Reactions of 3,5-Dimethyl-1,2,4,3,5-trithiadiborolane with Secondary Amines: Formation of Diorganylamino(sulfhydryl)boranes*

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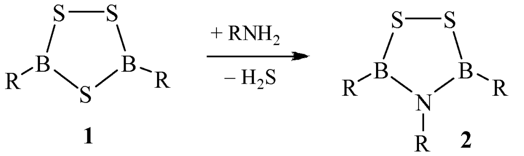
The 1 : 1 reaction of 3,5-dimethyl-1,2,4,3,5-trithiadiborolane, **3**, with dimethylamine in diethyl ether yielded a mixture of compounds from which only MeB(NMe$_2$)SH, **7**, could be separated. In the 1:2 reaction, insoluble Me$_2$NH(MeB(S$_2$)$_2$BMe)HNMe$_2$, **10**, could be isolated besides **7** and small amounts of MeB(NMe$_2$)$_2$. In the presence of NMe$_3$ the bis(methyl-dimethylamino-boryl)sulfide, **7** was obtained in good yield. Replacement of HNMe$_2$ by *N*-methylaniline or piperidine led to the corresponding amino(methyl)sulfhydrido boranes R$_2$N(MeB)SH in moderate yields. *t*BuNH(MeB)SH results in 61 % yield from the treatment of *t*Bu$_2$B$_2$S$_3$ with *t*BuNH$_2$ in a 1 : 1 ratio.

Key words: Diorganylamino(sulfhydryl)methylboranes,
Dimeric Dimethylamino(sulfhydryl)methylborane

Introduction

It is well known that the five-membered 1,2,4,3,5-trithiadiborolanes R$_2$B$_2$S$_3$, **1** [1, 2], are more reactive than the five-membered triazadiborolidines (R$_2$B)$_2$(NR$'$)$_3$ [3], and this corresponds with the higher reactivity of the six-membered 1,3,5,2,4,6 trithiatriboranes (RB=S)$_3$ [1] compared to borazines (RB=NR$'$)$_3$ [4, 5]. This difference in chemical behavior is due to the stronger B–N bonds compared with B–S bonds. BN π-bonding in borazines [4 – 7] makes the boron atoms less electrophilic than the boron atoms in trithiatriboranes. Whether the B–S bonds of B$_n$S$_m$ heterocycles have π-bond character is still a matter of debate [8]. Thus, the B–S bond lengths in bis(dithiaborolanyl)sulfide points to a small π-bond contribution, as shown by significantly different B–S bond lengths: 1.788 Å for the ring B–S bonds and 1.812 Å for the bridge B–S bonds [9]. The former are also shorter than the B–S bonds in B(SR)$_3$ with 1.805 Å [10], which indicates some π-bond character in the B–S–B bond [8].

In the case of Br$_2$B$_2$S$_3$ the B–Br bond is generally more reactive than the B–S bond, as shown by reactions with electrophilic borane derivatives BY$_3$ (Y = Hal, OR, NR$_2$ R) which yield trithiadiborolanes Y$_2$B$_2$S$_3$ by Br/Y exchange [11, 12]. Aminolysis of Br$_2$B$_2$S$_3$ leads to 3,5-diamino-trithiadiborolanes (Eq. 1) [13], and diorganylaminotrimethylsilanes react with Br$_2$B$_2$S$_3$ to generate the corresponding bis(diorganylamino)-trithiadiborolanes [14]. However, reactions of 3,5-diorganyltrithiadiborolanes with primary amines can lead to diorganyl-dithiadiborazolines, **2**, as shown in Eq. 1 [15]. However, the reaction of Me$_2$B$_2$S$_3$, **3**, with primary amines is much more complex depending on the reaction conditions, the molar ratio of Me$_2$B$_2$S$_3$: RNH$_2$ as well as on the steric requirements of the primary amines used (Scheme 1) [16].



1 **2** (1)

Results and Discussion

It was, therefore, of interest to study the reaction of Me$_2$B$_2$S$_3$ with secondary amines because neither borazines nor thiaborazines can form only non-cyclic dialkylamino-sulfhydryl-methylboranes. It was also expected that the 1 : 1 reaction with secondary amines

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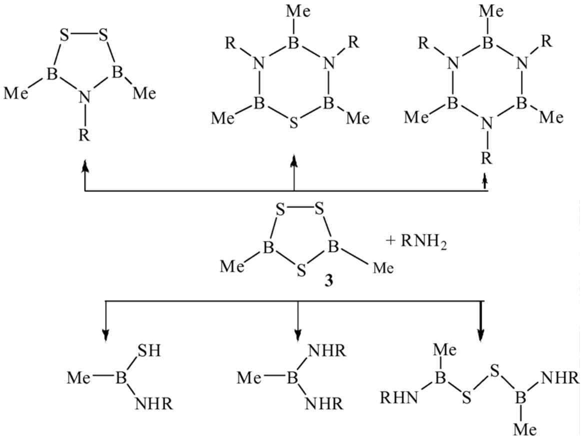
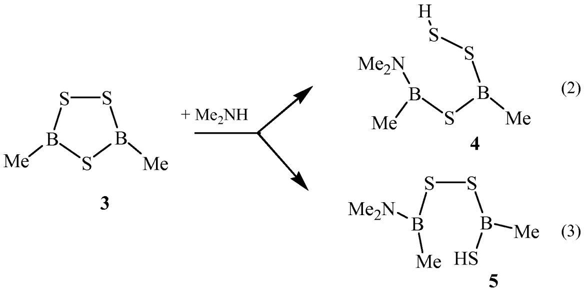


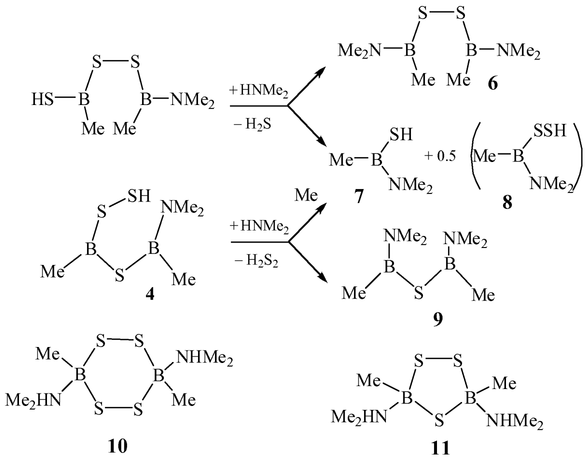
Scheme 1.

shows whether the B–S–B unit is affected by ring opening, or the B–S–S–B unit, as proposed in Eqs. 2 and 3.



Reactions with dimethylamine

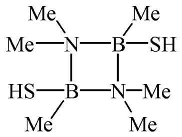
The reaction of **3** with dimethylamine in diethyl ether at −70 °C led to an insoluble product which dissolved almost completely at r. t. After filtration three ^{1}H NMR signals were recorded from the filtrate at δ = 0.45, 0.88 and 2.56 (d) ppm (ratio 1 : 1 : 2) which indicated the presence of either a 1 : 1 or a 1 : 2 dimethylamine adduct of **3** (**11**). It is unlikely that the solvolysis products **4** or **5** are formed, because we found no signal for an SH group. After removal of most of the solvent a sticky solid remained. Distillation at 70 °C/10^{-3} Torr yielded an oily product that crystallized on standing. Its ^{11}B NMR spectrum showed three signals at δ = 70.7 (50 %), 42.3 (25 %) and 8 ppm (25 %). These signals can be assigned to **3**, $Me_2N(Me)BSH$, **7**, and its dimer. Further fractionation at 98 °C/10^{-3} Torr led to a solid compound of m. p. 84 °C. This compound is not dimeric **4** (= **8**), but its isomer **10** because the IR spectrum did not show SH stretching bands in contrast to an NH band (*v. i.*). Scheme 2 shows possible and observed reactions.



Scheme 2.

A somewhat less complex course can be expected for the reaction of **3** with Me_2NH in a 1 : 2 ratio because the B–S bonds should be cleaved with formation of H_2S or H_2S_2 (or H_2 and sulfur). Indeed, now the main product is $MeB(NMe_2)SH$, **7** (Scheme 2). In addition, a small amount of $MeB(NMe_2)_2$ could also be detected in the ^{11}B NMR spectrum. The solid that precipitated at the beginning of the reaction proved to be $[Me_2NH(Me)BSS]_2$, **10**, but not its isomer **8** because its IR spectrum shows an NH band at 3210 cm^{-1}, but no SH band around 2620 cm^{-1}. Its structure was also characterized by its NMR and mass spectra. Heating the precipitate to 100 °C *in vacuo* produced small quantities of a solid condensate which reacted rapidly with a solution of bromine in CH_2Cl_2. This indicates the presence of B–S bonds in this material. The solid residue proved to be pure **10**. It melts at 160 – 162 °C.

The formation of gel-like material from the clear condensates points to the formation of associates. This behavior is well known for $Me_2B–S–BMe_2$ [17]. The ^{11}B NMR spectrum of a freshly prepared clear condensate showed a signal at 42.2 ppm for **7**, and at 11 ppm for a tetra-coordinated boron atom. The latter most likely results from the Me_2NH adduct **11** of the trithiadiborolane **3**. The aminolysis of the reaction of **3** with dimethylamine at −10 °C led after a short reaction time (2 h), to a filtrate with two ^{11}B NMR signals at 42 and 11 ppm, in a ratio of 10 : 1. Within 2 h the less intense signal at 11 ppm became more and more intense until the ratio was about 1 : 1. In addition, a new signal appeared for a tetra-coordinated ^{11}B atom



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at 3 ppm, which may be due to the four-membered ring compound **12**.

In order to prevent the formation of products carrying SH groups, trimethylamine was added to the reaction mixture of Me_2NH and **3**. Astonishingly, the trimethylamine could be completely recovered *in vacuo*. Nevertheless it had an important influence on the course of the reaction because the ratio of **5** to $MeB(NMe_2)_2$ was now 4 : 1, corresponding to a 54 % yield of **5**. The yield of the insoluble **10** rose to 95 %.This, however, gives no clear evidence whether the B–S–B or the B–S–S–B groups are preferentially attacked by dimethylamine. Compounds **6** and **9** could not be isolated or detected spectroscopically.

Reaction of $R_2B_2S_3$ with N-methylaniline, piperidine and tert-butylamine

The addition of *N*-methylaniline to a diethyl ether solution of **3** at −70 °C resulted in a precipitate which dissolved on heating the mixture to reflux. On cooling, a solid formed, and distillation of the filtrate yielded MeB(NMePh)SH in 21 % yield. Similarly, the reaction of **3** with piperidine in a 1 : 2 ratio led to the isolation of MeB(pip)SH in 32 % yield. It was, however, surprising that the reaction of $t\mathrm{BuNH_2}$ with $t\mathrm{Bu_2B_2S_3}$ yielded *t*BuB(NH*t*Bu)SH in 61 % yield, as shown in Eq. 4. This demonstrates that the bulky *tert*-butyl amine reacts like secondary amines with the sterically shielded boron atoms of $(t\mathrm{Bu})_2\mathrm{B_2S_3}$.

$$t\mathrm{Bu_2B_2S_3} + 2\ \mathrm{H_2N}t\mathrm{Bu} \rightarrow 2\ t\mathrm{BuB(NH}t\mathrm{Bu)SH} + 1/8\ \mathrm{S_8} \tag{4}$$

Conclusions

The reaction of $Me_2B_2S_3$ with secondary amines leads, like the reaction of $Me_2B_2S_3$ with primary amines, to various products by ring opening reactions. However, it could not be proved whether the boron-sulfur bonds of the B–S–B or the B–S–S–B group are preferentially attacked, because $MeB(NMe_2)SH$ and $[MeB(NHMe_2)SS]_2$ are formed. In case of sterically more demanding secondary amines the main products are of the type $MeB(NR_2)SH$. Moreover, the trithiadiborolane $(t\mathrm{Bu})_2\mathrm{B_2S_3}$ reacts with $t\mathrm{BuNH_2}$, as shown in Eq. 4, similar to the secondary amines. This shows that steric effects are controlling the aminolysis of the $R_2B_2S_3$ heterocycle.

Experimental Section

All reactions were performed under anhydrous conditions using Schlenk techniques under argon gas. Amines were of high-purity commercial quality. $Me_2B_2S_3$ was prepared according to the literature [13]. Solvents were dried by standard procedures and distilled prior to use. Elemental analyses were conducted in the Microanalytical Laboratory of the Department. ^{1}H and ^{11}B NMR spectra were recorded with a Varian EM 360 instrument and $SiMe_4$ as internal or BF_3OEt_2 as external standard. Mass spectra were recorded with a CH-7 instrument of Atlas, and IR spectra with a Perkin-Elmer 324 spectrometer.

Reaction of $Me_2B_2S_3$ with dimethylamine

a) Ratio 1 : 1

At −78 °C Me_2NH (1.35 g, 30 mmol) was condensed into a solution of $Me_2B_2S_3$ (4.44 g, 30 mmol) in diethyl ether (30 mL). A white solid formed rapidly which dissolved after warming the suspension to ambient temperature. However, a small amount of a solid (0.5 g) precipitated from the solution within 6 h. This solid was separated by filtration. From the filtrate about 50 % of the solvent was removed *in vacuo*. The ^{1}H NMR spectrum showed singlet signals at 0.45, 0.88 and 2.54 and 2.58 ppm (ratio 1 : 1 : 1: 1), indicating the formation of compound $Me(SH)B–S–S–BMe(NMe_2)$ with hindered rotation about the BN bond. Further removal of the solvent produced oil-covered crystals (5.25 g) which became liquid at about 35 °C. Distillation of this material at 70 °C/10^{-3} Torr led to 4.2 g of an oily product which became solid at ambient temperature. Its ^{11}B NMR spectrum showed the presence of $Me_2B_2S_3$ (δ = 70.7 ppm, 50 %), and of $Me_2N(Me)BSH$ (δ = 42.3 ppm, 25 %), and a broad signal at 8 ppm (25 %) most likely due to $(Me_2NHB(Me)S_2)_2$, **10**. The ^{1}H NMR spectrum showed several signals including those of $Me_2B_2S_3$ at 1.19 ppm and of $HS_2BMe–S–BMe(NMe_2)$ at 0.55 (3H), 0.95 (1H), and 2.75 ppm (6H), besides signals that could not be reliably assigned at 0.33, 0.99, 2.3, 2.56 and 2.65 ppm. The distillation of this product mixture at 98 °C/10^{-3} Torr (1.33 g) gave a solid fraction with m. p. 84 °C which according to its ^{1}H NMR spectrum was almost pure $HS_2BMe–S–BMe(NMe_2)$. The distillation residue proved to be a mixture of $Me_2B_2S_3$ (40 %) and $Me_2N(Me)BSH$ (60 %), as shown by their ^{1}H NMR signals.

The elemental analysis of the first part of the insoluble material suggested that it consisted mainly of compound $[MeB(HNMe_2)S_2]_2$, **10**: $C_6H_{20}N_2B_2S_2$ (270.1): calcd. C 26.68, H 7.46, N 10.37; found C 24.26, H 7.26, N 9.22.

b) Ratio 1 : 2

As described above, $HNMe_2$ (2.7 g, 60 mmol) was condensed into a solution of $Me_2B_2S_3$ (4.44 g, 30 mmol) dissolved in diethyl ether (10 mL). A yellowish precipitate formed on warming the mixture to r. t. On heating for 16 h to reflux most of the solid went into solution. After removal of the solvent distillation at b. p. 40 °C/40 Torr (redistillation at 52 °C/90 Torr) yielded $MeB(NMe_2)SH$ (0.98 g, 32 %) as a colorless moisture-sensitive product. – NMR (CH_2Cl_2): $\delta^1H = 0.55$ (3 H), 0.95 (1 H), 2.73 (6 H) ppm; $\delta^{11}B$ (CH_2Cl_2) = 42.2 ppm. A second fraction obtained at b. p. 28 °C/10 Torr consisted of $MeB(NMe_2)SH$ (20 %), and $MeB(NMe_2)_2$ ($\delta^1H = 0.16$, 2.62 ppm, ratio 4 : 1). Small signals at $\delta^1H = 0.53$, 0.79, 2.78, and 2.9 ppm may be due to $Me_2NB(Me)–S–B(Me)NMe_2$, **9**.

The non-volatile residue (4.5 g) was insoluble in chloroform, toluene and THF and could not be characterized.

Reaction of $Me_2B_2S_3$ with $HNMe_2$ in the presence of trimethylamine

To a stirred solution of $Me_2B_2S_3$ (4.44 g, 30 mmol) in diethyl ether (60 mL) were condensed at −78 °C NMe_3 (3.55 g, 30 mmol) and $HNMe_2$ (2.70 g, 30 mmol). A slightly yellow precipitate formed which on warming to ambient temperature produced a yellow solution. After removal of the solvent and trimethylamine *in vacuo* all volatile material of the residue was condensed up to 100 °C/10^{-3} Torr. The condensate was recondensed at 100 °C/10^{-3} Torr to give a mixture of 2.13 g of $MeB(NMe_2)SH$ and $MeB(NMe_2)_2$ (ratio 4 : 1). 3.86 g of $[(Me_2NH)MeBSS)]_2$ remained as a residue, m. p. 158 – 160 °C. It was characterized by its mass spectrum (*m/z* = 270 calcd. for ^{11}B), its IR spectrum and elemental analysis. – $C_6H_{20}N_2B_2S_2$ (270.1): calcd. C 26.7, H 7.40, N 10.37; found C 27.22, H 6.95, N 10.45. – IR (cm^{-1}): ν = 3180 w, 3160 w, 3120 vst (NH), 3030 m, 3000 m, 2960 st, 2960 st, 2930 w, 2895 w, 2825 w, 2760 m, 1455 st, 1450 st, 1422 m, 1390 st, 1309 vst, 1300 vst, 1290 sh, 1270 w, 1130 st, 1013 st, 990 m, 965 st, 945 st, 928 st, 897 st, 800 br, m, 673 st, 645 st, 530 m, 346 m, 270 st, 230 st.

Methyl-phenylmethylamino-sulfhydryl-borane

A solution of *N*-methylaniline (6.43 g, 60 mmol) in diethyl ether (30 mL) was dropped into a stirred solution of $Me_2B_2S_3$ (4.44 g, 30 mmol) in diethyl ether (10 mL) at −78 °C. On warming to ambient temperature a solid formed which went into solution on heating the mixture to reflux. On cooling to −20 °C a solid precipitated which was removed by filtration. The filtrate was subjected to distillation *via* a Vigreux column. At b. p. 41 °C/10^{-3} Torr liquid PhMeNB(Me)SH (1.1 g, 21 %) was obtained. All other fractions contained only mixtures of products (^{11}B NMR). – $C_8H_{12}BNS$ (165.1): calcd. C 58.21, H 7.33, N 8.48; found C 59.62, H 7.11, N 8.81. – NMR (C_6D_6): $\delta^1H = 0.54$ (3 H), 1.15 (1 H), 3.1 (3 H), 7.17 ppm (5 H); $\delta^{11}B = 43.8$ ppm. – IR (cm^{-1}): ν = 3200 (br), 3060 m, 3040 m, 2940 st, 2580 w, 1595 vst, 1580 sh, 1490 vst, 1470 st, 1440 st, 1385 vst, 1305 vst, 1280 m, 1240 vst, 1170 w, 1120 st, 1095 m, 1080 m, 1060 vst, 1040 st, 1020 w, 910 w, 880 w, 860 w, 770 st, 750 st, 969 vst, 620 w, 610 st, 550 st, 540 vst.

Methyl(piperidinyl)-sulfhydryl-borane

As described above, $Me_2B_2S_3$ (4.44 g, 30 mmol) was allowed to react with piperidine (5.11 g, 60 mmol) in diethyl ether (30 mL). The precipitate that formed was removed by filtration. Distillation of the filtrate at 29 °C/10^{-2} Torr $(C_5H_{10}N)MeBSH$ as the only well characterized product (1.36 g, 31.7 %). – NMR (CH_2Cl_2): $\delta^1H = 0.55$ (3 H), 0.84 (1 H), 1.56 ppm (10 H); $\delta^{11}B = 41.0$ ppm. – MS: *m/z* = 143 (^{11}B). – $C_6H_{14}NBS$ (143.06), calcd. C 50.38, H 10.04, N 9.77; found C 49.92, H 10.06, N 9.56.

t-Butylamino(t-butyl)-sulfhydryl-borane

To a stirred solution of t-$Bu_2B_2S_3$ (2.32 g, 10 mmol) in diethyl ether (20 mL) was added at −78 °C a solution of t-$BuNH_2$ (1.46 g, 20 mmol) in diethyl ether (10 mL). The solution was kept at reflux for 24 h. Then the ether was removed by distillation. The residue was fractionally distilled yielding 1.1 g (63.5 %) of *t*-BuB(NH*t*-Bu)(SH) at b. p. 25 °C/8 Torr. – NMR (CH_2Cl_2): $\delta^1H = 0.91$ (9 H), 1.28 (9 H), 2.3 (1 H), 4.3 ppm (1 H); $\delta^{11}B = 44.5$ ppm. – MS: *m/z* = 173 (^{11}B). – $C_8H_{20}NBS$ (173.13): calcd. C 55.45, H 11.64, N 8.09; found C 55.36, H 11.53, N 7.99.

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