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Reaction of Tetrachalcogenastannolanes with Triphenylphosphine. A Novel Mode of Generation for Overcrowded Stannanethiones and Stannaneselones†

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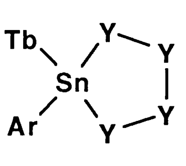
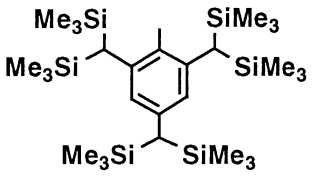
Dechalcogenation of overcrowded 1,2,3,4,5-tetrachalcogenastannolanes with triphenylphosphine resulted in the formation of the corresponding 1,3,2,4-dichalcogenadistannetanes via [2+2]cycloaddition of intermediary stannanethione and stannaneselone. Molecular structures of the newly obtained 1,3,2,4-dichalcogenadistannetanes were examined by X-ray analysis.

Metallathiones and metallaselones of group 14 metals (RR'M=Y; M=Si, Ge, Sn, and Pb; Y=S, Se) are among a novel class of multiple bond compounds of current interest. Although several recent reports have described some examples of silanethione,1) silaneselone,1) and germanethiones2) stabilized by taking advantage of thermodynamic stablilization (electronic perturbation due to strongly electron-donating heteroatoms in the substituents), very little is known of the chemistry of tin-chalcogen double bond compounds because of their low bond energy. It has been known that sterically unhindered stannanethiones and stannaneselones undergo oligomerization. For example, Ph_2SnS and Me_2SnS were found to have the corresponding trimeric structures with puckered six-membered rings as evidenced by X-ray analysis,3) while di-*t*-butyltin chalcogenides *t*-Bu_2SnY (Y= S, Se, and Te) occur as dimers both in the solid state and in solution with flat four-membered 1,3,2,4-dichalcogenadistannetane rings.4)



1a; Ar = Mes, Y = S
1b; Ar = Mes, Y = Se
2a; Ar = Tip, Y = S
2b; Ar = Tip, Y = Se
Mes = mesityl
Tip = 2,4,6-triisopropylphenyl

Tb =


We have recently reported the first synthesis of 1,2,3,4,5-tetrachalcogenastannolanes Tb(Ar)SnY_4 (**1a**, Ar=mesityl (Mes), Y=S; **2a**, Ar=2,4,6-triisopropylphenyl (Tip), Y=S; **1b**, Ar=Mes, Y=Se; **2b**, Ar=Tip, Y=Se)5) by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl

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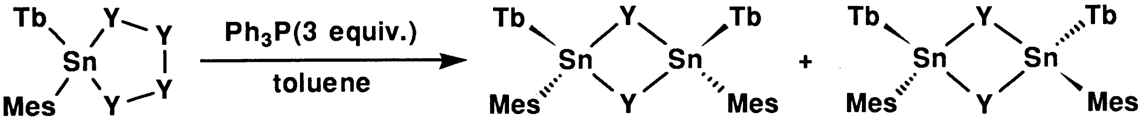
†Dedicated to Professor Emeritus Osamu Simamura of The University of Tokyo on the occasion of his 80th birthday.

(denoted as Tb hereafter).[6)] In this paper, we report on a novel mode of generation for overcrowded stannanethiones and stannaneselones by dechalcogenation of the corresponding tetrachalcogenastannolanes and also on the characteristic reactivites of these tin-chalcogen double bond species in their [2+2]cycloaddition reactions together with the crystallographic structure analysis of the resulting 1,3,2,4-dichalocogenadistannetanes.

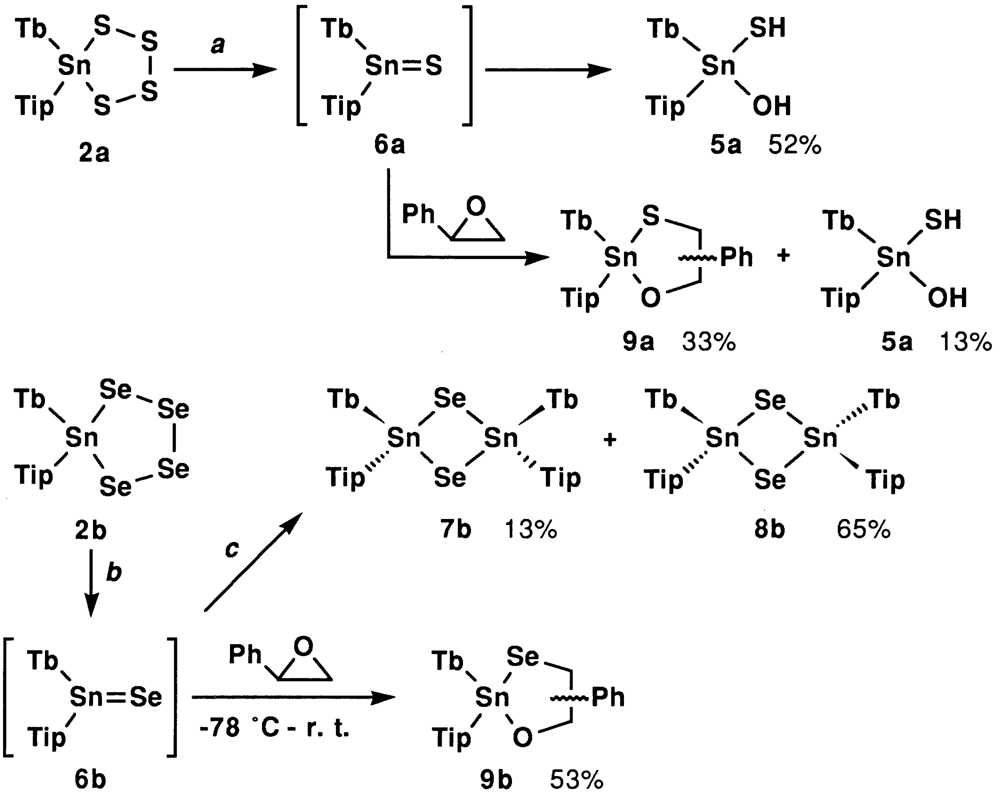


1a; Y=S
1b; Y=Se

3a(Y=S) ; 83%
3b(Y=Se) ; 38%

4a(Y=S) ; 0%
4b(Y=Se) ; 3%

When tetrathiastannolane **1a** having Tb and mesityl substituents (150.0 mg, 0.164 mmol) was treated with 3 equivalent moles of triphenylphosphine (129.0 mg, 0.492 mmol) in toluene (2 ml) at room temperature for 1.5 h, *cis*-1,3,2,4-dithiadistannetane **3a** (111.3 mg, 83%), probably formed by dimerization of intermediary stannanethione Tb(Mes)Sn=S, was exclusively obtained. Tetraselenastannolane **1b** was more readily deselenated with Ph_3P (3 equiv.) at -78 °C in toluene to afford both *cis*- and *trans*-substituted 1,3,2,4-diselenadistannetanes, **3b** (38%) and **4b** (3%).



Scheme 1. *a*: Ph_3P(3 equiv.)/toluene/r. t./10 h; *b*: Ph_3P(3 equiv.)/toluene/-78 °C/30 min; *c*:-78 °C - r. t./10 h.

On the other hand, dechalcogenation of more crowded tetrachalcogenastannolanes bearing Tb and Tip groups (**2a** and **2b**) gave quite different results. Tetrathiastannolane **2a** was readily desulfurized with Ph_3P (3 equiv.) in toluene at room temperature to give hydroxystannanethiol **5a** in 52% without any 1,3,2,4-

dithiadistannetane derivatives, suggesting that the steric hindrance of the bulky aryl groups prevented the [2+2]cycloaddition of the intermediary stannanethione **6a**, which instead reacted with water during work-up to give **5a**. However, in the case of deselenation of tetraselenastannolane **2b** with Ph_3P under similar reaction conditions, both *cis*- and *trans*-isomers of 1,3,2,4-diselenadistannetanes (**7b** and **8b**) were isolated in 13 and 65%, respectively. In both cases, the intermediary stannanethione **6a** and stannaneselone **6b** were effectively trapped with styrene oxide to afford the corresponding cycloadducts, 1,3,2-oxachalcogenastannolanes (**9a** and **9b**),7) respectively, as shown in Scheme 1.

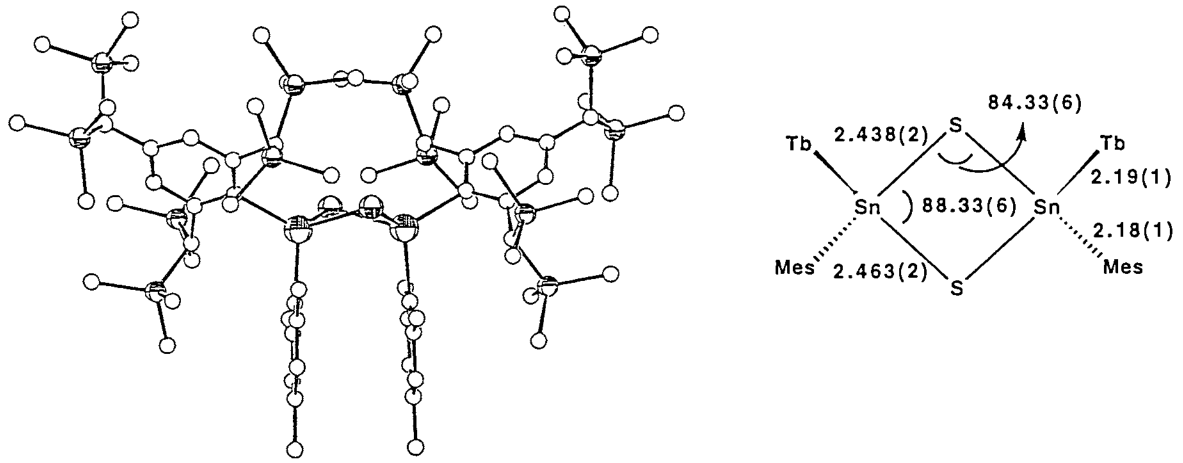


Fig. 1. Molecular Structure of *cis*-[Tb(Mes)SnS]$_2$ (**3a**).

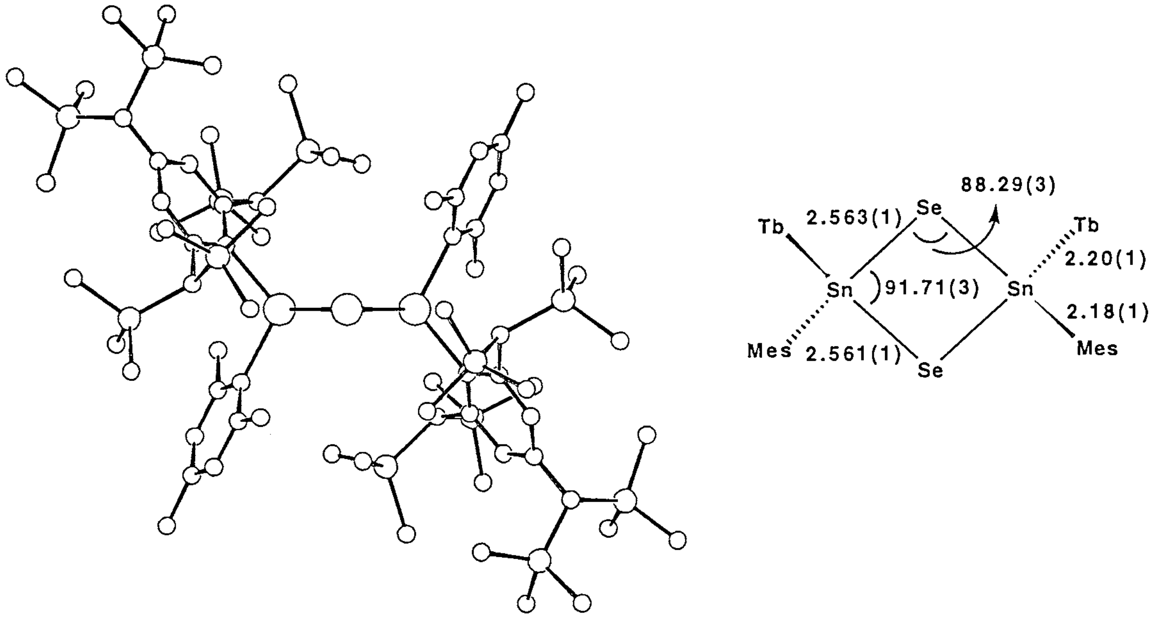


Fig. 2. Molecular Structure of *trans*-[Tb(Mes)SnSe]$_2$ (**4b**).

Of particular note in the dechalcogenation of tetrachalcogenastannolanes here described is the non-stereospecificity in the formation of 1,3,2,4-diselenadistannetanes which is in sharp contrast to the stereospecific dimerization of Tb(Mes)Sn=S leading to exclusive formation of the *cis*-substituted 1,3,2,4-dithiadistannetane. A similar exclusive *cis*-dimerization was also observed in the case of Tb(Mes)Ge=S.8) The above results suggest that the stereochemical outcome in the [2+2]cycloaddition of the intermediary tin-chalcogen double bond compounds is controlled by both the steric bulkiness of the aromatic substituents on the tin atom and the tin-chalcogen bond length.

The newly obtained 1,3,2,4-dichalcogenadistannetanes (**3a**, **3b**, **4b**, **7b**, and **8b**) showed satisfactory spectral data and their final structures were definitely determined by X-ray crystallographic analysis.9) The molecular structures of **3a** and **4b** were shown as the representatives in Fig. 1 and 2 along with the selected interatomic bond lengths (Å) and angles (deg).10) The central four-membered rings of the *trans*-substituted distannetanes (**4b** and **8b**) were found to be completely planar as in the case of the previously reported 1,3,2,4-dichalcogena-distannetanes,4) whereas the *cis*-substituted distannetanes (**3a** and **3b**) showed unprecedentedly large fold angles (**3a**; 39.8° for S-S axis and 40.9° for Sn-Sn axis, **3b**; 43.6° for Se-Se axis and 41.3° for Sn-Sn axis) probably due to the remarkable steric hindrance of the two Tb groups facing each other.

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References

1) P. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot, and C. Priou, *Angew. Chem., Int. Ed. Engl.*, **28**, 1016 (1989).
2) M. Veith, S. Becker, and V. Huch, *Angew. Chem., Int. Ed. Engl.*, **28**, 1237 (1989); M. Veith, A. Detemple, and H. Huch, *Chem. Ber.*, **124**, 1135 (1991).
3) H. Schumann, *Z. Anorg. Allg. Chem.*, **354**, 192 (1967); B. Menzebach and P. Bleckmann, *J. Organomet. Chem.*, **91**, 291 (1975).
4) H. Puff, R. Gattermayer, R. Hundt, and R. Zimmer, *Angew. Chem., Int. Ed. Engl.*, **16**, 547 (1977).
5) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki, and M. Goto, *J. Am. Chem. Soc.*, **113**, 7047 (1991); N. Tokitoh, M. Takahashi, T. Matsumoto, H. Suzuki, Y. Matsuhashi, and R. Okazaki, *Phosphorus, Sulfur, and Silicon*, **59**, 161 (1991).
6) R. Okazaki, M. Unno, and N. Inamoto, *Chem. Lett.*, **1987**, 2293; R. Okazaki, M. Unno, N. Inamoto, and G. Yamamoto, *ibid.*, **1989**, 493; R. Okazaki, M. Unno, and N. Inamoto, *ibid.*, **1989**, 791.
7) All the four possible regio- and stereo-isomers capable of separation by column chromatography, were obtained. 4-Phenyl-1,3,2-oxachalcogenastannolanes were yielded predominantly over the corresponding 5-phenyl derivatives although their stereochemical orientation has not been determined yet.
8) N. Tokitoh, T. Matsumoto, H. Ichida, and R. Okazaki, *Tetrahedron Lett.*, **32**, 6877 (1991).
9) Details for the X-ray structure analyses of **3b**, **7b**, and **8b** will be described elsewhere as a full paper.
10) Crystal data for **3a**; $C_{72}H_{140}S_2Si_{12}Sn_2$, MW = 1644.52, *monoclinic*, C2/c, a = 20.916(5), b = 15.390(1), c = 30.396(5) Å, β = 103.82(1) °, V = 9501.4 Å^3, Z = 4, D_c = 1.149 g cm^{-3}, μ = 63.55 cm^{-1}, $R(R_w)$ = 0.047(0.056). Crystal data for **4b**; $C_{72}H_{140}Se_2Si_{12}Sn_2$, MW = 1738.31, *monoclinic*, C2/c, a = 16.416 (3), b = 20.365(2), c = 29.241(6) Å, β = 101.13(1) °, V = 9591.8 Å^3, Z = 4, D_c = 1.203 g cm^{-3}, μ = 68.99 cm^{-1}, $R(R_w)$ = 0.046(0.054). Total 6986 and 6538 independent reflections with $|F_o| > 3.0\sigma|F_o|$ ($4 < 2\theta < 130$ °) were used for calculation of **3a** and **4b**, respectively. The structures were solved by direct method using *UNICS III* and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms.

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