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Reactions of 1,3,5,2,4,6-trichalcogenatristannins and their derivatives with a nitrile oxide: synthesis, structure, and thermal behavior of oxachalcogenazastannoles

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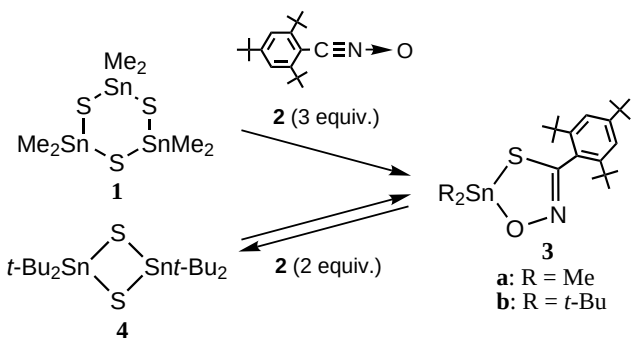
Abstract—2,2,4,4,6,6-Hexamethyl-1,3,5-trithia- and 1,3,5-triselena-2,4,6-tristannins reacted with 2,4,6-tri-*t*-butylbenzonitrile oxide to give 2,2-dimethyl-1,3-oxathia- and 1,3,5,2-oxaselenazastannoles. The reaction of 2,2,4,4-tetra-*t*-butyl-1,3,2,4-dithiadistannetane with 2,4,6-tri-*t*-butylbenzonitrile oxide gave 2,2-di-*t*-butyl-1,3,5,2-oxathiazastannole. The unusual thermal behavior of the oxachalcogenazastannole is also described. © 2001 Elsevier Science Ltd. All rights reserved.

Double-bond compounds between heavier group 14-group 16 elements are known to be useful building blocks for the synthesis of chalcogen-containing heterocyclic compounds via cycloaddition reactions such as [2+2]cycloaddition and 1,3-dipolar cycloaddition.[1] Generation of such double-bond species with small substituents is accomplished by thermolysis or photolysis of 1,3,5-trichalcogenane derivatives as confirmed by trapping reactions with various reagents,[2,3] a useful method for the synthesis of heterocyclic compounds having group 14 elements. To the best of our knowledge, however, there is no report on the formation of tin-containing heterocyclic compounds by the reaction of 1,3,5,2,4,6-trichalcogenatristannins with appropriate reagents. Since the Sn–X (X = O, S, Se) σ-bond energies are much smaller than those of the Si–X and Ge–X bonds,[4] the thermal dissociation mode of the Sn–X bond is of interest. We report here novel reactions of 1,3,5,2,4,6-trichalcogenatristannins with 2,4,6-tri-*t*-butylbenzonitrile oxide[5] to afford 1,3,5,2-oxachalcogenazastannole, a new method for the synthesis of organotin heterocycles, and the first X-ray structural analysis of 1,3,5,2-oxathiazastannole. We also report an unexpected thermal dissociation behavior of the resulting 1,3,5,2-oxachalcogenazastannoles, different from that of oxachalcogenazoles.[3a,6]

When mesitonitrile oxide (3 equiv.) was added to a benzene solution of 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-trithiatristannin (**1**), a white precipitate that had a melting point of around 240°C[7] was immediately formed. Unfortunately, the structure of this product could not be assigned, because of the very low solubility to most organic solvents, to record the NMR spectrum. Next, we examined the reaction of 2,4,6-tri-*t*-butylbenzonitrile oxide (**2**)[5] with **1**. Monitoring the reaction of 1,3,5,2,4,6-trithiatristannin **1** with nitrile oxide **2** (3 equiv.) by ^{1}H NMR in benzene-d_6 at room temperature showed the reaction proceeded cleanly to afford 2,2-dimethyl-1,3,5,2-oxathiazastannole **3a**[8] (Scheme 1). Although, some 1,3,5,2-oxachalocogenazastannoles have been synthesized by the reaction of overcrowded stable tin–chalcogen double-bond compounds with mesitonitrile oxide,[9] the compound **3a** is the first example of 1,3,5,2-oxachalocogenazastannole having small substituents on the tin, suggesting that a bulky group on the tin is not essential for the isolation of 1,3,5,2-oxachalocogenazastannole. Reaction of 2,2,4,4-tetra-*t*-butyl-1,3,2,4-dithiadistannetane (**4**)[10]



Scheme 1.

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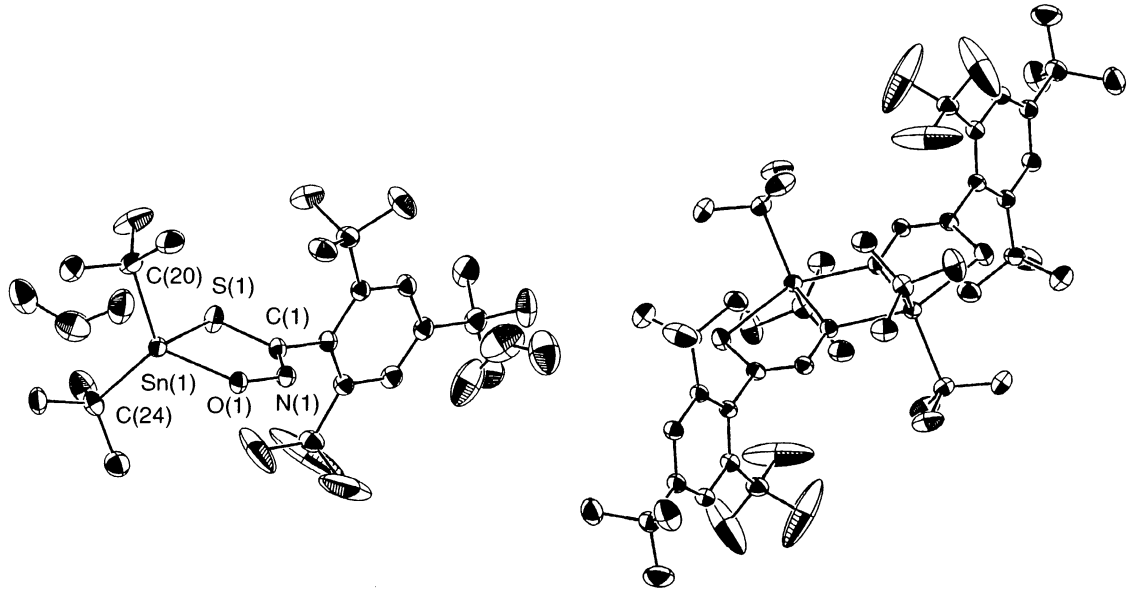
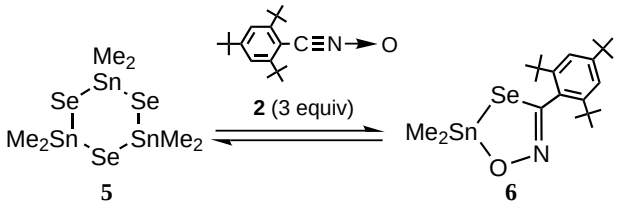


Figure 1. ORTEP drawing of oxathiazastannole **3b**·C_6H_6 with thermal ellipsoids plots (40% probability for non-hydrogen atoms). Asymmetric unit (left) and benzene molecules were omitted in the unit cell (right). Selected bond lengths (Å) and angles (°): Sn(1)–S(1), 2.5077(6); Sn(1)–O(1), 2.127(1); C(1)–S(1), 1.746(2); N(1)–O(1), 1.413(2); C(1)–N(1), 1.269(2); C(20)–Sn(1)–C(24), 118.5(1); S(1)–Sn(1)–O(1), 77.4(1).

with **2** was also investigated. The reaction proceeded slowly but quantitatively to form 2,2-di-*t*-butyl-1,3,5,2-oxathiazastannole **3b**,[11] the structure of which was established by X-ray crystallographic analysis carried out at 203 K.[12] As shown in an ORTEP drawing, the compound **3b** crystallized by solvation to benzene (**3b**·C_6H_6) (Fig. 1). The five-membered ring has a planar structure. The lengths of the Sn–S and Sn–O bonds in **3b**·C_6H_6 are 2.5077(6) and 2.127(1) Å, respectively, longer than the standard bond lengths of Sn–S (2.43 Å) and Sn–O (1.94 Å)[13] and comparable to those of 2,2-di-*t*-butyl-1,3,2-oxathiastannolane (d(Sn–S) = 2.49 Å, d(Sn–O) = 2.08 Å).[14] In a unit cell, **3b**·C_6H_6 forms a dimer with Sn---O interactions (2.289(1) Å), similar to the dimeric Sn---O interactions reported in the X-ray crystallographic analysis of 2,2-di-*t*-butyl-1,3,2-oxathiastannolane (d(Sn---O) = 2.29 Å).[14] It has been reported that 2,2-di-*n*-butyl-1,3,2-oxathiastannolane exists as a polymer in its crystalline form.[14] Since the five-membered ring in **3b** is surrounded by two *t*-butyl groups and a bulky aromatic moiety, **3b**·C_6H_6 cannot exist as a polymer but as a dimer.

Interestingly, when the reaction of **4** and **2** was monitored by ^{1}H NMR in benzene-d_6, the formation of the stannole **3b** was observed at room temperature. However, the stannole **3b** disappeared completely on heating the solution at 80°C and appeared again quantitatively after cooling down the solution to room temperature.[15] The oxachalcogenazoles were reported to undergo thermal transformation into the isochalcogenocyanate and the ketone with the cleavage of the O–N bond followed by the shift of the C_5-substituent to nitrogen.[3a,6] The analogous cleavage of **3b** to isochalcogenocyanate would give the tin–oxygen double-bond compound that has not been isolated so far. On the contrary, the oxathiazastannole **3b** underwent thermal cleavage of the S–C bond instead of the O–N bond to reproduce the starting **4** and **2**. To the best of our knowledge, this type of thermal behavior of oxachalcogenazoles is unprecedented and is of interest.

This method was next applied to the synthesis of a selenium-containing organotin heterocycle. Treatment of 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-triselenatristannin (**5**) with nitrile oxide **2** (3 equiv.) afforded an equilibrium mixture of 1,3,5,2-oxaselenazastannole **6**,[16] **2** and **5** in a ratio of 3:3:1 in sharp contrast to the complete reaction with the sulfur analog (Scheme 2). The oxaselenazastannole **6** was isolated as a solid sparingly soluble to benzene. On heating the reaction mixture at 80°C, the oxaselenazastannole **6** disappeared completely as in the case of **3b** and appeared again after cooling down to room temperature with the same **6**:**2**:**5** ratio as that before heating. As already mentioned, the oxachalcogenazastannole showed the unusual dissociation behavior, which may be explained by the thermal cleavage of the Sn–O and X–C (X = S, Se) bonds to produce the nitrile oxide and dimethylstannanechalocogenone [Me_2Sn=X] which trimerized rapidly to 1,3,5,2,4,6-trichalcogenatristannin. Alternatively, the trichalcogenatristannin may be produced



5 6

Scheme 2.

through the trimeric molecular unit, connected by intermolecular Sn···X interactions. Dräger reported that tin–sulfur heterocycles of the type $[R_2SnS]_3$ underwent exchange reaction (redistribution) through the intermolecular Sn···S interactions.[17]

In summary, the reaction of 1,3,5,2,4,6-trichalcogenatristannins with nitrile oxide provided a novel method for the synthesis of 1,3,5,2-oxachalcogenazastannoles which showed unusual thermal behavior.

Experimental

Synthesis of 2,4,6-tri-*t*-butylbenzonitrile oxide (2)

2,4,6-Tri-*t*-butylbenzonitrile oxide (**2**) was synthesized according to the private communication.[5]

(a) Synthesis of 2,4,6-tri-t-butylbenzaldehyde oxime. To an ethanol (50 mL) solution of 2,4,6-tri-*t*-butylthiobenzaldehyde[18] (1602 mg, 5.51 mmol) and hydroxyamine hydrochloride (906 mg, 13.0 mmol) was added triethylamine (1.8 mL, 12.9 mmol). After it was refluxed for 10 min, the mixture was allowed to stand at room temperature. After removal of a solvent, the residue was subjected to WCC (SiO_2, hexane:methylene chloride = 2:1) to afford 2,4,6-tri-*t*-butylbenzaldehyde oxime (1035 mg, 65%). Mp 170–171°C (methylene chloride). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.34 (s, 9H), 1.37 (s, 18H), 7.41 (s, 2H), 8.49 (s, 1H), 9.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 31.40 (q), 32.41 (q), 35.05 (s), 36.92 (s), 121.56 (d), 127.04 (s), 149.63 (s), 150.27 (s), 153.66 (d). EI MS [M], calcd for $C_{19}H_{31}NO$: 289.2406. Found: 289.2394. Anal. calcd for $C_{19}H_{31}NO$: C, 78.84; H, 10.80; N, 4.84. Found: C, 79.01; H, 10.91; N, 4.98.

(b) Synthesis of 2,4,6-tri-t-butylbenzonitrile oxide (2). To a DMF (13 mL) solution of 2,4,6-tri-*t*-butylbenzaldehyde oxime (1123 mg, 3.88 mmol) was added a DMF (6 mL) solution of *N*-bromosuccinimide (763 mg, 4.28 mmol). After it was stirred for 10 min at room temperature, the reaction mixture was treated with triethylamine (0.6 mL, 4.30 mmol). After addition of water, the solid (1320 mg) was filtered and subjected to WCC (Al_2O_3, hexane) to give 2,4,6-tri-*t*-butylbenzonitrile oxide (**2**) (985 mg, 88%). Compound **2**: mp 113–118°C (hexane+methylene chloride). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.32 (s, 9H), 1.48 (s, 18H), 7.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 30.73 (q), 31.12 (q), 35.50 (s), 36.24 (s), 106.18 (s), 121.28 (d), 153.15 (s), 154.83 (s); EI MS [M], calcd for $C_{19}H_{29}NO$: 287.2249. Found: 287.2255. Anal. calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.37; H, 10.28; N, 4.59.

Reaction of 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-trithiatristannin (1) with 2,4,6-tri-*t*-butylbenzonitrile oxide (2)

A benzene-d_6 (0.5 mL) solution of 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-trithiatristannin (**1**) (8 mg, 0.014 mmol) and 2,4,6-tri-*t*-butylbenzonitrile oxide (**2**) (12 mg, 0.042 mmol) was placed in a 5ϕ mm NMR tube, degassed by freeze-pump-thaw cycles and sealed. The solution was allowed to stand at room temperature overnight. Monitoring the reaction by ^{1}H NMR showed the quantitative formation of **3a**. 2,2-Dimethyl-1,3,5,2-oxathiazastannole (**3a**) (6 mg, 31%) was obtained as white precipitates.

Reaction of 2,2,4,4-tetra-*t*-butyl-1,3,2,4-dithiadistannetane (4) with 2

A benzene-d_6 (0.5 mL) solution of 2,2,4,4-tetra-*t*-butyl-1,3,2,4-dithiadistannetane (**4**) (7 mg, 0.014 mmol) and **2** (7 mg, 0.023 mmol) was placed in a 5ϕ mm NMR tube, degassed by freeze-pump-thaw cycles and sealed. The solution was allowed to stand at room temperature overnight. 2,2-Di-*t*-butyl-1,3,5,2-oxathiazastannole solvated with a benzene-d_6, **3b**·C_6D_6 (3 mg, 20%) was obtained as colorless crystals.

Reaction of 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-triselenatristannin (5) with 2

A benzene-d_6 (0.5 mL) solution of 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-triselenatristannin (**5**) (26 mg, 0.039 mmol) and **2** (33 mg, 0.12 mmol) was placed in a 5ϕ mm NMR tube, degassed by freeze-pump-thaw cycles and sealed. The solution was allowed to stand at room temperature overnight. 2,2-Dimethyl-1,3,5,2-oxaselenazastannole (**6**) (25 mg, 43%) was obtained as white precipitates.

X-ray crystallographic data for 3b·C_6H_6

$C_{33}H_{52}NOSSn$, $M = 629.54$, triclinic, $a = 9.9670(7)$, $b = 12.2290(8)$, $c = 14.5660(8)$ Å, $\alpha = 97.886(4)$, $\beta = 106.732(4)$, $\gamma = 95.450(3)°$, $V = 1667.1(2)$ Å^3, $Z = 2$, $D = 1.254$ Mg m^{-3}, space group $P\bar{1}$. Data were collected on Mac Science Xdip diffractometer at 203 K with Mo Kα radiation ($\lambda = 0.71073$ Å) and the structure was solved by direct methods. There are two independent halves of a benzene molecule in the asymmetric unit. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed at calculated positions (d(C–H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 6802 observed reflections [$I > 3.00\sigma(I)$] and 334 variable parameters with $R(_wR2) = 0.042$ (0.103).

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References

1. For examples of reviews, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509; (b) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283–319.

2. (a) Thompson, D. P.; Boudjouk, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1466–1467; (b) Boudjouk, P.; Bahr, S. R.; Thompson, D. P. *Organometallics* **1991**, *10*, 778–782.
3. (a) Lavayssière, H.; Satgé, J.; Barrau, J.; Traore, M. *J. Organomet. Chem.* **1982**, *240*, 335–348; (b) Barrau, J.; Rima, G.; Lavayssière, H.; Dousse, G.; Satgé, J. *J. Organomet. Chem.* **1983**, *246*, 227–242.
4. Basch, H.; Hoz, T. In *The chemistry of organic germanium, tin and lead compounds*; Patai, S., Ed.; John Wiley: Chichester, England, 1995; pp. 1–96.
5. Matsumoto, T.; Tokitoh, N.; Okazaki, R., private communication.
6. Minoura, M.; Kawashima, T.; Okazaki, R. *Chem. Lett.* **1994**, 1691–1692.
7. Anal. calcd for $C_{12}H_{17}NOSSn$: C, 42.14; H, 5.01; N, 4.10. Found: C, 41.48; H, 4.93; N, 3.92.
8. Compound **3a**: mp 206–208°C (recrystallized from benzene). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.92 (s, 6H), 1.32 (s, 9H), 1.61 (s, 18H), 7.66 (s, 2H); ^{13}C NMR (C_6D_6, 100 MHz): δ 6.05 (q), 31.47 (q), 33.96 (q), 35.03 (s), 38.80 (s), 123.69 (d), 132.10 (s), 148.49 (s), 150.10 (s), 161.46 (s). Anal. calcd for $C_{21}H_{35}NOSSn$: C, 53.86; H, 7.53; N, 2.99. Found: C, 54.10; H, 7.64; N, 2.88.
9. (a) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 43–48; (b) Saito, M.; Tokitoh, N.; Okazaki, R. *Organometallics* **1996**, *15*, 4531–4536.
10. Puff, H.; Gattermayer, R.; Hundt, R.; Zimmer, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 547.
11. Compound **3b**: mp 155–158°C (recrystallized from benzene). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.29 (s, 9H), 1.55 (s, 18H), 1.70 (s, 18H), 7.66 (s, 2H); ^{13}C NMR (C_6D_6, 100 MHz): δ 31.38 (q), 31.50 (q), 34.69 (q), 34.91 (s), 39.05 (s), 46.12 (s), 123.95 (d), 132.53 (s), 148.62 (s), 149.70 (s), 161.68 (s). Anal. calcd for $C_{27}H_{47}NOSSn$: C, 58.70; H, 8.58; N, 2.54. Found: C, 59.05; H, 8.52; N, 2.47.
12. Crystallographic data for **3b**·C_6H_6 deposited at CCDC 162230.
13. Mackay, K. M. In *The chemistry of organic germanium, tin and lead compounds*; Patai, S., Ed.; John Wiley: Chichester, England, 1995; p. 101.
14. Bates, P. A.; Hursthouse, M. B.; Davies, A. G.; Slater, S. D. *J. Organomet. Chem.* **1989**, *363*, 45–60.
15. The stannole **3a** remained almost unchanged even after heating at 80°C for 1 h. The reason for the different thermal behavior of **3a** and **3b** is not at all clear.
16. Compound **6**: mp 160°C (recrystallized from toluene). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.07 (s, 6H), 1.32 (s, 9H), 1.62 (s, 18H), 7.65 (s, 2H); ^{13}C NMR (C_6D_6, 100 MHz): δ 8.00 (q), 31.43 (q), 34.35 (q), 34.97 (s), 38.93 (s), 123.91 (d), 132.80 (s), 147.96 (s), 150.00 (s), 158.76 (s). Anal. calcd for $C_{21}H_{35}NOSeSn$: C, 48.96; H, 6.85; N, 2.72. Found: C, 48.34; H, 6.75; N, 2.63.
17. Flöck, O. R.; Dräger, M. *Organometallics* **1993**, *12*, 4623–4632.
18. Ishii, A.; Ishida, T.; Kumon, N.; Fukuda, N.; Oyama, H.; Inamoto, N.; Iwasaki, F.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 709–717.