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Formation and Reactions of a Thioxoborane, a Novel Boron–Sulfur Double-bond Compound

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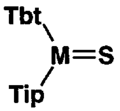
Abstract: Thermolysis of an overcrowded tin-containing four-membered boracycle, 1,3,2-dithiastannaboretane derivative **6**, bearing an extremely bulky aryl group, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt), on the boron atom in the presence of several 1,3-dienes in toluene at 120 °C gave the corresponding diene adducts of an initially formed thioxoborane (Tbt-B=S; **7**) together with a trimer of diphenylstannanethione **8**. Retro [4+2]cycloaddition of the diene adducts into the thioxoborane **7** is also described. Copyright © 1996 Elsevier Science Ltd

In recent years remarkable progress has been made in the chemistry of multiple-bond compounds containing heavier typical elements, especially in the field of thiocarbonyl compounds[1] and their heavy congeners.[2] In the course of our study on the kinetic stabilization of highly reactive organoheteroatom compounds, we have recently succeeded in the syntheses and isolations of the first stable silanethione [Tbt(Tip)Si=S (**1**); Tip = 2,4,6-triisopropylphenyl][3] and germanethione [Tbt(Tip)Ge=S (**2**)],[4] *i. e.* heavier group 14 element analogues of thioketones, by taking advantage of a new and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), and revealed their unique structures and reactivities. On the other hand, very little is known for the chemistry of boron–sulfur double-bond compounds (thioxoboranes).[5] The parent molecule, H–B=S, has been postulated as an intermediate in the reaction of hydrogen sulfide with elemental boron at 1000 °C,[6] but no stable monomeric thioxoboranes have been known although some of them are isolated as oligomeric products such as dimer or trimer.[7] In addition to the high reactivity and instability of thioxoboranes, the lack of a suitable synthetic route to the boron–sulfur double-bond species may hamper the progress of this field. Here, we wish to delineate the first example of the generation and trapping of a thioxoborane.

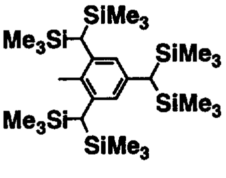


1; M=Si
2; M=Ge

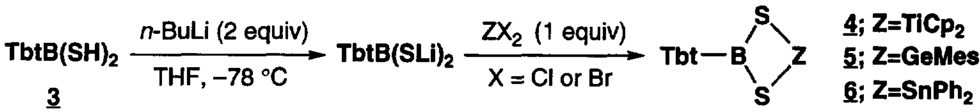
$\boxed{R-B=S}$

thioxoborane

Tbt =

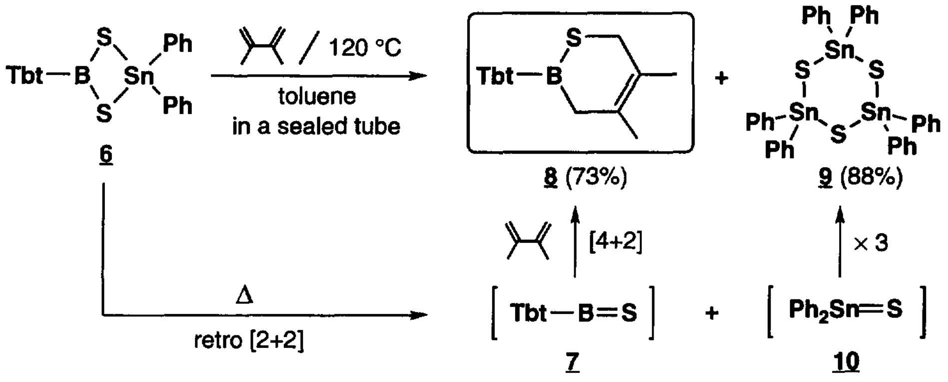


Recently, we have reported the synthesis and crystallographic structural analysis of the first stable dimercaptoborane bearing Tbt group, TbtB(SH)$_2$ **3**, and found that **3** can be utilized as a good precursor for the synthesis of a novel titanium-containing four-membered boracycle **4** (Z = TiCp$_2$; Cp = cyclopentadienyl) by way of its lithiation.[8] Using this methodology we have succeeded in the synthesis of new types of dithiaboretane derivatives containing heavier group 14 elements, a 1,3,2-dithiagermaboretane derivative **5** (Z = GeMes$_2$; Mes = mesityl) and its tin-analogue **6** (Z = SnPh$_2$), as stable crystalline compounds (Scheme 1).[9,10]



Scheme 1

Since the structures of the four-membered rings of **5** and **6** are exactly those of [2+2]cycloaddition products of thioxoborane **7** (Tbt–B=S) with the corresponding germanethione ($Mes_2Ge=S$) and stannanethione ($Ph_2Sn=S$), respectively, we examined the thermal retrocycloaddition of **5** and **6** in the presence of appropriate 1,3-dienes in the hope of trapping the regenerated thioxoborane **7**. On heating a toluene solution (20 ml) of the dithiastnnaboretane **6** (53.1 mg, 0.059 mmol) at 120 °C for 5 days in a sealed tube in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (0.6 ml, 94 equiv.), 4,5-dimethyl-1,2-thiaboracyclohex-4-ene **8** (29.0 mg, 73%) was obtained together with the trimer of diphenylstannanethione **9** (15.9 mg, 88%) as shown in Scheme 2,[10] while no change was observed for **5** even under severer reaction conditions (180 °C, 20 h).

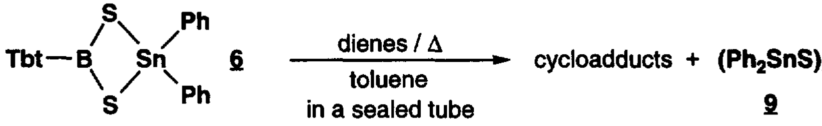


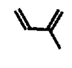
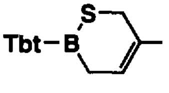
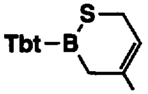
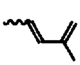
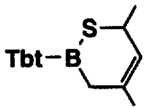
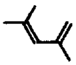
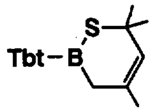
Scheme 2

The formation of **8** and **9** in the thermolysis of **6** can be reasonably interpreted in terms of the initial retro [2+2]cycloaddition of the dithiastannaboretane ring into the expected two 2π systems, *i. e.* thioxoborane **7** and diphenylstannanethione **10**, followed by [4+2]cycloaddition reaction of **7** with co-existing 2,3-dimethyl-1,3-butadiene and the self-trimerization of **10**, respectively. To the best of our knowledge, this is the first example of generation and trapping reactions of a thioxoborane.

The effective generation of **7** from **6** and its high reactivity toward 2,3-dimethyl-1,3-butadiene prompted us to examine [4+2]cycloaddition reactions of **7** with other unsymmetric dienes, *i. e.* isoprene, 2-methyl-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene. As shown in Table 1, all the three dienes afforded expected [4+2]cycloadducts with **7** in moderate to good yields. Although the cycloaddition reactions of **7** with dienes were found to proceed regiosepcifically in the cases of the latter two 1,3-pentadienes (entries 2 and 3) probably due to the considerable steric hindrance for the boron side of the thioxoborane unit in **7**, thermolysis of **6** at 120 °C in the presence of isoprene afforded both of the two possible regioisomers **11** and **12** in 62 and 31% yields, respectively (entry 1). The regioselectivity of cylcoaddition of **7** with isoprene was almost lost at higher temperature (170 °C), suggesting an equilibrium between **11** and **12** via their retro [4+2]cycloaddition. Furthermore, we have found that the thermolysis of a 1:1 mixture of the isoprene adducts **11** and **12** at 170 °C in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene resulted in exclusive formation of the diene-exchanged cycloadduct **8** in 70% yield.

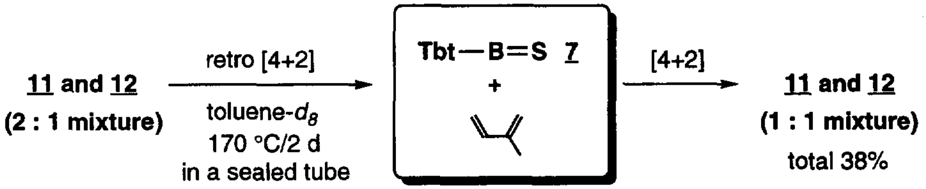
Table 1. Thermolysis of Dithiastannaboretane 6 in the Presence of Unsymmetrical Dienes



entry	diene	temp / °C	product (yield)	
1				+ 
		120	11 (62%)	12 (31%)
		170	11 (33%)	12 (37%)
2		120	 13 (68%)	—[a]
3		120	 14 (59%)	—[a]

[a] No the other regioisomer was obtained in these cases.

Cycloadduct 8 also underwent ready retro [4+2]-cycloaddition reaction at 170 °C in the presence of isoprene (excess) to give a 1:1 mixture of 11 and 12 (total 59%). These results showed that not only the dithiastannaboretane 6 but also the 1,2-thiaboracyclohex-4-enes here obtained can be used as good precursors for thioxoborane 7 .



Scheme 3

Finally, we have examined the retro [4+2]cycloaddition reaction of the diene adduct of thioxoborane 7 in the absence of an external trapping reagent. Monitoring by ^{1}H NMR spectroscopy of the thermolysis of the 2:1 mixture of 11 and 12 in toluene-d_8 at 170 °C for 2 days showed a gradual decrease of the molar ratio of 11 to 12 to 1:1, and a mixture of 11 and 12 (almost 1:1) was obtained in 38% yield after chromatographic separation (Scheme 3). These results suggest that thioxoborane 7 thus formed does not dimerize instantaneously but can survive as a monomeric species even in a hot solution at 170 °C and has a sufficient lifetime to undergo [4+2]cycloaddition reaction with equimolar amount of the dissociated diene (isoprene) to regenerate an equilibrated mixture of the starting cycloadducts **11** and **12**.

In summary, we have succeeded in the generation of a kinetically stabilized thioxoborane Tbt-B=S (**7**), which is among a novel class of unsaturated organoboron compounds, and revealed its high dienophilic reactivity in the [4+2]cycloaddition reactions with 1,3-dienes. Further investigation on the structure and reactivity of **7** is currently in progress.

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9. The molecular structures of newly obtained boron-containing metallacycles **5** and **6** have been determined definitively by X-ray crystallographic analysis, the details of which will be described elsewhere.
10. All the new compounds described here gave satisfactory spectral and analytical data, among which those for compounds **6** and **8** are listed as representatives as follows.
    6: colorless crystals, mp 175 °C (decomp); ^{1}H NMR(500 MHz, $CDCl_3$) δ 0.05 (s, 18H), 0.10 (s, 36H), 1.34 (s, 1H), 2.03 (br s, 2H), 6.24 (br s, 1H), 6.35 (br s, 1H), 7.55 (m, 6H), 7.90 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.64 (q), 0.85 (q), 29.70 (d), 30.18(d), 120.64 (d), 124.95 (d), 129.48 (d), 131.18 (d), 136.06 (d), 138.18 (s), 139.52 (s), 143.25 (s), 143.57 (s); ^{11}B NMR(86.4 MHz, $CDCl_3$) δ 74.5; ^{119}Sn NMR(100 MHz, $CDCl_3$) δ -73.97. HRMS(FAB): m/z Calcd for $C_{39}H_{69}Si_6S_2BSn$: 900.2571. Found: 900.2475. Anal. Calcd for $C_{39}H_{69}Si_6S_2BSn \cdot 0.5H_2O$: C, 51.52; H, 7.76; S, 7.05. Found: C, 51.23; H, 7.77; S, 7.52.
    8: colorless crystals, mp 176 °C (decomp); ^{1}H NMR(500 MHz, $CDCl_3$) δ -0.01 (s, 18H), 0.02 (s, 18H), 0.03 (s, 18H), 1.07 (br s, 2H), 1.29 (s, 1H), 1.82 (br s, 3H), 1.83 (br s, 3H), 2.14 (br s, 2H), 3.22 (br s, 2H), 6.19 (br s, 1H), 6.31 (br s, 1H);.^{13}C NMR(125 MHz, $CDCl_3$) δ 0.65 (q). 0.94 (q), 19.75 (q), 21.51 (q), 29.51 (d), 29.97 (d), 33.37 (t), 35.77 (t), 120.87 (d), 124.87 (s), 125.31 (d), 127.91 (s), 128.18 (s), 142.51 (s), 143.69 (s). ^{11}B NMR(86.4 MHz, $CDCl_3$) δ 75.3. HRMS(FAB): m/z Calcd for $C_{33}H_{69}Si_6SB$: 676.3843. Found: 676.3829. Anal. Calcd for $C_{33}H_{69}Si_6SB \cdot 0.5CH_2Cl_2$: C, 55.90; H, 9.80; S, 4.45. Found C, 55.63; H, 9.71; S, 5.04.

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