Crystal Structure of Bis(triphenylstannyl)sulfite

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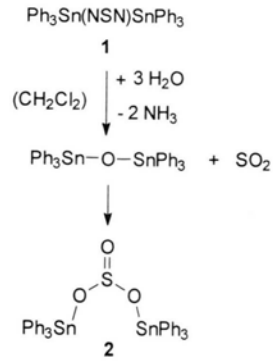
The reaction of bis(triphenylstannyl)sulfur diimide **1** with water in CH_2Cl_2 provides an alternative route to bis(triphenylstannyl)sulfite **2**, affording crystalline material suitable for X-ray structural analysis (monoclinic, space group $P2_1/n$). The sulfite **2** is monomeric in solution but forms polymeric chains in the solid state with both tetra- and penta-coordinate tin atoms.

The reaction of bis(triorganostannyl)oxides, $(R_3Sn)_2O$, with sulfur dioxide has been studied repeatedly [1,2] with the result that bis(triorganostannyl)sulfites, R_3SnO-S(O)-$OSnR_3$, can be prepared by insertion of SO_2 into the Sn-O bond. These compounds are difficult to crystallize for R = alkyl [1,2], and although a microcrystalline solid was isolated in the case of R = Ph [2], direct structural evidence could not be obtained. Structural information would be of interest for comparison with the structural properties of bis(triorganostannyl)carbonates, R_3SnO-C(O)-$OSnR_3$ [3] or bis(trimethylstannyl)selenite, Me_3SnO-Se(O)-$OSnMe_3$ [4], for which polymeric chains were observed. Here we report that controlled hydrolysis of bis(triphenylstannyl)sulfur diimide **1** [5] provides an alternative route to bis(triphenyltin)sulfite **2**, and that crystalline material suitable for X-ray structural analysis can be obtained.

The most likely (simplified) reaction pathway from **1** to **2** is shown in Scheme 1, although the proposed intermediates could not be isolated.



Since it is assumed that NH_3 and SO_2 are formed in the presence of water, the reaction may be much more complex than indicated in Scheme 1.

The properties of **2** are as described [2], and single crystals were obtained directly from the reaction in CH_2Cl_2 saturated with water. The δ^{119}Sn value for **2** in solution (δ -49.7) indicates the presence of a monomeric species containing tetra-coordinate tin atoms, in agreement with the finding for bis(trimethyltin)selenite [4]. This is in accordance either with a static structure of **2** as shown in Scheme 1 or with a fluxional structure due to fast exchange of the Ph_3Sn groups between the three oxygen sites either intra- or intermolecularly.

The crystal structure of **2** is illustrated in the Figs 1 and 2. The structure of **2** reminds of that of the carbonate [3] with respect to the presence of both tetra-and penta-coordinate tin atoms. Polymeric chains are formed by penta-coordination of tin atoms through O-Sn-O linkages. The crystal structure of **2** is very similar to that of bis(trimethylstannyl)selenite which, however, crystallizes with one equivalent of water. It had been pointed out that the particular arrangement of the polymeric chains in the selenite is stabilized by hydrogen bonding [4]. An analogous arrangement of the polymeric chains is also observed in **2**, although without hydrogen bonding. The bond lengths and angles in **2** are found in the expected ranges. In the case of the penta-coordinate tin atom, the axial Sn(2)-O bonds (225.2(3) pm) are significantly elongated (compare with $d_{Sn(1)-O(1)}$ = 203.2(2) pm). The surroundings of the Sn(2) atom are close to trigonal bipyramidal. (*e.g.*, angle O2-Sn(2)-O(3A) 176.9(1)°). The surroundings of the sulfur atom are pyramidal with slightly different O-S-O bond angles (101.4(1), 103.4(1), 105.7(1)°) and different S-O bond lengths (156.8(3), 151.9(3),

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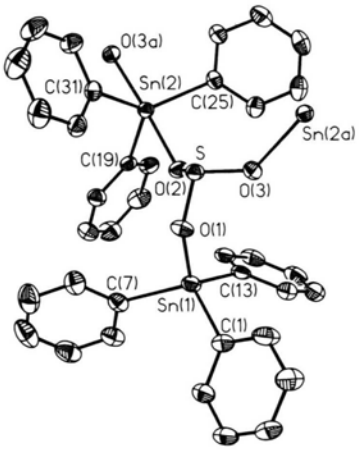

Fig. 1. Part of the structure of Ph_3SnO-S(O)-$OSnPh_3$ (**2**) showing the numbering scheme. Selected bond lengths [pm] and angles [°]: Sn(1)-O(1) 203.2(2), Sn(1)-C 212.8 (mean value), Sn(2)-O(2) 226.4(3), Sn(2)-O(3A) 225.2(3), Sn(2)-C 213.3 (mean value), S-O(1) 156.8(3), S-O(2) 151.9(3), S-O(3) 151.1(3); Sn(1)-O(1)-S 124.7(1), Sn(2)-O(2)-S 130.7(1), Sn(2A)-O(3)-S 125.0(1), O(2)-Sn(2)-O(3A) 176.9(1), O(1)-S-O(2) 101.4(1), O(1)-S-O(3) 103.4(1), O(2)-S-O(3) 105.7(1).

151.1(3) pm), with the longer distance to the oxygen which is linked to the terminal stannyl group.

Experimental

Bis(triphenylstannyl)sulfur diimide **1** was prepared as described [5]. When **1** (1.0 g; 1.32 mmol) was kept in 20 ml of H_2O-saturated CH_2Cl_2, colorless crystals of **2** precipitated within several days in almost quantitative yield (m.p. 146-148 °C, decomp.).

^{119}Sn NMR spectra were measured using a Bruker ARX 250 instrument (δ^{119}Sn with respect to external neat Me_4Sn).

X-Ray structure analysis of **2** [6]: A single crystal (colorless prism) of dimensions 0.55 x 0.40 x 0.15 mm was sealed under argon in a glass capillary. The dimensions of the monoclinic unit cell are a = 1566.2(2), b = 1119.5(2), c = 1834.8(2) pm, β = 93.90(2)° with Z = 4 in the space group $P2_1/n$. The absorption coefficient is μ = 1.665 mm^{-1}. The reflection intensities were collected at 173 K on a Siemens P4 diffractometer with MoK_α -radiation (λ = 71.073 pm, graphite monochromator). 7378 reflections were measured in ω scan mode with a scan width of 1.10° (ω) in the range 3° $\leq 2\theta \leq$ 50°. Three check reflections monitored every 100 reflections controlled the stability of the primary beam. After applying Lorentz and polarization corrections and merging, 5652 unique reflections remained which were assigned to be observed ($F_0 > 0.0\ \sigma(F_0)$). The absorption correction was done semi-empirically by ψ-scans of 10 different reflections, the min./max. transmission factors were 0.3104/0.3425. The crystal structure was solved by Direct Methods (Siemens SHELXTL PLUS System). The refinement of all non-hydrogen atoms by the full-matrix-least-squares method with anisotropic temperature factors and 180 parameters converged at R/wR 0.0283/0.0259, the weighting scheme was $w^{-1} = \sigma^2(F_0)$. The hydrogen atoms were refined in calculated positions with fixed temperature factors (0.08 Å^2) using the riding model. The max./min. residual electron density was 0.60/-0.64 eÅ^{-3}.

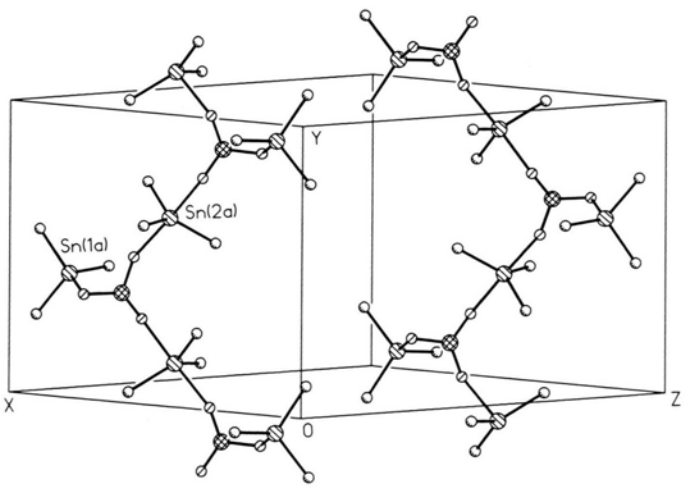

Fig. 2. View of the unit cell of Ph_3SnO-S(O)-$OSnPh_3$ (**2**); for clarity only the *ipso*-carbon atoms of the Ph_3Sn groups are shown.

Acknowledgements

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[1] A. G. Davies, J. D. Kennedy, J. Chem. Soc. (C) **1968**, 2630.
[2] U. Kunze, H. P. Völker, Chem. Ber. **107**, 3818 (1974).
[3] J. Kümmerlen, A. Sebald, H. Reuter, J. Organomet. Chem. **427**, 309 (1992).
[4] A. Diasse-Sarr, L. Diop, M. F. Mahon, K. C. Molloy, Main Group Met. Chem. **20**, 223 (1997).
[5] M. Herberhold, S. Gerstmann, B. Wrackmeyer, Phosphorus, Sulfur and Silicon, **66**, 273 (1992).
[6] Further details of the crystal structure analysis can be obtained on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-407573.