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The Synthesis of *bis* (Tri-*N*-Butyl)tin-113 Oxide

Kenneth S. TENNY and Alfred M. TENNY
The Metropolitan Sanitary District of Greater Chicago

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SUMMARY

Bis(*tri*-n-*butyl)tin-113 oxide was prepared from tetrabutyltin and tin-113 tetrachloride by redistribution reaction between alkyl groups, with the formation of the intermediate tri*-n-*butyltin-113 chloride, which was hydrolyzed to form the desired product. Purification of the reaction mixture by alumina column chromatography, followed by thin layer chromatography, revealed a pure sample. The sample was also distilled under vacuum as a further check on the efficiency of the purification methodology; radioactivity resided in the* bis*(tri*-n-*butyl)tin oxide fraction. Infra-red analysis of similarly prepared non-radioactive sample showed the Sn-O-Sn bond; the spectra agreed with published spectra, and with the spectra obtained in our laboratory from commercial samples.*

1. — INTRODUCTION.

The Metropolitan Sanitary District of Greater Chicago has experimentally applied "Biocide" (Drew Chemical Co.), a commercial product containing *bis*(tri-*n*-butyl)tin oxide (TBTO) as an active ingredient, to a vacuum filter cloth used for separation of activated sludge in the production of fertilizer. Fungus growths on the filters has caused clogging. In the process of using Biocide to kill the fungus it was necessary to synthesize TBTO to carry out studies pertaining to the application of the fungicide. The purpose of the synthesis was to evaluate how to utilize "Biocide" through a tracer examination of its course once added to the activated sludge. The synthesis of *bis*-(tri-*n*-butyl)tin oxide can be described by the following reactions :

(*a*). $SnCl_4 + 3Bu_4Sn \rightarrow 4Bu_3SnCl$
(*b*). $2Bu_3SnCl + 2KOH \xrightarrow[\text{(aq.)}]{} (Bu_3Sn)_2O + 2KCl + H_2O$

(side products = $Bu_4Sn + Bu_2SnO$)

Mendelsohn, Marchand, and Valada (2) prepared tri-*n*-butyltin chloride by the redistribution of alkyl groups between tetrabutyltin and tin tetrachloride. By alkaline hydrolysis of the latter, they obtained *bis*(tri-*n*-butyl)tin oxide.

Intensive infra-red studies by these authors of numerous tin compounds showed that the Sn-O-Sn bond gave an asymmetric vibration peak at 784 cm^{-1} distinctive in identifying the tin oxide.

Radioactive tin (Sn-113) has also been utilized in the redistribution reaction by several authors to prepare organo-tin-113 intermediates.

Frye and Horst (3) prepared dibutyltin-113 dichloride by refluxing tin-113 tetrachloride with non-radioactive tetrabutyltin.

Otto and Luijten (4) utilized the same reaction to prepare tri-n-butyltin-113 chloride. From that intermediate they prepared the tributyltin-113 benzoate.

In the present report, we utilized tri-*n*-butyltin-113 chloride as an intermediate for the synthesis of TBTO.

Organo-tin preparations in general, as well as TBTO have been routinely purified and fractioned by vacuum distillation (1, 5).

Radioactive organo-tin compounds have also been purified by the same method of vacuum distillation (3, 4).

Due to the hazards of contaminating the laboratory with Sn-113 by possible leakage in a distillation, an alternative method of purification of the TBTO was investigated, namely alumina column chromatography.

The alumina column was found to give good resolution of tetrabutyltin and TBTO. Physical and chemical parameters of the TBTO compared favorably to that reported in the literature and obtained by distillation.

2. — METHODOLOGY.

Alumina column chromatography:

Columns were prepared with Bio Rad Basic Alumina (AG 10, 100-200 mesh) and eluted with hexane and ether. Tetra-*n*-butyltin (Aldrich Chem. Co.) eluted 97 percent in the hexane fraction. *Bis*(tri-*n*-butyl)tin oxide eluted 92 percent in the ether fraction.

Infra-red:

The non-radioactive "cold run" of the synthesis was fractionated as described above and examined on the I.R. The distinctive Sn-O-Sn peak of bis(tri-*n*-butyl)tin oxide appeared at 784 cm^{-1} on the ether fraction and the spectra was identical to that reported in the literature (2). The radioactive preparation was assumed to be similar and not itself analyzed on the I.R.

Comparison of the alumina column with vacuum distillation :

The two methods for treating organo-tin compounds were evaluated with commercially available tetrabutyltin and bis(tri-*n*-butyl)tin oxide (Aldrich Chemical Company).

Tetra-*n*-butyltin (Aldrich $n_D^{20} = 1.4738$) purified by alumina column gave $n_D^{20} = 1.4735$. Vacuum distillation gave $n_D^{20} = 1.4735$. Various literature references give $n_D^{20} = 1.4746$ (1), $n_D^{20} = 1.4735$ (6), and $n_D^{20} = 1.4730$ (8).

Bis(tri-*n*-butyl)tin oxide (Aldrich $n_D^{20} = 1.4868$) purified by alumina column gave $n_D^{20} = 1.4872$. Vacuum distillation of the same material gave $n_D^{20} = 1.4868$. The literature gives $n_D^{20} = 1.4870$ (1), $n_D^{20} = 1.4862$ (6) and $n_D^{20} = 1.4871$ (7).

3. — EXPERIMENTAL PROCEDURE :

Tin-113 tetrachloride in 4M. HCl (2.1 mC, 0.2 gm tin tetrachloride, Union Carbide Corp.), was continuously extracted with ethyl ether until the ether phase contained most of the radioactivity as measured by a "Ludlum count rate meter". Ether was evaporated on a rotating vacuum evaporator (Rinco Co.). The resulting tin-113 tetrachloride hydrate was mixed with anhydrous tin tetrachloride (4.38 gm) and tetrabutyltin (17.0 gm) in a round bottomed flask equipped with condenser, calcium chloride tube, and magnetic stirrer and heated on an oil bath to 200° to 210° C for 4 ½ hours.

The reaction mixture was cooled to room temperature, potassium hydroxide (5.75 gm) in water (16.5 ml) together with ethyl ether (30 ml) was added, and the mixture was refluxed at 60° C for 45 minutes.

The white precipitate was filtered from the reaction mixture; the filtered product was presumably $(Bu_2SnO)_x$ as reported in the literature (1). The ether filtrate was dried with sodium sulfate, and the ether was evaporated on the rotating vacuum evaporator. The reaction mixture was dissolved in hexane and applied to a 2 cm diameter alumina column (140 gm Basic Alumina) and eluted with 700 ml each of hexane and ether.

Radioactivity was assayed on a deep well gamma counter (Nuclear Chicago). The isotopic yield of the reaction was 16 percent (345 μC). In addition, the hexane yielded 304 μC, and an undetermined amount of radioactivity was retained on the column. The chemical yield, determined on a non-radioactive "cold run", was 52 %.

Vacuum distillation :

Bis(tri-*n*-butyl)tin-113 oxide, purified as previously described, was diluted with a mixture of non-radioactive carrier *bis*(tri-*n*-butyl)tin oxide and tetrabutyltin. The mixture was distilled under vacuum.

Tetrabutyltin distilled at 140-148° C at 2 mm Hg; the literature gives 145° C at 10 mm (8).

Bis(tri-*n*-butyl)tin oxide distilled at 203-205° C at 1.70 mm Hg; the literature gives 210-214° C at 10 mm Hg (1).

Radioactivity of the fractions was assayed. Tetra-*n*-butyltin contained about 7 percent of the radioactivity of the bis(tri-*n*-butyl)tin oxide, which does not indicate an impurity in the TBTO for the activity of the fraction could have resulted from decomposition of the TBTO during distillation. *Bis*(tri-*n*-butyl)tin oxide decomposes to tetrabutyltin and dibutyltin oxide (5). The activity of the TBTO fraction does establish the identity of the Sn-113 with the synthesized TBTO.

Thin layer chromatography.

The radiochemical purity of the *bis*(tri-*n*-butyl)tin oxide was determined by thin layer chromatography, after the procedure of Otto and Luijten (4) as described below.

Chloroform solutions containing 10 μg organotin were applied to a silicagel layer 0.25 mm thickness (Silic AR TLC-7GF Mallinckrodt) activated at 100° C for one hour. The chromatograms were developed with a mixture of hexane and acetic acid (12 : 1), dried at 100° C for 30 minutes, exposed to bromine vapor for 30 minutes, and sprayed with a 0.1 percent solution of pyrocatechol violet in ethanol. The developed chromatographic spots were scratched off into tubes for radioactivity measurement. Remaining portions of the chromatograms were also transferred to tubes and counted.

The $(Bu_3Sn)_2O$ spot ($R_f = 0.3\text{-}0.4$) yielded 96 percent of the radioactivity while the residual activity at the origin amounted to only 1 percent. Between the origin and the spot, a tail of radioactivity occurred amounting to 2 percent of the total. The remainder of the chromatogram from $R_f = 0.4$ to 1.0 yielded only 1 percent of the total radioactivity.

4. — CONCLUSION.

Bis(tri-*n*-butyl)tin-113 oxide was synthesized. Alumina column chromatography purified the product. Isotopic yield was 16 percent for the reaction. The identity of the product was established by vacuum distillation. Radiochemical purity of the product was between 96-98 percent as established by thin layer chromatography.

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