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

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Summary Stoicheiometric 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-RSB_2H_5 in moderate yield.

Relatively little is known about sulphur substituted boranes and borohydride ions. We report the extension of earlier work[1-3] to the preparation and characterization of a number of new *S*-alkyl substituted compounds.

$$MSR + B_2H_6 \longrightarrow M[RS(BH_3)_2] \qquad (1)$$

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 stoicheiometric 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).

$$K[EtS(BH_3)_2] \xrightarrow{80^\circ} KBH_4 + \tfrac{1}{n}(EtSBH_2)_n \qquad (2)$$

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-$EtSB_2H_5$ may be effected as shown in equations (3)—(5).

$$K[EtS(BH_3)_2] + HX \longrightarrow H_2 + KX + \mu\text{-}EtSB_2H_5 \qquad (3)$$
$$HX = HCl,\ H_2SO_4,\ (HPO_3)_x$$

$$K[EtS(BH_3)_2] + \tfrac{1}{2}B_2H_6 \xrightarrow{\text{xylene}} \mu\text{-}EtSB_2H_5 + KBH_4 \qquad (4)$$

$$K[EtS(BH_3)_2] + \tfrac{1}{2}I_2 \xrightarrow{\text{toluene}} \mu\text{-}EtSB_2H_5 + KI + \tfrac{1}{2}H_2 \qquad (5)$$

Decomposition of μ-$EtSB_2H_5$ at 25° occurs slowly in the gas phase and rapidly in the liquid phase in accord with equation (6).

$$\mu\text{-}EtSB_2H_5 \longrightarrow \tfrac{1}{2}B_2H_6 + \tfrac{1}{n}(EtSBH_2)_n \qquad (6)$$

Reactions (3) and (4) are convenient methods for the preparation of free μ-$EtSB_2H_5$; 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-$EtSB_2H_5$. In this case yields are generally much higher, since isolation of liquid μ-$EtSB_2H_5$ 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 Et_2O,BF_3.

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