[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DREXEL INSTITUTE OF TECHNOLOGY]

# REACTIONS OF BIS-(TRIETHYLTIN) OXIDE WITH ACIDS. TRIETHYLTIN MERCAPTIDES

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*Received March 9, 1953*

Recent studies of Anderson (1, 2) have shown that bis-(trialkylgermanium) oxides react with various weak acids such as acetic, mercaptoacetic, and hydrocyanic to form the corresponding esters. Because of the relative position of tin with respect to germanium in the periodic table, it was expected that bis-(trialkyltin) oxides are more basic than bis-(trialkylgermanium) oxides, and therefore, capable of reacting with a variety of weak acids.

This study was undertaken to demonstrate the basicity of bis-(triethyltin) oxide by allowing it to react with acids whose ionization constants range between $10^{-1}$ and $10^{-10}$. Bis-(triethyltin) oxide is sufficiently basic to react with trifluoroacetic, acetic, propionic, butyric, and benzoic acids; ethyl, isopropyl, *n*-butyl, isobutyl, *tert*-butyl, isoamyl, and benzyl mercaptans; *o*-thiocresol, *m*-thiocresol, *p*-thiocresol, phenol, *p*-cresol, and hydrogen sulfide to form the corresponding esters. The properties of the esters prepared are summarized in Table I.

The method of preparing trialkyltin phenoxides by treating bis-(triethyltin) oxide with phenol or *p*-cresol appears to be more convenient than the one previously reported (3) which involves the reaction of trimethyltin bromide with sodium phenoxide. Bis-(triethyltin) oxide reacts readily with mercaptans and thiocresols to form, in quantitative yields, triethyltin mercaptides. The author believes that this is the first synthesis of trialkyltin mercaptides.

Kulmiz had previously shown (4) that hydrogen sulfide reacts with bis-(triethyltin) oxide, but he did not succeed in isolating the product. The product of this reaction was isolated by distillation at 1 mm. and found to be bis-(triethyltin) sulfide. The following is suggested as a plausible mechanism for the formation of the sulfide.

$$(R_3Sn)_2O + 2\ H_2S \rightarrow 2\ R_3SnSH + H_2O$$
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Triethyltin benzoate was previously prepared by Kulmiz (5) by treating triethyltin iodide with silver benzoate. The melting point of the benzoate reported by Kulmiz is 80°; the melting point of our sample of triethyltin benzoate is 71°. This discrepancy is undoubtedly due to the difference in the methods used in determining the melting points. All melting points in this study were determined by stirring a bulb thermometer immersed in the cooling molten compounds, and recording that temperature for melting points at which the compound partially solidified. Triethyltin acetate and butyrate were previously prepared (6) by treating the oxide with acetic and butyric acids respectively, but since little physical data were reported on these compounds, it

TRIETHYLTIN ESTERS

| COMPOUND | B.P. |  | M.P., °C. | $d_4^{20}$ | $n^{20}$ | ANALYSES |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Mol. Wt. |  | Sulfur |  | Tin |  |
|  | °C. | Mm. |  |  |  | Calc'd | Found | Calc'd | Found | Calc'd | Found |
| $(C_2H_5)_3Sn(CF_3COO)$ | 218 | 760 | 107 |  |  | 318.9 | 312 |  |  | 37.2 | 36.7 |
| $(C_2H_5)_3Sn(CH_3COO)$[a] | 224 | 760 | 119 |  |  | 264.9 | 281 |  |  |  |  |
| $(C_2H_5)_3Sn(CH_3CH_2COO)$ | 226 | 760 | 103 |  |  | 278.9 | 268 |  |  | 42.5 | 42.9 |
|  | 238 | 760 |  |  |  |  |  |  |  |  |  |
| $(C_2H_5)_3Sn(CH_3CH_2CH_2COO)$[b] | 96–98 | 1 | 92 |  |  | 293.0 | 285 |  |  |  |  |
|  | 286 | 760 |  |  |  |  |  |  |  |  |  |
| $(C_2H_5)_3Sn(C_6H_5COO)$[c] | 132–134 | 1 | 71 |  |  | 326.0 | 317 |  |  | 36.4 | 36.7 |
|  | 230 dec. | 760 |  |  |  |  |  |  | 11.8 |  |  |
| $(C_2H_5)_3Sn(C_2H_5S)$ | 125–126 | 12 |  | 1.278 | 1.5150 | 267.0 | 258 | 12.0 | 11.7 |  |  |
|  | 240 | 760 |  |  |  |  |  |  | 11.1 |  |  |
| $(C_2H_5)_3Sn(iso\text{-}C_3H_7S)$ | 78–79 | 1 |  | 1.236 | 1.5132 | 281.0 | 276 | 11.4 | 11.4 |  |  |
|  | 256 | 760 |  |  |  |  |  |  | 10.5 |  |  |
| $(C_2H_5)_3Sn(n\text{-}C_4H_9S)$ | 88–91 | 1 |  | 1.234 | 1.5133 | 295.1 | 302 | 10.8 | 10.6 |  |  |
|  | 248 dec. | 760 |  |  |  |  |  |  | 10.4 |  |  |
| $(C_2H_5)_3Sn(iso\text{-}C_4H_9S)$ | 86–88 | 1 |  | 1.244 | 1.5122 | 295.1 | 290 | 10.8 | 10.5 | 40.2 | 40.5 |
|  | 243 dec. | 760 |  |  |  |  |  |  |  |  |  |
| $(C_2H_5)_3Sn(tert\text{-}C_4H_9S)$ | 84–86 | 1 |  | 1.240 | 1.5051 | 295.1 | 286 |  |  | 40.2 | 40.3 |
|  | 254 | 760 |  |  |  |  |  |  | 10.0 |  |  |
| $(C_2H_5)_3Sn(iso\text{-}C_5H_{11}S)$ | 96–97 | 1 |  | 1.188 | 1.5060 | 309.1 | 315 | 10.3 | 10.0 |  |  |
|  | 285 dec. | 760 |  |  |  |  |  |  | 9.7 |  |  |
| $(C_2H_5)_3Sn(o\text{-}CH_3C_6H_5S)$ | 132–135 | 1 |  | 1.295 | 1.5740 | 329.1 | 339 | 9.7 | 9.6 |  |  |
|  | 292 dec. | 760 |  |  |  |  |  |  | 9.9 |  |  |
| $(C_2H_5)_3Sn(m\text{-}CH_3C_6H_5S)$ | 132–134 | 1 |  | 1.283 | 1.5705 | 329.1 | 340 | 9.7 | 9.8 |  |  |
|  | 288 | 760 |  |  |  |  |  |  | 9.7 |  |  |
| $(C_2H_5)_3Sn(p\text{-}CH_3C_6H_5S)$ | 128–130 | 1 |  | 1.288 | 1.5712 | 329.1 | 342 | 9.7 | 9.6 |  |  |
|  | 300 | 760 |  |  |  |  |  |  | 9.8 |  |  |
| $(C_2H_5)_3Sn(C_6H_5CH_2\text{-}S)$ | 136–138 | 1 |  | 1.304 | 1.5682 | 329.1 | 336 | 9.7 | 9.8 |  |  |
|  | 260 | 760 |  |  |  |  |  |  |  |  |  |
| $(C_2H_5)_3Sn(C_6H_5O)$ | 115–116 | 1 |  | 1.315 | 1.5422 | 293.0 | 302 |  |  | 39.6 | 39.5 |
|  | 280 | 760 |  |  |  |  |  |  |  |  |  |
| $(C_2H_5)_3Sn(p\text{-}CH_3C_6H_5O)$ | 124–127 | 1 |  | 1.283 | 1.5365 | 313.0 | 298 |  |  | 37.9 | 37.9 |
|  | 303 dec. | 760 |  |  |  |  |  |  |  |  |  |
| $(C_2H_5)_3SnS\text{-}Sn\text{-}(C_2H_5)_3$ | 133–137 | 1 |  | 1.429 | 1.5468 | 443.8 | 431 |  |  | 53.6 | 53.8 |

[a] Reported by Cahours (6) as sublimable needles, b.p. 230°. [b] Reported by Cahours (6) as sublimable needles. [c] Prepared by Kulmiz (5) by treating triethyltin iodide with silver benzoate, m.p. 80°.

seemed advisable to prepare them and to measure their boiling and melting points to facilitate their future identification.

## EXPERIMENTAL

All melting points are corrected, and were determined by stirring a bulb thermometer immersed in the cooling molten compounds, recording that temperature for melting points at which the compound partially solidified. All boiling points at 760 mm. pressure are corrected and were measured by the dynamic method. All compounds, unless otherwise stated, were distilled at the lowest pressure listed in Table I.

*Bis-(triethyltin) oxide.* Three liters of 1.85 *molar* ethyl magnesium bromide (5.55 moles) were added over a 3-hour period, with occasional shaking, to 482 g. of stannic chloride (1.85 moles) dissolved in 500 ml. of dry benzene immersed in an ice-water bath. The reaction mixture was allowed to stand overnight. After gradual aqueous decomposition of the unreacted ethylmagnesium bromide, the organotin layer was separated and shaken with 400 ml. of 3 *M* sodium hydroxide solution for 30 minutes to convert triethyltin chloride to bis-(triethyltin) oxide. The ether-benzene layer was separated from the aqueous layer, and to complete the recovery of organotin, the aqueous layer was extracted with hexane. The organotin solution was then dried overnight over sodium sulfate. The solvent was removed by distillation at atmospheric pressure; further distillation under 100 mm. pressure yielded 50 g. of crude tetraethyltin at 110–118°. Distillation under 1 mm. pressure yielded 102 g. of bis-(triethyltin) oxide at 100–102° [boiling point at 760 mm. reported (6), 272°]; boiling point at 760 mm. obtained was 270°. Thus only 25.5% of stannic chloride was converted to bis-(triethyltin) oxide. A solid residue, presumably polymeric diethyltin oxide, remained in the distilling flask; it was discarded.

*Triethyltin acetate, propionate, butyrate, and trifluoroacetate.* When 4.3 g. (0.01 mole) of bis-(triethyltin) oxide was mixed with 0.02 mole of the appropriate acid heat was evolved, and the esters precipitated almost immediately. After gentle heating under reflux for ten minutes, water and the excess acid were removed by distillation. The esters were then distilled; all of the esters solidified. The yields were essentially quantitative.

*Triethyltin ethyl, isopropyl, n-butyl, isobutyl, tert-butyl, and isoamyl mercaptides.* When 4.3 g. (0.01 mole) of bis-(triethyltin) oxide was mixed with 0.03 mole of the appropriate mercaptan heat was evolved and an emulsion formed. The reaction mixture was heated under reflux for ten minutes. After the removal of water and excess mercaptan by distillation, the esters were distilled. The yields were essentially quantitative.

*Triethyltin benzoate, phenoxide, and p-cresoxide and benzyl, o-tolyl, m-tolyl, and p-tolyl mercaptides.* When 4.3 g. (0.01 mole) of bis-(triethyltin) oxide was mixed with 0.0105 mole of benzoic acid or the appropriate phenol or thiocresol heat was evolved and an emulsion formed. After gentle heating under reflux for ten minutes, water and the excess reactant were removed by distillation under 100 mm. pressure. The esters were then distilled under 1 mm. pressure; the yields were essentially quantitative.

*Bis-(triethyltin) sulfide.* When excess hydrogen sulfide was bubbled into 4.3 g. (0.01 mole) of bis-(triethyltin) oxide, the reaction mixture became quite warm. After the removal of water by distillation under 100 mm. pressure, bis-(triethyltin) sulfide was distilled at 1 mm. The yield was essentially quantitative.

*Analyses and properties of the esters.* Triethyltin acetate, propionate, butyrate, benzoate and trifluoroacetate are white solids; all the other esters prepared are colorless liquids. Sulfur, in all of the mercaptides except in *tert*-butyl mercaptide, was determined by the titration with standard iodine solution of an alcoholic solution of the mercaptide which was acidified with hydrochloric acid. Tin was determined as $SnO_2$ by the method of Kulmiz (5).

## SUMMARY

1. The basicity of bis-(triethyltin) oxide was studied.
2. Trialkyltin mercaptides were prepared.

3. Trialkyltin propionate, trifluoroacetate, phenoxide, *p*-cresoxide, and sulfide; and ethyl, isopropyl, *n*-butyl, isobutyl, *tert*-butyl, isoamyl, benzyl, *o*-thiocresyl, and *p*-thiocresyl mercaptides were prepared.

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