Reaction of an Overcrowded Distibene with Elemental Sulfur and Crystallographic Analysis of the Sulfurization Products

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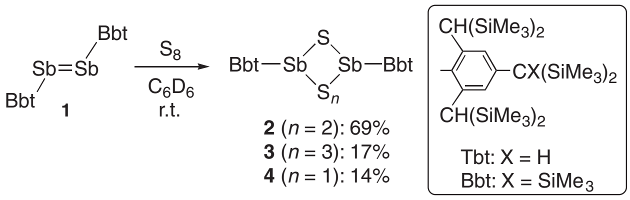
The reaction of a kinetically stabilized distibene bearing 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl (denoted as Bbt) groups with elemental sulfur resulted in the formation of three types of sulfurization products containing two antimony atoms. The first structural identification of the 1,2,4,3,5-trithiadistibolane derivative was achieved by X-ray crystallographic analysis.

Recent active works on the chemistry of doubly-bonded systems between heavier group 15 elements have demonstrated that they are not fictitious any longer and have real existence as stable compounds even in the case of the heaviest group 15 element, bismuth, when they are kinetically well stabilized.[1] Currently, there is a widespread interest in the reactivity of these fascinating doubly-bonded systems. Although several reactions of diphosphenes (RP=PR) and diarsenes (RAs=AsR) have been reported,[1a,b,d] the reactivities of their heavier congeners, distibenes (RSb=SbR) and dibismuthenes (RBi=BiR), are not fully explored. Up to date, only three examples of stable distibenes and dibismuthenes have been recently reported,[2,3] and we have succeeded in the synthesis and characterization of the first stable distibene (TbtSb=SbTbt)[2b] and dibismuthene (TbtBi=BiTbt)[2a] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group. In addition, we have already reported the unique oxidation reactions of TbtSb=SbTbt and TbtBi=BiTbt with atmospheric oxygen in the solid state to give the corresponding 1,3,2,4-dioxadipnictogetane derivatives.[2] Although further studies on the reactivities of TbtE=ETbt (E=Sb, Bi) in solution have been thwarted by their extremely low solubility in common organic solvents, we have recently succeeded in the synthesis of soluble distibene and dibismuthene bearing a new substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl (denoted as Bbt) group,[2c] and started studies on the reactivities of BbtE=EBbt (E=Sb, Bi) in solution. At the first stage of studies on reactivities of heavier dipnictenes ("pnictogen" is the general term for group 15 elements), we decided to elucidate the reactivity of the soluble distibene and dibismuthene with elemental chalcogens from the viewpoint of comparison with the oxidation reaction by atmospheric oxygen. Here, we wish to describe the reaction of BbtSb=SbBbt with elemental sulfur leading to the formation of three types of antimony-containing cyclic polysulfides, all of which were structurally characterized by X-ray crystallographic analysis.

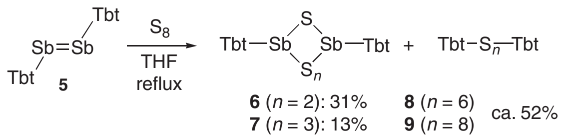
When a benzene-d_6 solution (0.7 mL) of **1** (96 mg, 0.064 mmol), which was easily prepared by reductive coupling reaction of $BbtSbBr_2$ with Mg in almost quantitative yield, was mixed with an excess amount of elemental sulfur (S_8, 20 mg, 9.8 equiv. as S) at room temperature, deep-orange color of the solution gradually changed to yellow. After standing the solution for 1 h, three types of antimony-containing cyclic polysulfides, 1,2,4,3,5-trithiadistibolane **2** (69%), 1,2,3,5,4,6-tetrathiadistibinane **3** (17%), and 1,3,2,4-dithiadistibetane **4** (14%) were obtained without any other identifiable compounds as judged by the ^{1}H NMR spectrum of the crude solution.[4] It was very difficult to perform the complete separation of **2**, **3**, and **4** from each other by HPLC and column chromatography, because they gradually decomposed through separation procedures. However, small amounts of pure **2**, **3**, and **4** were isolated and identified via persistent purification by recrystallization and column chromatography. This result contrasts with the case of diphosphenes, the lighter analogue of distibenes, which are known to react with elemental sulfur to give three-membered ring compounds, thiadiphosphiranes.[5] We examined the reaction of **1** with 1 equiv. (as S) of elemental sulfur at room temperature in the hope of obtaining Bbt-substituted thiadistibirane, a possible intermediate to give **2**, **3**, and **4**. As a result, ^{1}H NMR spectrum showed that the reaction mixture contained unidentified compound **X** as a main product together with **1**, **2**, and **4**. Unfortunately, compound **X**, which might be a thiadistibirane derivative, could not be isolated because of its extreme sensitivity toward air and moisture.[6]



Scheme 1.

On the other hand, we have already revealed that the reaction of TbtSb=SbTbt (**5**) with elemental sulfur in THF, in which **5** may be slightly more soluble than in C_6D_6, did not proceed at room temperature probably due to the extremely low solubility of **5**. Refluxing the reaction mainly produced a mixture of the linear polysulfides **8** and **9** (ca. 52%) containing no Sb atom, together with Tbt-substituted 1,2,4,3,5-trithiadistibolane **6** (31%) and 1,2,3,5,4,6-tetrathiadistibinane **7** (13%).[7] The linear polysulfides **8** and **9** are most likely generated via the over reaction of **6** and/or **7** with S_8 at such high temperature. Since the soluble distibene **1** was found to react with S_8 easily at room temperature, it can be concluded that the results of the reaction of BbtSb=SbBbt (**1**) with S_8 described here might reflect the more inherent reactivity of a distibene with S_8.

Single crystals of the new 1,2,4,3,5-trithiadistibolane [**2**·hexane] were obtained by the recrystallization from hexane, and its unique molecular structure was revealed by X-ray crystallographic analysis.[8] It should be noted that this is the first ex-



Scheme 2.

ample of a 1,2,4,3,5-trithiadistibolane ring system. In Figure 1 are shown the ORTEP drawing and the selected structural parameters of **2**. One can see the half-chair geometry for the central 1,2,4,3,5-trithiadistibolane ring skeleton. The two sulfur atoms S2 and S3 lie at almost equal distance on both sides of the plane defined by Sb1, Sb2, and S1 [Figure 1a]. The Sb–S bond lengths [2.4349(8), 2.4806(7), 2.4398(7), and 2.4833(7) Å] in **2** are comparable with those of W(CO)$_5$ complex of *cyclo*-R$_2$Sb$_2$S$_2$ [R = CH(SiMe$_3$)$_2$; Sb–S: 2.425(1), 2.428(1) Å].[9] The S–S bond-length [2.0586(9) Å] in **2** is within a range of normal single bond lengths.

We also succeeded in the structural characterization of **3**.[8] Figure 2 shows the chair-conformation of the central 1,2,3,5,4,6-tetrathiadistibinane ring of **3**. It was found that the 1,2,3,5,4,6-tetrathiadistibinane ring was disordered (78:22) due to the flipping of the six-membered ring. In both cases of the two types of chair-conformations, two Bbt groups on the antimony atoms are in equatorial positions. The structural parameters of **3** are similar to those of previously reported **7**.[10] Although the structural parameters of **4** were not determined definitively due to the low quality of the single crystals, the 1,3,2,4-dithiadistibetane skeleton of **4** was confirmed by X-ray crystallographic analysis.[8]

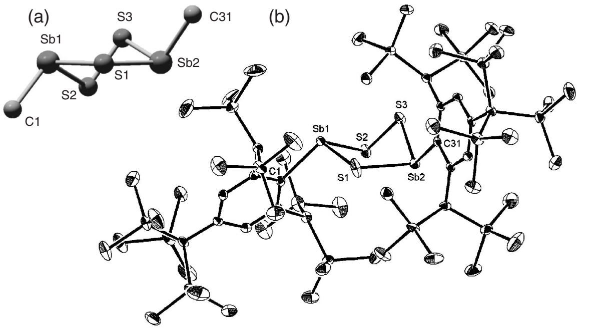


Figure 1. (a) Side view of the Sb$_2$S$_3$ ring in **2**. (b) ORTEP drawing of **2** with thermal ellipsoid plot (50% probability). The solvated hexane molecule was omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb1–S1 2.4349(8), Sb1–S2 2.4806(7), Sb2–S1 2.4398(7), Sb2–S3 2.4833(7), S2–S3 2.0586(9), Sb1–S1–Sb2 101.90(3), S1–Sb1–S2 94.40(2), Sb1–S2–S3 91.04(3), S2–S3–Sb2 91.21(3), S1–Sb2–S3 94.96(2).

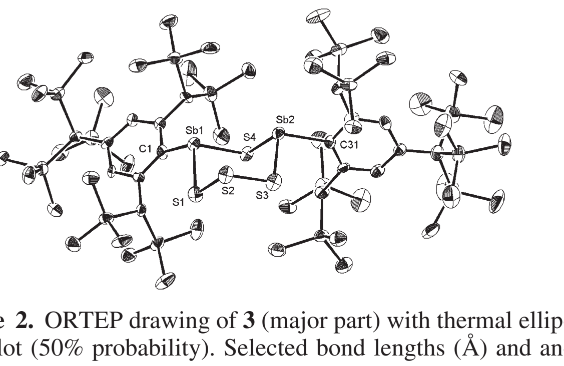


Figure 2. ORTEP drawing of **3** (major part) with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and angles (deg) for the major part: Sb1–S1 2.473(3), Sb1–S4 2.449(4), Sb2–S3 2.455(4), Sb2–S4 2.443 (4), S1–S2 2.067(5), S2–S3 2.068(5), S1–Sb1–S4 95.18(13), Sb1–S1–S2 95.10(16), S1–S2–S3 107.4(2), S2–S3–Sb2 97.54(17), S3–Sb2–S4 97.75(13), Sb1–S4–Sb2 93.20(13).

It should be noted again that the reaction products of distibenes with elemental sulfur are different from those reported for diphosphenes, though their formation mechanism is not clear at present. Further elucidation of the chemical properties of heavier dipnictenes is currently in progress.

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4 All the new products here obtained (**2**–**4**) showed satisfactory spectral and analytical data. The spectral data for **2** as the representative are shown as follows. **2**: yellow crystals, mp 186.0–186.7 °C (dec.); ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.34 (s, 126H), 2.59 (s, 4H), 7.04 (s, 4H); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 1.70 (q), 1.89 (q), 5.60 (q), 22.74 (s), 34.84 (d), 128.12 (d), 147.61 (s), 147.94 (s), 151.12 (s). HRMS(FAB) *m/z* Obsd 1589.4515 ([M + H]$^+$) Calcd for $C_{60}H_{135}S_3{}^{123}Sb_2\ Si_{14}$: 1589.4586. Anal. Found: C, 47.66; H, 9.00%. Calcd for $C_{60}H_{134}S_3Sb_2Si_{14}\cdot C_6H_{14}$: C, 47.65; H, 8.95%.

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6 The spectral data for compound **X** are shown as follows: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.32 (s, 126H), 2.96(s, 4H), 6.94(s, 4H). Compound **X** gave a complicated mixture containing BbtH on exposure to the air and moisture.

7 N. Tokitoh, Y. Arai, and R. Okazaki, unpublished results (Y. Arai, Thesis, The University of Tokyo, 1996.)

8 The intensity data for single crystals of [**2**·hexane], **3** and **4** were collected on a Rigaku/MSC Mercury CCD diffractometer. Crystallographic data for [**2**·hexane]: $C_{66}H_{148}S_3Sb_2Si_{14}$, $FW = 1674.78$, $T = 103(2)$ K, triclinic, $P-1$ (#2), $a = 12.9972(16)$ Å, $b = 18.119(2)$ Å, $c = 21.906(2)$ Å, $\alpha = 69.779(3)°$, $\beta = 73.807(4)°$, $\gamma = 87.957(5)°$, $V = 4638.3(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.199\ \mathrm{g\,cm^{-3}}$, $R_1 = 0.0312$ [$I > 2\sigma(I)$], w$R_2 = 0.0781$ [all data] (CCDC222751); **3**: $C_{60}H_{134}S_4Sb_2Si_{14}$, $FW = 1620.67$, $T = 103(2)$ K, monoclinic, $P2_1/a$ (#14), $a = 24.764(10)$ Å, $b = 12.656(5)$ Å, $c = 28.522(12)$ Å, $\beta = 103.468(4)°$, $V = 8693(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.238\ \mathrm{g\,cm^{-3}}$, $R_1 = 0.1059$ [$I > 2\sigma(I)$], w$R_2 = 0.2307$ [all data] (CCDC222752); **4**: $C_{60}H_{134}S_3Sb_2Si_{14}$, $FW = 1588.61$, $T = 103(2)$ K, monoclinic, $P2_1/c$ (#14), $a = 8.918(19)$ Å, $b = 12.90(3)$ Å, $c = 36.44(7)$ Å, $\beta = 91.16(2)°$, $V = 4192(15)$ Å^3, $Z = 2$, $D_{calcd} = 1.259\ \mathrm{g\,cm^{-3}}$.

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