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β-SUBSTITUTED ALKYLTIN HALIDES

III *. SYNTHESIS OF TRIALKYLTIN HALIDES AND TETRAALKYLTINS

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Summary

(β-Carboalkoxyethyl)tin trihalides and bis(β-carboalkoxyethyl)tin dihalides react with metallic zinc to give mixtures of the corresponding tris(β-carboalkoxyethyl)tin halides and the tetra(β-carboalkoxyethyl)tins. Bis(β-carboalkoxyethyl)tin diacetates react with metallic zinc to give only the corresponding tetra(β-carboalkoxyethyl)tin compounds. The mechanisms of these reactions are discussed. Conversion of the bis(β-carboalkoxyethyl)tin dihalides into the tris(β-carboalkoxyethyl)tin halides is believed to occur by a two-step process, with the tetra(β-carboalkoxyethyl)tin compounds as intermediate products. The 270 MHz NMR spectra of the (β-carbobutoxyethyl)tin compounds are presented.

Introduction

In the previous papers of this series we described the synthesis of functionally substituted mono- and di-alkyltin halides from reactions between hydrogen halides, functionally substituted olefins, and $SnCl_2$ or Sn, respectively. In that work the activated olefins were largely acrylates, and eq. 1 and 2 illustrate the methods [1,2].

$$HX + SnX_2 + CH_2{=}CHCO_2R \rightarrow X_3SnCH_2CH_2CO_2R \quad (1)$$

$$2HX + Sn + 2CH_2{=}CHCO_2R \rightarrow X_2Sn(CH_2CH_2CO_2R)_2 + X_3SnCH_2CH_2CO_2R \quad (2)$$

(X = Cl, Br, I; R = alkyl, aryl)

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[*] For part II see ref. 2.

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As a 'direct reaction' route to mixed alkyltin halides reaction 2 is somewhat unique, since only mono- and di-alkyltin halides are produced. Other 'direct reaction' routes to these materials (typically from alkyl halides and metallic tin) also give trialkyltin halides as (from a commercial point of view) unwanted impurities (eq. 3), [3].

$$RX + Sn \rightarrow RSnX_3 + R_2SnX_2 + R_3SnX \qquad (3)$$

$$(X = Br, I;\ R = Me, Bu, Oct)$$

Sisido and coworkers have shown that under appropriate conditions it is also possible to influence the distribution of the alkyltin halides produced by reaction 3 so that relatively high yields of the trialkyltin halides are produced [4]. The same workers studied the synthesis of trialkyltin halides from reactions between dialkyltin halides and metallic tin or zinc (eq. 4) [5].

$$R_2SnX_2 + M \xrightarrow[160°C]{\text{Base } (\pm RX)} R_3SnX + R_4Sn \qquad (4)$$

$$(R = Bu;\ X = Cl;\ M = Sn, Zn)$$

More recently, Bulten and Van den Hurk have demonstrated that similar reactions between methyltin trichloride or β-carbomethoxyethyltin trichloride (β-CMESnCl$_3$) and tin or zinc proceed under mild conditions to give the corresponding di- and tri-alkyltin halides. (eq. 5) [6].

$$RSnCl_3 + M \xrightarrow[20°C]{Et_2O} R_2SnCl_2 + R_3SnCl \qquad (5)$$

$$(R = Me, CH_2CH_2CO_2Me;\ M = Sn, Zn)$$

Results and discussion

I. Synthetic reactions

I.i. Reactions between β-carboalkoxyethyltin trihalides and zinc (or tin). (β-Carboalkoxyethyl)tin trihalides react with metallic zinc to give high yields of tris(β-carboalkoxyethyl)tin halides or tetra(β-carboalkoxyethyl)tins depending on the conditions used (see Table 1). Some 60 MHz NMR data for several compounds are listed in Table 2, but they are of relatively little use for (β-carboalkoxyethyl)tin compounds with $R > Et$, and 270 MHz NMR spectra are also given for the (β-carbobutoxyethyl)tin compounds (Table 3).

From a limited study it appears that β-CMESnBr$_3$ will also undergo reaction, but to give lower yields. Higher alkyl and aromatic esters also react under mild conditions with metallic zinc. The overall reaction is represented by eq. 6.

$$X_3SnCH_2CH_2CO_2R + Zn \rightarrow XSn(CH_2CH_2CO_2R)_3 + Sn(CH_2CH_2CO_2R)_4 \qquad (6)$$

$$(X = Cl, Br;\ R = Me, Et, Bu, Ph)$$

With a Zn/organotin ratio of 2.63, β-CMESnCl$_3$ reacts with zinc in Et_2O at room temperature to give exclusively (β-CME)$_3$SnCl (73%), but with a lower Zn/organotin ratio, under similar conditions, Bulten and Van den Hurk found that (β-CME)$_2$SnCl$_2$ is also a major product [6]. They also obtained a high yield of Me$_3$SnCl from a facile reaction between MeSnCl$_3$ and Zn in refluxing ether. The

TABLE 1

REACTIONS BETWEEN β-CARBOALKOXYETHYLTIN COMPOUNDS AND ZINC

Reagent (mol)		Solvent (Volume (ml))		Molar ratio zinc/organotin compound	Reaction time (h)	Temperature (°C)	Yield (%) $R'_3SnCl + R'_4Sn$	$\%R'_4Sn$[a]
$Cl_3SnCH_2CH_2CO_2Me$	(0.192)	Et_2O	(300)	2.63	20	22	73	–
$Cl_3SnCH_2CH_2CO_2Me$	(0.135)	Et_2O	(350)	2.95	36	R	80	74
$Br_3SnCH_2CH_2CO_2Me$	(0.011)	Tol.[d]	(50)	2.73	5	R	ca. 58	6
$Cl_3SnCH_2CH_2CO_2Et$	(0.275)	Et_2O	(900)	2.00	16	R	86	4
$Cl_3SnCH_2CH_2CO_2Bu$	(0.169)	Et_2O	(300)	2.71	20	22	75	–
$Cl_3SnCH_2CH_2CO_2Ph$	(0.027)	Tol.	(100)	2.26	12	R	ca. 47	[b]
$Cl_2Sn(CH_2CH_2CO_2Me)_2$	(0.165)	Et_2O	(300)	1.30	36	R	69	70
$Cl_2Sn(CH_2CH_2CO_2Me)_2$	(0.055)	MeOAc	(30)	1.11	2	R	81	12
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.022)	Et_2O	(100)	3.43	72	22	c	
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.112)	Et_2O	(75)	1.37	8	R	76	8
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.446)	Et_2O	(1000)	1.03	21	R	84	7
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.134)	Et_2O	(300)	1.37	36	R	79	75
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.045)	Bulk		1.37	20	100	ca. 76	[b]
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.022)	Tol.	(100)	2.74	1.5	R	ca. 67	[b]
		$+ ClCH_2CH_2CO_2Bu$ (4 g)						
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	(0.022)		(100)	5.49	5	R	ca. 50	30
		$+ ClCH_2CH_2CO_2Bu$ (8 g)						
$Br_2Sn(CH_2CH_2CO_2Bu)_2$	(0.019)	Tol.	(100)	1.64	5	R	ca. 71	[b]
$Cl_2Sn(CH_2CH_2CO_2Ph)_2$	(0.062)	Tol.	(200)	0.99	20	R	ca. 62	[b]
$ClSn(CH_2CH_2CO_2Bu)_3$	(0.009)	Tol.	(100)	1.66	50	R	[c]	
$ClSn(CH_2CH_2CO_2Bu)_3$	(0.018)	Tol.	(100)	3.33	10	R	[c]	
		$+ ClCH_2CH_2CO_2Bu$ (4 g)						
$(MeCO_2)_2Sn(CH_2CH_2CO_2Me)_2$	(0.433)	Tol.	(200)	1.77	3	R	83	95
$(MeCO_2)_2Sn(CH_2CH_2CO_2Bu)_2$	(0.020)	Tol.	(100)	3.03	8	R	83	100

[a] $R' = CH_2CH_2CO_2R$. [b] Not determined. [c] No reaction. [d] Tol. = toluene; R = reflux.

TABLE 2

60 MHz NMR DATA FOR β-CARBOALKOXYETHYLTIN COMPOUNDS

Compound	Chemical shifts (τ) [a]			Coupling constants [b] (Hz)	
	CH(α)	CH(β)	OCH_n	J(Sn–H(α))	J(Sn–H(β))
$ClSn(CH_2CH_2CO_2Me)_3$	8.59	7.25	6.33	50	90
$Sn(CH_2CH_2CO_2Me)_4$	9.06	7.48	6.40	51	62
$ClSn(CH_2CH_2CO_2Et)_3$	8.60	7.27	5.87	72(?)	91
$ClSn(CH_2CH_2CO_2Bu)_3$	[c]	7.27	5.93	[d]	94
$Sn(CH_2CH_2CO_2Bu)_4$	[c]	7.43	5.95	[d]	[d]

[a] Spectra recorded in $CDCl_3$ solution - internal TMS (τ = 10.0). [b] The reported values are the mean of the ^{117}Sn–H and ^{119}Sn–H coupling constants. [c] Spectra not resolved. [d] The Sn–H satellite peaks are masked by the other signals.

reaction between alkyltin trihalides and zinc does, however, appear to be moderated by increasing alkyl chain length, since in our hands $BuSnCl_3$ reacted with zinc in Et_2O at room temperature during 96 hours to give approximately 50% conversion of $BuSnCl_3$, mainly to Bu_2SnCl_2 and a small amount of Bu_3SnCl (eq. 7). No tetrabutyltin was detected.

$$\mathrm{BuSnCl_3 + Zn \xrightarrow[96\ h]{Et_2O} Bu_2SnCl_2 + Bu_3SnCl} \tag{7}$$

Reaction 5 ($R = CH_2CH_2CO_2Me$; M = Sn) in Et_2O at room temperature gives small quantities (2%) of $(\beta\text{-CME})_3SnCl$ [6] and larger quantities (12%) after 10 h in refluxing dimethoxyethane (DME). In view of these observations, it is perhaps surprising that the formation of tris(β-carboalkoxyethyl)tin halides is not detected in the hydrostannation reaction (eq. 2) [2], in which the β-carboalkoxyethyltin trihalides are generated in the presence of a relatively large excess of Sn, at least in the early stages of the reaction. However, mechanistic studies showed that in the presence of HCl the alkylation of β-carboalkoxyethyltin trihalides to the corresponding bis(β-carboalkoxyethyltin)tin dihalides does not occur by the same process as the reaction in absence of HCl [2]. Furthermore, the absence of tris(β-carboalkoxyethyl)tin halides in reaction 2 may be a consequence of the relatively facile redistribution with β-carboalkoxyethyltin trihalides [7].

$$\mathrm{ClSn(CH_2CH_2CO_2R)_3 + Cl_3SnCH_2CH_2CO_2R \rightarrow 2Cl_2Sn(CH_2CH_2CO_2R)_2} \tag{8}$$

(R = alkyl)

I.ii. Reaction between bis(β-carboalkoxyethyl)tin dihalides and Zn. Bis(β-carboalkoxyethyl)tin dihalides also react with metallic zinc to give mixtures of the corresponding tris(β-carboalkoxyethyl)tin halides and tetra(β-carboalkoxyethyl)tins (eq. 9). The bis(β-carboalkoxyethyl)tin dihalides are less reactive than the corresponding trihalides. Short reaction times favour the tris(β-carboalkoxyethyl)tin halides and longer times the tetra(β-carboalkoxyethyl)tins, in line with observations

$$\mathrm{X_2Sn(CH_2CH_2CO_2R)_2 + Zn \rightarrow XSn(CH_2CH_2CO_2R)_3 + Sn(CH_2CH_2CO_2R)_4} \tag{9}$$

(X = Cl, Br; R = alkyl, aryl)

TABLE 3

270 MHz NMR DATA FOR β-CARBOBUTOXYETHYLTIN COMPOUNDS[a]

Compound	Chemical Shifts (τ)[b]						Coupling constants (Hz)[c]	
	H(α)	H(β)	H(a)	H(b)	H(c)	H(d)	J(Sn–H(α))	J(Sn–H(β))
$Cl_3SnCH_2CH_2CO_2Bu$	7.78	7.04	5.62	8.27	8.58	9.03	105	190
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	8.11	7.08	5.86	8.33	3.62	9.05	105	151
$ClSn(CH_2CH_2CO_2Bu)_3$	8.56	7.24	5.92	8.38	8.63	9.06	[d]	85
$Sn(CH_2CH_2CO_2Bu)_4$	8.97	7.43	5.93	8.38	8.63	9.07	[d]	58

[a] $\underset{\alpha}{SnCH_2}\,\underset{\beta}{CH_2}CO_2\,\underset{a}{CH_2}\,\underset{b}{CH_2}\,\underset{c}{CH_2}\,\underset{d}{CH_3}$ [b] Spectra recorded in $CDCl_3$ solution - internal TMS (τ = 10.0). [c] The reported values are the mean of the ^{117}Sn–H and ^{119}Sn–H coupling constants. [d] The Sn–H satellite peaks are masked by the other signals.

TABLE 4

ATTEMPTED REACTIONS BETWEEN β-CARBOALKOXYETHYLTIN COMPOUNDS AND TIN

Reagent (mol)	Solvent (volume (ml))	Molar ratio tin/organotin compound	Reaction time (h)	Temper-ature (°C)	Yield (%)
$Cl_3SnCH_2CH_2CO_2Me$ (0.032)	DME[c] (100)	2.63	10	R	78[a]
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$ (0.022)	Tol[d] (50)	5.49	21	R	[b]
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$ (0.011)	Tol (50) + $ClCH_2CH_2CO_2Bu$(2 g)	3.01	21	R	[b]
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$ (0.011)	DMD[e] (50) + $ClCH_2CH_2CO_2Bu$(2 g)	6.02	40	160	[b]

[a] 88% (β-CME)$_2$SnCl$_2$ + 12% (β-CME)$_3$SnCl. [b] No reaction. [c] DME = dimethoxyethane. [d] Tol = toluene. [e] DMD = dimethyldigol. R = reflux.

on reactions of the trihalides. Bis(β-carboalkoxyethyl)tin dibromides also undergo reaction with Zn. A limited study suggests that longer alkyl chain esters and aromatic esters also react, the latter compounds somewhat more slowly than the alkyl esters.

Unlike the β-carboalkoxyethyltin trihalides, the dihalides do not react with metallic Sn (see Table 4). Use of large molar excesses of tin in combination with butyl-3-chloropropionate as cosolvent [5] did not enhance the reaction. Reactions between $(\beta\text{-CBE})_2SnCl_2$ and Zn were similarly unaffected by the addition of butyl-3-chloropropionate. Attempts to bring $(\beta\text{-CBE})_3SnCl$ into reaction with Zn in refluxing toluene were unsuccessful. The bis(β-carboalkoxyethyl)tin diacetates also react with metallic zinc to give high yields of relatively pure tetra(β-carboalkoxyethyl)tin (Table 1). This appears to be the first example of an alkylation involving an organotin carboxylate.

$$2(CH_3CO_2)_2Sn(CH_2CH_2CO_2R)_2 + Zn \rightarrow Sn(CH_2CH_2CO_2R)_4 + Zn(OAc)_2 + Sn(OAc)_2 \qquad (10)$$

$(R = Me, Bu)$

II. Reaction mechanisms

In an attempt to elucidate the mechanism of the alkylation reactions of the bis(β-carboalkoxyethyl)tin dihalides (and diacetates) with zinc, a comprehensive study of the effects of reaction variables was undertaken.

II.i. Effect of solvent. The effects of solvents on the reaction between $(\beta\text{-CBE})_2SnCl_2$ and zinc at 80°C are shown in Table 5. Reactions were deemed to be complete when all traces of $(\beta\text{-CBE})_2SnCl_2$ had disappeared as judged by TLC analysis. Only in cyclohexane, the least polar of the solvents, was the reaction relatively slow. There seems to be little correlation between yield and/or $(\beta\text{-CBE})_4Sn$ formation and reaction time.

II.ii. Effect of temperature. The results of experiments performed on $(\beta\text{-CBE})_2SnCl_2$ over a range of temperatures are presented in Fig. 1. Reactions were fast above 60°C whereas below 40°C no reaction at all was detected. It thus appears, that there is a critical initiation temperature between 40 and 60°C.

II.iii. Effect of concentration. The results of this study are presented in Fig. 2.

TABLE 5

EFFECT OF SOLVENT UPON THE REACTION BETWEEN $Cl_2Sn(CH_2CH_2CO_2Bu)_2$ (0.022 mol) AND ZINC (0.031 mol) AT 80°C

Solvent	Reaction time (h)	Yield $R'_3SnCl + R'_4Sn$	%R'_4Sn [a]
Cyclohexane	6	89	11.2
Benzene	1	89	12.0
Di/Sec-butyl ether	1	86	15.6
Dimethoxyethane	2.5	94	28.0
Butyl formate	1	67	2.0
Butan-2-one	2	91	12.8

[a] $R' = CH_2CH_2CO_2Bu$.

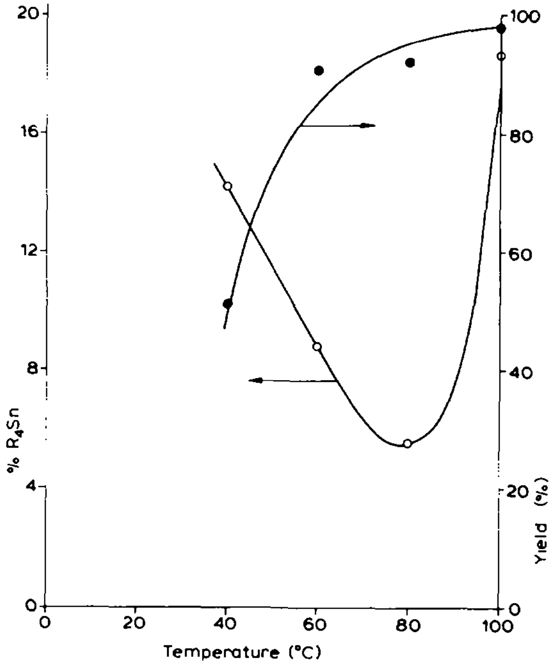


Fig. 1. The effect of temperature upon yield (●), $R_3SnCl + R_4Sn$; and upon product composition (○), % R_4Sn; in the reaction between (β-CBE)$_2$SnCl$_2$ (0.022 mol) and Zn (0.031 mol) in toluene (20 ml) (R = β-CBE). Reaction times; 336 h at 40°C, 2 h at 60°C, 1 h at 80°C, and 0.5 h at 100°C.

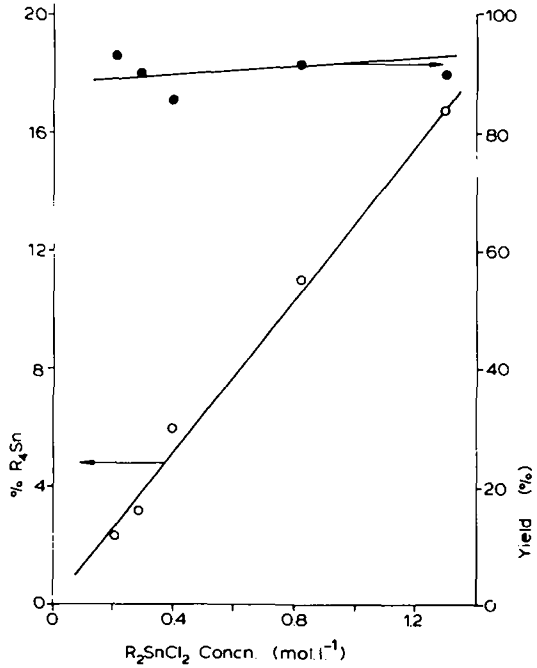


Fig. 2. The effect of concentration upon yield (●), $R_3SnCl + R_4Sn$; and upon product composition (○), % R_4Sn; in the reaction between (β-CBE)$_2$SnCl$_2$ (0.022 mol) and Zn (0.031 mol) in toluene at 80°C (R = β-CBE).

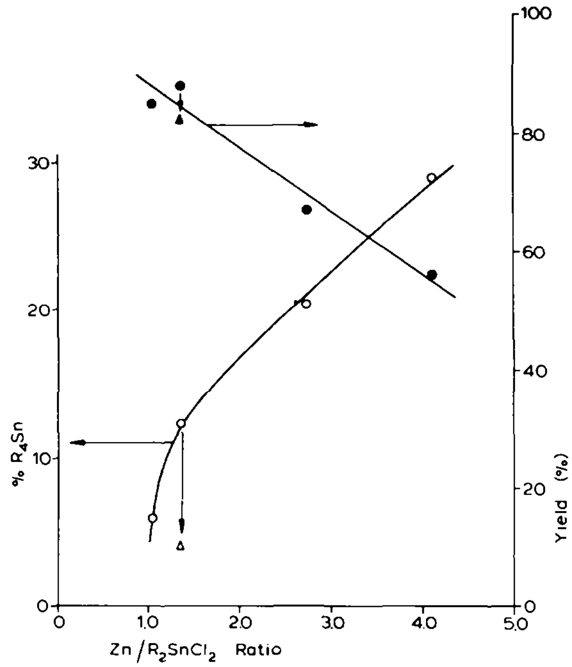


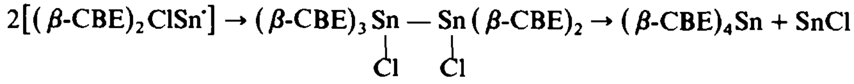
Fig. 3. The effect of Zn/R_2SnCl_2 mole ratio upon yield (●), $R_3SnCl + R_4Sn$; and upon product composition (○), % R_4Sn; in the reaction between $(\beta\text{-CBE})_2SnCl_2$ (0.022 mol) and Zn in toluene (40 ml) at 80°C (R = β-CBE). The effect of added $ZnCl_2$ (0.015 mol) upon yield (▲) and upon product composition (△).

The organotin concentration was varied in these experiments by varying the solvent volume.

II.iv. Effect of zinc/organotin ratio. Both yield and composition, of the product mixture are greatly affected by variation in the ratio of zinc to $(\beta\text{-CBE})_2SnCl_2$ (see Fig. 3).

II.v. Effect of zinc chloride. Addition of zinc chloride to a reaction between $(\beta\text{-CBE})_2SnCl_2$ and Zn in toluene gave a significant reduction in the proportion of $(\beta\text{-CBE})_4Sn$ in the product mixture without markedly affecting the overall yield (Fig. 3).

II.vi. Proposed mechanism. We believe that the experimental observations are consistent with the following scheme (eq. 11):



$$2(\beta\text{-CBE})_2SnCl_2 + Zn \rightarrow 2[(\beta\text{-CBE})_2ClSn^{\cdot}] + ZnCl_2$$

$$2[(\beta\text{-CBE})_2ClSn^{\cdot}] \rightarrow (\beta\text{-CBE})_3\underset{\displaystyle Cl}{\underset{|}{Sn}} - \underset{\displaystyle Cl}{\underset{|}{Sn}}(\beta\text{-CBE})_2 \rightarrow (\beta\text{-CBE})_4Sn + SnCl_2 \qquad (11)$$

$$(\beta\text{-CBE})_4Sn + (\beta\text{-CBE})_3SnCl_2 \rightarrow 2(\beta\text{-CBE})_3SnCl$$

The first step in this sequence corresponds to reduction of $(\beta\text{-CBE})_2SnCl_2$ by Zn to give a radical intermediate and $ZnCl_2$. Devaud has reported the electrochemical reduction of substituted trihalides [8] and also the electrochemical reduction of dialkyl and bis(β-carboalkoxyethyl)tin dihalides [9]. In both cases radical species are generated, and in the case of substituted (or unsubstituted) dialkyltin compounds, the radical $R_2ClSn^{\cdot}$ is proposed as an intermediate. (We previously reported a similar chemical reduction of β-carboalkoxyethyltin trihalides with Sn involving initial generation of $RCl_2Sn^{\cdot}$ [2]. Formation of $(\beta\text{-CBE})_4Sn$ and $SnCl_2$ from the radical intermediate, possibly via the di-tin species $(\beta\text{-CBE})_2ClSn\text{-}SnCl(\beta\text{-CBE})_2$, could then occur. $(\beta\text{-CBE})_3SnCl$ and $\beta\text{-CBESn}^{II}Cl$ or $(\beta\text{-CBE})_2SnCl_2$ and $(\beta\text{-CBE})_2Sn^{II}$ are possible alternative product pairs, but the greater overall thermodynamic stability of the $(\beta\text{-CBE})_4Sn/SnCl_2$ product pair should favour these products. Devaud also concludes that $R_2ClSn^{\cdot}$ radicals (generated electrochemically) dimerise to $R_2ClSnSnClR_2$.

In the reaction between $(\beta\text{-CBE})_2SnCl_2$ and Zn, $(\beta\text{-CBE})_3SnCl$ is believed to arise from the redistribution reaction between $(\beta\text{-CBE})_2SnCl_2$ and $(\beta\text{-CBE})_4Sn$ (eq. 8) ($R = Bu$). A study of this reaction has shown that the β-CBE/Cl exchange process is much faster than, e.g., Bu/Cl exchange in the analogous butyltin redistribution reaction [7]. This type of exchange is catalysed by either inter- or intra-molecular carbonyl to Sn coordination. However, it is unlikely that this reaction, in isolation, is sufficiently fast to explain the rate of formation of $(\beta\text{-CBE})_3SnCl$.

In an attempt to clarify this point, some of these redistributions were examined (see Table 6). A reaction between equimolar quantities of $(\beta\text{-CBE})_4Sn$ and $(\beta\text{-CBE})_2SnCl_2$ during 2 hours at 120°C in toluene resulted in only approximately 30% conversion to $(\beta\text{-CBE})_3SnCl$, whereas many reactions (between $(\beta\text{-CBE})_2SnCl_2$ and Zn) in toluene at 80°C are complete in only 1.5 hours. This redistribution is also extremely slow in Et_2O at 35°C, with less than 5% conversion in 20 hours. Again the reaction between $(\beta\text{-CBE})_2SnCl_2$ and Zn in Et_2O under reflux conditions is complete within this period. However, the addition of $ZnCl_2$ to the redistribution reactions resulted in very large catalysis such that the generation of $(\beta\text{-CBE})_3SnCl$ from $(\beta\text{-CBE})_2SnCl_2$ and Zn can easily be accounted for by the redistribution process. Consistent with these observations is the fact that addition of $ZnCl_2$ to a reaction between $(\beta\text{-CBE})_2SnCl_2$ and Zn gave a lower proportion of $(\beta\text{-CBE})_4Sn$ in

TABLE 6

REDISTRIBUTION REACTIONS BETWEEN $Sn(CH_2CH_2CO_2Bu)_4$ AND ORGANOTIN COMPOUNDS OF THE TYPE $X_2Sn(CH_2CH_2CO_2Bu)_2$ ($X = Cl, CH_3CO_2$)

Organotin	Solvent	Catalyst (% w/w)	Temperature (°C)	Time (h)	Conversion (%)
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	–	–	120	2	ca. 30
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	–	$ZnCl_2$ (5)	120	< 0.5	100
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	Et_2O	–	35	20	< 5
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	Et_2O	$ZnCl_2$ (5)	35	20	95
$(CH_3CO_2)_2Sn(CH_2CH_2CO_2Bu)_2$	Tol	–	50	60	ca. 20
$(CH_3CO_2)_2Sn(CH_2CH_2CO_2Bu)_2$	Tol	$Zn(OAc)_2$ (10)	50	60	ca. 20
$(CH_3CO_3)_2Sn(CH_2CH_2CO_2Bu)_2$	Tol	$ZnCl_2$ (10)	50	60	90

the product mixture. The $ZnCl_2$ catalyst for the redistribution step is generated in the first step of the reaction. Furthermore, the level of zinc in the majority of the alkylation reactions is sufficient to generate higher levels of $ZnCl_2$ by reaction with $SnCl_2$ (also generated in the first step). Indeed, inorganic tin appears as metallic tin rather than $SnCl_2$.

$$\mathrm{Zn + SnCl_2 \rightarrow ZnCl_2 + Sn} \qquad (12)$$

Also consistent with the proposed mechanism are the observations that higher molar ratios of Zn to $(\beta\text{-CBE})_2SnCl_2$ and higher concentrations of $(\beta\text{-CBE})_2SnCl_2$ give a higher proportion of $(\beta\text{-CBE})_4Sn$ in the product mixture. This is to be expected, since both factors will enhance the $(\beta\text{-CBE})_2SnCl_2 \rightarrow (\beta\text{-CBE})_4Sn$ transformation and so give lower residual amounts of $(\beta\text{-CBE})_2SnCl_2$. Conceivably the effect of DME as solvent (reported in Table 5) might also be explained in terms of eq. 11. Possibly the catalytic efficiency of $ZnCl_2$ in the redistribution process is reduced by DME solvation.

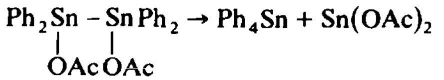
By far the highest yields of $Sn(CH_2CH_2CO_2R)_4$ (R = Me, Bu) recorded in Table 1 were obtained from the corresponding diacetates ($(CH_3CO_2)_2Sn(CH_2CH_2CO_2R)_2$). This observation can again be rationalised in terms of a similar mechanism to that shown in eq. 11 (i.e. eq. 13):

$$2(\beta\text{-CBE})_2\mathrm{Sn(OAc)_2 + Zn} \rightarrow (\beta\text{-CBE})_4\mathrm{Sn + Sn(OAc)_2 + Zn(OAc)_2} \qquad (13)$$

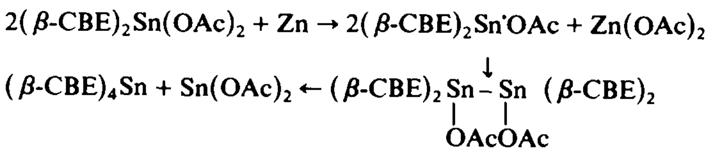
$$(\beta\text{-CBE})_4\mathrm{Sn} + (\beta\text{-CBE})_2\mathrm{Sn(OAc)_2} \xrightarrow{\text{v. slow}} 2(\beta\text{-CBE})_3\mathrm{SnOAc}$$

In this case, the second step, the redistribution, is very slow, and apparently not catalysed by $Zn(OAc)_2$ (see Table 6). Hence, the first step, the initial conversion of $(\beta\text{-CBE})_2Sn(OAc)_2$ into $(\beta\text{-CBE})_4Sn$, is the only efficient step in this case. $ZnCl_2$ has been shown to catalyse the redistribution reaction between $(\beta\text{-CBE})_4Sn$ and $(\beta\text{-CBE})Sn(OAc)_2$.

That $(\beta\text{-CBE})_2AcOSnSnOAc(\beta\text{-CBE})_2$ should be proposed as an intermediate in the formation of $(\beta\text{-CBE})_4Sn$ in the first step of reaction 13 is consistent with the report that $(Ph)_2AcOSnSnOAc(Ph)_2$ decomposes thermally to give $(Ph)_4Sn + Sn(OAc)_2$ [10] (eq. 14). In the light of that report, the suggestion that $(\beta\text{-CBE})_2ClSnSnCl(\beta\text{-CBE})_2$ is an intermediate in the formation of $(\beta\text{-CBE})_4Sn$ is all the more plausible.



$$\underset{\mathrm{OAc}}{\mathrm{Ph_2Sn}}-\underset{\mathrm{OAc}}{\mathrm{SnPh_2}} \rightarrow \mathrm{Ph_4Sn + Sn(OAc)_2} \qquad (14)$$



$$\begin{array}{c} 2(\beta\text{-CBE})_2\mathrm{Sn(OAc)_2 + Zn} \rightarrow 2(\beta\text{-CBE})_2\mathrm{Sn^{\cdot}OAc + Zn(OAc)_2} \\ \hspace{4cm}\downarrow \\ (\beta\text{-CBE})_4\mathrm{Sn + Sn(OAc)_2} \leftarrow (\beta\text{-CBE})_2\underset{\mathrm{OAc}}{\mathrm{Sn}}-\underset{\mathrm{OAc}}{\mathrm{Sn}}\ (\beta\text{-CBE})_2 \end{array} \qquad (15)$$

Experimental

Reagents

β-Carboalkoxyethyltin trihalides and bis(β-carboalkoxyethyl)tin dihalides were prepared by published methods [1,2]. Bis(β-carboalkoxyethyl)tin diacetates were prepared from the corresponding dichlorides by reaction with acetic acid in the presence of $NaHCO_3$. $BuSnCl_3$(Aldrich), powdered Zn (AR, B.D.H.) and powdered Sn (Steetley Chemical Co.) were used without purification. Solvents were AR grade and were dried over molecular sieve (type 4A). Butyl-3-chloropropionate was prepared from the reaction between butyl acrylate and gaseous HCl in Et_2O at 0°C and was purified by distillation; b.pt. 82°C/8 mmHg. (lit. [11] 77°C/6 mmHg.)

Spectroscopy

NMR spectra were recorded as $CDCl_3$ solutions on a Perkin Elmer R12B 60MHz spectrometer and/or a Bruker WH270, 270 mHZ spectrometer.

Reactions

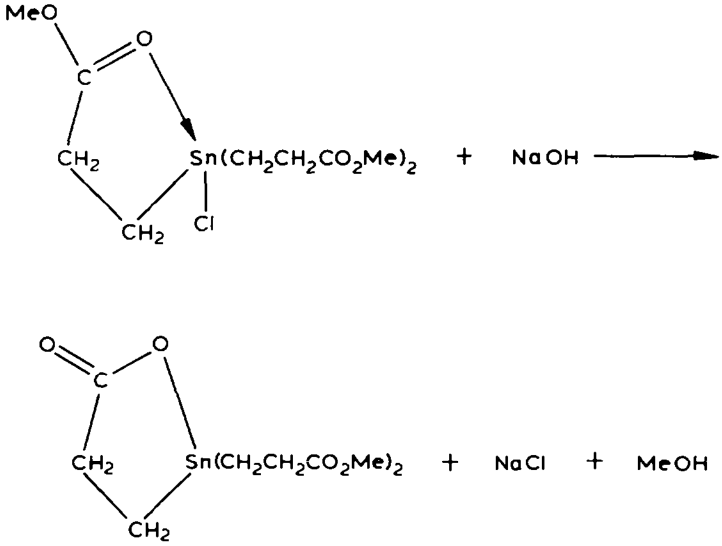
All reactions were performed under an atmosphere of dry nitrogen. Typical reactions are described below.

Reaction of (β-CBE)$_2$SnCl$_2$ and Zn in toluene at 80°C. (β-CBE)$_2$SnCl$_2$ (0.022 mol) was dissolved in dried toluene (20 ml) and powdered Zn (0.031 mol) was added. The temperature was quickly raised to 80°C and kept there for 1 hour. The reaction was monitored by TLC (hexane was used as eluting solvent and the plates were plastic-backed cellulose; the detection spray was dithizone in chloroform) and was deemed to be complete when the amount of (β-CBE)$_2$SnCl$_2$ was below the detection limit. At this point the mixture was filtered to remove solids which were washed with DME (2 × 10 ml). The filtrate was treated with gaseous HCl then washed with 3 × 50 ml portions of 2 *N* HCl and then with water until neutral. The organic phase was dried ($MgSO_4$) and concentrated to give 7.4 g of a pale yellow oil. This was identified as a mixture of (β-CBE)$_3$ SnCl (94.4%) and (β-CBE)$_4$Sn (5.6%) by elemental analysis (Cl and Sn) and 270 MHz NMR spectroscopy. From the analytical data the yield of organotins was estimated to be 92% (based upon the β-carboalkoxyethyl groups).

Reactions of β-CMESnCl$_3$ with Zn in diethyl ether. β-CMESnCl$_3$ (0.135 mol) was dissolved in Et_2O (350 ml) and powdered Zn (0.398 mol) was added. The mixture was refluxed for 36 hours and the solid was filtered off and washed with DME. The combined filtrates were treated with HCl and washed with 3 × 100 ml portions of 2 *N* HCl. The ethereal phase was then washed with water until the aqueous phase was neutral, and concentrated to give 12.5 g of a colourless oil. Elemental analysis (Cl and Sn) and NMR spectroscopy indicated that the product consisted of a mixture of (β-CBE)$_3$SnCl (25%) and (β-CBE)$_4$Sn (75%).

Isolation of (β-CME)$_4$Sn from a mixture of (β-CME)$_4$Sn and (β-CME)$_3$SnCl. The above mixture of (β-CME)$_4$Sn and (β-CME)$_3$SnCl was dissolved in 50 ml of Et_2O at room temperature 7.5 ml of 1 *N* NaOH solution was added during 30 min. After 3 h stirring, water (100 ml) was added and the ethereal phase was separated. The aqueous phase was extracted with 3 × 50 ml portions of Et_2O and the combined ethereal extracts were dried ($MgSO_4$) and concentrated on a thin film evaporator to give 9.4 g of a colourless oil. This was shown by NMR spectroscopy to be pure (β-CME)$_4$Sn, which was obtained in 60% yield based on the amount of β-CMESnCl$_3$ initially taken.

The purification procedure utilizes the greater susceptibility of one ester group in (β-CME)$_3$SnCl to base hydrolysis; in this compound one ester group is intramolecularly coordinated to Sn and two are 'free' (uncoordinated) [7]. Hence, the coordinated group is prone to attack by OH^- [12], giving an 'inner salt' compound which is ether-insoluble (eq. 16).



(16)

Under mild hydrolysis conditions ester groups not coordinated to Sn are not susceptible to base hydrolysis, and $(\beta\text{-CME})_4Sn$ is recovered unchanged.

Reaction of $(\beta\text{-CBE})_2Sn(OAc)_2$ with Zn in toluene. $(\beta\text{-CBE})_2Sn(OAc)_2$ (0.020 mol) was dissolved in toluene (100 ml) and powdered Zn (0.060 mol) was added. The mixture was then heated under reflux for 8 hours then cooled to room temperature and filtered. The filtrate was washed with 3 × 100 ml of H_2O and then dried over $MgSO_4$. Concentration of the toluene solution gave 5.3 g of a pale yellow oil, which was shown to be pure $(\beta\text{-CBE})_4Sn$ by NMR spectroscopy. The yield was 83%.

Reaction of $BuSnCl_3$ with Zn in diethyl ether. $BuSnCl_3$ (0.035 mol) was dissolved in Et_2O (50 ml) and Zn powder (0.031 mol) was added. The mixture was stirred at room temperature for 96 hours and filtered. Evaporation of the filtrate left a residue, which was extracted with hexane. Concentration of the hexane solution yielded a pale brown residue (6.0 g) which was shown by GLC (after methylation with MeMgI [7]) to be a mixture of unchanged $BuSnCl_3$ (46.4%), Bu_2SnCl_2 (48.3%) and Bu_3SnCl (4.0%). These figures correspond to approximately 50% conversion of $BuSnCl_3$ to Bu_2SnCl_2 and Bu_3SnCl.

Redistribution reactions. Redistributions between equimolar quantities of $(\beta\text{-CBE})_4Sn$ and either $(\beta\text{-CBE})_2SnCl_2$ or $(\beta\text{-CBE})_2Sn(OAc)_2$ were carried out under dry nitrogen under the conditions described in Table 6. Conversions in reactions which involved the chlorides were determined directly by NMR analysis (Et_2O was first removed by evaporation under reduced pressure at 0°C from the reactions performed in Et_2O). Conversions in the reactions which involved the acetates were determined by conversion of the acetates to the corresponding chlorides by treatment with hydrochloric acid and washing with water (to remove acetic acid).

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