higher intensity bands. Finally, there is no observable splitting of the d → d band for either isomer.

The mechanism of the *cis* → *trans* isomerization is not known. In order to learn something more about this interesting reaction, we are currently studying the thermodynamics and kinetics of the isomerization.

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Preparation of Stannic Chloride Sulfide

BY CHRISTIAN H. STAPFER

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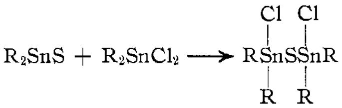
The reaction of dialkyltin sulfides with corresponding dialkyltin dichlorides is known to involve halogen transfer yielding 1,1,3,3-tetraalkyl-1,3-dichlorodistanthianes[1,2]



$$R_2SnS + R_2SnCl_2 \longrightarrow R\overset{Cl}{\underset{R}{Sn}}S\overset{Cl}{\underset{R}{Sn}}R$$

When $SnCl_4$ is used in place of R_2SnCl_2, a more complex reaction is observed,[3] *i.e.*

$$3(C_4H_9)_2SnS + 2SnCl_4 \longrightarrow 3(C_4H_9)_2SnCl_2 + Sn_2Cl_2S_3$$

The resulting $Sn_2Cl_2S_3$ is a white, reactive solid which is amorphous to X-rays. It reacts with water forming H_2S and uncharacterized oxides and oxychlorides. It is unstable in air or in inert atmosphere and decomposes rapidly into stannic sulfide and $SnCl_4$

$$2SnCl_2S_3 \xrightarrow{\Delta} 3SnS_2 + SnCl_4$$

The character of the new compound was not affected by varying the ratio of dibutyltin sulfide and $SnCl_4$. An excess of $(C_4H_9)_2SnS$ leads to the formation of 1,1,3,3-tetrabutyl-1,3-dichlorodistanthiane along with dibutyltin dichloride and $Sn_2Cl_2S_3$.

Experimental Section

In a modular drybox containing a nitrogen atmosphere, 7.95 g of pure di-*n*-butyltin sulfide, prepared from recrystallized di-*n*-butyltin dichloride and sodium sulfide following the reported procedure,[4] was dissolved into 50 ml of anhydrous *n*-hexane. Slowly and under magnetic agitation, 5.21 g of reagent grade stannic chloride was added to this solution. After 15 minutes of vigorous agitation at room temperature, the white precipitate was filtered, washed several times with hexane, and vacuum dried; yield, 3.92 g. *Anal.* Calcd for $Sn_2Cl_2S_3$: Sn, 58.6; Cl, 17.5; S, 23.7. Found: Sn, 56.9; Cl, 17.0; S, 24.0. A 2.8-g amount of di-*n*-butyltin dichloride was recovered by evaporation of the filtrate. When $Sn_2Cl_2S_3$ was heated in a crucible at 120° until the evolution had subsided, a quantitative amount of SnS_2 was recovered.

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Organotin Sulfates from the Oxidation of Organotin Sulfides with Hydrogen Peroxide

BY CHRISTIAN H. STAPFER AND ROBERT D. DWORKIN

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The subject of this paper is the investigation of the reaction of aqueous hydrogen peroxide with *n*-butyl-substituted stannyl sulfides which led to the preparation of several organotin sulfate derivatives. The preparation of bis(trialkyltin) sulfates either by ester-exchange reactions of trialkyltin mercaptides[1] or by reaction of sodium hydrosulfate with bis(trialkyltin) oxides or hydroxides[2] has been previously described. It is also known that acyl peroxides and esters of some peracids react with various organometallic compounds, in particular triethyltin halides[3,4] and bis(triethyltin) sulfide.[5] In the latter case, benzoyl peroxide was shown to cleave both tin–sulfur bonds of the organotin sulfide to form triethyltin benzoate and elemental sulfur. No other work has been reported on the oxidation of the tin–sulfur bonds of organotin sulfides.

Experimental Section

Bis(tri-*n*-butyltin) Sulfate.—To a solution of 30.6 g (0.05 mol) of pure bis(tri-*n*-butyltin) sulfide in 50 ml of *n*-hexane was added dropwise under vigorous agitation 9.7 g (0.1 mol) of a 35% aqueous solution of hydrogen peroxide. After maintaining the agitation at room temperature until all peroxide had been consumed (potassium iodide test), the water was eliminated by azeotropic distillation. The remaining white precipitate was filtered, washed with hexane, and dried under vacuum over calcium chloride. Twenty-seven grams of pure bis(tri-*n*-butyltin) sulfate melting at 140–144° was obtained in 80% yield. *Anal.* Calcd for $C_{24}H_{54}O_4SSn_2$: C, 42.63; H, 8.05; O, 9.47; S, 4.74; Sn, 35.11. Found: C, 41.72; H, 8.13; O, 10.00; S, 4.69; Sn, 35.39. Infrared spectrum [potassium bromide wafer on Perkin-Elmer Infracord 337 grating spectrometer (in cm^{-1})]: 2900 (vs), 1450 (s), 1270 (s), 1100 (vs), 870 (w), 665 (v), 620 (s), 520 (vw), 470 (vw).

Di-*n*-butyltin Sulfate.—Fifty-seven grams (0.1 mol) of pure, recrystallized bis(chlorodi-*n*-butyltin) sulfide, prepared by heating at 100° for 1 hr equimolar amounts of di-*n*-butyltin sulfide and di-*n*-butyltin dichloride and recrystallized from *n*-hexane, was dissolved in 100 ml of *n*-hexane. To this solution, 19.5 g (0.2 mol) of 35% aqueous hydrogen peroxide was added dropwise under agitation. The agitation was maintained until completion of the reaction and the water was eliminated by azeotropic distil-

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