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DIRECT SYNTHESIS OF ORGANOTIN COMPOUNDS VI*. CONVERSION OF DIALKYLTIN DICHLORIDE INTO TRIALKYLTIN CHLORIDE AND TETRAALKYLTIN

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It has been shown that dibenzyltin dichloride is converted into tribenzyltin chloride in a polar solvent in presence of some metals, and that in water bis(dibenzylchlorotin) oxide is an intermediate[1]. In the direct reaction of alkyl (ethyl, n-propyl and n-butyl) chloride with tin, it was observed that increase of the amount of metallic tin and triethylamine (catalyst) raised the yield of trialkyltin chloride at the expense of dialkyltin dichloride[2].

The conversion of dialkyltin dichloride into trialkyltin chloride was found to occur in water in the presence of metallic tin powder at high temperature (160°). The reaction did not occur at 100°, although dibenzyltin dichloride was changed into tribenzyltin chloride in boiling water almost quantitatively. When tin powder was

TABLE 1

CONVERSION OF DIALKYLTIN DICHLORIDE INTO TRIALKYLTIN CHLORIDE[a]

R_2SnCl_2	*Metal (g-atom)*	*Reaction medium*	*Reaction temperature (°C)*	*Yield*[b] (%)		*Recovered* R_2SnCl_2
				R_3SnCl	$(R_2SnCl)_2O$	
Et_2SnCl_2	Sn 0.10	Water	160	76	4	20
Pr_2SnCl_2	Sn 0.10	Water	160	62	14	25
Bu_2SnCl_2	Sn 0.05	Water	160	45	30	17
Bu_2SnCl_2	Sn 0.05	Water	100	0	97	0
Bu_2SnCl_2	None	Water	160	0	66	30
Bu_2SnCl_2	Sn 0.05	MeOH	160	32	27	40
Bu_2SnCl_2	Sn 0.05	THF[f]	160	5	22	65
Bu_2SnCl_2	Fe 0.20	Water	160	56	29	0
Bu_2SnCl_2	Mg 0.20	Water	160	4	0[c]	0
Bu_2SnCl_2	Al 0.20	Water	160	42	40	16
Bu_2SnCl_2	Ni 0.10	Water	160	9	60	23
Bu_2SnCl_2	Co 0.10	Water	160	15	64[d]	10
Bu_2SnCl_2	Zn 0.10	Water	160	54	14[e]	0

[a] All reactions were carried out with 0.05 mole of dialkyltin dichloride in 100 ml of solvent, in an autoclave with stirring (1000 rpm) for 4 h. [b] Yields are based on alkyl group. [c] Di-n-butyltin oxide was obtained in 94% yield. [d] Di-n-butyltin oxide was obtained in 10% yield. [e] Di-n-butyltin oxide was obtained in 13% yield. [f] Tetrahydrofuran.

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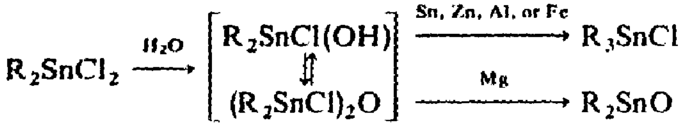
* For Part V see ref. 2.

absent the conversion did not occur even at 160°. In boiling water or in the absence of tin powder, partial hydrolysis occurred to give bis(dialkylchlorotin) oxide (Table 1). In the presence of both metallic tin and water at higher temperature (160°) this oxide was shown to be converted into trialkyltin chloride in a good yield.

It was found that the reaction occurs when zinc, aluminium or iron is used in place of tin (Table 1). No tetraalkyltin was found in the products. With magnesium the same treatment afforded dialkyltin oxide in 94% yield, due presumably to the preferential hydrolysis of bis(dialkylchlorotin) oxide. When nickel or cobalt was used, the main product was the latter oxide. The reaction sequences in water can be considered to be the same as for benzyltin compounds[1] [sequence (A)]. When methanol or tetrahydrofuran was used as the medium, the yield was lower, presumably due to the lower polarity[1].



$$R_2SnCl_2 \xrightarrow{H_2O} \left[\begin{matrix} R_2SnCl(OH) \\ \Updownarrow \\ (R_2SnCl)_2O \end{matrix}\right] \begin{matrix} \xrightarrow{\text{Sn, Zn, Al, or Fe}} R_3SnCl \\ \xrightarrow{\text{Mg}} R_2SnO \end{matrix} \qquad (A)$$

Dialkyltin dichloride was also converted into trialkyltin chloride in the presence of metallic tin in good yield when both alkyl chloride and organic base were used instead of water (Table 2). In the absence of either metallic tin or organic base,

TABLE 2

CONVERSION OF DI-n-BUTYLTIN DICHLORIDE INTO TRI-n-BUTYLTIN CHLORIDE AND TETRA-n-BUTYLTIN IN THE PRESENCE OF ORGANIC BASE[a]

Metal	*Organic base*	*Reaction medium*	*Yield*[b] *Bu_4Sn*	*Bu_3SnCl*	*Recovered (%) Bu_2SnCl_2 and/or $(Bu_2SnCl)_2O$*[d]
None	Et_3N[c]	Et_3N	0	18	82
Sn	None	BuCl	0	5	89
Sn	Et_3N	Et_3N	0	11	86
Sn	Et_3N	BuCl	0	117[e]	0
Sn	Et_3N	Benzene	0	26	72
Sn	Pyridine	BuCl	0	96	2
Fe	None	BuCl	0	0	98
Fe	Et_3N	BuCl	0	61	42
Fe	Et_3N	Toluene	0	26	70
Fe	Pyridine	BuCl	0	44	63
Zn	Et_3N	Et_3N	58	0	0
Zn	Et_3N	BuCl	88	22[e]	2
Zn	Pyridine	BuCl	34	41	3
Zn	Pyridine	Toluene	69	1	0
Al	Et_3N	BuCl	73	21	2
Mg	Et_3N	BuCl	46	66[e]	28
Na	None	BuCl	84	28[e]	26

[a] All reactions were carried out with 0.05 mole of di-n-butyltin dichloride, 0.1 g-atom of metal, 0.1 mole of organic base and 100 ml of solvent in an autoclave with stirring (1000 rpm) at 160° for 6 h. [b] Yields are based on n-butyl group of di-n-butyltin dichloride. [c] Triethylamine. [d] Bis(dialkylchlorotin) oxide was obtained by treating dialkyltin dichloride–organic base complex with water. [e] Over 100% yield means that n-butyl group was introduced from n-butyl chloride.

the conversion scarcely occurs. The presence of alkyl chloride raises the conversion yield remarkably. Iron powder can be used in place of metallic tin to obtain trialkyltin chloride.

When zinc, aluminium, magnesium or sodium was used instead of tin or iron, a mixture of trialkyltin chloride and tetraalkyltin was formed from dialkyltin dichloride (Table 2). Tin, iron or a mixture of them did not give tetraalkyltin. Metals having stronger affinity for halogen or stronger ionization tendency than tin or iron gave tetraalkyltin.

Although the production of tetraalkyltin by the direct reaction of alkyl halide with tin–zinc[3,4] tin–sodium[3–10] or tin–magnesium[11] alloy is known, the conversion from di- or trialkyltin halides into tetraalkyltin has not been previously reported.

For the conversion of a trialkyltin chloride into tetraalkyltin, tri-n-butyltin chloride was treated with zinc in triethylamine tetra-n-butyltin and a little hexa-n-butylditin being obtained [eqn. (1)]. The yields listed under each compound were based on the tin content of the trialkyltin chloride.

$$Bu_3SnCl \xrightarrow[160^\circ]{Zn,\ Et_3N} \underset{(56\%)}{Bu_4Sn} + \underset{(5.5\%)}{Bu_3SnSnBu_3} \qquad (1)$$

When triethyltin chloride was treated with zinc in the presence of n-butyl chloride and triethylamine, both tetraethyltin and n-butyltriethyltin were obtained together with small amounts of other tetraalkyltin compounds [eqn. (2)].

$$Et_3SnCl + BuCl \xrightarrow[160^\circ]{Zn,\ Et_3N} \underset{(38\%)}{Et_4Sn} + \underset{(20\%)}{Et_3BuSn} + \underset{(4\%)}{Et_2Bu_2Sn} + \underset{(3\%)}{EtBu_3Sn} + \underset{(2\%)}{Bu_4Sn} \qquad (2)$$

The reaction of sodium with triethyltin chloride in n-butyl chloride gave n-butyltriethyltin as well as small amounts of tetraethyltin and hexaethylditin [eqn. (3)]. In this reaction triethylamine was not needed, since sodium afforded sufficient basicity. The yields were based on the utilized triethyltin chloride.

$$Et_3SnCl + BuCl \xrightarrow[160^\circ]{Na} \underset{(5\%)}{Et_4Sn} + \underset{(61\%)}{Et_3BuSn} + \underset{(3.5\%)}{Et_3SnSnEt_3} \qquad (3)$$

In the absence of n-butyl chloride, the treatment of tri-n-butyltin chloride with sodium afforded only hexa-n-butylditin[12] [eqn. (4)].

$$Bu_3SnCl \xrightarrow[160^\circ]{Na\ in\ benzene\ or\ Et_3N} \underset{(92\%)}{Bu_3SnSnBu_3} \qquad (4)$$

The formation of mixed tetraalkyltin, *e.g.* n-butyltriethyltin in eqns. (2) and (3), showed that n-butyl group was introduced from n-butyl chloride into triethyltin chloride. In order to find out the mechanism of this reaction several experiments were carried out.

In the case of sodium, it should seem that both alkyl chloride (R'Cl) and trialkyltin chloride (R_3SnCl) reacted with sodium to give alkylsodium (R'Na)[13] and trialkyltinsodium (R_3SnNa)[14], respectively, which gave rise to produce mixed tetraalkyltin ($R_3R'Sn$) as shown in sequences (B) and (C). It was not clear which sequence was predominant. When tri-n-butyltin chloride was treated with sodium in benzene [eqn. (4)] Wurtz–Fittig type reaction occurred. This might indicate an intermediary

$$R'Cl + Na \rightarrow [R'Na] \xrightarrow{R_3SnCl} R_3R'Sn \qquad (B)$$

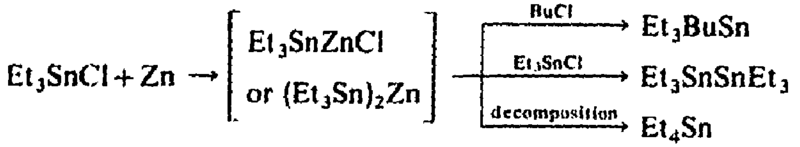
$$R_3SnCl + Na \rightarrow [R_3SnNa] \xrightarrow{R'Cl} R_3R'Sn \qquad (C)$$

formation of highly reactive tri-n-butyltinsodium[14]. Since treatment of hexa-n-butylditin with ethyl chloride in the presence of sodium afforded no tri-n-butylethyltin, the possibility that the mixed tetraalkyltin ($R_3R'Sn$) was formed from hexaalkylditin (R_3SnSnR_3) and alkyl chloride ($R'Cl$) can be excluded.

The reaction of a free radical triethyltin, $Et_3Sn^{\bullet}$, with n-butyl chloride can be ruled out, since the radical would preferentially abstract the chlorine atom of alkyl chloride rather than the alkyl group, as shown by the disproportionation reactions of dialkyltin in the presence of alkyl halide[15].

In the case of zinc, intermediary formation of n-butylzinc chloride or di-n-butylzinc was excluded, since n-butyl chloride gave no alkylzinc compounds at the reaction condition. The reaction of n-butyl chloride with hexaethylditin was also not the case, since no reaction occurred between them on heating at 160° in the presence of zinc.

Reaction of triethyltin chloride with zinc would give, similar to the case with sodium, triethyltinzinc compounds, $Et_3SnZnCl$ or $(Et_3Sn)_2Zn$, which would immediately react with n-butyl chloride or with triethyltin chloride to afford n-butyltriethyltin or hexaethylditin, respectively as shown in sequence (D). Sequence (D) is supported by the result that no hexaethylditin was obtained when n-butyl chloride was present in a large excess [eqn. (2)].



$$Et_3SnCl + Zn \rightarrow \left[\begin{array}{l} Et_3SnZnCl \\ \text{or } (Et_3Sn)_2Zn \end{array}\right] \rightarrow \begin{array}{l} \xrightarrow{BuCl} Et_3BuSn \\ \xrightarrow{Et_3SnCl} Et_3SnSnEt_3 \\ \xrightarrow{\text{decomposition}} Et_4Sn \end{array} \qquad (D)$$

Attempted isolation of the tri-n-butyltinzinc compound in a form of tri-n-butylmethyltin failed. When methyl iodide was added, after removal of triethylamine, to the reaction product from tri-n-butyltin chloride and zinc powder in triethylamine at the refluxing temperature (90°), no tri-n-butylmethyltin but hexa-n-butylditin and zinc chloride were obtained [eqn. (5)]. The hitherto unknown trialkyltinzinc com-

$$Bu_3SnCl + Zn \xrightarrow[90°]{Et_3N,\ CH_3I} \underset{(1.4\%)}{Bu_4Sn} + \underset{(76\%)}{Bu_3SnSnBu_3} + ZnCl_2 \qquad (5)$$

pound could be so reactive that it combined immediately with remaining trialkyltin chloride. Such lability would be reminiscent of the analogous case of triphenyltinmagnesium compounds reported by Tamborski and Solonski[16].

All the ethyl groups in tetraethyltin obtained in equation (2) are thought to come from triethyltin chloride via thermal disproportionation. The possibility that an ethyl group originated from triethylamine could be excluded, since no ethyltin compound was obtained by the reaction of tri-n-butyltin chloride with zinc in the presence of triethylamine [eqn. (1)]. The poor yield of tetra-n-butyltin from the reaction of equation (5) carried out at lower temperature (90°), as compared with that from the reaction of eqn. (1) at higher temperature (160°), suggested that the simple tetraalkyltin might be produced by thermal decomposition of trialkyltinzinc compound.

The reaction of di-n-butyltin dichloride with zinc in triethylamine in the absence of n-butyl chloride gave tetra-n-butyltin as a sole product (58 % yield, Table 2). When di-n-butyltin dichloride was treated with ethyl chloride in the presence of zinc powder and triethylamine, a mixture of tetra-n-butyltin, tetraalkyltins with mixed ethyl and n-butyl groups, and tetraethyltin was obtained [eqn. (6)]. In this case no trialkyltin chloride was found. The ethyl group was apparently introduced into di-n-butyltin compound from ethyl chloride.

$$\mathrm{Bu_2SnCl_2 + EtCl} \xrightarrow[160^\circ]{\mathrm{Zn,\ Et_3N}} \underset{(24\,\%)}{\mathrm{Bu_4Sn}} + \underset{(20\,\%)}{\mathrm{Bu_3EtSn}} + \underset{(4\,\%)}{\mathrm{Bu_2Et_2Sn}} + \underset{(5\,\%)}{\mathrm{BuEt_3Sn}} + \underset{(8\,\%)}{\mathrm{Et_4Sn}} \tag{6}$$

In the case of iron, when no tetraalkyltin was formed as stated above, the alkyl group of the alkyl chloride was also introduced into dialkyltin compounds. When di-n-butyltin dichloride was treated with ethyl chloride in the presence of iron powder and triethylamine, tri-n-butyltin chloride and di-n-butylethyltin chloride were produced [eqn. (7)]. Similar treatment of diethyltin dichloride with n-butyl chloride gave triethyltin chloride and n-butyldiethyltin chloride [eqn. (8)].

$$\mathrm{Bu_2SnCl_2 + EtCl} \xrightarrow[160^\circ]{\mathrm{Fe,\ Et_3N}} \underset{(46\,\%)}{\mathrm{Bu_3SnCl}} + \underset{(26\,\%)}{\mathrm{Bu_2EtSnCl}} + \underset{(5\,\%)}{\mathrm{BuEt_2SnCl}} + \underset{(2\,\%)}{\mathrm{Et_3SnCl}} \tag{7}$$

$$\mathrm{Et_2SnCl_2 + BuCl} \xrightarrow[160^\circ]{\mathrm{Fe,\ Et_3N}} \underset{(36\,\%)}{\mathrm{Et_3SnCl}} + \underset{(17\,\%)}{\mathrm{BuEt_2SnCl}} + \underset{(3\,\%)}{\mathrm{Bu_2EtSnCl}} + \underset{\text{(trace)}}{\mathrm{Bu_3SnCl}} \tag{8}$$

In the conversion of dialkyltin dichloride into trialkyltin chloride in the presence of metal, a dialkyltin–metal compound or a dialkyltin fragment may be formed as an intermediate. Zietz, Biltzer, Redman and Robinson[10] proposed that a dialkyltin fragment might be formed as an intermediate in the direct reaction of alkyl halide with tin–sodium–zinc alloy to give trialkyltin halide or tetraalkyltin, while Frankland[17] obtained diethyltin by the reaction of diethyltin dichloride with zinc. It was reported in a previous paper[15] that polymeric dialkyltin reacted with alkyl chloride in the presence of organic base. An unsuccessful attempt was made to prove the existence of either dialkyltin–zinc compound or dialkyltin among the reaction products obtained from dialkyltin dichloride and zinc. This failure might be due to the thermal unstability and/or ready reactivity of the dialkyltin–zinc compound or the dialkyltin fragment. In the case of sodium, formation of both dialkyltin–sodium compounds and dialkyltin fragment can be expected, since dialkyltin–sodium and dialkyltin can be prepared by the reaction of sodium with dialkyltin dichloride[3,18,19]. In the case of iron, a dialkyltin fragment might be formed rather easier than a dialkyltin–iron compound. Since even if the tin–iron compound could be formed, it might be very unstable at the reaction temperature, and would probably decompose to give a dialkyltin fragment, analogous to the bibenzyl formation from benzyl halide[20–30].

Treatment of diethyltin with n-butyl chloride in the presence of triethylamine afforded triethyltin chloride and n-butyldiethyltin chloride together with minor products [eqn. (9)][15]. This result was similar to the result obtained by the reaction

$$(Et_2Sn)_m + BuCl \xrightarrow[160^\circ]{Et_3N} \underset{(17.8\%)}{Et_3SnCl} + \underset{(13.7\%)}{Et_2BuSnCl} + \underset{(2.8\%)}{EtBu_2SnCl} + \underset{(0.4\%)}{Bu_3SnCl} \qquad (9)$$

of diethyltin dichloride with n-butyl chloride in the presence of iron [eqn. (8)]. Triethyltin and n-butyldiethyltin chlorides were considered to be formed by the disproportionation and the addition reaction, respectively[15].

Bis(dialkylchlorotin) oxide was converted into trialkyltin chloride in the presence of metallic tin and amine in alkyl chloride (Table 3). In the absence of either metal or organic amine, no conversion occurred. Presence of zinc powder brought about the formation of tetra-n-butyltin.

TABLE 3

CONVERSION OF BIS(DIALKYLCHLOROTIN) OXIDE INTO TRIALKYLTIN CHLORIDE[a]

$(R_2SnCl)_2O$	*Metal (g-atom)*	*Reaction medium*	*Reaction time (h)*	*Yield[b] (%)*			*Recovered (%) $(R_2SnCl)_2O$*
				R_4Sn	*R_3SnCl*	*R_2SnCl_2*	
$(Et_2SnCl)_2O$	Sn 0.10	Water	4	0	79	0	0
$(Pr_2SnCl)_2O$	Sn 0.10	Water	4	0	84	0	0
$(Bu_2SnCl)_2O$	Sn 0.10	Water	4	0	49	12	23
$(Bu_2SnCl)_2O$	Sn 0.05	Water	4	0	32	3	64
$(Bu_2SnCl)_2O$	None	Water	4	0	0	0	98
$(Bu_2SnCl)_2O$	Sn 0.10	BuCl	6	0	1	0	98
$(Bu_2SnCl)_2O$	Sn 0.10	BuCl[c]	6	0	73	30	19
$(Bu_2SnCl)_2O$	Zn 0.10	BuCl[c]	6	80	35	0	0
$(Bu_2SnCl)_2O$	Fe 0.10	BuCl	6	0	0	0	100

[a] All reactions were carried out with 0.025 mole of bis(dialkylchlorotin) oxide in 100 ml of solvent in an autoclave with stirring at 160°. [b] Yields are based on alkyl group of bis(dialkylchlorotin)oxide. [c] 0.10 mole of triethylamine was added.

EXPERIMENTAL

Gas chromatography

The composition of alkyltin compounds was determined by gas chromatography with helium gas flowing at 40 ml/min through a stainless steel column of 3 m × 3 mm o.d. packed with "Polyethylene Glycol-6000" at the column bath temperature of 200° and sample chamber temperature of 270°. Retention times (min) of organotin compounds are shown in parentheses: Et_4Sn (1.1), Et_3BuSn (1.5), Et_2Bu_2Sn (2.1), $EtBu_3Sn$ (2.9), Bu_4Sn (3.9), Et_3SnCl (3.5), $BuEt_2SnCl$ (5.3), $Bu_2EtSnCl$ (8.0), Bu_3SnCl (11.1), Et_2SnCl_2 (10.9) and Bu_2SnCl_2 (18.5). Each compound was also characterized by the infrared spectrum.

Reaction of dialkyltin dichloride with metal in water (Table 1)

A representative procedure was as follows. A mixture of 11.4 g (0.050 mole) of diethyltin dichloride, 11.8 g (0.10 g-atom) of tin powder and 100 ml of water was heated in a stainless steel autoclave with a high speed rotatory stirrer (1000 rpm) at 160° for 4 h. Ethyltin compounds were extracted three times with 200 ml portions of ether. Combined ethereal solution was concentrated and the residue was distilled *in vacuo* to give 6.1 g (76 % based on ethyl group) of distillate, b.p. 140–141°/104 mm, identified as pure triethyltin chloride by gas chromatography and infrared spectrum.

Reaction of bis(dialkylchlorotin) oxide with metal in water (Table 3)

A mixture of 10.8 g (0.025 mole) of bis(diethylchlorotin) oxide, 11.9 g (0.10 g-atom) of tin powder and 100 ml of water was heated in a stainless steel autoclave and treated as above, when 6.2 g (79 %) of pure triethyltin chloride, b.p. 110–116°/40 mm, was obtained.

Reaction of di-n-butyltin dichloride with n-butyl chloride in the presence of organic base and metal (Table 2)

A representative procedure was as follows. A mixture of 15.2 g (0.050 mole) of di-n-butyltin dichloride, 5.6 g (0.10 g-atom) of commercial reduced iron powder, 10.1 g (0.10 mole) of triethylamine and 100 ml of n-butyl chloride was heated in an autoclave with vigorous stirring at 160° for 6 h. The reaction product, dissolved in 200 ml of acetone, was filtered to remove the unchanged iron. The filtrate was concentrated and the residue was shaken with 200 ml of ether and 100 ml of 1 *N* hydrochloric acid to extract n-butyltin compounds. The aqueous layer was extracted twice with 200 ml portions of ether. The combined ethereal layer was concentrated and the residue was distilled *in vacuo* to give 9.4 g of distillate, b.p. 130–135°/4 mm, including 6.6 g (61 % based on n-butyl group in the starting dichloride) of tri-n-butyltin chloride and 2.8 g (19 %) of di-n-butyltin dichloride. The distillation residue was 3.2 g (23 %) of pale brown crystals which were identified as bis(di-n-butylchlorotin) oxide, when recrystallized from acetone, m.p. 110–112° (lit.[24], m.p. 110–112°).

The aqueous layer gave positive test both for stannous[25] and ferrous cations.

Reaction of bis(dialkylchlorotin) oxide[24] with metal in the presence of organic base was carried out by the same procedure (Table 3).

In the absence of organic base, addition of acetone and hydrochloric acid as well as extraction with ether were omitted.

Reaction of tri-n-butyltin chloride with zinc in triethylamine [eqn. (1) and (5)]

A mixture of 16.3 g (0.050 mole) of tri-n-butyltin chloride, 6.5 g (0.10 g-atom) of zinc powder and 100 ml of triethylamine was heated in an autoclave with stirring at 160° for 6 h. The reaction product was concentrated and was shaken with 100 ml of 1 *N* hydrochloric acid and 200 ml of ether. The aqueous layer was shaken twice with 200 ml portions of ether. Combined ethereal layer was concentrated and the residue was distilled *in vacuo* to give 9.8 g (56 % based on tin atom) of tetra-n-butyltin, b.p. 128–129°/4 mm, n_D^{20} 1.4715, and 0.8 g (5.5 %) of hexa-n-butylditin, b.p. 200–208°/3.5 mm. No ethyltin compound was found in the product by gas chromatography.

The same reactants were heated to reflux (90°) in a glass flask with stirring. After 2 h refluxing, 5.9 g of unchanged zinc powder was separated by filtration. The filtrate was concentrated to 20 ml to give white needles which were removed by filtration. The needles deliquesced on exposure to air and were identified as zinc chloride. To the filtrate was added 20 ml of methyl iodide, and the mixture was kept at 30° for 10 h. All procedures were carried out in a nitrogen atmosphere. Methyl iodide was evaporated and the residue was distilled to give two fractions. The first fraction, b.p. 124–133°/3.5 mm, included 9.4 g (58 %) of unchanged tri-n-butyltin chloride and 0.1 g (0.6 %; 1.4 % based on the tin atom of consumed tri-n-butyltin chloride) of tetra-n-butyltin. The second fraction, b.p. 170–208°/3.5 mm, was hexa-n-butylditin, 4.6 g (32 %; 76 % as above). No tri-n-butylmethyltin was found by gas chromatography.

Reaction of triethyltin chloride with zinc in the presence of n-butyl chloride and triethylamine [*eqn.* (2)]

Reaction of 6.5 g (0.027 mole) of triethyltin chloride and 3.5 g (0.054 g-atom) of zinc powder was carried out with 5.5 g (0.054 mole) of triethylamine and 100 ml of n-butyl chloride in an autoclave stirred at 160° for 6 h. To the reaction product was added 100 ml of 1 *N* hydrochloric acid and organotin compounds were extracted three times with each 200 ml portion of ether. The combined ethereal layer was concentrated and the residue was distilled *in vacuo* to give 4.6 g of distillate, b.p. 64–135°/8 mm, including 2.4 g (38 %) of tetraethyltin, 1.4 g (20 %) of n-butyltriethyltin, 0.3 g (4 %) of di-n-butyldiethyltin, 0.3 g (3 %) of tri-n-butylethyltin and 0.2 g (2 %) of tetra-n-butyltin. The yields are based on tin atom.

Reaction of triethyltin chloride with sodium in n-butyl chloride [*eqn.* (3)]

A mixture of 12.1 g (0.050 mole) of triethyltin chloride and 2.3 g (0.10 g-atom) of sodium and 100 ml of n-butyl chloride was heated in an autoclave with stirring at 160° for 6 h. After cooling, n-butyl chloride layer was concentrated and distilled *in vacuo* to give 10.3 g of distillate, b.p. 78–88°/10 mm, including 5.2 g (43 %) of unchanged triethyltin chloride, 4.7 g (35 %; 61 % based on the tin atom of consumed triethyltin chloride) of n-butyltriethyltin chloride, 0.4 g (3 %; 5 % as above) of tetraethyltin and 0.2 g (2 %; 3.5 % as above) of hexaethylditin.

Reaction of tri-n-butyltin chloride with sodium in triethylamine or in benzene [*eqn.* (4)]

A mixture of 16.3 g of tri-n-butyltin chloride, 2.3 g (0.10 g-atom) of sodium and 100 ml of triethylamine was heated in an autoclave with stirring at 160° for 6 h. After cooling, 100 ml of methanol was added to the product to convert unchanged sodium to sodium methoxide. The product was concentrated and shaken with 100 ml of water and 200 ml of ether. The aqueous layer was extracted twice with 200 ml portions of ether. The combined ethereal layer was concentrated and the residue was distilled *in vacuo* to give 13.4 g (92 % based on tin atom) of hexa-n-butylditin, b.p. 170–200°/5 mm, including a trace of bis(tri-n-butylchlorotin) oxide.

When 100 ml of benzene was used as a solvent instead of triethylamine and the product was treated with ethyl iodide, no ethyltin compound but 12.5 g (86 %) of hexa-n-butylditin, b.p. 186–190°/3 mm, was obtained. It is possible that any tri-n-butyltinsodium was completely consumed before the treatment with ethyl iodide.

Reaction of hexaethylditin with n-butyl chloride in the presence of triethylamine and zinc

On heating 4.1 g (0.010 mole) of hexaethylditin[14] (b.p. 151–152°/15 mm), 5.2 g

(0.08 g-atom) of zinc powder and 5.0 g (0.050 mole) of triethylamine in 100 ml of n-butyl chloride in an autoclave with stirring at 160° for 6 h, all starting materials were recovered unchanged.

Reaction of hexa-n-butylditin with sodium in ethyl chloride

To a mixture of 11.6 g (0.02 mole) of hexa-n-butylditin and 1.8 g (0.08 g-atom) of sodium in an autoclave cooled in solid carbon dioxide–methanol bath was added 100 ml of ethyl chloride. The reaction was carried out at 160° for 6 h, when all sodium had been consumed. After removal of ethyl chloride, 100 ml of water and 600 ml of ether was added to the product. The combined ethereal layer was concentrated and the residue was distilled *in vacuo* to give 10.8 g (93 %) of unchanged hexa-n-butylditin. No ethyltin compound was obtained.

Reaction of di-n-butyltin dichloride with zinc in the presence of ethyl chloride and triethylamine (eqn. 6)

To a mixture of 15.2 g (0.050 mole) of di-n-butyltin dichloride, 6.5 g (0.10 g-atom) of zinc powder and 10.1 g (0.10 mole) of triethylamine in an autoclave cooled in solid carbon dioxide/methanol bath was added 100 ml of ethyl chloride, and the reaction was carried out at 160° for 6 h. After recovery of ethyl chloride, the product was shaken with 200 ml of 1 *N* hydrochloric acid and 200 ml of ether. The aqueous layer was extracted twice with 200 ml portions of ether. The combined ethereal layer was concentrated and the residue was distilled to give 9.6 g of liquid, b.p. 43°/3–119°/2 mm, including 4.2 g (24 %) of tetra-n-butyltin, 3.2 g (20 %) of tri-n-butylethyltin, 0.6 g (4 %) of di-n-butyldiethyltin, 0.7 g (5 %) of n-butyltriethyltin and 0.9 g (8 %) of tetraethyltin. The yields are based on tin atom.

Reaction of di-n-butyltin dichloride with zinc in triethylamine. Attempted isolation of dialkyltin–zinc compound

A mixture of 15.2 g (0.05 mole) of di-n-butyltin dichloride, 6.5 g (0.10 g-atom) of zinc powder and 100 ml of triethylamine was heated in an autoclave with stirring at 130° for 6 h. The triethylamine layer was separated by decantation and was concentrated to give 2.2 g of white precipitate which was a mixture of bis(di-n-butylchlorotin) oxide and di-n-butyltin dichloride–triethylamine complex. The precipitate was removed by filtration in a nitrogen atmosphere. Half of the filtrate was treated with 17 ml of ethyl bromide at 140° for 4 h and the product was distilled *in vacuo* to give a distillate, b.p. 135–137°/4 mm, including 6.0 g of tri-n-butyltin chloride and 1.5 g of tetra-n-butyltin and no ethyltin compound. On exposing half the remaining filtrate to air for 5 days no white precipitate of di-n-butyltin oxide was obtained, while the other half was distilled *in vacuo* to give 7.3 g of distillate, b.p. 133°/4 mm, including 5.9 g of tri-n-butyltin chloride and 1.4 g of tetra-n-butyltin.

Reaction of di-n-butyltin dichloride with ethyl chloride in the presence of triethylamine and iron

Ethyl chloride (100 ml) was added to a mixture of 30.4 g (0.10 mole) of di-n-butyltin dichloride, 11.2 g (0.20 g-atom) of iron powder and 20.2 g (0.20 mole) of triethylamine in an autoclave cooled in a solid carbon dioxide-methanol bath, and the reaction was carried out at 160° for 6 h. To the reaction product was added 100 ml of 1 *N* hydrochloric acid and the mixture was shaken three times with 200 ml portions of ether. The combined ethereal layer was concentrated and the residue was distilled to give 23.6 g of distillate, b.p. 96–123°/4 mm, whose constituents were found by gas chromatography to be (yields are based on tin atom): 14.1 g (43 %; 46 % based on consumed di-n-butyltin dichloride) of tri-n-butyltin chloride, 7.0 g (24 %; 26 % as above) of di-n-butylethyltin chloride, 1.3 g (5 %) of n-butyldiethyltin chloride, 0.5 g (2 %) of triethyltin chloride, 1.5 g (6 %) of unchanged di-n-butyltin dichloride, 0.1 g (0.4 %) of di-n-butyldiethyltin and 0.1 g (0.3 %) of tetra-n-butyltin.

Reaction of diethyltin dichloride with n-butyl chloride in the presence of triethylamine and iron [*eqn.* (8)]

A mixture of 24.8 g (0.010 mole) of diethyltin dichloride, 11.2 g (0.20 g-atom) of iron powder, 20.2 g (0.20 mole) of triethylamine and 100 ml of n-butyl chloride was heated in an autoclave with stirring at 160° for 6 h. The product was shaken with 100 ml of 1 *N* hydrochloric acid and 200 ml of ether. The aqueous layer was shaken three times with 200 ml portions of ether. The combined ethereal layer was concentrated and the residue was distilled to give 16.1 g of distillate, b.p. 90–113°/12 mm, which included 2.7 g (11 %) of unchanged diethyltin dichloride, 7.7 g (32 %; 36 % based on consumed diethyltin dichloride) of triethyltin chloride, 4.1 g (15 %; 17 % as above) of n-butyldiethyltin chloride, 0.4 g (1 %) of di-n-butylethyltin chloride, 0.8 g (3 %) of n-butylethyltin dichloride, 0.1 g (0.6 %) of tetraethyltin, 0.2 g (0.6 %) of tri-n-butylethyltin, and a trace of n-butyltriethyltin and tri-n-butyltin chloride. The yields are based on the tin atom of the diethyltin dichloride.

SUMMARY

Dialkyltin dichloride is converted into trialkyltin chloride via bis(dialkylchlorotin) oxide in water in presence of a metal. The conversion also takes place without water in the presence of alkyl chloride, organic base, and metallic tin or iron. Zinc, magnesium, aluminium or sodium can be used instead of tin or iron, but in these cases a mixture of trialkyltin chloride and tetraalkyltin was formed from di- or trialkyltin chloride. Possible reaction schemes are discussed.

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