circ$  shows a triplet of doublets with  $\delta +24.8$  p.p.m.,  $J_{\text{terminal}}$  141 Hz.,

and  $J_{\text{bridge}}$  39 Hz thus confirming the bridge structure. The thermal stability of  $\mu$ - $HSB_2H_5$  in both the gas and the liquid phase is poor. Typically, in a gas-phase experiment  $\mu$ - $HSB_2H_5$  (0.35 mole) in a 60-ml. bulb underwent 45% decomposition in 5 hr. at room temperature. Decomposition in the liquid phase is considerably faster. The mechanism of decomposition depends upon whether the reaction occurs in the gas or the liquid phase, as evidenced by different ultimate products. Gas-phase decomposition yields hydrogen sulphide, diborane, and involatile solid; liquid-phase decomposition yields hydrogen, diborane, and involatile solid.

Diethyl ether is cleaved by  $\mu$ - $HSB_2H_5$  at room temperature and the product distribution is approximately consistent with the following reaction:



The ether appears to catalyse the decomposition of the  $\mu$ - $HSB_2H_5$  as well, since less diethyl ether is lost than  $\mu$ - $HSB_2H_5$ , and a small amount of hydrogen sulphide is also found among the reaction products.

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† The  $^{11}B$  n.m.r. spectra reported were obtained using a Varian HA-100 spectrometer equipped with a 32.1 MHz. probe and standard low-temperature accessories. Chemical shifts are relative to  $Et_2OBF_3$ .

<sup>1</sup> J. D. Cotton and T. C. Waddington, *J. Chem. Soc. (A)*, 1966, 789.

<sup>2</sup> J. W. Gilje, K. W. Morse, and R. W. Parry, *Inorg. Chem.*, 1967, **6**, 1761.

<sup>3</sup> N. R. Thompson, *J. Chem. Soc.*, 1965, 6290.