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

REACTIONS WITH ESTERS, HALIDES, AND HALOGENOIDS. I. BIS-(TRIETHYLTIN) OXIDE AND SULFIDE

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In Group IV-regular there is a gradual increase in basicity from the nearly neutral carbon to the clearly basic tin; this order of increasing basicity depends on experimental results mainly in aqueous or non-aqueous solutions.

An exploratory publication on organogermanium esters established $(Et_3Ge)_2O$ as the most basic, $(Et_2GeO)_4$ as the next most basic and $[(EtGeO)_2O]_n$ as the least basic ethylgermanium oxide (1). This work suggested that bis-(trialkyltin) oxides would react with numerous acids weaker than acetic acid; recent researches at this Institute demonstrate the reaction of $(Et_3Sn)_2O$ with H_2S or C_2H_5SH (2), or with HCN (3).

This present paper, exploratory in nature, clearly demonstrates the capture of halogen, halogenoid, or an ester group by tin at the expense of silicon, germanium, phosphorus, arsenic, or antimony. It also shows the transfer of halogen from tin of a higher oxidation number to tin of a lower oxidation number.

The basicity of organotin oxides decreases progressively as the oxygen content increases $Et_4Sn > (Et_3Sn)_2O > (Et_2SnO)_n > [(EtSnO)_2O]_n > SnO_2$. Tin in the lowest oxidation number holds chlorine most firmly, while tin in the highest oxidation number holds chlorine least firmly: Et_3SnCl, oxidation number 1, holds halogen more firmly than Et_2SnCl_2, of oxidation number 2, which in turn holds halogen more firmly than $EtSnCl_3$, of oxidation number 3, which in turn holds halogen more firmly than $SnCl_4$, of oxidation number 4.

Table I lists no new compounds; there is good agreement between physical properties of the organotin products obtained and the published physical properties of the compounds—as shown in the experimental section.

Comparison of Table I and other experiments reported outside the Table shows that $(Et_3Sn)_2O$ is a more reactive base than either $(Et_3Sn)_2S$ or Et_3SnSMe, as might be expected. In Table I the organotin oxide reacts with $Me_3SiOCOMe$, $Et_3Si(CN)$, or Me_3SiNCS, while $(Et_3Sn)_2S$ reacts with none of these. Also, $(Et_3Sn)_2O$ reacts easily and rather completely with $Me_3SiOCOMe$, $MeSi(OCOCF_3)_3$ and Ph_2SiF_2, while Et_3SnSMe reacts partially with the esters and not at all with the fluoride.

Upon consideration of the boiling points of the compounds, it is quite obvious that these reactions do not depend on the escape of the most volatile compound from the system under careful distillation, as in an earlier paper (4).

EXPERIMENTAL

Equipment consisted of fully-interchangeable distilling units and receivers with 10/30 standard taper ground joints, including thermometers; a drying tube with $CaCl_2$ excluded moisture from the system. Distillations usually were under reduced pressure in the leak-proof systems.

TABLE I

REACTIONS OF BIS-(TRIETHYLTIN) OXIDE AND SULFIDE

Starting Materials				Reaction Products					
Compound	Wt., g.	Compound	Wt., g.	Compound	Compound	Wt., g.	B.p., °C.	n^{20}	Yield, %
$EtOBCl_2$	2.5	$(Et_3Sn)_2O$	1.57	$(EtOBO)_n$	Et_3SnCl	0.65	206	1.507	37
$EtOCOMe$	2.30	$(Et_3Sn)_2O$	1.40	$EtOEt^a$	$Et_3SnOCOMe$	1.60	^{b}	—	92
$EtOCOPh$	1.00	$(Et_3Sn)_2O$	1.55	$EtOEt^a$	$Et_3SnOCOPh$	0.85	124^c	—	36
$Me_2Si(OCOCF_3)_2$	0.68	$(Et_3Sn)_2O$	1.40	$(Me_2SiO)_n{}^a$	$Et_3SnOCOCF_3$	1.32	140^d	—	63
$Me_3SiOCOMe$	1.28	$(Et_3Sn)_2O$	1.50	$(Me_3Si)_2O^a$	$Et_3SnOCOMe$	1.90	214	—	98
$MeOSi(NCO)_3$	.50	$(Et_3Sn)_2O$	1.63	$(MeOSiO)_2O$	$Et_3Sn(NCO)$	1.73	160^e	—	90
$Me_3Si(NCS)$	1.46	$(Et_3Sn)_2O$	1.57	$(Me_3Si)_2O$	$Et_3Sn(NCS)$	1.65	130^c	1.582	86
$Et_3Si(CN)$	.3	$(Et_3Sn)_2O$	0.3	$(Et_3Si)_2O$	$Et_3Sn(CN)$	.2	—	—	—^{f}
$MeSiCl_3$	1.30	$(Et_3Sn)_2O$	1.25	$(MeSiO)_2O$	Et_3SnCl	1.10	208	1.506	77
$SiBr_4$	.48	$(Et_3Sn)_2O$	1.29	SiO_2	Et_3SnBr	1.57	221	1.531	91
$DodSiI_3$	1.74	$(Et_3Sn)_2O$	1.93	$(DodSiO)_2O$	Et_3SnI	2.64	234	1.564	88
Ph_2SiF_2	.2	$(Et_3Sn)_2O$	.2	$(Ph_2SiO)_n$	Et_3SnF	—	—	—	—^{f}
n-Pr_3GeF	.22	$(Et_3Sn)_2O$	.40	$(n$-$Pr_3Ge)_2O$	Et_3SnF	—	—	—	—^{f}
i-Pr_3GeOH	.3	$(Et_3Sn)_2O$	.3	(i-$Pr_3Ge)_2O$	Et_3SnOH	.2	—	—	—^{f}
$GeCl_4$	.50	$(Et_3Sn)_2O$	2.00	GeO_2	Et_3SnCl	2.10	209	1.509	93
$SnCl_4$	.76	$(Et_3Sn)_2O$	1.84	SnO_2	Et_3SnCl	2.10	211	1.516	99
$SnBr_4$	.68	$(Et_3Sn)_2O$	1.35	SnO_2	Et_3SnBr	1.51	221	1.531	84
n-$BuSnCl_3$	.82	$(Et_3Sn)_2O$	1.87	$(n$-$BuSnO)_2O$	Et_3SnCl	1.95	210	1.508	92
$SnCl_2$	.80	$(Et_3Sn)_2O$	1.70	SnO	Et_3SnCl	1.83	208	1.507	95
Et_2SnCl_2	1.10	$(Et_3Sn)_2O$	2.00	$(Et_2SnO)_n$	Et_3SnCl	1.83	210	1.508	86
PCl_3	.60	$(Et_3Sn)_2O$	1.40	P_4O_6	Et_3SnCl	1.15	207	1.509	74
$AsCl_3$	.46	$(Et_3Sn)_2O$	1.67	As_4O_6	Et_3SnCl	1.66	208	1.507	88
$SbCl_3$	.50	$(Et_3Sn)_2O$	1.40	Sb_2O_3	Et_3SnCl	1.37	210	1.516	87
$SiBr_4$	.70	$(Et_3Sn)_2S$	1.40	SiS_2	Et_3SnBr	1.60	218	1.529	88
$DodSiI_3$	1.10	$(Et_3Sn)_2S$	1.08	$(DodSiS)_2S$	Et_3SnI	1.36	231	1.566	83
$GeCl_4$	.45	$(Et_3Sn)_2S$	1.89	GeS_2	Et_3SnCl	1.84	208	1.508	91
$SnCl_4$	.55	$(Et_3Sn)_2S$	1.86	SnS_2	Et_3SnCl	1.78	209	1.513	88
$SnCl_2$	.67	$(Et_3Sn)_2S$	1.50	SnS	Et_3SnCl	1.20	211	1.511	74
PCl_3	.30	$(Et_3Sn)_2S$	1.45	$P_4S_{10} + P$	Et_3SnCl	1.43	210	1.510	92
$AsCl_3$	.48	$(Et_3Sn)_2S$	1.75	As_2S_3	Et_3SnCl	1.68	209	1.511	89

[a] Distilled before organotin product.

[b] M.p. 105–110°.

[c] One mm. pressure. M.p. of $Et_3SnOCOPh$, 71°.

[d] M.p. 107–108°. 100 mm. pressure.

[e] M.p. 53°. 70 mm. pressure.

[f] Organotin compound crystallized out; no distillation performed.

Dod is n-$C_{12}H_{25}$. Ph is C_6H_5.

Typically, the *average run* consisted of weighing the distilling unit empty, then adding the $GeCl_4$ (for example) with reweighing to 0.01 g., and finally adding the $(Et_3Sn)_2O$ (for example) in three or four portions until the calculated quantity was present. Solids such as $SnCl_2$ were always added first of all. In the reaction between $GeCl_4$ and $(Et_3Sn)_2O$ 5–10 minutes of reflux at 760 mm. produced a large amount of solid GeO_2; then the Et_3SnCl was distilled at 129–134° under 67 mm. pressure. After reweighing the main distilling unit, the weight of the Et_3SnCl was the same as the loss of weight of the system. Remeasurement in a test tube yield the accurate boiling point of the Et_3SnCl.

Actual separations are best when the two reaction products are a readily volatile organotin compound (a pressure as low as one mm. is acceptable in distillation) and a nonvolatile second compound; thus a reaction with $MeSiCl_3$ is preferable to one with Me_2SiCl_2 or one with Me_3SiCl.

Organosilicon impurities contaminated $Et_3SnOCOMe$ which boiled at only 214°. Mechanical trapping with $EtOBCl_2$ and an apparent azeotrope with ethyl benzoate produced low yields. A reaction between $SnCl_2$ and $(Et_3Sn)_2S$ yielded SnS and Et_3SnCl as expected, but the SnS coated over the $SnCl_2$ and a two-hour distillation was necessary. In less than 30 minutes Et_3SnF, $Et_3Sn(CN)$ or Et_3SnOH crystallized from the appropriate reaction mixture almost without heating. After centrifugal separation the Et_3SnOH melted at 43° and the acetate made therefrom melted at 118–119°. After a double recrystallization from CCl_4 the $Et_3Sn(CN)$ melted at 152–153°.

Reactions not in Table I. These show the limitations of the method. No reactions occurred in the following combinations: $Et_3SnSMe + Ph_2SiF_2$; $(Et_3Sn)_2S + Me_3SiOCOMe$; $(Et_3Sn)_2S + Et_3Si(CN)$; $(Et_3Sn)_2S + Me_3SiNCS$. Five minutes reflux of 1.6 g. each of $Me_3SiOCOMe$ and Et_3SnSMe, followed by standing overnight, yielded 0.7 g. of $Et_3SnOCOMe$, m.p. 120° after drying in a vacuum; tin occurred in the supernatant liquid almost completely as Et_3SnSMe. One g. of Et_3SnSMe and 2 g. of $MeSi(OCOCF_3)_3$ produced much $Et_3SnOCOCF_3$, which could be purified only by recrystallization. In a vigorous reaction $(Et_3Sn)_2O$ and an equivalent quantity of $PO(NCO)_3$ yielded chiefly a non-volatile solid, probably $(Et_3Sn)_3PO_4$; $(Et_3Sn)_2O$ and an equivalent quantity of $PO(NCS)_3$ gave a product with n^{20} 1.581, mainly $Et_3Sn(NCS)$. In a vigorous reaction of no preparative value, $TiCl_4$ and $(Et_3Sn)_2O$ yielded lower halides of titanium. Reflux of $HgCl_2$ and $(Et_2Sn)_2O$ produced a small amount of free mercury.

Test tubes served in the following reactions. Reaction of $(Et_2SnO)_n$ with either $SnCl_2$ or $SnCl_4$ yielded Et_2SnCl_2, although neither reaction was complete. In one direction SnO and $SnCl_4$ yielded a product containing very little $SnCl_4$; in the reverse direction $SnCl_2$ and SnO_2 furnished very little $SnCl_4$. *n*-Butyltin trichloride reacted fairly well with SnO, reacted partially with $(Et_2SnO)_n$, and reacted not at all with SnO_2.

Physical properties of known tin compounds listed as products in Table I. The chief properties follow, with refractive indices for white or for sodium D light. Et_3SnF, m.p. 302° (5); Et_3SnCl, b.p. 210°, m.p. 15°, n^{20} 1.508 (5); Et_3SnBr, b.p. 224°, m.p. −13°, n^{20} 1.5821 (5); Et_3SnI, b.p. 231°, m.p. −34°, n^{20} 1.5648 (5); $Et_3Sn(NCO)$, b.p. 239°/760 mm. or 162°/80 mm., 48° (3); $Et_3Sn(NCS)$, b.p. 282° dec./760 mm. or 130°/1 mm., m.p. 33°, n^{20} 1.583 on supercooled liquid (3); $Et_3Sn(CN)$, b.p. 249° dec., m.p. 153° (3); Et_3SnOH, m.p. 44–45° (5); $Et_3SnOCOMe$, b.p. 224°, m.p. 119° (2, 3); $Et_3SnOCOCF_3$, b.p. 218°, m.p. 107° (2); $Et_3SnOCOPh$, b.p. 132–134°/1 mm., m.p. 71° (2). *These published values are consistent with those listed in Table I.* In addition, qualitative tests showed the absence of sulfide in the liquid reaction products. Properties of the starting materials were usually unlike those of the products; $(Et_3Sn)_2S$ has b.p. 303° dec., n^{20} 1.5365 (2); $(Et_3Sn)_2O$, b.p. 272° (3, 5); Et_3SnSMe, b.p. 224°, n^{20} 1.529 (3).

As a whole, the preparative methods in Table I cannot compete with the traditional preparative methods.

Starting materials. *n*-Butyltin trichloride was available through the courtesy of Metal & Thermit Corp., New York, N. Y. Preparation of large amounts of $(Et_3Sn)_2O$ and $(Et_3Sn)_2S$ followed the published directions (2) or modifications thereof. Recent publications describe the preparation of Et_3SnSMe (3), $Me_2Si(OCOCF_3)_2$ and $MeSi(OCOCF_3)_3$ (6), $MeOSi(NCO)_3$ (7), Me_3SiNCS (8), $Et_3Si(CN)$ (9), $DodSiI_3$ (10), *n*-Pr_3GeF (11), and iso-Pr_3GeOH (12).

Related studies are well under way; the oxide $(Et_3Ge)_2O$ reacts in much the same manner as $(Et_3Sn)_2O$ herein.

SUMMARY

Thirty successful reactions listed in Table I demonstrate the formation of a triethyltin ester, halide, or halogenoid through reaction of $(Et_3Sn)_2O$ or $(Et_3Sn)_2S$ with an ester, halide, or halogenoid of an element other than tin—or of tin in an oxidation number of 2, 3, or 4. Under gentle reflux without a solvent the average reaction is complete within 5 or 10 minutes and furnishes a yield of approximately 90%. An organotin halide forms at the expense of the less-basic silicon in the typical reactions $SiBr_4 + 2\ (Et_3Sn)_2O \rightarrow SiO_2 + 4\ Et_3SnBr$ and

$SiBr_4 + 2\ (Et_3Sn)_2S \rightarrow SiS_2 + 4\ Et_3SnBr$. Halogen transfers easily from tin of oxidation number 2 in Et_2SnCl_2, 3 in *n*-$BuSnCl_3$, or 4 in $SnCl_4$ to the more-basic tin of oxidation number 1 in the reactions $(Et_3Sn)_2O + Et_2SnCl_2 \rightarrow 2\ Et_3SnCl + (Et_2SnO)_n$, also $3\ (Et_3Sn)_2O + 2\ n\text{-}BuSnCl_3 \rightarrow 6\ Et_3SnCl + (n\text{-}BuSnO)_2O$, also $2\ (Et_3Sn)_2O + SnCl_4 \rightarrow 4\ Et_3SnCl + SnO_2$. Basicity appears the decisive factor in all thirty successful reactions, which illustrate a method still little explored. A dozen reactions described outside the Table have no preparative value, and show some limitations of the method.

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