[Contribution from the Chemistry Department, Drexel Institute of Technology]

"CONVERSION SERIES" FOR TRIETHYLTIN DERIVATIVES USING SILVER SALTS

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Before the present research there has been no systematic investigation of organotin esters, halides, halogenoids, oxides and sulfides to demonstrate the conversion of one compound into another.

This paper offers a complete "conversion series" for triethyltin derivatives using dry silver salts with or without an inert solvent such as benzene, carbon tetrachloride, toluene, or xylene. In the "conversion series", Et_3SnSCH_3 and $(Et_3Sn)_2S \rightarrow Et_3SnI \rightarrow Et_3SnBr \rightarrow Et_3Sn(CN) \rightarrow Et_3Sn(NCS) \rightarrow Et_3SnCl \rightarrow (Et_3Sn)_2O \rightarrow Et_3Sn(NCO) \rightarrow Et_3SnOCOCH_3 \rightarrow Et_3SnF$ heating with the appropriate silver salt converts a triethyltin compound into any other triethyltin compound to the right of it in the series. Reactions proceed only slightly to the left, if at all. Silver iodide converts $(Et_3Sn)_2S$ into Et_3SnI; silver bromide converts anhydrous Et_3SnSCH_3, $(Et_3Sn)_2S$ and Et_3SnI all into Et_3SnBr; silver cyanide changes Et_3SnSCH_3, $(Et_3Sn)_2S$, Et_3SnI, and Et_3SnBr all into $Et_3Sn(CN)$. No other atom or radical in this "conversion series" can displace the fluorine atom in Et_3SnF. We may also write the "conversion series" as SCH_3 and $S \rightarrow I \rightarrow Br \rightarrow CN \rightarrow NCS \rightarrow Cl \rightarrow O \rightarrow NCO \rightarrow OCOCH_3 \rightarrow F$ in considering ester groups, halide, halogenoid, oxygen, sulfur (sulfide), and methylmercaptide group only.

Several publications nearly a century ago demonstrated the use of silver salts in changing Et_3SnI into $Et_3Sn(CN)$ (1), Et_3SnI into unanalyzed $Et_3Sn(NCS)$ (1), also Et_3SnCl into $Et_3Sn(NCO)$ (1, 2)—but omitted boiling points and melting points. We have reexamined $Et_3Sn(NCO)$, $Et_3Sn(NCS)$, and $Et_3Sn(CN)$, furnishing boiling points, melting points, and other information.

Our best center-fraction $Et_3Sn(NCO)$ melted at 48°, boiled at 239° at 760 mm., 162–163° at 80 mm., or 120–121° at 11 mm.; made from Et_3SnBr and AgNCO, there was no bromine present in the $Et_3Sn(NCO)$. Our center-fraction $Et_3Sn(NCS)$, prepared from Et_3SnI and AgNCS, contained no iodine; the $Et_3Sn(NCS)$ boiled at 130°/1 mm., or at 282° with much decomposition under 760 mm.; $Et_3Sn(NCS)$ melts at 33°, but easily supercools to 20° without crystallization, furnishing (on supercooled liquid) d_4^{20}, 1.458 and n^{20}, 1.5825. Our best $Et_3Sn(CN)$ melted at 153° and boiled at 249° under 760 mm., with formation of an infusible white solid. $Et_3Sn(CN)$ must be sublimed at 8 mm. to avoid excessive decomposition; it hydrolyzes easily in moist air. Our center-fraction Et_3SnSCH_3, a new compound, prepared from $(Et_3Sn)_2O$ and CH_3SH, boiled at 224°, had d_4^{20} 1.319 and n^{20} 1.5290.

As expected, $(Et_3Sn)_2O$ reacts with either anhydrous liquid hydrogen cyanide or a solution of isothiocyanic acid in diethyl ether to yield $Et_3Sn(CN)$ and

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$Et_3Sn(NCS)$ respectively, but $(Et_3Sn)_2O$ does not react with anhydrous isocyanic acid to give $Et_3Sn(NCO)$. Perhaps HNCO polymerizes too rapidly into cyanuric acid, a trimer, for reaction with the organotin oxide.

Other researches undertaken in this department by one of us have centered around "conversion series" for organosilicon and organogermanium esters, halides, halogenoids, oxides, and sulfides (3). Eaborn (4) presents excellent evidence of a "conversion series" for organosilicon compounds not including esters.

It is beyond the present publication to explain the mechanism of the reactions with silver salts, or to compare numerous differences in the four individual series for silicon, gemanium, tin, or phosphorus.

The "conversion series" does not follow the solubility products of silver salts (using data for pure aqueous solutions); oxide and sulfide are usually not in the relative positions which solubility products could predict, assuming formation of the least soluble silver salt.

Specific examination of the reported "conversion series" for organotin derivatives shows that sulfide may be changed into any other atom or group in the series. This is the only instance yet of sulfide as the most replaceable in a series. Reactions using silver oxide are surprisingly difficultly performed, since the organotin derivatives often reduce silver oxide to the metal in the absence of a solvent.

In a number of combinations the forward reaction such as $Et_3SnBr + AgF \rightarrow Et_3SnF + AgBr$ was quantitative while the reverse reaction $Et_3SnF + AgBr \rightarrow Et_3SnBr + AgF$ went 2% to completion in the absence of a solvent. Perhaps the small bromine content of the Et_3SnF sublimate was actually due to hydrogen bromide. We consider this small percentage without effect on the "conversion series". Reactions of $Et_3Sn(NCO)$ with the appropriate silver salt yielded 10% of the chloride, 8% of the thiocyanate, or 5% of the cyanide which a pure chloride, thiocyanate or cyanide would contain—while silver cyanate converted the organotin chloride, thiocyanate, and cyanide quantitatively into (iso) cyanate. We consider this slight contradiction to be due to the known decomposition of silver cyanate.

EXPERIMENTAL

I. "CONVERSION SERIES"

Reactions of Et_3SnSCH_3. In each reaction 0.2 g. of Et_3SnSCH_3 and 0.4 g. of the silver salt were subjected to an hour of reflux, except for the reaction with silver fluoride which was instantaneous and violent, yielding Et_3SnF, and the reaction with Ag_2O, which was quite violent. Silver cyanate yielded $Et_3Sn(NCO)$ in 5 ml. of toluene; AgNCS in toluene yielded $Et_3Sn(NCS)$. In the absence of a solvent AgCl, AgCN, AgBr and AgI yielded Et_3SnCl, $Et_3Sn(CN)$, Et_3SnBr, and Et_3SnI respectively, whereas reactions in toluene were quite slow in rate. Silver acetate and 1 g. of $Et_3SnS\text{-}iC_3H_7$ (5) yielded $Et_3SnOCOCH_3$, m.p. 121°, b.p. 217°, after ten minutes of reflux under 60 mm.

Reactions of $(Et_3Sn)_2S$. When not specified, 0.3 g. of $(Et_3Sn)_2S$ and 0.8 g. of the silver salt were used in an hour of reflux. Gentle warming with AgF produced cotton-like Et_3SnF easily. A 60-minute reflux of 0.20 g. of Ag_2O and 0.30 g. of $(Et_3Sn)_2S$ in 3 ml. of toluene gave a product about 96% $(Et_3Sn)_2O$ and 4% $(Et_3Sn)_2S$. One gram of $(Et_3Sn)_2S$ and 1.50 g. of $AgOCOCH_3$ after 15 minutes reflux at 50 mm. yielded 1.15 g. of $Et_3SnOCOCH_3$ (5), m.p.

120°, b.p. about 220°. Using AgNCO in 3 ml. of benzene, AgCl in 2 ml of CCl_4, AgNCS in 3 ml. of benzene, AgBr in 3 ml. of xylene, AgCN without a solvent, and AgI in 3 ml. of xylene we obtained the corresponding organotin derivatives free of sulfide content, after a 30-minute reflux.

Reactions of Et_3SnI. Et_3SnI and AgF (0.5 g. each) yielded Et_3SnF in 30-minutes reflux in 3 ml. of xylene. One g. of Ag_2O and 0.7 g. of Et_3SnI in 5 ml. of CCl_4 yielded pure $(Et_3Sn)_2O$, free from iodine, in ten-minutes reflux. One g. of $AgOCOCH_3$ and 0.8 g. of Et_3SnI in 5 ml. of CCl_4 yielded pure $Et_3SnOCOCH_3$ after ten-minutes reflux. One g. of AgNCO and 0.7 g. of Et_3SnI in 5 ml. of CCl_4 yielded iodine-free $Et_3Sn(NCO)$ after ten-minutes reflux. Two g. of AgCl and 1.1 g. of Et_3SnI without a solvent yielded iodine-free Et_3SnCl, b.p. 209°, n^{30} 1.504. Et_3SnI (20 g.) and 17 g. of AgNCS after two-hours reflux in 35 ml. of CCl_4 yielded a liquid of apparently low miscibility with CCl_4; the silver salt was washed with benzene and later with 100% ethanol. The ethanol fraction was kept apart from other material for study of properties of $Et_3Sn(NCS)$. Rather pure $Et_3Sn(NCS)$ resulted when the compound was distilled at 1 mm. and the center fraction was taken. One g. of AgCN and 0.8 g. of Et_3SnI in a reaction without solvent during 30-minutes reflux gave an iodine-free solid of m.p. roughly 100°, perhaps partially hydrolyzed. Two g. of AgBr and 1 g. of Et_3SnI in a 30-minutes reflux without a solvent yielded iodide-free Et_3SnBr of n^{33} 1.521. Ten g. each of Ag_2S and Et_3SnI in two-hours reflux without a solvent yielded a liquid containing much iodine and boiling at about 225°—unchanged Et_3SnI.

Reactions of Et_3SnBr. When 0.6 g. of Et_3SnBr and 0.8 g. of AgF in 4 ml. of xylene were refluxed 30 min., bromine-free Et_3SnF was obtained. One g. of Ag_2O and 0.7 g. of Et_3SnBr in 5 ml. of xylene after an hour of reflux yielded $(Et_3Sn)_2O$ containing only a trace of bromide. Et_3SnBr and $AgOCOCH_3$ (0.5 g. each) without a solvent yielded solid (long white needles) $Et_3SnOCOCH_3$ after 15-minutes reflux. Forty-minutes reflux of 14 g. of Et_3SnBr and 11 g. of AgNCO in 30 ml. of benzene and 30 ml. of CCl_4 finally yielded bromine-free $Et_3Sn(NCO)$, b.p. 239°/760 mm. and m.p. 48°; actual purification utilized distillation at 120–121°/11 mm. pressure. A four-hour reflux, without solvent, of 1.34 g. of Et_3SnBr and 2.20 g. of AgCl yielded organotin material of d_4^{20} 1.462, containing some bromine—approximately 10% Et_3SnBr at most; the main product was Et_3SnCl. Ninety-minutes reflux of 2 g. of AgNCS and 2.80 g. of Et_3SnBr in 5 ml. of benzene finally yielded 1.63 g. of $Et_3Sn(NCS)$, m.p. 32°C, n^{20} 1.572, b.p. 135°/1 mm. A reaction in a test tube between 0.5 g. each of Et_3SnBr and AgCN yielded a sublimate of white needles, $Et_3Sn(CN)$. When 3 g. of Et_3SnBr was given an hour of reflux, without solvent, with either Ag_2S or AgI, no test for sulfide and only a slight test for iodide resulted; the density of Et_3SnBr rose only 0.1% in the iodide treatment.

Reactions of $Et_3Sn(CN)$. Gentle warming of 0.3 g. of $Et_3Sn(CN)$ and 0.4 g. of AgF produced cotton-like, cyanide-free Et_3SnF. One-hour reflux of 0.3 g. each of Ag_2O and $Et_3Sn(CN)$ in 3 ml. of toluene gave a cyanide-free product evidently $(Et_3Sn)_2O$. One hour of reflux of 0.3 g. of $Et_3Sn(CN)$ and 0.6 g. of $AgOCOCH_3$ in 3 ml. of toluene gave a cyanide-free product, $Et_3SnOCOCH_3$. An hour reflux of 0.2 g. of $Et_3Sn(CN)$ and 0.50 g. of AgNCO in 3 ml. of toluene yielded a product shown to be all cyanate and no cyanide—$Et_3Sn(NCO)$. Ten-minutes free reflux of 0.50 g. of $Et_3Sn(CN)$ and 1.10 g. of AgCl, without a solvent, gave liquid Et_3SnCl, b.p. 207°, n^{23} 1.502. Ten-minutes reflux of 1 g. of $Et_3Sn(CN)$ and 2.2 g. of AgNCS, without a solvent, under 80 mm. pressure, yielded $Et_3Sn(NCS)$ distilled at 130–135°/1 mm.; found n^{27} 1.541, also much thiocyanate present, although some decomposition occurred. Triethyltin cyanide did not react with Ag_2S, AgBr, or AgI under comparable conditions.

Reactions of $Et_3Sn(NCS)$. Gentle warming of 0.4 g. each of $Et_3Sn(NCS)$ and AgF yielded cotton-like Et_3SnF. Using CCl_4 as solvent, an hour reflux of 0.3 g. each of Ag_2O and $Et_3Sn(NCS)$ yielded $(Et_3Sn)_2O$ containing very little thiocyanate. Similarly, $AgOCOCH_3$ furnished $Et_3SnOCOCH_3$, free of thiocyanate content; AgNCO furnished $Et_3Sn(NCO)$, free of thiocyanate content. A gram of $Et_3Sn(NCS)$ and 2.20 g. of AgCl in 5 ml. of xylene after one hour of reflux gave material 98% Et_3SnCl and 2% $Et_3Sn(NCS)$. However, $Et_3Sn(NCS)$

failed to react with AgCN, with AgBr (3 hours reflux of 2 g. of each in 5 ml. of benzene), AgI, or Ag_2S.

Reactions of Et_3SnCl. Gentle warming of Et_3SnCl and AgF furnished cotton-like Et_3SnF. One-hour reflux of 2 g. of Ag_2O and 0.9 g. of Et_3SnCl in 4 ml. of xylene furnished a solution of $(Et_3Sn)_2O$ containing no chloride. One g. of Et_3SnCl and 1.2 g. of $AgOCOCH_3$ without a solvent yielded white solid $Et_3SnOCOCH_3$, chloride-free, after 15-minutes reflux. Similarly, Et_3SnCl and AgNCO yielded chloride-free $Et_3Sn(NCO)$. Triethyltin chloride, usually 1.5 g., and an equal weight of AgNCS, AgCN, AgBr, AgI, and Ag_2S did not react under similar conditions.

Reactions of $(Et_3Sn)_2O$. Gentle warming of $(Et_3Sn)_2O$ and AgF in a small test tube produced cotton-like Et_3SnF. Exactly 1 g. of $(Et_3Sn_2)O$ and 2 g. of $AgOCOCH_3$, upon an hour of gentle reflux in CCl_4, ultimately furnished white solid $Et_3SnOCOCH_3$, m.p. 108° and b.p. 220°. Reflux of 0.6 g. of $(Et_3Sn)_2O$ and 1.1 g. of AgNCO in 4 ml. of xylene for 15 minutes, gave a black silver salt and a solution containing $Et_3Sn(NCO)$; treated with 80% ethanolic $AgNO_3$, white AgNCO precipitated, but was soluble in dilute nitric acid. Reflux of $(Et_3Sn)_2O$ and AgCl without a solvent gave a liquid boiling at 230°, predominately Et_3SnCl, formed when Ag_2O decomposed. However, $(Et_3Sn)_2O$ and AgCl did not react during an hour of reflux in xylene, nor did $(Et_3Sn)_2O$ and AgCN react. Two g. of $(Et_3Sn)_2O$ and 4 g. of AgNCS in one hour of free reflux without a solvent yielded a product containing very little $Et_3Sn(NCS)$. Likewise, $(Et_3Sn)_2O$ reacted not at all with AgI or Ag_2S and only 4% with AgBr.

Reactions of $Et_3Sn(NCO)$. Gentle warming of 0.4 g. each of $Et_3Sn(NCO)$ and AgF produced cotton-like Et_3SnF. Fifty-minutes reflux in 4 ml. of CCl_4 gave mainly no reaction with 0.22 g. of Ag_2O and 0.35 g. of $Et_3Sn(NCO)$, since the precipitate obtained with 80% ethanolic $AgNO_3$ solution was pure white. However, about 10% of the precipitated silver salt was insoluble in concentrated nitric acid—evidently, cyanide formed by overheating the $Et_3Sn(NCO)$. Similarly, $Et_3Sn(NCO)$ and $AgOCOCH_3$ furnished nearly pure $Et_3SnOCOCH_3$, which contained very little isocyanate according to a test with concentrated sulfuric acid, then sodium hydroxide and Nessler's reagent. A one-hour reflux of 1 g. of $Et_3Sn(NCO)$ and 2 g. of AgCl gave a product with about 10% of the chloride content which pure Et_3SnCl has; perhaps the known decomposition of AgNCO accounts for this. Heating 0.6 g. of $Et_3Sn(NCO)$ and a three-fold weight of AgNCS in 5 ml. of xylene for 90 minutes yielded a product with 4% of the thiocyanate which pure $Et_3Sn(NCS)$ has. Heating equal weights of $Et_3Sn(NCO)$ and AgCN gave a product with 5% of the cyanide which $Et_3Sn(CN)$ has; the decomposition of AgNCO seems responsible. However, $Et_3Sn(NCO)$ did not react with AgBr, AgI, or Ag_2S.

Reactions of $Et_3SnOCOCH_3$. Gentle warming of 0.2 g. each of $Et_3SnOCOCH_3$ and AgF without a solvent easily produced cotton-like Et_3SnF in a small test tube; no acetate was present in the Et_3SnF. Silver oxide and $Et_3SnOCOCH_3$ without a solvent gave a rapid evolution of gases; in CCl_4 there was no reaction in a 30-minute reflux. According to a Nessler test for nitrogen, $Et_3SnOCOCH_3$ and AgNCO did not react. Likewise, $Et_3SnOCOCH_3$ reacted either not at all or 1% with AgCl, AgNCS, AgCN, AgBr, AgI, and Ag_2S.

Reactions of Et_3SnF. Neglecting a 2% reaction with AgBr, Et_3SnF did not react with anything except $AgOCOCH_3$; Et_3SnF reacted with $AgOCOCH_3$ in the absence of a solvent, but not in benzene solution. Probably the decomposition of $AgOCOCH_3$ was responsible.

II. PREPARATION OF STARTING MATERIALS

Bis(triethyltin) oxide, $(Et_3Sn)_2O$, was prepared either by reaction of $SnCl_4$ and a deficiency of EtMgBr (5)—or from Et_4Sn and iodine, followed by treatment with aqueous sodium hydroxide. This key material boils at 272/760 mm., or at approximately 100°/1 mm. Reaction of $(Et_3Sn)_2O$ with hydrofluoric acid gave Et_3SnF; with acetic acid gave $Et_3SnOCOCH_3$ (1, 5); with hydrochloric, hydrobromic, and hydriodic acid gave Et_3SnCl, Et_3SnBr.

and Et_3SnI respectively. Reaction of $(Et_3Sn)_2O$ and hydrogen sulfide gave $(Et_3Sn)_2S$ (5), and with CH_3SH gave Et_3SnSCH_3, a new compound.

An excess of gaseous CH_3SH bubbling through 10 g. of $(Et_3Sn)_2O$, followed by drying with Na_2SO_4, separation of the liquid by pipetting, and then distillation yielded pure Et_3SnSMe, of d_4^{20} 1.319, n^{20} 1.529, b.p. 224°.

Anal. for SCH_3; Found, 18.8, 18.9, 18.8. Calc'd, 18.6.

Described among the reactions of Et_3SnBr, the reaction with AgNCO yielded $Et_3Sn(NCO)$, m.p. 48°, but often supercooling, and b.p. 239°/760 mm.; 162–163°/80 mm.; or 120–121°/11 mm. There was no bromine present in the small crystals of $Et_3Sn(NCO)$.

Described among the reactions of Et_3SnI, the reaction with AgNCS yielded pure $Et_3Sn(NCS)$, m.p. 33°, but supercooling to 20° easily; b.p. 130°/1 mm. or 282°/760 mm. with severe decomposition. On the supercooled liquid $Et_3Sn(NCS)$ had d_4^{20} 1.458, n^{20} 1.5825.

Anal. Calc'd: M. W., 264.0; Neut. equiv., 264.

Found: M. W. (in camphor), 267; Neut. equiv. (to $AgNO_3$ with ferric ion), 272, 269.

Condensing excess liquid anhydrous hydrogen cyanide in a solution of 10 g. of $(Et_3Sn)_2O$ in 30 ml. of CCl_4 at 0°, after drying with Na_2SO_4 and distillation of solvent, yielded $Et_3Sn(CN)$. This $Et_3Sn(CN)$ had m.p. 153°, b.p. 249° with severe decomposition; the sample was sublimed at 8 mm.

III. REACTIONS OF $(ET_3SN)_2O$ WITH ACIDS

Thiocyanic acid. Exactly 1 g. of $(Et_3Sn)_2O$ and 2.5 ml. of 2.23 *M* HNCS in diethyl ether stood four hours over Na_2SO_4. Distillation of the solvent, after pipetting, was followed by distillation of $Et_3Sn(NCS)$ at 180° under 9 mm. The m.p. was above 20°, n^{20} was 1.580, with a yield of 0.85 g. or 70%.

Isocyanic acid and sulfur dioxide. Both of these were passed separately into $(Et_3Sn)_2C$ in the absence of a solvent. No reactions occurred.

Hydrogen cyanide. This successful reaction is described in the previous section.

IV. RELATED INVESTIGATIONS IN PROGRESS

A "conversion series" for organosilicon compounds including esters is complete (6), while another "conversion series" for organogermanium compounds including esters is nearly complete.

Information assembled at this institute shows that Cahours' boiling point of $Et_3SnOCOCH_3$, 230° (1) is approximately 6° too high, while the melting point is very nearly 121°.

SUMMARY

1. Using dry silver salts with or without an inert solvent such as benzene, carbon tetrachloride, toluene, or xylene, the "conversion series" for triethyltin esters, halides, halogenoids, oxide, and sulfide is Et_3SnSCH_3 and $(Et_3Sn)_2S \rightarrow Et_3SnI \rightarrow Et_3SnBr \rightarrow Et_3Sn(CN) \rightarrow Et_3Sn(NCS) \rightarrow Et_3SnCl \rightarrow (Et_3Sn)_2O \rightarrow Et_3Sn(NCO) \rightarrow Et_3SnOCOCH_3 \rightarrow Et_3SnF$ respectively. Heating with the appropriate silver salt converts a triethyltin compound into any triethyltin compound to the right of it in this series. Reactions proceed only very slightly, if at all, to the left. Organotin derivatives like these often react quite vigorously with silver oxide to yield silver metal.

2. Bis(triethyltin) oxide reacts easily with anhydrous liquid hydrogen cyanide or with ethereal thiocyanic acid furnishing $Et_3Sn(CN)$ and $Et_3Sn(NCS)$ respectively, but does not react with isocyanic acid. New physical data are presented for some compounds: $Et_3Sn(CN)$ has m.p. 153° and b.p. 249°; $Et_3Sn(NCO)$ has m.p. 48° and b.p. 239°; $Et_3Sn(NCS)$ has m.p. 33° and b.p. 282°; and the new

compound Et_3SnSMe has b.p. 224°. These halogenoid formulas carry no structural implication.

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