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### Reactions of some thiolatotin compounds

During investigations of cyclic dithiolatotin compounds<sup>1</sup> we became interested in the general reactivity of the tin-sulphur bond about which there is little information. One method of investigation used was to examine the behaviour of triphenyltin thiophenoxide with various reagents and the results obtained, together with some reactions of cyclic dithiolatotin compounds are now reported. While this work was in progress, reactions of alkyltin thiolates with halogens<sup>2</sup> and metal halides<sup>3</sup> were described.

The tin-sulphur bond in triphenyltin thiophenoxide is stable to water and the compound can be recovered unchanged after several hours boiling in aqueous ethanol; addition of sodium hydroxide caused hydrolysis to triphenyltin hydroxide.

Reactions of triphenyltin thiophenoxide with metal halides gave similar results to those obtained by Abel<sup>3</sup> with cleavage of the tin-sulphur bond and formation of the metal thiophenoxide. One point of difference is that mercuric chloride gave chloro-mercury thiophenoxide whereas with trimethyltin butanethiolate only the fully thiolated product was formed<sup>3</sup>.

A strikingly different reaction occurred when mercuric acetate was used in place of the chloride, under mild conditions tin-carbon bond cleavage accompanied the tin-sulphur cleavage and the principal product was phenylmercury thiophenoxide PhHgSPh. Although cleavage of phenyl-tin bonds by mercuric chloride is known<sup>4</sup> the conditions employed were much more energetic than in the present case. At present only speculative attempts can be made to interpret the course of the reaction since the other major product isolated appeared to be the partially hydrolysed compound  $[\text{Ph}_2(\text{AcO})\text{Sn}-\text{O}-\text{SnPh}_2(\text{OAc})]_2$ , an attempt to make diphenyltin diacetate by the treatment of diphenyltin oxide with acetic acid gave the same product.

Attempts to isolate compounds of the type  $\text{SnCl}_x(\text{SPh})_{4-x}$  by treatment of stannic chloride with less than 4 equivalents of triphenyltin thiophenoxide gave only tin tetrathiophenoxide and unchanged stannic chloride. Using a 1:4 ratio of the reactants good yields were obtained of tin tetrathiophenoxide which was characterised by formation of its 2,2'-bipyridine derivative,  $\text{bipy}-\text{Sn}(\text{SC}_6\text{H}_5)_4$ .

The reactions were extended to include some cyclic compounds and (ethane-1,2-dithiolato)dibutyltin reacted with iodine to give dibutyltin diiodide and the polymeric sulphide  $(\text{S}-\text{CH}_2\text{CH}_2-\text{S})_n$ . The spirocyclic bis(ethane-1,2-dithiolato)tin with

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one molecular proportion of iodine gave stannic iodide and polymeric products containing tin. (Ethane-1,2-dithiolato)dibutyltin reacted with mercuric acetate to give dibutyltin diacetate and  $(\text{SCH}_2\text{CH}_2\text{SHg})_n$ . Although organotin monothiolates react with methyl iodide<sup>2</sup> this reagent had no effect upon bis(ethane-1,2-dithiolato)tin.

#### EXPERIMENTAL

##### *Reactions of triphenyltin thiophenoxide*

(a) *With mercuric chloride*. Addition of a solution of mercuric chloride (0.27 g) in ether (10 ml) to a solution of triphenyltin thiophenoxide (0.46 g) in ether (10 ml) gave an immediate white precipitate. Filtration and crystallisation of the product from benzene gave chloromercury thiophenoxide (0.30 g), m.p. 192–194° unchanged on admixture with an authentic<sup>5</sup> sample. Evaporation of the ether filtrate and crystallisation of the residue from light petroleum gave triphenyltin chloride, m.p. 104–106° (lit.<sup>6</sup> m.p. 106°).

(b) *With mercuric acetate*. Mercuric acetate (0.32 g) in ethanol (10 ml) was added to a hot solution of triphenyltin thiophenoxide (0.92 g) in ethanol (30 ml). On cooling a small quantity (0.08 g) of mercury dithiophenoxide m.p. and mixed m.p. 150–151° crystallised and was filtered off. On cooling the filtrate in ice a second product was obtained which, after recrystallisation from ethanol, was shown to be phenylmercury thiophenoxide (0.30 g), m.p. and mixed m.p. 104–105°. (Found: C, 37.85; H, 2.9.  $\text{C}_{12}\text{H}_{10}\text{HgS}$  calcd.: C, 37.3; H, 2.6%.)

Concentration of the mother liquor gave triphenyltin acetate (0.10 g) m.p. 119–121° (lit.<sup>6</sup> m.p. 121–122°), while complete evaporation gave material which, after recrystallisation from benzene gave a product (0.26 g), m.p. > 250° (this product had an infrared spectrum identical with a compound (m.p. > 250°) obtained by the treatment of diphenyltin oxide with acetic acid and tentatively identified as  $[(\text{AcO})\text{Ph}_2\text{Sn}-\text{O}-\text{SnPh}_2(\text{AcO})]_n$ . (Found: Sn, 35.3.  $\text{C}_{28}\text{H}_{26}\text{O}_5\text{Sn}_2$  calcd.: Sn, 34.9%.)

(c) *With stannic chloride*. A solution of stannic chloride (0.24 g) in dry (Na) benzene (10 ml) was added to triphenyltin thiophenoxide (1.72 g, 4 mol.) in the same solvent (10 ml). Evaporation and extraction of the residue with cold petroleum (b.p. 40–60°) gave a product which, after crystallisation from ethanol, was shown to be tin tetrathiophenoxide (0.51 g), m.p. 66–67° (lit.<sup>7</sup> m.p. 67°). This was characterized by formation of its 2,2'-bipyridine adduct, m.p. 135–6°. (Found: C, 57.3; H, 4.15; N, 4.0.  $\text{C}_{44}\text{H}_{38}\text{N}_2\text{S}_4\text{Sn}$  calcd.: C, 57.4; H, 4.0; N, 3.9%.)

The residue which was insoluble in cold petroleum (b.p. 40–60°) was crystallised from this solvent giving triphenyltin chloride (1.10 g), m.p. 105–6°.

##### *Reaction of (ethane-1,2-dithiolato)dibutyltin with iodine*

Iodine (0.25 g) in chloroform (25 ml) was added dropwise to a solution of (ethane-1,2-dithiolato)dibutyltin (0.33 g, 1 mol.) in chloroform (10 ml) when rapid decolourisation occurred. After allowing to stand for 1 hour the mixture was filtered from a trace of insoluble material and the filtrate evaporated. The residue was extracted with petroleum (b.p. 40–60°, 20 ml) the insoluble material (0.06 g) was a tin-free sticky solid with an infrared spectrum consistent with  $(-\text{SCH}_2\text{CH}_2\text{S}-)_n$ .

2,2'-Bipyridyl (0.16 g) in benzene (5 ml) was added to the petroleum solution, the adduct crystallised out and was recrystallised from ethanol giving pure dibutyl-

(2,2'-bipyridine)tin diiodide (0.57 g) m.p. 163°, undepressed on admixture with an authentic<sup>9</sup> specimen.

*Reaction of (ethane-1,2-dithiolato)dibutyltin with mercuric acetate*

Addition of a warm solution of mercuric acetate (0.64 g) in ethanol (5 ml) to (ethane-1,2-dithiolato)-dibutyltin (0.65 g) in ethanol (10 ml) gave an immediate white precipitate of the polymeric  $(-\text{Hg}-\text{S}-\text{CH}_2\text{CH}_2\text{S}-)_n$  (0.62 g), m.p. 145° decomp. (lit.<sup>9</sup> m.p. 150–155° decomp.), infrared spectrum identical with that of an authentic specimen. (Found: C, 9.0; H, 1.4.  $\text{C}_2\text{H}_4\text{HgS}_2$  calcd.: C, 8.2; H, 1.4%.)

Evaporation of the filtrate gave an oil (0.43 g) which had an infrared spectrum identical with that of authentic dibutyltin diacetate.

*Reaction of bis(ethane-1,2-dithiolato)tin with iodine*

Iodine (0.80 g) in chloroform (40 ml) was added to a solution of bis(ethane-1,2-dithiolato)tin (0.95 g, 1 mol.) in chloroform (30 ml). The iodine colour rapidly disappeared and a yellow solid (0.20 g), m.p. 135–138°, was precipitated. (Found: C, 21.5; H, 3.8; Sn, 10.4%.) Concentration of the filtrate gave a second product (0.37 g), m.p. 150° decomp. (Found: C, 13.1; H, 2.8; Sn, 24.6%.) Attempts to isolate pure compounds from these products were unsuccessful.

Complete evaporation and crystallisation of the residue from benzene gave stannic iodide (0.72 g.), m.p. and mixed m.p. 143–145°. A portion of this product was converted to its 2,2'-bipyridine derivative, m.p. > 350° (lit.<sup>10</sup> m.p. > 400°), infrared spectrum identical with that of an authentic specimen.

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