

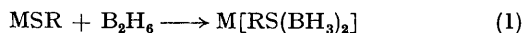
Formation and Properties of Bis(borane)alkanethiolate Salts and Their Conversion into μ -Alkylthiodiboranes

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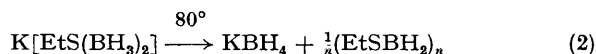
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Summary Stoichiometric quantities of KSR and B_2H_6 react in THF to form the thermally stable salts $K[RS(BH_3)_2]$; treatment of $K[RS(BH_3)_2]$ with anhydrous acids, diborane, or iodine produces μ -RSB₂H₅ in moderate yield.

RELATIVELY little is known about sulphur substituted boranes and borohydride ions. We report the extension of earlier work¹⁻³ to the preparation and characterization of a number of new S-alkyl substituted compounds.

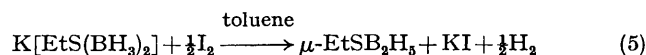
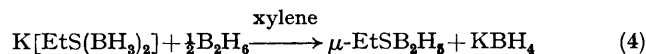
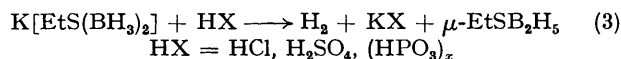


The preparation equation (1) and characterization of $K[EtS(BH_3)_2]$ is typical. Treatment of a stirred THF slurry of KSEt with an exact stoichiometric quantity of B_2H_6 results in rapid dissolution of the solid. Evaporation gives pure solvent-free $K[EtS(BH_3)_2]$; no KBH_4 or $(EtSBH_2)_n$ forms under these conditions. $K[EtS(BH_3)_2]$ dissolves in glyme ethers and THF, but reacts with protic solvents. The boron-11 n.m.r. spectrum† (THF) consists of a quartet at 22.6 p.p.m., J 97 Hz; the i.r. spectrum shows the following bands in the B-H stretching region (in cm^{-1}): 2375 (s, sh), 2330 (s), 2295 (s), and 2202 (m). $K[EtS(BH_3)_2]$ is indefinitely stable at room temperature in the absence of air and moisture and decomposes smoothly at 80° in agreement with equation (2).

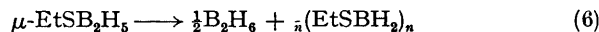


The thermal stability of $K[EtS(BH_3)_2]$ stands in contrast to the behaviour of $[Et_4N][HS(BH_3)_2]$, which decomposes vigorously with loss of hydrogen above -78° .⁴ The instability of the latter probably results from the acidic proton on sulphur.

Conversion of $K[EtS(BH_3)_2]$ into μ -EtSB₂H₅ may be effected as shown in equations (3)–(5).



Decomposition of μ -EtSB₂H₅ at 25° occurs slowly in the gas phase and rapidly in the liquid phase in accord with equation (6).



Reactions (3) and (4) are convenient methods for the preparation of free μ -EtSB₂H₅; the product may be isolated in 20–30% yield by trap to trap vacuum line fractionation. Reaction (5) is most suitable for the preparation of a toluene solution of μ -EtSB₂H₅. In this case yields are generally much higher, since isolation of liquid μ -EtSB₂H₅ and resultant accelerated decomposition are avoided.

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† The boron-11 n.m.r. spectra were obtained using a Varian HA-100 spectrometer equipped with a 32.1 MHz probe. Chemical shifts are relative to Et₂O, BF₃.

¹ P. C. Keller, *Chem. Comm.*, 1969, 209.

² P. C. Keller, *Inorg. Chem.*, 1969, **8**, 1695.

³ P. C. Keller, *Inorg. Chem.*, 1969, **8**, 2457.

⁴ J. D. Cotton and T. C. Waddington, *J. Chem. Soc. (A)*, 1966, 789.