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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CONTRIBUTION FROM CARLISLE CHEMICAL WORKS, INC.,
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Preparation of Stannic Chloride Sulfide

BY CHRISTIAN H. STAPFER

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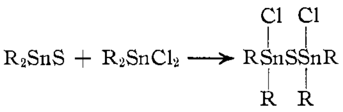
The reaction of dialkyltin sulfides with corresponding dialkyltin dichlorides is known to involve halogen transfer yielding 1,1,3,3-tetraalkyl-1,3-dichlorodistanthianes[1,2]



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

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

Received September 8, 1969

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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lation. An additional 50 ml of hexane was added to the reaction mixture, and, upon filtration and drying, 21.5 g of infusible white di-*n*-butyltin sulfate was obtained in 65% yield. The solvent was eliminated from the filtrate by evaporation and the remaining mixture yielded 17 g of di-*n*-butyltin dichloride and residual unreacted starting material by fractional recrystallization from *n*-hexane. *Anal.* Calcd for $C_8H_{18}O_4SSn$: C, 29.21; H, 5.51; O, 19.45; S, 9.75; Sn, 36.08. Found: C, 28.55; H, 5.42; O, 19.67; S, 9.99; Sn, 37.01. Infrared spectrum [KBr wafer (in cm^{-1})]: 2950 (vs), 2920 (s), 1455 (s), 1420 (w), 1370 (m), 1290 (s), 1100 (vs), 880 (s), 685 (s), 650 (m), 620 (s), 590 (vs), 535 (vw), 510 (vw), 415 (vw).

Poly[oxybis(di-*n*-butyltin) sulfate].—A solution of 53 g (0.02 mol) of di-*n*-butyltin sulfide in 50 ml of *n*-hexane was oxidized by slowly adding to it 38.9 g (0.4 mol) of 35% aqueous hydrogen peroxide, under vigorous agitation. The exothermic reaction was maintained at 30–40° during the addition of the peroxide and the agitation was maintained for 2 hr after completion of the addition. Thirty-two milliliters of water was eliminated by azeotropic distillation and the off-white precipitate formed was filtered and extracted several times with carbon disulfide. From the carbon disulfide, 1.2 g of elemental sulfur was recovered. The residual 42 g of infusible white powder represented a 32% yield of pure poly[oxybis(di-*n*-butyltin) sulfate]. *Anal.* Calcd for $(C_{16}H_{36}O_5SSn_2)_n$: C, 33.25; H, 6.28; O, 13.84; S, 5.55; Sn, 41.08. Found: C, 32.31; H, 6.22; O, 13.5; S, 5.91; Sn, 40.50. Infrared spectrum [KBr wafer (in cm^{-1})]: 2950 (vs), 2900 (s), 1455 (s), 1420 (w), 1300 (s), 1100 (vs), 1000 (s), 880 (s), 685 (s), 620 (s), 590 (s), 510 (w).

Bis(acetoxydi-*n*-butyltin) Sulfate.—A mixture of 100 g of poly[oxybis(di-*n*-butyltin) sulfate] and 200 g of acetic anhydride was refluxed for 30 min until the reaction mixture became clear. After cooling, crystallization occurred and the resulting solid was filtered, washed with 60 ml of cold acetic anhydride, and dried under vacuum over sodium hydroxide. Seventy-six grams of pure bis(acetoxydi-*n*-butyltin) sulfate melting at 288–289° was obtained (65% yield). *Anal.* Calcd for $C_{20}H_{42}O_8SSn_2$: C, 35.32; H, 6.22; O, 18.82; S, 4.71; Sn, 34.91. Found: C, 34.52; H, 5.97; O, 19.01; S, 4.92; Sn, 35.18. Infrared spectrum [KBr wafer (in cm^{-1})]: 2950 (vs), 2900 (s), 1725 (vs), 1645 (m), 1550 (w), 1455 (s), 1420 (w), 1370 (m), 1280 (s), 1200 (vs), 1050 (vs), 900 (w), 870 (w), 825 (w), 785 (2), 630 (m), 595 (m), 555 (w), 530 (s).

Poly(*n*-butylstannoxy) Acid Sulfate.—Twenty nine grams (0.3 mol) of a 35% aqueous solution of hydrogen peroxide was added dropwise to a refluxing suspension of 24.2 g (0.1 mol) of freshly prepared butylthiostannoic acid in 100 ml of *n*-hexane. After 2 hr of agitation at reflux and complete elimination of the water by azeotropic distillation, the resulting off-white polymeric solid was filtered, washed with petroleum ether and acetone, and then dried in a vacuum desiccator over phosphorus pentoxide. The 30 g of white powder obtained represented a quantitative yield of poly(*n*-butylstannoxy) acid sulfate melting with decomposition at 255–260°. *Anal.* Calcd for $(C_4H_{10}O_5SSn)_n$: C, 16.60; H, 3.46; O, 27.68; S, 11.07; Sn, 41.07. Found: C, 16.50; H, 3.92; O, 28.11; S, 11.30; Sn, 40.99. Infrared spectrum [KBr wafer (in cm^{-1})]: 3500 (s), 2990 (vs), 1400 (s), 1100 (vs), 1020 (vs), 880 (m), 750 (w), 595 (s). When treated with aqueous potassium hydroxide, poly(*n*-butylstannoxy) acid sulfate yielded quantitative amounts of *n*-butylstannoic acid which, in turn, reverted to the acid sulfate above by treatment with sulfuric acid.

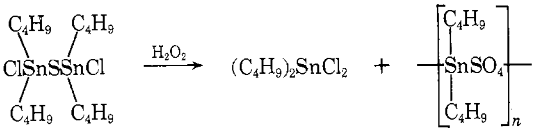
Results and Discussion

Bis(tri-*n*-butyltin) sulfide reacts readily with hydrogen peroxide to yield bis(tri-*n*-butyltin) sulfate

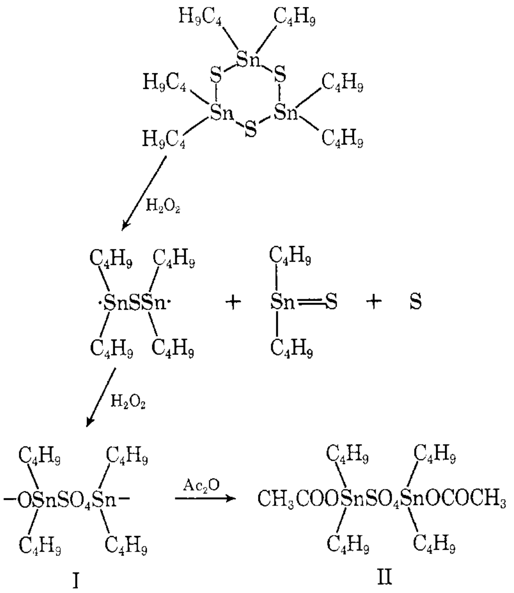
$$(C_4H_9)_3SnSSn(C_4H_9)_3 \xrightarrow{H_2O_2} (C_4H_9)_3SnSO_4Sn(C_4H_9)_3 \qquad (1)$$

The reaction is slightly exothermic and the resulting sulfate corresponds to the compound prepared by treating tri-*n*-butyltin isopropyl mercaptide with sulfuric acid following a reported general procedure.[1]

An attempt to prepare bis(chlorodi-*n*-butyltin) sulfate by the same process, using recrystallized bis(chlorodi-*n*-butyltin) sulfide[6] as a starting material, failed when the exothermic reaction with hydrogen peroxide led, by a redistribution reaction, to di-*n*-butyltin dichloride and di-*n*-butyltin sulfate (eq 2). The latter was comparable to the compound obtained from the reaction of di-*n*-butyltin oxide or di-*n*-butyltin sulfide with concentrated sulfuric acid.[7] It is reasonable to believe that the redistribution reaction took place after the oxidation of the halogenated organotin sulfide proceeded rather than before. If a redistribution into di-*n*-butyltin dichloride and di-*n*-butyltin sulfate had preceded the formation of the sulfate ion, one would expect dibutyltin sulfate to be the major product of the oxidation of dibutyltin sulfide with hydrogen peroxide. This is not the case and di-*n*-butyltin sulfide, which is known to assume a trimeric form,[8] seems to undergo a ring cleavage to form poly[oxybis(di-*n*-butyltin) sulfate] (I) and elemental sulfur. The formation of an intermediate free thiobis(di-*n*-butylstannyl) radical readily undergoing oxidation into the stannoxy derivative is a probable cause for the elimination of unreacted elemental sulfur. Residual di-*n*-butyltin sulfide resulting from the cleavage obviously may trimerize and undergo the same cleavage–oxidation sequence



$$ClSn(C_4H_9)_2SSn(C_4H_9)_2Cl \xrightarrow{H_2O_2} (C_4H_9)_2SnCl_2 + \left[Sn(C_4H_9)_2SO_4\right]_n \qquad (2)$$



I II

Poly[oxybis(di-*n*-butyltin) sulfate] reacts with acetic anhydride to form bis(acetoxydi-*n*-butyltin) sulfate (II) but does not react with mercaptans. *n*-Butylthiostannoic acid oxidizes quantitatively into *n*-butylstannoxy acid sulfate when treated with hydrogen peroxide (eq 3).

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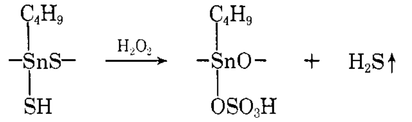
(6) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 943 (1964).
(7) C. H. Stapfer and A. C. Shah, unpublished results.
(8) W. T. Reichle, *J. Org. Chem.*, **26**, 4634 (1961).



$$-\overset{\displaystyle C_4H_9}{\underset{\displaystyle SH}{Sn}}S- \xrightarrow{H_2O_2} -\overset{\displaystyle C_4H_9}{\underset{\displaystyle OSO_3H}{Sn}}O- + H_2S\uparrow \qquad (3)$$

Potassium hydroxide easily hydrolyzes the sulfate into *n*-butylstannoic acid which, in turn, can be treated with sulfuric acid to revert to the *n*-butylstannoxy acid sulfate.

In summary, we can see that the reaction of hydrogen peroxide with alkyltin sulfides leads to the oxidation of tributyltin sulfide into the corresponding sulfate and to partial cleavage of dibutyltin sulfide and butylthiostannoic acid to form stannoxy sulfates with elimination of sulfur and hydrogen sulfide, respectively. Similar oxidation reactions were attempted with phenyl-substituted stannyl sulfides but extensive decomposition was observed in all cases.

The infrared spectra of most *n*-butyl-substituted stannyl sulfates show common vibrations at about 1100, 880, and 685 cm^{-1} which have been assigned to the stretching and deformation bands of the sulfate ion.[9,10] However, we feel that these spectra are insufficient to determine the exact structure of organotin sulfates. This question is the object of a separate investigation[11] showing that the tin atom in bis(tri-*n*-butyltin) sulfate is most likely to be pentacoordinate.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Triphenylphosphine and Triphenylarsine Complexes of Mercury(II) Thiocyanate, Nitrate, and Perchlorate[1,2]

BY A. R. DAVIS, C. J. MURPHY,[3] AND R. A. PLANE

Received June 9, 1969

A variety of tertiary phosphine and arsine derivatives of mercury(II) halides have been known for some time.[4] Recently the infrared spectra of the series of compounds $[(C_6H_5)_3P]_2HgX_2$ and $[(C_6H_5)_3P\cdot HgX_2]_2$ (X = Cl, Br, or I) have been studied by Deacon and Green.[5,6] The replacement of halides by such potentially multidentate ligands as thiocyanate, nitrate, and perchlorate offer a number of interesting bonding possibilities.

This paper reports a study of the complexes formed between triphenylphosphine (TPP) or triphenylarsine (TPA) and mercury(II) thiocyanate, nitrate, or perchlorate. The structures of the solid complexes have been deduced from their stoichiometry, infrared spectra, and a comparison with previous investigations of the similar mercury(II) halide complexes.[4-6]

Experimental Section

Materials.—All inorganic compounds were of reagent grade and were used as received. Triphenylphosphine was obtained from Matheson Coleman and Bell and was used without further purification. Triphenylarsine was purchased from Alfa Inorganics and was recrystallized from ethanol before use. All solvents were reagent grade.

Analytical Procedures.—Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Infrared Spectra.—The infrared spectra were obtained with a Perkin-Elmer 521 spectrophotometer. The samples were prepared as Nujol mulls pressed between either KBr or AgCl plates.

Preparation of Compounds.—All the compounds reported in this paper were prepared by the same general method. TPP or TPA and the appropriate mercury(II) salt were allowed to react in either a 2:1 or a 1:1 molar ratio in the boiling solvent indicated in Table I. The only exception is the preparation of $(TPA)_2Hg(SCN)_2$, which required a 10% excess of TPA to give the required product. After boiling for several minutes, the reaction mixtures were cooled. The colorless crystals which appeared were filtered off and washed thoroughly with absolute ether to remove any unreacted ligand. The thiocyanate and nitrate complexes were air dried and used without further treatment. The $(TPP)_2Hg(ClO_4)_2$ and $(TPA)_2Hg(ClO_4)_2$ complexes were recrystallized from nitromethane. The $[(TPP)Hg(ClO_4)_2]_2$ and $[(TPA)Hg(ClO_4)_2]_2$ complexes were thoroughly washed with nitromethane to remove any contaminating 2:1 complex present. The melting points and analytical data for the various compounds prepared are summarized in Table I. Preparation of $[(TPP)Hg(SCN)_2]_2$ was repeated three times and the surprisingly low melting point was obtained each time. All of the compounds are stable in air.

Caution! On several occasions the TPP complexes of mercury(II) perchlorate exploded when heated above their melting points. The analogous TPA complexes merely decomposed slowly under the same conditions. All should be treated with caution, however.

Results and Discussion

Class 1 compounds, prepared by the reaction of either triphenylphosphine or triphenylarsine with mercury(II) thiocyanate, nitrate, or perchlorate, in a 2:1 molar ratio, gave analyses consistent with the formulation

$$[(C_6H_5)_3E]_2HgX_2$$

1

where E = P or As and $X^- = SCN^-, NO_3^-$, or ClO_4^-. Class 2 compounds were prepared by using a 1:1 molar ratio of $(C_6H_5)_3E$ to mercury(II) salt. Analyses of the products are consistent with the formulation

$$[(C_6H_5)_3E\cdot HgX_2]_2$$

2

The major infrared peaks of the compounds are recorded in Table II. Absorptions characteristic of triphenylphosphine or -arsine are not tabulated. Evans, *et al.*,[4] and Deacon and Green[5,6] have prepared analogous series of halide complexes. X-Ray crystallographic studies[4] and infrared studies[5,6] of these halide complexes have been interpreted in terms of class 1 com-

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[2] Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[3] Visiting Professor on leave from Ithaca College, 1967–1968. Now at East Stroudsburg State College, East Stroudsburg, Pa. 18301.

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