Heteroatom Chemistry
Volume 12, Number 4, 2001

Formation of Antimony–Sulfur Double-Bond Compounds and Their Trapping with Nitrile Oxides

Norihiro Tokitoh,[1] Yoshimitsu Arai,[2] Takahiro Sasamori,[3] Nobuhiro Takeda,[1] and Renji Okazaki[2]

[1]*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan; tokitoh@boc.kuicr.kyoto-u.ac.jp*

[2]*Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan*

[3]*Department of Chemistry and Physics of Condensed Matter, Graduate School of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*

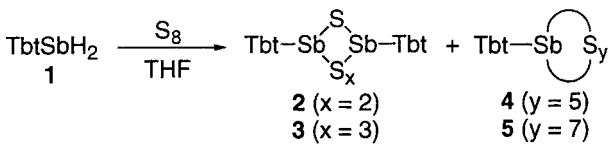
Received 12 December 2000; revised 5 February 2001

ABSTRACT: *The reaction of a highly crowded dihydrostibine [2,4,6-tris[bis(trimethylsilyl)methyl]phenyl-SbH_2 ($TbtSbH_2$) (**1**)] with elemental sulfur in the presence of nitrile oxides resulted in the formation of [2 + 3]cycloaddition reaction products of a thioxostibine [TbtSb=S (**6**)] and a dithioxostiborane [TbtSb(S)=S (**7**)], which are among a novel class of antimony–sulfur double-bond compounds. The structures of the [2 + 3] cycloadducts of dithioxostiborane **7** with nitrile oxides were determined by X-ray structural analysis. Desulfurization of highly crowded antimony-containing cyclic polysulfides [$TbtSbS_x$ (**4**: x = 5; **5**: x = 7)] with phosphine reagents also resulted in the formation of* **6** *and* **7**. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:244–249, 2001

INTRODUCTION

The chemistry of compounds featuring double-bond-containing heavier group 15 elements has attracted attention in recent years [1]. Various double bonds of group 15–group 15 and group 14–group 15 elements have already been reported. As for the low-coordinated double-bond compounds between group 15 and group 16 elements, dithioxophosphorane [RP(S)=S][2] and diselenoxo-phosphorane [RP(Se)=Se][3], have been synthesized as stable compounds, and thioxophosphines [RP=S][4] and selenoxophosphines [RP=Se][5] stabilized by the coordination of an amino group have been observed in solution by NMR spectroscopy. However, there are no reports about the double bond of antimony with sulfur.

On the other hand, we have already reported the synthesis of antimony-containing cyclic polysulfides (**2–5**) by the reaction of dihydrostibine **1** with elemental sulfur (Scheme 1) together with their struc-



SCHEME 1

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

Correspondence to: Norihiro Tokitoh.

Contract Grant Sponsor: Ministry of Education, Science, Sports, and Culture, Japan.

© 2001 John Wiley & Sons, Inc.

tural analysis [6]. From the mechanistic point of view, intermediacy of reactive species containing a Sb=S bond, that is, thioxostibine [TbtSb=S (**6**)] and/or dithioxostiborane [TbtSb(S)=S (**7**)], is conceivable in this reaction. In this article, we describe the formation of thioxostibine **6** and dithioxostiborane **7**, intermediates that were confirmed by trapping reactions with nitrile oxides.

RESULTS AND DISCUSSION

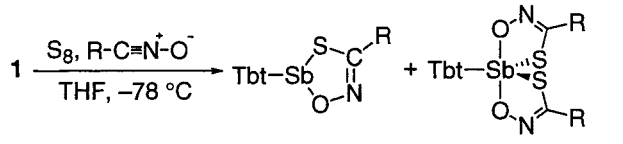
When the reaction of dihydrostibine **1** with elemental sulfur was performed in the presence of RCNO {R = mesityl (Mes) [7], 2,4,6-trimethoxyphenyl (Tmp) [8]}, two new products **8** and **9** containing the nitrile oxide unit were obtained (Scheme 2). Both **8** and **9** have a novel antimony-containing five-membered ring system, namely, a 1,3,5,2-oxathiazastibole skeleton, and can be regarded as the [2 + 3] cycloaddition products of the nitrile oxide with the thioxostibine (TbtSb=S) and the dithioxostiborane [TbtSb(S)=S],
respectively (Scheme 3). Especially, the formation of spirocyclic compounds **9a** and **9b** is very interesting because these compounds have a pentacoordinate antimony atom, with the two Mes and Tmp groups appearing to be equivalent in the ^{1}H and ^{13}C NMR spectra.

Interestingly, no cycloaddition product was obtained when the much bulkier nitrile oxide 2,4,6-tri-*tert*-butylphenyl–CNO (Mes*CNO) was used, probably due to the steric repulsion between the large substituents, Tbt and Mes* groups.

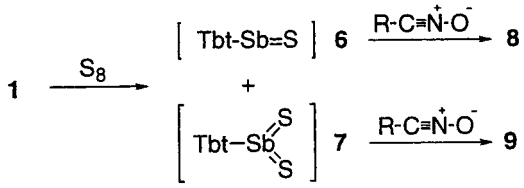
The molecular structures of **9a** and **9b** were determined by X-ray crystallographic analyses. Figures 1 and 2 show the ORTEP drawings of these cyclic compounds. Selected bond lengths and angles are listed in Tables 1 and 2. Figures 1 and 2 show the distorted trigonal bipyramidal structures of the spiro compounds **9a** and **9b**, with the oxygen atoms in apical positions. The sums of the angles around the antimony atom in the equatorial plane are 359.99° (for **9a**) and 360.01° (for **9b**), and the angles of O–Sb–O are slightly deviated [166.1° (for **9a**) and 166.4° (for **9b**)] from the ideal trigonal bipyramidal (*TBP*) structure (180°). The structures of the 1,3,5,2-oxathiazastibole rings of **9a** and **9b** are very similar to each other.

The X-ray structural analysis of **8b** [9] was also performed and the preliminary results supported the proposed structure, although the data were not good enough for publication, probably due to the poor quality of the crystal.

Since the cyclic polysulfides **4** and **5** can also be



SCHEME 2



SCHEME 3

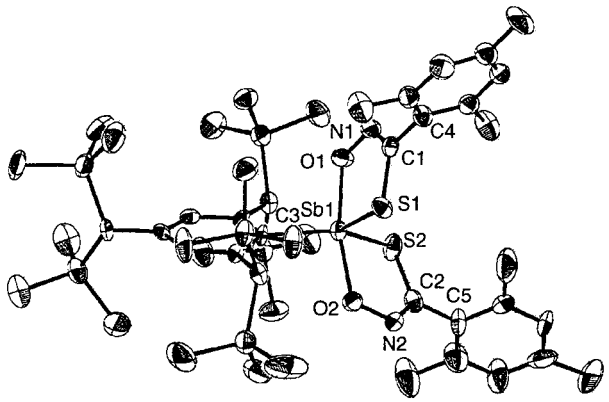


FIGURE 1 ORTEP drawing of **9a** with thermal ellipsoid plots (30% probability for nonhydrogen atoms).

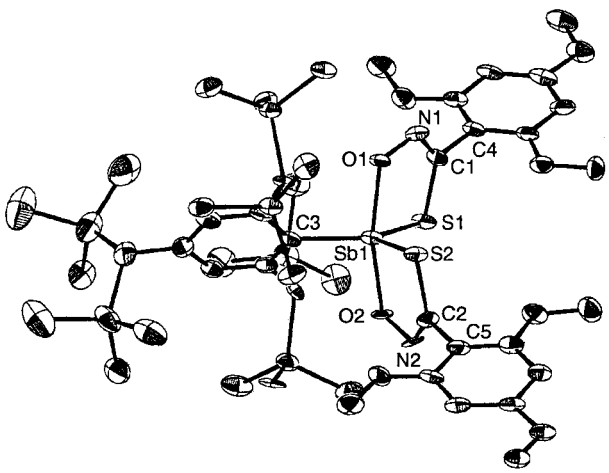


FIGURE 2 ORTEP drawing of **9b** with thermal ellipsoid plots (50% probability for nonhydrogen atoms).

TABLE 1 Selected Bond Lengths (Å) and Angles (°) of **9a**

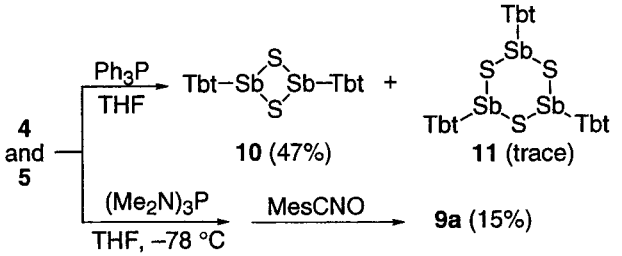
Sb(1)–C(3)	2.161(10)		
Sb(1)–O(1)	2.041(8)	Sb(1)–O(2)	2.047(8)
Sb(1)–S(1)	2.404(3)	Sb(1)–S(2)	2.386(4)
S(1)–C(1)	1.779(13)	S(2)–C(2)	1.754(14)
N(1)–C(1)	1.287(13)	N(2)–C(2)	1.286(14)
N(1)–O(1)	1.359(11)	N(2)–O(2)	1.392(12)
C(1)–C(4)	1.481(16)	C(2)–C(5)	1.495(17)
O(1)–Sb(1)–O(2)	166.1(3)		
S(1)–Sb(1)–S(2)	111.39(13)		
S(1)–Sb(1)–C(3)	126.2(3)	S(2)–Sb(1)–C(3)	122.4(3)
O(1)–Sb(1)–C(3)	95.3(4)	O(2)–Sb(1)–C(3)	95.3(4)
S(1)–Sb(1)–O(1)	82.0(2)	S(2)–Sb(1)–O(2)	82.4(3)
Sb(1)–S(1)–C(1)	94.1(4)	Sb(1)–S(2)–C(2)	93.7(5)
S(1)–C(1)–N(1)	123.4(9)	S(2)–C(2)–N(2)	124.0(11)
O(1)–N(1)–C(1)	118.6(10)	O(2)–N(2)–C(2)	117.9(11)
Sb(1)–O(1)–N(1)	120.8(6)	Sb(1)–O(2)–N(2)	117.2(6)

TABLE 2 Selected Bond Lengths (Å) and Angles (°) of **9b**

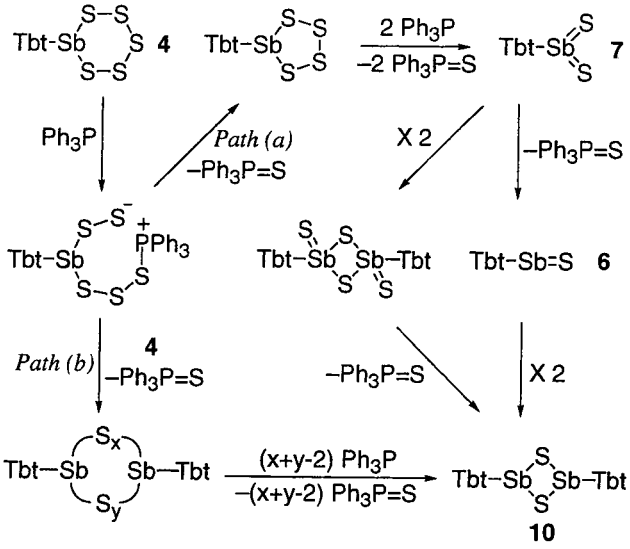
Sb(1)–C(3)	2.137(8)		
Sb(1)–O(1)	2.058(4)	Sb(1)–O(2)	2.051(4)
Sb(1)–S(1)	2.390(2)	Sb(1)–S(2)	2.394(2)
S(1)–C(1)	1.769(7)	S(2)–C(2)	1.804(8)
N(1)–C(1)	1.300(10)	N(2)–C(2)	1.257(10)
N(1)–O(1)	1.413(8)	N(2)–O(2)	1.413(8)
C(1)–C(4)	1.473(10)	C(2)–C(5)	1.500(10)
O(1)–Sb(1)–O(2)	166.4(2)		
S(1)–Sb(1)–S(2)	116.41(8)		
S(1)–Sb(1)–C(3)	121.6(2)	S(2)–Sb(1)–C(3)	122.0(2)
O(1)–Sb(1)–C(3)	97.2(2)	O(2)–Sb(1)–C(3)	96.4(2)
S(1)–Sb(1)–O(1)	83.19(15)	S(2)–Sb(1)–O(2)	83.26(15)
Sb(1)–S(1)–C(1)	94.4(3)	Sb(1)–S(2)–C(2)	93.8(2)
S(1)–C(1)–N(1)	125.1(6)	S(2)–C(2)–N(2)	124.9(5)
O(1)–N(1)–C(1)	116.8(6)	O(2)–N(2)–C(2)	118.1(5)
Sb(1)–O(1)–N(1)	118.9(4)	Sb(1)–O(2)–N(2)	119.4(4)

regarded as possible precursors of the antimony-sulfur doubly bonded compounds, as in the cases of double-bond compounds between heavier group 14 and group 16 elements, that is, heavy ketones [10–12], the desulfurization reactions of **4** and **5** were investigated using triphenylphosphine as a desulfurizing reagent. When the mixture of **4** and **5** was treated with an excess amount of Ph_3P in THF [13], the orange precipitate of 1,3,2,4-dithiadistibetane **10** was obtained (47%), together with a trace amount of trithiatristibane **11** (Scheme 4).

A plausible mechanism of this reaction is shown in Scheme 5, where the reaction starting from **4** is depicted for simplicity. First, triphenylphosphine attacks **4** to open the polysulfide ring. When it recyclizes with the loss of triphenylphosphine sulfide, there are two possible reaction pathways: (*a*) an intramolecular recyclization or (*b*) an intermolecular recyclization. If it proceeds by path (*a*), repeated desulfurization generates dithioxostiborane **7**. The dithioxostiborane **7** can then dimerize to give the Lawesson's Reagent-type of compound, which will lose two more sulfur atoms to afford **10**. On the other hand, the dithioxostiborane **7** may lose a sulfur atom, first to give thioxostibine **6**, which will then dimerize to give **10**. If it proceeds by path (*b*), the cyclic compound with two TbtSb units will continue to be desulfurized by Ph_3P until **10** is obtained.



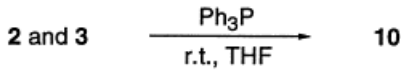
SCHEME 4



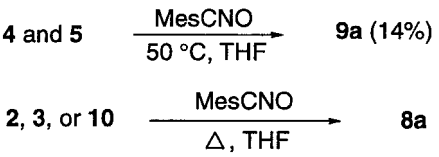
SCHEME 5

To clarify the mechanism of this reaction, MesCNO was added to the reaction mixture shortly after the treatment of **4** and **5** with the desulfurizing reagent at −78°C. The reaction afforded the double [2 + 3] cycloadduct **9a**, albeit in low yield (15%) (Scheme 4). This fact suggests that the reaction does take path (*a*), where the nitrile oxide can trap the intermediary dithioxostiborane **7**. But this does not rule out the possibility that some part of the reaction proceeds by path (*b*). The feasibility of path (*b*) is supported by the reactions of the cyclic compounds **2** and **3** with Ph_3P, giving dithiadistibetane **10** (Scheme 6).

In anticipation of generating the Sb=S doubly



SCHEME 6



SCHEME 7

bonded species in the process of thermal decomposition of antimony-containing cyclic polysulfides, a THF solution of the mixture of **4** and **5** was heated at 50°C for 30 hours in the presence of MesCNO. This reaction afforded **9a**, the double [2 + 3] cycloaddition product of dithioxostiborane **7** (Scheme 7).

By way of contrast, the thermolyses of the cyclic compounds **2, 3**, and **10** in the presence of MesCNO gave quite a different result. No double cyclization product **9a** was obtained in any of these reactions, but instead the 1:1 cycloadduct **8a** (Scheme 7) was formed, indicating the intermediacy of thioxostibine **6**.

Thermolyses of **9a** and **8a** were also examined in the hope of regeneration of **7** and **6**, since their high-resolution mass spectra showed prominent peaks of $[M\text{-}MesCNO]^+$. When **9a** was heated in toluene-d_8 at 120°C for 50 hours, the pentavalent antimony was reduced to give the trivalent antimony compound **8a**. This type of reduction to organoantimony(III) compounds is often observed in the thermolyses of organoantimony(V) compounds. Compound **8a** was further decomposed by thermolysis at higher temperature to give TbtH and MesNCS, together with the formation of white inorganic salts. This type of thermal cycloreversion of five-membered ring systems is reported in the cases of oxathiazole and oxaselenazole [14]. The thermal decomposition of the oxathiazastibole ring of **8a** probably gives MesNCS and TbtSb=O, which will further decompose to give TbtH and Sb_2O_3.

In summary, formation of thioxostibine **6** and dithioxostiborane **7** was strongly suggested in the reaction of dihydrostibine **1** with elemental sulfur and also in the desulfurization reaction of polysulfides **4** and **5** with phosphine reagents. Further investigations of the properties of **6** and **7** are currently in progress.

EXPERIMENTAL

Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. Tetrahydrofuran (THF) was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 or LC-908-C60 with JAIGEL 1H and 2H columns (Japan Analytical Industry) with chloroform or toluene as the solvent. Dry column chromatography (DCC) was performed with ICN silica DCC 60A. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker AM-500, JEOL α-500, or JEOL EX-270 spectrometer using $CHCl_3$ as an internal standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Reaction of TbtSbH$_2$ **1***[6] with Elemental Sulfur in the Presence of MesCNO [7]*

To a mixture of TbtSbH$_2$ **1** (615 mg, 0.65 mmol), elemental sulfur (84 mg, 0.33 mmol as S_8), and MesCNO (314 mg, 1.95 mmol), 40 mL of THF was added at −78°C. Then the reaction mixture was warmed to room temperature, and the solvent was evaporated under reduced pressure. Purification by GPLC afforded TbtSbS·MesCNO **8a** (180 mg, 32%) and TbtSbS$_2$·2MesCNO **9a** (136 mg, 20%). TbtSbS·MesCNO **8a**: yellow crystals; m.p. 195–198°C (dec); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 18H), 0.09 (s, 18H), 0.11 (s, 18H), 1.34 (s, 1H), 1.79 (s, 2H), 2.22 (s, 6H), 2.28 (s, 3H), 6.33 (s, 1H), 6.48 (s, 1H), 6.85 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 0.65 (q), 0.72 (q), 0.91 (q), 1.11 (q), 19.8 (q), 21.1 (q), 30.2 (d), 30.7 (d), 123.7 (d), 125.3 (s), 128.4 (d), 128.5 (d), 143.9 (s), 145.6 (s), 148.7 (s), 149.8 (s). High-resolution fast atom bombardment mass spectrometry FABMS: observed *m/z* 866.2910; calcd for $C_{37}H_{71}ONSi_6SSb$ 866.2910. Anal. Calcd for $C_{37}H_{71}ONSi_6SSb$: C, 51.24; H, 8.14; N, 1.61; S, 3.70. Found: C, 51.06; H, 8.05; N, 1.90; S, 4.55. TbtSbS$_2$·2MesCNO **9a**: yellow crystals; m.p. 219–221°C; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18H), 0.11 (s, 9H), 0.127 (s, 9H), 0.134 (s, 9H), 0.15 (s, 9H), 1.47 (s, 1H), 2.09 (s, 1H), 2.13 (s, 1H), 2.16 (s, 12H), 2.28 (s, 6H), 6.56 (s, 1H), 6.66 (s, 1H), 6.87 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 0.60 (q), 0.89 (q), 1.06 (q), 19.6 (q), 21.1 (q), 31.2 (d), 35.1 (d), 35.6 (d), 122.3 (d), 126.9 (d), 128.4 (d), 129.4 (s), 142.3 (s), 146.2 (s), 149.0 (s), 149.1 (s), 149.2 (s). High-resolution FABMS: observed *m/z* 1061.3414; calcd for $C_{47}H_{82}O_2N_2Si_6S_2Sb$ 1061.3475

([M + H]$^+$). Anal. Calcd for $C_{47}H_{81}O_2N_2Si_6S_2Sb$: C, 53.22; H, 7.69; N, 2.64; S, 6.04. Found: C, 52.35; H, 7.88; N, 3.29; S, 6.38.

Reaction of TbtSbH$_2$ **1** *with Elemental Sulfur in the Presence of 2,4,6-Trimethoxyphenylnitrile Oxide (TmpCNO) [8]*

To a mixture of TbtSbH$_2$ **1** (154 mg, 0.20 mmol), elemental sulfur (51.7 mg, 0.20 mmol as S_8), and TmpCNO (92 mg, 0.44 mmol), 15 mL of THF was added at −78°C. Then the reaction mixture was warmed to room temperature, and the solvent was evaporated under reduced pressure. Purification by GPLC and DCC ($CHCl_3$:EtOH = 100:1) afforded TbtSbS·TmpCNO **8b** (31 mg, 17%) and $TbtSbS_2$·2TmpCNO **9b** (21.6 mg, 9%). TbtSbS·TmpCNO **8b**: yellow crystals; m.p. 225–226°C (dec); ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 18H), 0.07 (s, 18H), 0.09 (s, 18H), 1.32 (s, 1H), 1.84 (s, 2H), 3.65 (s, 6H), 3.80 (s, 3H), 6.07 (s, 2H), 6.30 (s, 1H), 6.44 (s, 1H). High-resolution FABMS: observed *m/z* 916.2795; calcd for $C_{37}H_{71}O_4NSi_6SSb$ 916.2762. Anal. Calcd for $C_{37}H_{71}O_4NSi_6SSb$: C, 48.55; H, 7.70; N, 1.53; S, 3.50. Found: C, 48.92; H, 7.75; N, 2.05; S, 4.17. $TbtSbS_2$·2TmpCNO **9b**: yellow crystals; m.p. 242–244°C (dec); ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 18H), 0.10 (s, 18H), 0.12 (s, 18H), 1.43 (s, 1H), 2.14 (s, 1H), 2.17 (s, 1H), 3.65 (s, 12H), 3.81 (s, 6H), 6.07 (s, 4H), 6.48 (s, 1H), 6.58 (s, 1H). High-resolution FABMS: observed *m/z* 1157.3254; Calcd for $C_{47}H_{82}O_8N_2Si_6S_2Sb$ 1157.3170 ([M + H]$^+$). Anal. Calcd for $C_{47}H_{81}O_8N_2Si_6S_2Sb$: C, 48.80; H, 7.05; N, 2.42; S, 5.54. Found: C, 47.68; H, 7.17; N, 2.64; S, 5.95.

X-ray Data Collection of Compounds **9a** *and* **9b**

Single crystals of **9a** and **9b** were grown by the slow evaporation of its saturated solution in hexane and chloroform at room temperature. The intensity data ($2\theta \leq 50.02$ for **9a** and $2\theta \leq 54.34$ for **9b**) were collected on a Rigaku AFC5R (for **9a**) and Rigaku MSC Mercury CCD (for **9b**) diffractometers, respectively, with graphite monochromated MoKα radiation (λ = 0.71069 Å). The structures were solved by direct methods with SIR97[15] and refined by the full matrix least-squares procedures on F^2 (SHELX-97[16]). All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of the least square refinement was based on 10590 observed reflections and 565 variable parameters with $R1 = 0.0909$ [$I > 2.00\sigma(I)$] and $wR2 = 0.2401$ (all data) for **9a** and based on 13076 observed reflections and 619 variable parameters with $R1 = 0.0814$ [$I > 2.00\sigma(I)$] and $wR2 = 0.2515$ (all data) for **9b**. Crystal data for **9a**: $C_{47}H_{81}O_2N_2Si_6S_2Sb$, M = 1060.55, temperature 296 K, monoclinic, space group $P2_1/c$, a = 11.464(8) Å, b = 21.407(5) Å, c = 24.525(5) Å, β = 92.25(3)°, V = 6014(4) Å^3, $Z = 4$, D_c = 1.171 g cm^{-3}, $R1 = 0.0909$ [$I > 2.00\sigma(I)$], $wR2 = 0.2401$ (all data), goodness of fit = 0.949. Crystal data for **9b**: $C_{47}H_{81}O_8N_2Si_6S_2Sb$, M = 1156.55, temperature 93(2) K, triclinic, space group $P\bar{1}$, a = 11.174(3) Å, b = 11.8631(15) Å, c = 25.149(3) Å, α = 90.624(6)°, β = 94.280(5)°, γ = 95.6562(13)°, V = 3307.5(9) Å^3, $Z = 2$, D_c = 1.161 g cm^{-3}, $R1 = 0.0814$ [$I > 2.00\sigma(I)$], $wR2 = 0.2515$ (all data), goodness of fit = 0.908.

Desulfurization Reaction of Cyclic Polysulfides **4** *and* **5** *with Ph$_3$P*

To a mixture of **4** and **5** (53.3 mg, **4:5** = 10:1) in 5 mL of THF, Ph_3P (52.9 mg, 0.2 mmol) was added at −70°C. The reaction mixture was warmed to room temperature, and the orange precipitate was filtered off to give 14.3 mg of **10** (47%). $Tbt_2Sb_2S_2$ **10**: orange crystals; m.p. >300°C; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 36H), 0.09 (s, 72H), 1.34 (s, 2H), 2.34 (s, 2H), 2.36 (s, 2H), 6.35 (s, 2H), 6.48 (s, 2H). High-resolution FABMS: observed *m/z* 1410.3998; calcd for $C_{54}H_{118}Si_{12}S_2Sb_2$ 1410.3987.

Desulfurization Reaction of Cyclic Polysulfides **4** *and* **5** *with (Me$_2$N)$_3$P in the Presence of MesCNO*

To a mixture of **4** and **5** (115 mg, **4:5** = 4:1) in 6 mL of THF, $(Me_2N)_3P$ (52.9 mg, 0.48 mmol) was added at −78°C. MesCNO (86.7 mg, 0.5 mmol) was added after stirring of the mixture at −78°C for a few minutes. The reaction mixture was warmed to room temperature, and after removal of the solvent, separation by GPLC afforded 16.7 mg of **9a** (15%).

Thermolysis of Cyclic Polysulfides **4** *and* **5** *in the Presence of MesCNO*

To a mixture of **4** and **5** (103 mg, **4:5** = 3:1) and MesCNO (28.4 mg, 0.18 mmol) was added 2.5 mL of THF. The reaction mixture was warmed to 50°C for 30 hours, and the solvent was evaporated under reduced pressure. Purification by GPLC afforded 15.2 mg of **9a** (14%).

Thermolysis of 1,3,4,5,2,6-Tetrathiadistibane **2** *in the Presence of MesCNO*

A mixture of **2** (35.0 mg, 0.024 mmol) and MesCNO (29.0 mg, 0.18 mmol) in 5 mL of THF was warmed

to 60°C for 36 hours. After removal of the solvent, purification by GPLC afforded 5.3 mg of **8a** (13%).

Thermolysis of 1,3,5,2,4-Trithiadistibolane **3** *in the Presence of MesCNO*

A mixture of **3** (40.0 mg, 0.028 mmol) and MesCNO (24.0 mg, 0.15 mmol) in 1.5 mL of THF was warmed to 70°C for 24 hours. After removal of the solvent, purification by GPLC afforded 3.5 mg of **8a** (conversion yield 17%) and the starting material (62%).

Thermolysis of 1,3,2,4-Dithiadistibetane **4** *in the Presence of MesCNO*

A mixture of **4** (37.0 mg, 0.026 mmol) and MesCNO (46.3 mg, 0.29 mmol) in 3 mL of THF was warmed to 120°C for 30 hours. After removal of the solvent, purification by GPLC afforded 1.8 mg of **8a** (conversion yield 5%) and 7.8 mg of the starting material (21%).

Thermolysis of TbtSbS$_2$ · 2MesCNO **9a**

A solution of **9a** (26.4 mg, 0.025 mmol) in toluene-d_8 (0.6 mL) was heated at 80°C for 5 hours in a sealed tube. Further heating at 90°C for 7 hours at 100°C for 3 hours, at 110°C for 50 hours, and then at 120°C for 50 hours resulted in the almost disappearance of the signal of **9a** in the ^{1}H NMR spectrum. After removal of the solvent, purification of the mixture by GPLC afforded 5.0 mg (0.0058 mmol) of **8a** (conversion yield 28%) together with 4.8 mg of the starting material (18%).

Thermolysis of TbtSbS · MesCNO **8a**

A solution of **8a** (8.7 mg, 0.010 mmol) in toluene-d_8 (0.5 mL) was heated at 100°C for 3 hours in a sealed tube. Further heating at 120°C for 3 hours at 140°C for 3 hours, and then at 150°C for 10 hours resulted in the formation of white precipitates. The ^{1}H NMR spectrum of the mixture showed the presence of TbtH, MesNCS, and the starting material.

ACKNOWLEDGMENTS

We are grateful to Shin-etsu Chemical and Tosoh Akzo Co., Ltds for the generous gifts of chlorosilanes and alkyllithiums, respectively.

REFERENCES

[1] For a recent review, see: Power, P. P. Chem Rev 1999, 99, 3463–3503.
[2] Appel, R.; Knoch, F.; Kunze, H. Angew Chem Int Ed Engl 1983, 22, 1004.
[3] Yoshifuji, M.; Shibayama, K.; Inamoto, N. Chem Lett 1984, 603.
[4] Yoshifuji, M.; Sangu, S.; Hirano, M.; Toyota, K. Chem Lett 1993, 1715.
[5] Yoshifuji, M.; Hirano, M.; Toyota, K. Tetrahedron Lett 1993, 34, 1043–1046.
[6] Tokitoh, N.; Arai, Y.; Harada, J.; Okazaki, R. Chem Lett 1995, 959–960.
[7] Grundmann, C.; Richter, R. J Org Chem 1968, 33, 476–478.
[8] Grundmann, C.; Dean, J. M. J Org Chem 1965, 30, 2809–2812.
[9] Crystal data for **8b**: $C_{37}H_{70}O_4NSi_6SSb$, M = 915.29, temperature 296 K, monoclinic, space group $P2_1/a$, a = 19.20(2) Å, b = 11.040(6) Å, c = 24.90(3) Å, β = 106.27(8)°, V = 5067(8) Å^3, Z = 4, D_c = 1.200 g cm^{-1}.
[10] Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. J Am Chem Soc 1998, 120, 11096–11105.
[11] Tokitoh, N.; Matsumoto, T.; Okazaki, R. Bull Chem Soc Jpn 1999, 72, 1665–1684.
[12] Okazaki, R.; Tokitoh, N. Acc Chem Res 2000, 33, 625–630.
[13] The mixture of **4** and **5** was used as starting material in this reaction because the separation of these compounds is very difficult and gives only very small amount of pure cyclic polysulfides, **4** and **5**.
[14] Minoura, M.; Kawashima, T.; Okazaki, R. Chem Lett 1994, 1691–1692.
[15] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. Sir97: a new tool for crystal structure determination and refined. Submitted for publication.
[16] Sheldrick, G. M. SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.