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ON THE REACTION OF TIN DICHLORIDE AND OF METALLIC TIN WITH HYDROCHLORIC ACID IN THE PRESENCE OF ALKENES. THE QUESTION OF TRICHLOROSTANNANE(IV) OR CHLOROSTANNATE(II) INTERMEDIATES.

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Summary

Studies of the reaction of tin dichloride and of metallic tin with hydrochloric acid gas in diethyl ether are described. On the basis of spectroscopic and analytical data it is concluded that the product is not to be regarded as a tin–hydrogen bonded analog of chloroform, viz. trichlorostannane(IV), and the formation of an equilibrium mixture of hydrogen trichlorostannate(II) and dihydrogen tetrachlorostannate(II) is tentatively suggested. The complexes slowly decompose as a result of diethyl ether cleavage, yielding ethanol and ethyl chloride, together with traces of ethyltin trichloride.

The mechanism of addition of the complexes to methyl acrylate is discussed in terms of a 1,4-addition involving initial protonation of oxygen. Reaction of the resulting β -carbomethoxyethyltin trichloride with tin or with zinc gives rise to mixtures of bis(β -carbomethoxyethyl)tin dichloride and tris(β -carbomethoxyethyl)tin chloride. Similar reactions were observed for the first time with methyltin trichloride, the reaction with zinc being extremely fast at room temperature.

Introduction

The first report on the tin analogue of chloroform, viz. stannachloroform, dates back to 1889 when Engel reported the preparation of $\text{HSnCl}_3 \cdot 3\text{H}_2\text{O}$ (m.p. -27°C) by cooling down to -40°C an aqueous solution of tin dichloride saturated with hydrogen chloride [1]. On the basis of physico-chemical studies of a similar system Young obtained indications of the existence of a species H_2SnCl_4 [2], while Vanderzee and Rhodes [3] determined the equilibrium constants K_n for equilibria of type 1:

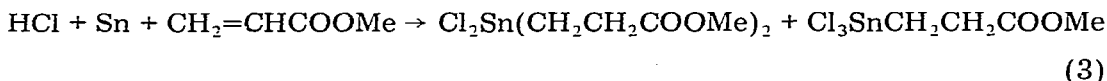


More recently Nefedov and coworkers extended their studies of trichlorogermane (for a review see ref. 4) to the corresponding trichlorostannane [5–7]. Reaction of tin dichloride with hydrogen chloride in diethyl ether was reported to give the dietherate of trichlorostannane, $\text{HSnCl}_3 \cdot 2\text{Et}_2\text{O}$ (I) and it was stated that I does not form organotin compounds with ethylene or other unsaturated hydrocarbons. In contrast, Reifenberg and Considine claimed in a patent application [8] that I does react with α -olefins to give the corresponding adducts (eq. 2)

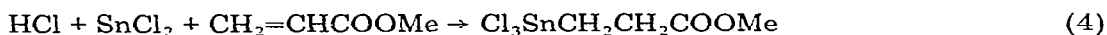


(R = alkyl, CN, functional groups)

Very recently, Burley, Hutton and Oakes described a new synthesis of β -substituted alkyltin halides via halogen-stannane intermediates [9–11]. They found that hydrogen halides react with metallic tin in the presence of α,β -unsaturated carbonyl compounds, such as acrylic esters, to produce mixtures of mono- and di- β -carboxyethyltin halides (e.g. eq. 3).



Similarly, reaction of hydrogen halides with tin dihalides in the presence of α,β -unsaturated carbonyl compounds was reported to give a semi-quantitative yield of β -carboxyethyltin trihalides (e.g. eq. 4).

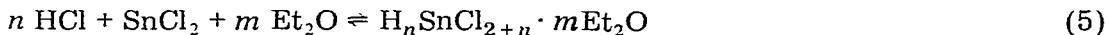


Reaction 4 was interpreted in terms of the intermediate formation of trichlorostannane, HSnCl_3 , and subsequent hydrostannation of the α -carbonyl alkene. For reaction 3 the transient formation of $[\text{H}_2\text{SnCl}_2]$ and/or $[\text{HSnCl}]$ was tentatively suggested.

Results and discussion

Reaction of tin dichloride and of metallic tin with hydrogen chloride in diethyl ether

Anhydrous tin dichloride dissolves rapidly in a saturated solution of hydrogen chloride in diethyl ether. In accord with the results obtained by Nefedov and coworkers [5–7], an etherate $\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}$ separated out as a clear faintly yellow oily liquid (I), insoluble in the clear colourless supernatant liquid.

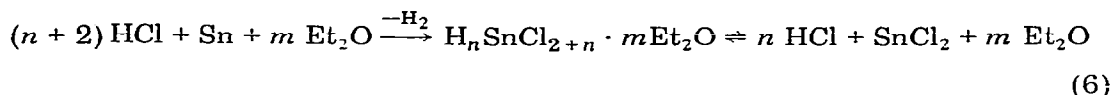


(I)

Addition of diethyl ether to product I causes precipitation of tin dichloride, which can be redissolved by passing hydrogen chloride. Similarly, addition of inert apolar substances such as toluene or tetramethylsilane, or evaporation of diethyl ether and/or hydrogen chloride immediately induces tin dichloride precipitation, indicative of a thermodynamically controlled equilibrium.

A similar reaction mixture is obtained by passing hydrogen chloride into a

suspension of tin powder in diethyl ether (eq. 6).



^1H NMR spectrometry of I shows a strongly ionized proton with a chemical shift varying in different experiments between 10.8 and 12.8 ppm (Table 1). Interaction of the proton with the diethyl ether oxygen is reflected by the down-field shift of the methylene and methyl protons. Comparison with the data reported [5] for $\text{HCl} \cdot n\text{Et}_2\text{O}$ ($n = 1, 2$) shows the considerably increased ionization caused by the interaction with tin dichloride.

The ^1H NMR data of the supernatant point to a composition quite similar to that of hydrogen chloride etherates. The chemical shifts of I are markedly affected by presence of minor amounts of impurities, such as TMS or ethanol. The latter product, resulting from the acidolysis of diethyl ether, is present even in freshly prepared I (see below). Accordingly, a quantitative interpretation of the chemical shift data cannot be given but the following qualitative conclusions can be drawn.

According to Nefedov and coworkers I consists of $\text{HSnCl}_3 \cdot 2\text{Et}_2\text{O}$, two different chemical shift values for the acidic proton being reported, viz. 11.8 ppm [5] and 12.81 ppm [6]. In a series of experiments (Table 1) we observed various m/n values (^1H NMR; integrated ratios) ranging from 1.1–1.5. Attempts to prepare compositions with exact stoichiometry (m/n 1.0 or 2.0) failed because of tin dichloride precipitation. The rather poor stability of the product strongly hampered accurate elemental analysis (sampling). Interestingly, however, in different samples the molar ratio Cl/Sn was found to be 3.8, 4.0 and 4.3, respectively.

Most likely product I does not consist of one single well-defined compound but of a product mixture resulting from a set of equilibria similar to that suggested previously for aqueous systems [3]. Approximately one molecule of

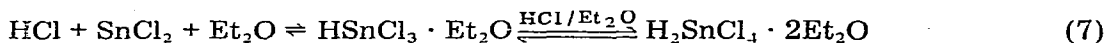
TABLE 1

^1H NMR DATA FOR $\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}$ AND RELATED COMPOUNDS

Compound	m/n	Chemical shifts (ppm; TMS = 0)		
		$\delta(\text{H}^+)$	$\delta(\text{CH}_3-\text{C})$	$\delta(\text{CH}_2-\text{O})$
$\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}$	1.1	10.9	1.40	4.05
$\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}$	1.2	10.8–11.9	1.37–1.40	4.02–4.10
$\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}$	1.4	11.9–12.8	1.40–1.42	4.13–4.14
$\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}$	1.5	12.5	1.44	4.20
$\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}^a$	2.0	11.8	—	—
$\text{H}_n\text{SnCl}_{2+n} \cdot m\text{Et}_2\text{O}^b$	2.0	12.8	1.70	4.42
$\text{HGeCl}_3 \cdot n\text{Et}_2\text{O}^b$	1.0	11.2	1.74	4.42
$\text{HGeCl}_3 \cdot n\text{Et}_2\text{O}^b$	2.0	14.9–15.3	1.48–1.54	4.10–4.26
Supernatant	1.7	7.5	1.18	3.53
Supernatant	2.6	6.9	1.16	3.49
$\text{HCl} \cdot n\text{Et}_2\text{O}^b$	1	6.8	1.25	3.54
$\text{HCl} \cdot n\text{Et}_2\text{O}^b$	2	6.8	1.25	3.54

^a Ref. 5. ^b Ref. 6.

diethyl ether per proton is present (eq. 5, $n = m$).



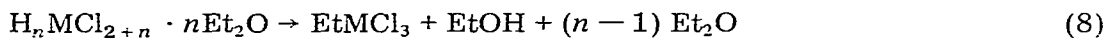
The equilibrium product composition is very near to $\text{H}_2\text{SnCl}_4 \cdot 2\text{Et}_2\text{O}$, intermediate compositions being due to arbitrary amounts of dissolved diethyl ether. The degree of dissociation, $\text{H}_n^+ \text{SnCl}_{2+n}^-$, tends to increase with increasing amounts of ether (m). A similar trend has been observed [6] for $\text{HGeCl}_3 \cdot n\text{Et}_2\text{O}$ ($n = 1, 2$)

As regards the structure of $\text{H}_n\text{SnCl}_{2+n} \cdot n\text{Et}_2\text{O}$, no $\nu(\text{Sn}-\text{H})$ stretching frequency could be detected in the IR 1700–2200 cm^{-1} region. For comparison, ethyldichlorotin hydride, EtCl_2SnH , shows an $\nu(\text{Sn}-\text{H})$ absorption band at 1934 cm^{-1} [12]. In the ^1H NMR spectrum of the latter compound the tin–hydrogen resonance is situated at $\delta(\text{Sn}-\text{H})$ 8.7 ppm, the coupling constants being $J(^{117/119}\text{Sn}-\text{H})$ 2974/3112 Hz [12]. In contrast, coupling constants could not be detected in the ^1H NMR spectrum of I in the range 0–6000 Hz.

The Mössbauer data (Table 2) show the product to be a tin(II) compound, rather than a tin(IV) species. The data are within the range generally observed for trichlorostannates(II). Following the model for the interpretation of the $^{119\text{m}}\text{Sn}$ Mössbauer parameters of triligandstannates(II) the relatively low isomer shift and large quadrupole splitting suggests a very low s -character (high p -character) of the tin non-bonding orbital [13].

Overall it can be concluded that the product obtained from the reaction of hydrogen chloride and tin dichloride or metallic tin in diethyl ether consists largely of solvated, strongly ionized dihydrogen tetrachlorostannate(II), $2\text{H}^+ \text{SnCl}_4^{2-} \cdot 2\text{Et}_2\text{O}$, rather than of trichlorostannane(IV), HSnCl_3 .

According to Nefedov and coworkers [6], aging of trichlorogermane etherate gives rise to diethyl ether cleavage according to eq. 8 ($M = \text{Ge}$). A ^1H NMR study of a sample of dihydrogen tetrachlorostannate(II) kept in the dark at room temperature for fifty days showed that reaction 8 also takes place with $M = \text{Sn}$, albeit to a very small extent.



($M = \text{Ge}$, $n = 1$; $M = \text{Sn}$, $n = 2$)

Within 24 h the ^1H NMR spectrum (CD_3OD solution) revealed signals characteristic of ethanol ($\delta(\text{CH}_2)$ 3.83 ppm; $\delta(\text{CH}_3)$ 1.28 ppm) and ethyl chloride ($\delta(\text{CH}_2)$ 3.60 ppm; $\delta(\text{CH}_3)$ 1.46 ppm), indicative of diethyl ether cleavage by

TABLE 2

$^{119\text{m}}\text{Sn}$ MÖSSBAUER DATA (relative to SnO_2 ; recorded at 77 K)

Compound	IS (mm/s)		QS (mm/s)
$\text{H}_2\text{SnCl}_4 \cdot 2\text{Et}_2\text{O}$	3.46	1.30	1.30
SnCl_2	4.07	0.58	0.58
KSnCl_3	3.77	0.92	0.92
SnCl_4	0.81		
K_2SnCl_6	0.45		

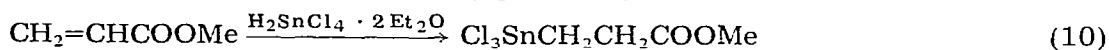
hydrogen chloride (eq. 9). The intensity of the signals increased with time. After 50 days at room temperature new sets of signals appeared at δ 1.32 and 2.23 ppm, and these are tentatively assigned to ethyltin trichloride. The formation of the latter species was confirmed by methylation of the reaction mixture and subse-



quent GLC-MS analysis for Me_3SnEt . In this way the formation of 0.05–0.15% of ethyltin trichloride was demonstrated.

Mechanism of the reaction of tin dihalides and of metallic tin with hydrogen chloride in the presence of alkenes

Reaction of preformed dihydrogen tetrachlorostannate(II) with an equimolar amount of methyl acrylate proceeds strongly exothermal at room temperature to give a semi-quantitative yield of β -carbomethoxyethyltin trichloride (eq. 10). When the reaction is carried out by passing hydrogen chloride into a mixture



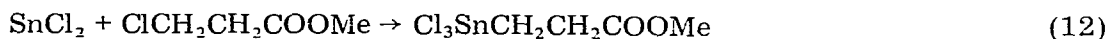
of tin dichloride and methyl acrylate in diethyl ether, the yields tend to be lower as the result of side-reaction 11. Replacement of diethyl ether as solvent



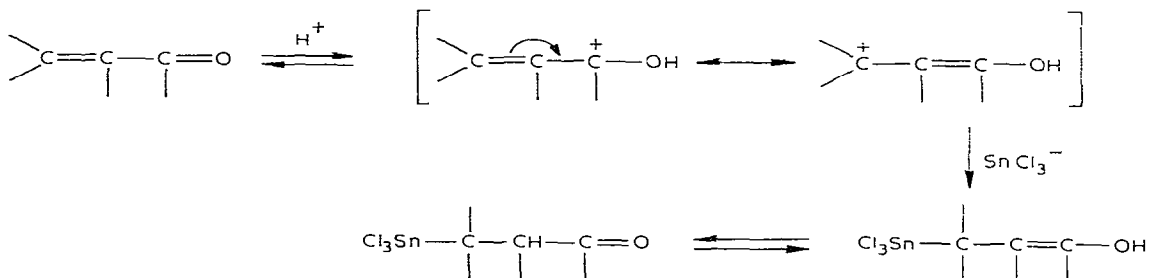
by an excess of methyl acrylate results in the formation of substantial amounts of the side-product methyl β -chloropropionate (eq. 11).

According to Burley et al. [9–11] reaction 10 may be explained in terms of a hydrostannation, that is a reaction in which a tin–hydrogen bond adds across an unsaturated linkage [15]. However, in view of the structural considerations discussed earlier the presence of a tin–hydrogen bond in I, and thus a hydrostannation mechanism, is highly unlikely.

An alternative mechanism is based on the oxidative addition of tin dichloride with β -chloropropionate, viz. eq. 5, 11 and 12. Examples of catalyzed and uncatalyzed oxidative addition reactions of tin(II) compounds have been reported [16]. However, attempts to accomplish reaction 12 under the conditions of reac-



tion 10 failed. Furthermore, it was observed that reaction 10 also proceeds quantitatively when carried out in the presence of hydrogen chloride etherate (the supernatant). Apparently the rate of reaction 10 is much higher than that of reaction 11.

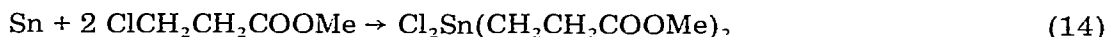


Most probably the mechanism of hydrogen trichlorostannate(II) and/or dihydrogen tetrachlorostannate(II) addition to methyl acrylate is similar to that of hydrogen chloride addition to α -carbonyl activated olefins, viz. a 1,4-addition involving initial protonation of oxygen [17].

For the mechanism for the formation of bis(β -carbomethoxyethyl)tin dichloride in the reaction of metallic tin with hydrogen chloride and methyl acrylate (eq. 13) the intermediate formation of $[H_2SnX_2]$ and/or $[HSnX]$ has been tentatively suggested [9–11]. By analogy with reaction 12, a direct synthesis mecha-



nism might be envisaged. However, metallic tin does not react with methyl β -chloropropionate under the conditions of reaction 13.



A plausible explanation for reaction 13 is offered by reaction 15 reported recently by Burley et al. [18]. We observed indeed that reaction of II with

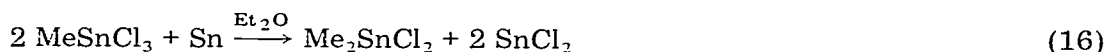


(II)

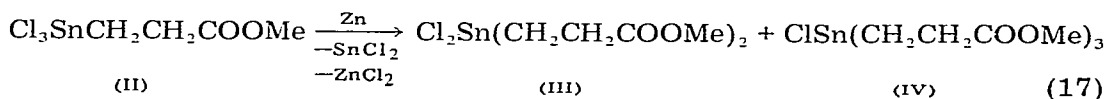
(III)

metallic tin in diethyl ether proceeds rapidly at room temperature according to eq. 15, compound III being the main product. However, according to ^1H NMR spectrometry (Table 3) small amounts of tris(β -carbomethoxyethyl)tin chloride (IV) are formed as well. This observation was confirmed by comparison with an authentic sample of IV prepared according to ref. 19.

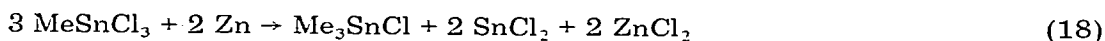
Reaction 15 appeared to be quite general. Reaction of methyltin trichloride with an excess of tin powder in diethyl ether for 24 h at 20°C gave a 100% conversion of starting materials into the mixture $\text{Me}_2\text{SnCl}_2/\text{Me}_3\text{SnCl}$ (17/1).



According to Des Tombe et al. reaction of phenyltin trichloride with zinc in THF gives triphenyltin chloride [20]. The results have been explained on the basis of phenylzinc intermediate species capable of phenylating phenyltin trichloride. Preliminary experiments showed that reaction of II with an excess of zinc in diethyl ether at room temperature results in the complete conversion of II into a mixture of III and IV (ratio 1/4).



The analogous reaction of methyltin trichloride with zinc in diethyl ether proceeds strongly exothermally at room temperature (eq. 18).



Further studies into these new type of reactions are planned. Reactions of dihydrogen tetrachlorostannate(II) with substrates other than unsaturated compounds will be reported in a separate paper.

TABLE 3

¹H NMR DATA FOR CARBOMETHOXYETHYL TIN COMPOUNDS IN ACETONE-*d*₆ SOLUTION

Compound	Chemical shift (ppm; TMS = 0)		
	$\delta(\text{CH}_3\text{OOC})$	$\delta(\text{CH}_2\text{CO})$	$\delta(\text{CH}_2\text{Sn})$
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{COOMe}$	4.00	3.09(t)	2.30(t) ^a
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{COOMe})_2$	3.83	2.95(t)	1.85(t) ^b
$\text{ClSn}(\text{CH}_2\text{CH}_2\text{COOMe})_3$	3.70	2.90(t)	1.45(t) ^c

^a $J(^{117/119}\text{Sn}-\text{CH}_2)$ 111/116 Hz. ^b $J(^{117/119}\text{Sn}-\text{CH}_2)$ 98/103 Hz. ^c $J(^{117/119}\text{Sn}-\text{CH}_2)$ 64/67 Hz.

Experimental

Unless otherwise indicated the starting materials were prepared by published procedures or purchased. Liquids were purified by distillation.

Pure anhydrous tin dichloride was prepared according to Christov and Karaivanov [21]. ¹H NMR spectra were recorded using on a Varian Associates HA 60 apparatus. The Mössbauer spectra were recorded at the Interuniversitair Reactor Instituut, Delft. GC-MS analyses were performed on a Finnigan Model 9500 gas chromatograph coupled to a Finnigan Model 3100D quadrupole mass spectrometer using a Finnigan Model 6110 data system. Elemental analyses were carried out by the Section Elemental Analysis of the Institute for Organic Chemistry TNO, Utrecht.

Typical experiments are described below.

Reaction of SnCl₂ with HCl in diethyl ether

A slow stream of dry hydrogen chloride was passed for 15 min through a suspension of 19.0 g (0.1 mol) of anhydrous SnCl₂, in 40 ml of diethyl ether kept at 0°C. Stirring was continued for 15 min and the mixture was warmed to room temperature. The resulting clear solution separated into two phases, a faintly yellow oily liquid and a colourless supernatant. The layers were separated and studied by IR, Mössbauer and ¹H NMR spectrometry.

A 10 g sample of the oily liquid was added slowly to an excess of aqueous 4 N NaOH at 0°C. After evaporation of the diethyl ether the remaining suspension of tin oxides and hydroxides was treated with concentrated nitric acid. The resulting colourless solution was adjusted to 100 ml and analyzed for tin and chlorine. In three different experiments the molar ratio Cl/Sn was found to be 3.8, 4.0 and 4.3, respectively. Together with the ¹H NMR data the results point to a product composition H₂SnCl₄ · 2Et₂O.

The supernatant liquid contained only residual amounts of tin, Cl/Sn ratios ranging from 21–26, the ratio Et₂O/HCl varying between 2.1 and 3.5.

Reaction of Sn with HCl in diethyl ether

A slow stream of dry hydrogen chloride was passed for 2.5 h through a suspension of 11.87 g (0.1 mol) of tin powder ($\phi < 0.05$ mm) in 40 ml of diethyl ether. As a result of the rather vigorous evolution of hydrogen substantial evaporation of diethyl ether occurred, and so the solvent was replenished continuously. As with the SnCl₂/HCl reaction a clear solution was obtained consisting

of two phases. However, when using tin powder the oily liquid tended to be less intensely coloured or even colourless.

Aging of chlorostannate(II) etherate

A sample of chlorostannate(II) etherate, prepared by treating SnCl_2 with HCl in diethyl ether, was stored at room temperature in the dark for 2 months. At regular time intervals samples were taken for ^1H NMR spectrometry. After 50 days at room temperature a 2.5 ml sample of the product was added dropwise to 35 ml of a 0.8 molar solution of methylmagnesium bromide in diethyl ether at 0°C . The mixture was refluxed for 4 h. After the usual work-up GC-MS analysis demonstrated the presence of Me_3SnEt . Based on the total intake of SnCl_2 the amount was calculated to be $0.1 \pm 0.05\%$.

Reaction of chlorostannate(II) etherate with methyl acrylate

By the procedure given above 28.4 g (0.15 mol) of tin dichloride in 50 ml of diethyl ether was treated with HCl gas for 15 min at 0°C . Dropwise addition of 13.0 g (0.152 mol) of methyl acrylate resulted in an exothermal reaction. The mixture was kept at 20°C . Reaction was complete in about 10 min and gave a clear homogeneous solution. Evaporation of the solvent in vacuo gave 46 g ($\sim 100\%$) of crude product (II, m.p. $62\text{--}67^\circ\text{C}$). Distillation gave 42 g (90%) of pure β -carbomethoxyethyltin trichloride (II); b.p. $136\text{--}138^\circ\text{C}/0.02$ mmHg; m.p. $67\text{--}69^\circ\text{C}$ (lit. [11] b.p. $174^\circ\text{C}/4$ mmHg; m.p. 70°C).

Similarly 2-methyl-2-carbomethoxyethyltin trichloride was obtained in 86.3% yield from methyl methacrylate.

Reactions carried out with tin dichloride as the starting material rather than pre-formed chlorostannate(II) etherate proceed similarly although the product yields tend to be slightly lower.

Reaction of β -carbomethoxyethyltin trichloride with tin in diethyl ether

A mixture of 5.0 g (0.022 mol) of II, 1.33 g (0.011 mol) of tin powder ($\phi < 0.05$ mm) and 20 ml of diethyl ether was stirred for 3 h at room temperature. The solvent was evaporated and the resulting solid residue was extracted with boiling chloroform. The chloroform-insoluble solid was treated with ethanol to give 0.5 g (38%) of recovered tin. ^1H NMR spectrometry (cf. Table 3) of the chloroform solution showed the presence of II, III and IV in the molar ratio 60/26/2.

Reaction of methyltin trichloride with tin in diethyl ether

A mixture of 17.5 g (0.07 mol) of methyltin trichloride, 8.67 g (0.07 mol) of tin powder ($\phi < 0.05$ mm) and 15 ml of diethyl ether was stirred for 24 h at room temperature. ^1H NMR spectrometry showed the presence of Me_2SnCl_2 together with Me_3SnCl and only a trace of residual MeSnCl_3 . The mixture was treated with methanol and acetone to give a 40% (3.5 g) recovery of tin. ^1H NMR spectrometry of the residue obtained after evaporation of the filtrate showed the presence of Me_2SnCl_2 and Me_3SnCl in the ratio 17/1.

Reaction of β -carbomethoxyethyltin trichloride with zinc in diethyl ether

A mixture of 10.0 g (0.032 mol) of II, 2.1 g (0.032 mol) of zinc powder and

30 ml of diethyl ether was stirred for 19 h at room temperature. A white precipitate formed and the mixture became increasingly viscous. After the addition of 15 ml of dry methanol, stirring was continued for 5 h. After standing for two days a sample of the mixture was filtered and studied by ^1H NMR spectrometry (acetone- d_6 added), and found to contain approximately equal molar amounts of III, $\delta(\text{CH}_3\text{OOC})$ 3.83 ppm, and IV, $\delta(\text{CH}_3\text{OOC})$ 3.70 ppm, together with residual traces of II, $\delta(\text{CH}_3\text{OOC})$ 4.00 ppm. The reaction mixture was treated with methanol and filtered to give a 42% recovery of metallic zinc. The filtrate was evaporated to dryness and the residue was extracted with methanol- d_4 . ^1H NMR spectrometry showed the presence of II, III and IV in the molar ratio 1/9/11.

Reaction of methyltin trichloride with zinc in diethyl ether

In an atmosphere of dry nitrogen a solution of 19.0 g (0.079 mol) of methyltin trichloride in 15 ml of diethyl ether was added drop-wise (20 min) to a stirred suspension of 3.43 g (0.053 mol) of zinc powder in 5 ml of diethyl ether. After an induction period of about 5 min an exothermic reaction started, causing reflux of the solvent. Stirring was continued for 1.5 h at room temperature and subsequently for 0.5 h under reflux. Dry methanol (15 ml) was added and refluxing was continued for 0.5 h. Residual zinc metal was removed by filtration (99.4% conversion of zinc). The filtrate was concentrated and the residue was taken up in methanol and analyzed by ^1H NMR. Methyltin trichloride appeared to be completely converted into a mixture of trimethyltin chloride (90%) and dimethyltin dichloride (10%).

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