β-SUBSTITUTED ALKYLTIN HALIDES

II*. DIALKYLTIN DIHALIDES: MECHANISTIC AND SPECTROSCOPIC ASPECTS

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Summary

Hydrogen halides, tin and α,β-unsaturated carbonyl compounds react together under mild conditions to give mixtures of β-substituted alkyltin trihalides and bis(β-substituted alkyl)tin dihalides: acrylonitrile is also active. Spectroscopic data for a number of pure functionally substituted dialkyltin compounds is presented. The monoalkyltin compounds are almost certainly formed by the in-situ formation of trihalogenostannanes from hydrogen halides and tin. Several possible mechanisms are discussed for the formation of the dialkyltin compounds. The substituted monoalkyltin compounds react with tin to give the corresponding dialkyltin compounds as well as products which are believed to be relatively stable tin—tin species.

Introduction

β-Substituted alkyltin halides have been prepared by a variety of methods. The synthesis of many of these compounds is described in a review by Omae [1] where the major reaction employed was the direct reaction between metallic tin and the corresponding β-substituted alkyl halide (eq. 1). Reifenberg and Con-

$$2 \ XCH_2CH_2R + Sn \rightarrow X_2Sn(CH_2CH_2R)_2 \tag{1}$$
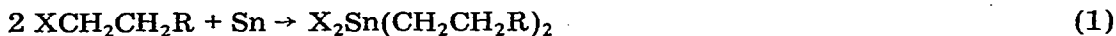
(X = Br, I; R = CO_2H, CO_2R^1, COR^1; R^1 = alkyl)
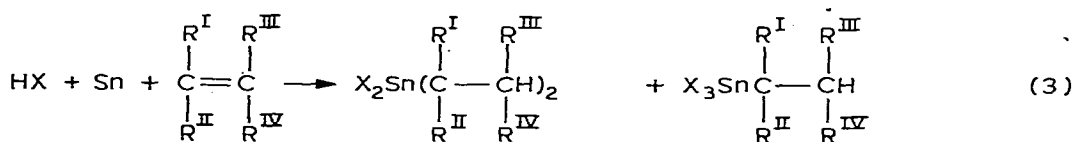
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* Part I see ref. 6.

TABLE 1

THE REACTION BETWEEN HCl, Sn (POWDER) AND VARIOUS MONOMERS IN DIETHYL ETHER AT 20°C (Sn/MONOMER 1/2)

Reaction no.	Monomer	Reaction time (hour)	Sn conversion (%)	Yield of organotin compounds (%, based on Sn consumed)	% Mono [a]	Yield of pure R_2SnCl_2 (%)	Analyses [b] (pure R_2SnCl_2) Sn (%)	Cl (%)
1	$CH_2=CHCO_2Me$	14	94	100	3.5	94 [g]	32.58 (32.64)	19.50 (19.52)
2	$CH_2=CHCO_2Me$ (HBr)	10	83	100	20	not isolated	(26.21)	(35.33)(Br)
3	$CH_2=CHCO_2Me$(HI)	12	100	~90	7	72 [g]	21.18 (21.71)	43.67 (44.60)(I)
4	$CH_2=CHCO_2Et$	25	100	94	15	60 [g]	30.20 (30.28)	18.20 (18.11)
5	$CH_2=CHCO_2Bu$	20	100	99	9.5	[d]	(26.54)	(15.86)
6	$CH_2=CHCO_2Ph$	10	100	81	6	not isolated	(24.32)	(14.56)
7	$CH_2=CMeCO_2Me$	13	45	85	~50	25 [g]	30.41 (30.28)	18.23 (18.11)
8	$MeCH=CHCO_2Me$	17	85	5.5 [c]	<3 [c]	5.5	30.17 (30.28)	17.95 (18.11)
9	$CMe_2=CHCOMe$	10	100	80	22	46 [h]	30.94 (30.60)	18.81 (18.32)
10	$CH_2=CHCOMe$	14	100	~80	~47	[f]	(35.76)	(21.39)
11	$CH_2=CHCONH_2$	23	82	79	<3 [c]	79	35.21 (35.55)	20.96 (21.26)
12	$CH_2=CHCO_2H$	6.5	66	70	<3 [c]	70 [h]	34.90 (35.35)	21.10 (21.14)
13	$MeOCOCH_2CH=CHCO_2Me$	13	100	6.2 [c]	<3 [c]	6.2	22.90 (23.40)	14.50 (14.00)
14	$CH_2=CHCN$	15	66	14 [c]	<3 [c]	14 [h]	39.71 (39.86)	23.78 (23.84)
15	$CH=CCO_2H$	12	100	~80	11	[f]	(35.77)	(21.40)

[a] Determined by NMR spectroscopy. [b] Values in parenthesis indicate theoretical values. [c] Values shown as <3 suggest non detectable by NMR. [d] Isolation of pure $Cl_2Sn(CH_2CH_2CO_2Bu)_2$ has not proved possible. [e] Low yields indicate a high conversion of tin to stannous chloride. [f] The product mixtures were difficult to purify and the pure dialkyltin compounds were not isolated. [g] The pure dialkyltin dihalides were isolated by crystallisation from the concentrated product liquors. [h] The pure dialkyltin dihalides were isolated by Et_2O washing of the reaction products.

sidine have prepared a range of cyanoethyltin halides by disproportionation of tetracyanoethyltin with stannic halides [2]. The other widely employed route to functionally substituted organotin compounds is hydrostannation and a review by Leusink adequately demonstrates the versatility of this approach [3]. Until recently, however, the hydrostannation route was limited to the synthesis of tetraalkyltin compounds and trialkyltin halides. It has now been demonstrated that, not only these, but also certain β-substituted mono- and dialkyltin halides can be prepared by this route. Preliminary results on the reactions between hydrogen halides, stannous halides and α,β-unsaturated carbonyl compounds (to give β-substituted alkyltin trihalides) and on the reactions between hydrogen halides, tin and the same α,β-unsaturated carbonyl compounds (to give largely bis(β-substituted alkyl)tin dihalides) have been reported [4,5]. Eq. 2 and 3 represent the overall reactions: halogenostannane intermediates are involved.

$$HX + SnX_2 + \begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C=C \\ | \quad | \\ R^{II} \quad R^{IV} \end{array} \longrightarrow X_3Sn-\begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C-CH \\ | \quad | \\ R^{II} \quad R^{IV} \end{array} \qquad (2)$$

$$HX + Sn + \begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C=C \\ | \quad | \\ R^{II} \quad R^{IV} \end{array} \longrightarrow X_2Sn(\begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C-CH \\ | \quad | \\ R^{II} \quad R^{IV} \end{array})_2 + X_3Sn\begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C-CH \\ | \quad | \\ R^{II} \quad R^{IV} \end{array} \qquad (3)$$

$$(X = Cl, Br, I; R^I, R^{II}, \text{ and } R^{III} \text{ are H or Me}; R^{IV} \text{ contains } -\overset{O}{\underset{||}{C}}-)$$

We present here a detailed account of the study of reaction 3 which complements a similar study of the spectroscopic and mechanistic aspects of reaction 2 [6].

Results and discussion

Hydrogen chloride and metallic tin react together in the presence of activated olefinic compounds to give high yields of functionally substituted organotin compounds [4,5]. Table 1 contains the results of experiments with a wide variety of monomers: largely these are α,β-unsaturated esters but α,β-unsaturated ketones, acids and amides are similarly reactive and acrylonitrile can also be employed. The products from these reactions were characterised by elemental analyses (Cl and Sn) and spectroscopic techniques (IR and NMR) and identified as mixtures of β-substituted mono- and dialkyltin halides. Eq. 4 and 5 represent the constituent reactions of eq. 3.
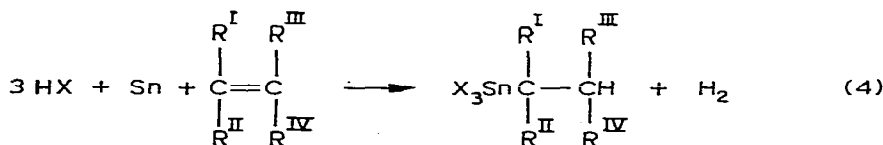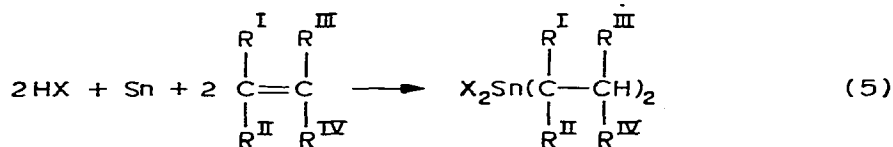
$$3 HX + Sn + \begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C=C \\ | \quad | \\ R^{II} \quad R^{IV} \end{array} \longrightarrow X_3Sn\begin{array}{c} R^I \quad R^{III} \\ | \quad | \\ C-CH \\ | \quad | \\ R^{II} \quad R^{IV} \end{array} + H_2 \qquad (4)$$

TABLE 2

MELTING POINT AND SPECTROSCOPIC DATA FOR FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

Compound	Melting point	ν(C=O) (± 2 cm^{-1})	Chemical shifts (ppm) [a]			Coupling constants (Hz) [b]	
			CH(α)	CH(β)	Others	J(Sn—H(α))	J(Sn—H(β))
Cl$_2$Sn(CH$_2$CH$_2$CO$_2$Me)$_2$	132	1677	8.07	7.07	6.18 (OMe)	98	150
Br$_2$Sn(CH$_2$CH$_2$CO$_2$Me)$_2$	137	1677	7.93	7.08	6.18 (OMe)	94	153
I$_2$Sn(CH$_2$CH$_2$CO$_2$Me)$_2$		1677	7.89	7.31	6.33 (OMe)	~100	152
Cl$_2$Sn(CH$_2$CH$_2$CO$_2$Et)$_2$		1677	8.10	7.11	5.75 (OCH$_2$—)	c	c
Cl$_2$Sn(CH$_2$CH$_2$CO$_2$Bu)$_2$	~10	1676	8.10	7.08	5.73 (OCH$_2$—)	c	c
Cl$_2$Sn(CH$_2$CH$_2$CO$_2$Ph)$_2$	93—94	1712	8.07	6.90	2.67 (Ph), 2.84 (Ph)	93	152
Cl$_2$Sn(CH$_2$CHMeCO$_2$Me)$_2$	111	1676	8.05	6.83	6.18 (OMe)	c	c
Cl$_2$Sn(CH$_2$CH$_2$COMe)$_2$	107—108	1672	8.28	6.81	8.66 (COMe)	~86	145
Cl$_2$Sn(CMe$_2$CH$_2$COMe)$_2$	158	1671		7.01 (CH$_2$), 8.57 (Me)	7.07 (COMe)	—	138 (CH$_2$), 129 (Me)
Cl$_2$Sn(CH$_2$CH$_2$CO$_2$H)$_2$	157	1676	8.25	7.08	-1.04 (CO$_2$H)	104	135
Cl$_2$Sn(CH$_2$CH$_2$CONH$_2$)$_2$	240—250	1669	8.65	7.36	1.53 (NH$_2$), 1.75 (NH$_2$)	114	141
Cl$_2$Sn(CH$_2$CH$_2$CN)$_2$	173	—	7.90	7.14	—	80	93

[a] τ(internal TMS) = 10.0 ppm. [b] The reported values are the mean of the ^{117}Sn—H and ^{119}Sn—H coupling constants. [c] The Sn—H satelite peaks are masked by other signals.

$$2\,HX + Sn + 2\ \underset{\underset{R^{II}}{\overset{R^{I}}{|}}}{C} = \underset{\underset{R^{IV}}{\overset{R^{III}}{|}}}{C} \longrightarrow X_2Sn(\underset{\underset{R^{II}}{\overset{R^{I}}{|}}}{C} - \underset{\underset{R^{IV}}{\overset{R^{III}}{|}}}{C}H)_2 \qquad (5)$$

Spectroscopic data for a number of pure bis(β-substituted alkyl)tin dihalides are presented in Table 2.

As with reactions between hydrogen halides, stannous halides and functionally substituted olefins [4—6] only the β-substituted products were isolated as described by reaction 3. With the reaction conditions described in Table 1 the dialkyltin dihalide is, in most cases, the major product although modification of the reaction conditions can significantly affect the proportion of the monoalkyltin component that is produced. In general reaction 3 exhibits the same versatility with respect to solvent and temperature as does the similar reaction 2 [6]. Temperatures between —10 and 120°C can be employed with equally good overall yields of organotin compounds (based on tin consumed) and solvents with widely different dielectric constant ($\sim$2 → 80) can also be utilised (see Table 3). Low temperatures (<10°C) favoured hydrogen chloride addition to some of the monomers (particularly esters) and high temperatures (>90°C) caused polymerisation to occur. Hydrogen bromide and hydrogen iodide can replace hydrogen chloride with good yields of organotin compounds (Table 1).

A number of reactions have been performed with methyl acrylate to determine the effects of solvent, temperature and hydrogen chloride flow rate upon the overall yield of organotin compounds and also upon the distribution of the products. In all cases the overall yield of organotin compounds was good (Table 3). The effect of reaction temperature can be seen from results obtained in dimethoxymethane (see experiment numbers 24 and 25) at —10 and 40°C. De-

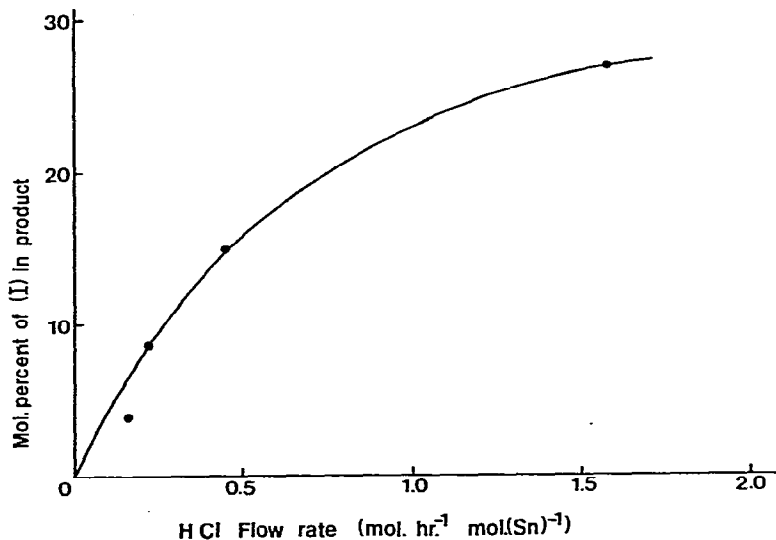Fig. 1. The effect of hydrogen chloride flow rate upon the production of $Cl_3SnCH_2CH_2CO_2Me$ (I) and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ (II) from hydrogen chloride, tin (0.5 mol) and methyl acrylate (1.0 mol) in diethyl ether (140 ml) at 20°C.

TABLE 3

THE REACTION BETWEEN HCl, Sn (POWDER) AND METHYL ACRYLATE IN VARIOUS SOLVENTS AT 20°C

Reaction no.	Solvent	Sn conversion (%)	HCl flow rate (mol/h/mol(Sn))	Yield of Organotin compounds (%, based on Sn consumed)	Mono (%)	Acrylate concentration (mol/1)	Reaction time (hour)	Dielectric constant of solvent
16	1,2-Dimethoxyethane	98.7	0.190	98	19.3	4.4	14.0	7.15
17	Toluene	99.7	0.152	100	16.8	5.5	19.5	2.38
18	n-Hexane	97.5	0.195	99	15.9	4.4	12.5	1.89
19	Ethyl acetate	100	0.195	99	16.5	4.4	14.0	6.02
20	Chloroform	99	0.302	100	15.8	4.6	12.0	4.8
21	Water	84.5	1.250	67	Not detected	2 phase system	3.0	80.1
22	Methanol	99.1	0.244	77	Not detected	4.6	11.0	32.63
23	Excess acrylate	96	0.219	100	5.0	11.0	10.0	
24	Dimethoxymethane (40°C)	100	2.407	99	10.0	1.1	0.8	
25	Dimethoxymethane (−10°C)	100	2.407	95	95	1.1	5.0	

creasing the temperature from 40°C, where the dialkyltin compound is the major component, to −10°C causes a dramatic change in the distribution of the organotin compounds such that the monoalkyltin compound becomes the major product.

Figure 1 shows the effect of hydrogen chloride flow rate upon the distribution of organotin compounds in the final product mixture. Increasing the hydrogen chloride flow rate causes an increase in the amount of the monoalkyltin component $Cl_3SnCH_2CH_2CO_2Me$ (I) which is produced.

Solvent nature, however, appears to have a less predictable effect upon the course of the reaction. In all cases but hydroxylic solvents (water and methanol) the overall yields were greater than 95% and mixtures of mono- and di-alkyltin compounds were produced (see Table 3). In hydroxylic solvents yields were somewhat lower (approximately 70%) but the monoalkyltin product was not observed. Although experimental conditions were not identical for the experiments performed in other solvents (expt. nos. 16—20) they were sufficiently similar to suggest that most solvents do not have a dramatic effect on the course of the reaction. Acrylate concentration does, however, appear to have a significant effect since a reaction in bulk methyl acrylate gave a product with a significantly lower monoalkyltin content than did most other solvents (expt. no. 23).

Mechanisms

In the above experiments the observation of β-substituted monoalkyltin trihalides is not difficult to explain since stannous chloride (and therefore trichlorostannane) can be formed simply from hydrogen chloride and tin. The monoalkyltin compounds then arise from reactions between trichlorostannane and the respective monomers according to reaction 2. Formation of the bis(β-substituted alkyl)tin dihalides is, however, somewhat more difficult to explain.

Initially we proposed a tentative mechanism which involved halogenostannane intermediates [5]: this mechanism, with a few small modifications to incorporate the phenomenon of monomer solvation of organotin intermediates, is presented in eq. 6.
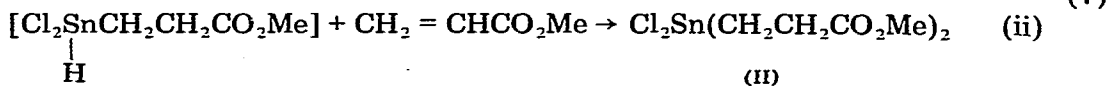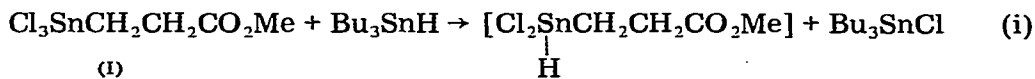
The first step envisaged is hydrogen chloride interaction with tin at the tin surface, to give [HSnCl]. This species can undergo further reaction with hydrogen chloride (also at the tin surface) to give stannous chloride and ultimately enter solution as [M : HSnCl$_3$]; as in eq. 2 (details in ref. 6). Alternatively [HSnCl] might interact with monomer and enter solution directly as [M : HSnCl] giving rise to [RSnCl] and ultimately to R_2SnCl_2. Some support for this mechanism has been obtained from an experiment where hydrogen chloride was passed into a suspension of powdered tin in excess butyl acrylate at 60°C. The change in concentration of each of the organotin compounds ($Cl_3SnCH_2CH_2CO_2Bu$ and $Cl_2Sn(CH_2CH_2CO_2Bu)_2$) was monitored throughout this experiment. Figure 2 shows that, under these conditions, the concentrations of both the mono- and the di-alkyltin compounds increased continuously throughout the experiment. This observation suggests that there is possibly a common intermediate ([HSnCl]) for the two organotin compounds. However, an alternative possibility is that $Cl_2Sn(CH_2CH_2CO_2Bu)_2$ is formed via $Cl_3SnCH_2CH_2CO_2Bu$ and that under these conditions the generation of the substituted monoalkyltin compound is faster than its transformation to the dialkyltin compound (see below).

$$HCl + Sn \longrightarrow [HSnCl] \xrightarrow{\quad M \quad} [M{:}HSnCl]$$

$$[H_2SnCl_2]? \xleftarrow{\quad HCl \quad}$$

$$\downarrow HCl$$

$$H_2 + SnCl_2 \qquad\qquad [RSnCl] \qquad\qquad (6)$$

$$\downarrow M{:}HCl \qquad\qquad\qquad \downarrow M{:}HCl$$

$$[M{:}HSnCl_3] \qquad\qquad [M{:}HSnRCl_2]$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$RSnCl_3 \qquad\qquad\qquad R_2SnCl_2$$

$$M = \begin{array}{c} R^{I} \quad R^{III} \\ | \quad\ | \\ C = C \\ | \quad\ | \\ R^{II} \quad R^{IV} \end{array} \qquad\qquad R = \begin{array}{c} R^{I} \quad R^{III} \\ | \quad\ | \\ C - CH \\ | \quad\ | \\ R^{II} \quad R^{IV} \end{array}$$
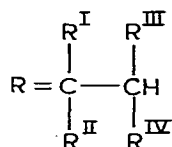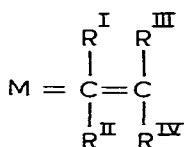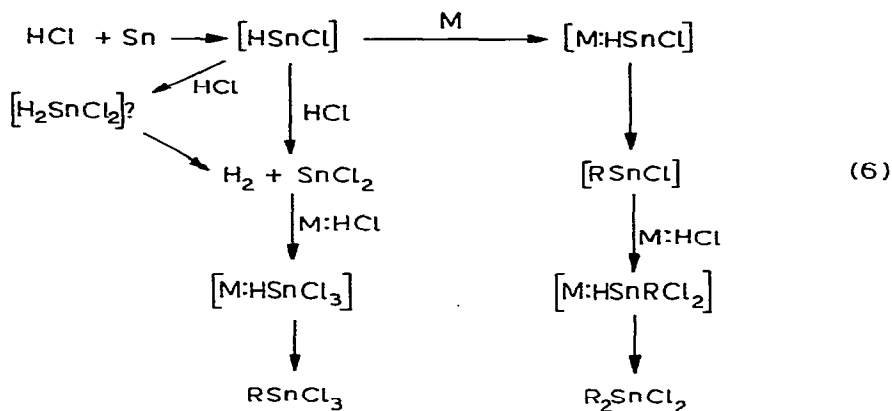
$(R^{I}, R^{II}$ and R^{III} are H or Me; R^{IV} contains $-\overset{\overset{\displaystyle O}{\|}}{C}-$)

Direct evidence for the occurrence of eq. 6 is indeed difficult to obtain. Oakes and Hutton have previously suggested [RSnBr] (R = Oct) as an intermediate in the direct reaction between Sn and octyl bromide [7] but evidence for the existence of such species has been obtained in only a very limited number of special cases [8]. Also, as far as we know, [HSnX] (X = halogen) has never before been suggested as an active halogenostannane intermediate although HGeX, RGeX, H_2GeX_2 and $RHGeX_2$ (R = alkyl) are all well documented halo-genogermane species [9—11]. The reactions of some of these species have also been studied [12]. Our own attempts to trap divalent tin species in the reactions between hydrogen halides, tin and α,β-unsaturated carbonyl compounds with alkyl halides were unsuccessful. However, evidence for the existence of $BuSnHCl_2$ has been obtained by Sawyer and Brown although it is highly unstable [13].

In an attempt to verify at least one step of this tentatively proposed scheme, that is the interaction of the halogenostannane $Cl_2SnHCH_2CH_2CO_2Me$ with mo-nomer, we have treated $Cl_3SnCH_2CH_2CO_2Me$ (I) with tributyltin hydride in a medium of methyl acrylate. From this experiment was obtained Cl_2Sn-$(CH_2CH_2CO_2Me)_2$ (II) (52%) formed we believe, by eq. 7. (Tributyltin chloride was also obtained but the formation of $Bu_3SnCH_2CH_2CO_2Me$ was not observed since the uncatalysed reaction between tributyltin hydride and methyl acrylate is slow under our experimental conditions [3,15,16].)

$$Cl_3SnCH_2CH_2CO_2Me + Bu_3SnH \rightarrow [Cl_2\underset{\overset{|}{H}}{Sn}CH_2CH_2CO_2Me] + Bu_3SnCl \qquad (i)$$

(I)

$$[Cl_2\underset{\overset{|}{H}}{Sn}CH_2CH_2CO_2Me] + CH_2 = CHCO_2Me \rightarrow Cl_2Sn(CH_2CH_2CO_2Me)_2 \qquad (ii)$$

(II)

(7)

This experiment illustrates that $Cl_2SnHCH_2CH_2CO_2Me$ can exist and that it
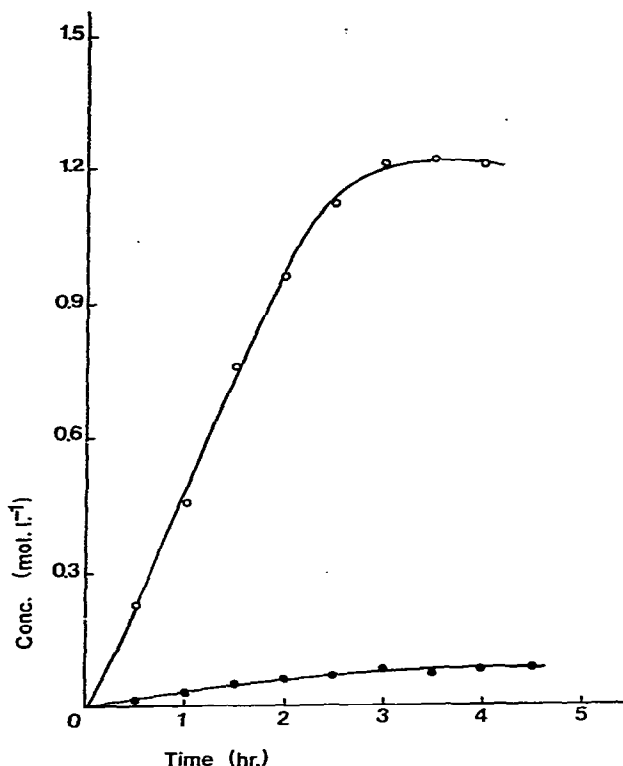
Fig. 2. The concentrations of $Cl_3SnCH_2CH_2CO_2Bu$ ($\bullet$) and $Cl_2Sn(CH_2CH_2CO_2Bu)_2$ ($\circ$) as a function of time in the reaction between hydrogen chloride, (0.94 mol/hour/mol tin), tin (3.37 mol) and butyl acrylate (15.33 mol) at $60°C$.

can be an intermediate in the formation of II. (The instability of this alkylchlorotin hydride was also easily demonstrated since when reaction 7i was performed in isolation the infrared absorption ($\nu(SnH)$) due to Bu_3SnH rapidly disappeared without the formation of any other Sn—H peak.)

Although relatively little direct evidence can be put forward in support of eq. 6 some steps have been shown to be possible and others are mechanistically likely and it is for these reasons that it is difficult to dismiss this reaction sequence entirely.

More recently however, [17] the discovery that ester substituted monoalkyltin trichlorides can react with metallic Sn to give the corresponding β-substituted dialkyltin dichlorides (reaction 8 $R^I = R^{II} = R^{III} = H$; $R^{IV} = CO_2R^V$; R^V = alkyl) suggested a simpler mechanism for the formation of the dialkyltin compounds in the reaction between hydrogen chloride, tin and α,β-unsaturated carbonyl compounds.

$$2\ RSnCl_3\ +\ Sn\ \longrightarrow\ R_2SnCl_2\ +\ 2\ SnCl_2 \qquad (8)$$

$$\left(R = \overset{\overset{\displaystyle R^I}{|}}{\underset{\underset{\displaystyle R^{II}}{|}}{C}} - \overset{\overset{\displaystyle R^{III}}{|}}{\underset{\underset{\displaystyle R^{IV}}{|}}{CH}}\ ;\quad R^I,\ R^{II},\ R^{III} = H\ \text{or Me}\ ;\ R^{IV}\text{contains} - \overset{\overset{\displaystyle O}{||}}{C} -\ \right)$$
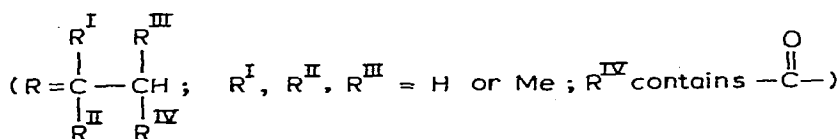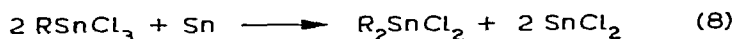
In this case it is suggested that $RSnCl_3$ produced initially as in eq. 6 is converted to R_2SnCl_2 by reaction with Sn (at the Sn surface). Stannous chloride produced according to eq. 8 (possibly in solution) can then be consumed by reaction with M:HCl (M = $R^I R^{II} C{=}CR^{III} R^{IV}$) to regenerate $RSnCl_3$: R_2SnCl_2 is therefore produced by a cyclic process with $RSnCl_3$ as an intermediate. An experiment was designed to test this hypothesis.

Hydrogen chloride was passed quickly into a suspension of powdered tin in a mixture of methyl acrylate and dimethoxymethane at 40°C. Figure 3 shows how the concentrations of $Cl_3SnCH_2CH_2CO_2Me$ (I) and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ (II) varied during the course of this reaction. In this case, the concentration of the monoalkyltin compound initially increased more rapidly than that of the dialkyltin compound. It reached a maximum value after approximately 20 min and then decreased gradually to zero. After the maximum concentration of I has been attained the concentration of II begins to increase more rapidly and at least partly at the expense of the monoalkyltin compound. These results suggest that, under these conditions, I can be an intermediate in the formation of II.
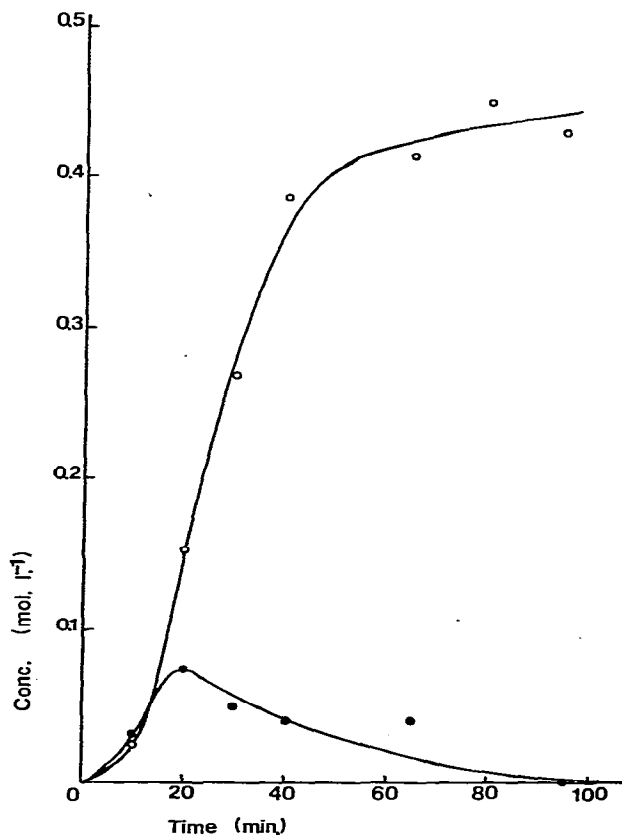

Fig. 3. The concentrations of $Cl_3SnCH_2CH_2CO_2Me$ (●) and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ (○) as a function as a of time in the reaction between hydrogen chloride (1.20 mol/hour/mol tin), tin (108 mmol) and methyl acrylate (26.9 mmol) in dimethoxymethane (25 ml) at 40°C.

Following the preliminary results which we reported previously [17] we have performed a more extensive study of the reaction between β-carboalkoxyethyltin trihalides and metallic Sn. A mass balance verified that the reactions in Et$_2$O (diethyl ether) proceeded with the stoichiometry suggested by eq. 8. Table 4 presents the results of further reactions which have been performed between Cl$_3$SnCH$_2$CH$_2$CO$_2$R^1 (R^1 = Me, i-Pr and n-Bu) and Sn under a variety of conditions. The reaction is markedly solvent sensitive as illustrated by the results for I in Et$_2$O, toluene and 1,1,2,2-*sym*-tetrachloroethane: Nonethereal media giving much lower rates of reaction. Therefore, if reaction 8 correctly represents a step in the formation of the dialkyltin compounds, it is perhaps surprising that the reaction between hydrogen chloride, tin and methyl acrylate is not more markedly solvent sensitive (Table 3). Obviously the crucial question is: how fast is reaction 8 (R = CH$_2$CH$_2$CO$_2$Me) under the conditions which prevail in the reactions between hydrogen chloride, tin and methyl acrylate. (It is, however, not possible to measure the rate of this step since (I), for the most part, is merely an intermediate in the formation of (II).)

In an attempt to determine what factors affect the rate of reactions under these conditions we have studied reactions between I and tin in butyl acrylate in the presence and in the absence of hydrogen chloride. Reactions performed in the presence of hydrogen chloride essentially correspond to doping reactions between hydrogen chloride, tin and butyl acrylate with I. The concentration of I in these experiments was monitored by NMR spectroscopy.

Initially I (approximately 0.8 molar in butyl acrylate) was treated under N$_2$ at 60°C with excess powdered Sn (100% - based on the stoichiometry of reaction 8). Figure 4a shows how the concentration of I decreased under these conditions. In fact, this detailed NMR study revealed that reaction 8 is not as simple as previously believed, since, besides the signal due to II (τ(CH$_3$OCO) = 6.21) two other ester methyl signals appeared, (τ(CH$_3$OCO)^1 = 6.15 and τ(CH$_3$OCO)^2 = 6.24), suggesting that other organotin compounds are produced. Neither of these signals corresponded to ClSn(CH$_2$CH$_2$CO$_2$Me)$_3$ since this compound shows τ(CH$_3$OCO) at 6.3. However, when this reaction was repeated with the continuous addition of hydrogen chloride throughout the experiment curve b (Fig. 4) was obtained for the disappearance of I. A reaction time of 4.5 h corresponded closely to the addition of the stoichiometric quantity of hydrogen chloride according to reaction 5. Coincident with this increase in the rate of disappearance of I there was a simplification in the NMR spectral changes. In this latter case only the signal at τ 6.21 appeared as I disappeared. Furthermore, the additional signals produced in the absence of hydrogen chloride were not easily removed by the post addition of hydrogen chloride. Further similar experiments were performed with a much larger excess of powdered Sn (700% excess). These reactions followed exactly similar paths and curves c and d of Fig. 4 represent these reactions. The NMR spectra of the solutions produced from these reactions, (a) with no added hydrogen chloride and, (b) with added hydrogen chloride are presented in Fig. 5. It is significant that I disappeared much more rapidly in these experiments. (That the increased rate of disappearance of I with hydrogen chloride present was not due to a removal of tin oxide from the tin surface was verified in a separate experiment where a small amount (0.5 g) of hydrogen chloride was initially added to the reaction between I (0.1 mole) and tin over a period of 10 min. A slight

TABLE 4

THE REACTION BETWEEN Cl₃SnCH₂CH₂CO₂R AND Sn

R	Solvent	Temperature (°C)	Reaction time (hours)	Ratio Sn/Cl₃SnCH₂CH₂CO₂R	Initial concentration of Cl₃SnCH₂CH₂CO₂R (mol l⁻¹)	Conversion of Cl₃SnCH₂CH₂CO₂R (%)
Me	Diethyl ether	22	3	1.83	0.110	100
Me	Tetrahydrofuran	60	3	2.15	0.113	100
Me	Toluene	120	5	2.20	0.093	13
Me	1,1,2,2-Tetrachloroethane	60	5	2.03	1.010	63
Me	Butyl acrylate	60	13	0.98	0.831	67
i-Pr	Diethyl ether	22	6	1.01	0.402	30
i-Pr	Dimethoxyethane	80	9	2.00	0.325	97
Bu		100	14	1.01	Bulk	55
Bu	Butyl acrylate	60	13	1.05	0.796	73
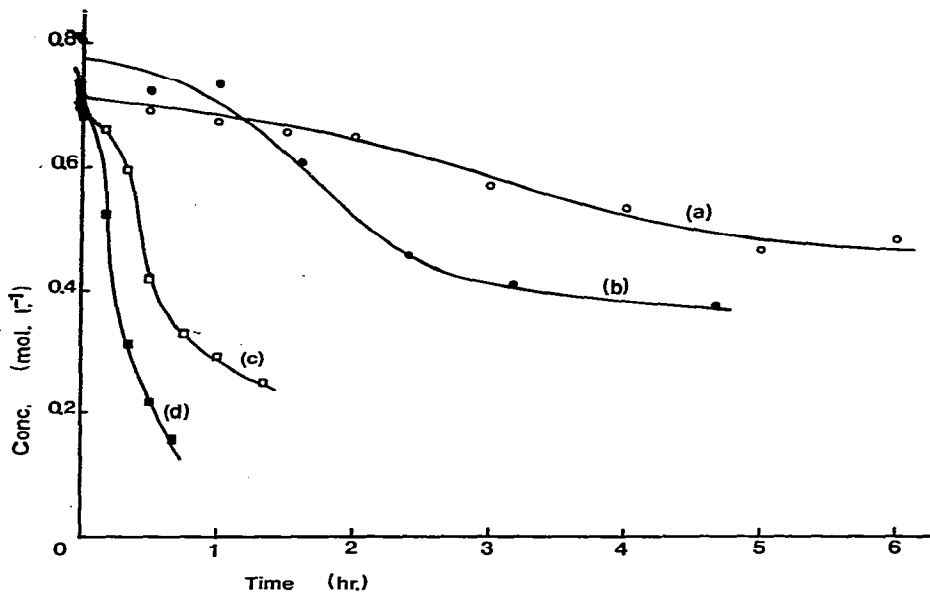
Fig. 4. The effects of excess tin and of hydrogen chloride upon the disappearance of $Cl_3SnCH_2CH_2CO_2Me$ in the reaction between I and tin in butyl acrylate at $60^\circ C$: (a) 100% excess tin; (b) 100% excess tin with a hydrogen chloride flow rate of 0.44 mol/hour/mol tin; (c) 700% excess tin and (d) 700% excess tin with a hydrogen chloride flow rate of 0.72 mol/hour/mol tin.
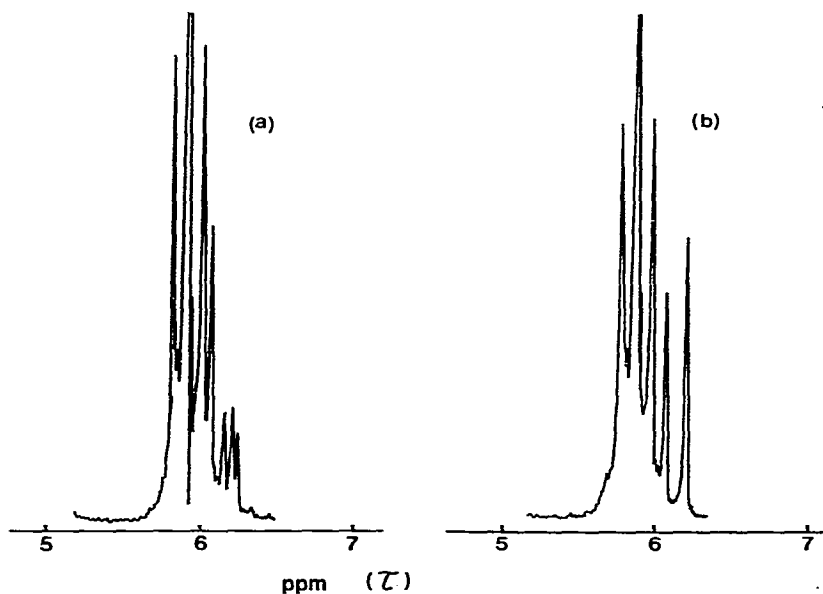

Fig. 5. ^{1}H NMR spectra of solutions from the reactions between $Cl_3SnCH_2CH_2CO_2Me$ (I) (approximately 0.68 molar) and tin (700% excess) in butyl acrylate at $60^\circ C$: (a) after 45 min with no added hydrogen chloride and (b) after 20 min with the addition of 3.4 g of hydrogen chloride.
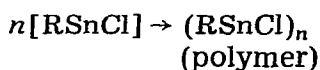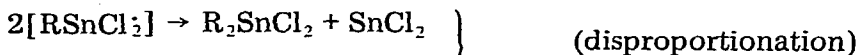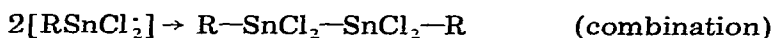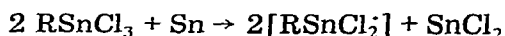
increase in initial rate for the disappearance of I was observed but the post hydrogen chloride addition rate of reaction was no faster than in the reaction with no added hydrogen chloride.)

If we now consider all but the latter stages of reactions between hydrogen chloride, tin and methyl acrylate the concentration of I will be small and the excess of tin will be large. Conditions very favourable for the conversion I to II will, therefore, prevail. Furthermore hydrogen chloride catalysis of this step has been demonstrated above (at least in butyl acrylate) and would simply be explained by the regeneration of I from hydrogen chloride, stannous chloride (produced in reaction 8) and methyl acrylate. Actually in the hydrogen chloride catalysis of the reaction between I and tin in butyl acrylate the overall concentration of substituted monoalkyltin compounds is maintained by the formation of $Cl_3SnCH_2CH_2CO_2Bu$. (Under the same conditions, $Cl_3SnCH_2CH_2CO_2Bu$ (0.1 molar) reacted with powdered tin (0.1 mol) in butyl acrylate at 60°C at a very similar rate to $Cl_3SnCH_2CH_2CO_2Me$ (see Table 4).)

The NMR study suggests that the reaction between I and tin in butyl acrylate is complex in the absence of hydrogen chloride but much simpler in the presence of hydrogen chloride therefore, it is believed that the two reactions probably follow different paths.

In the absence of further experimental data concerning the exact nature of the other organotin species which are produced in the absence of hydrogen chloride we can only speculate as to their nature.

Devaud [18] has proposed a mechanism for the electrochemical reduction of similarly substituted monoalkyltin compounds involving the formation of a radical intermediate (eq. 9) and it is possible that an exactly similar mechanism operates here: eq. 10 is proposed for the reaction between I and tin in the absence of hydrogen chloride.

$$R^1SnCl_3 + e^- \rightarrow Cl^- + R^1SnCl_2^{\cdot} \tag{9}$$

$$(R^1 = CHCO_2EtCH_2CO_2Et)$$

$$2\ RSnCl_3 + Sn \rightarrow 2[RSnCl_2^{\cdot}] + SnCl_2$$

$$2[RSnCl_2^{\cdot}] \rightarrow R-SnCl_2-SnCl_2-R \qquad \text{(combination)}$$

$$\left.\begin{array}{l} 2[RSnCl_2^{\cdot}] \rightarrow R_2SnCl_2 + SnCl_2 \\ 2[RSnCl_2^{\cdot}] \rightarrow RSnCl_3 + [RSnCl] \end{array}\right\} \quad \text{(disproportionation)} \tag{10}$$

$$n[RSnCl] \rightarrow (RSnCl)_n$$
$$\text{(polymer)}$$

$$(R = CH_2CH_2CO_2Me)$$
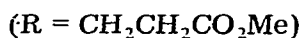
If $R_2Sn_2Cl_4$ and $(RSnCl)_n$ correctly represent the unidentified organotin species produced in the absence of hydrogen chloride their unexpected resistance to hydrogen chloride (demonstrated earlier) might be explained by inter-tin ester co-ordination as represented by III and IV.
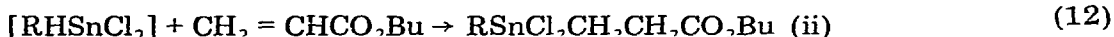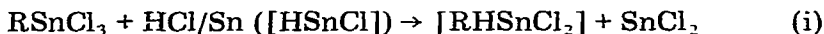
Since the proposed species III and IV are not produced in the presence of hydrogen chloride, neither do they react readily with hydrogen chloride; it is reasonable to propose that either (a) their precursor $[RSnCl_2^{\cdot}]$ (R =
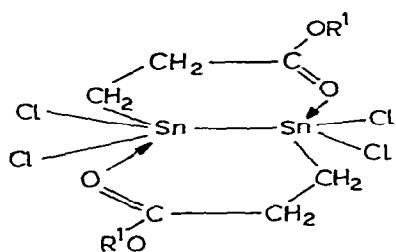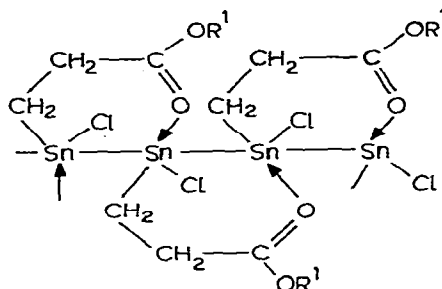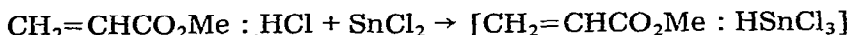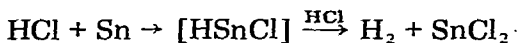
(III)   (IV)   (R¹= Me)

$CH_2CH_2CO_2Me$) (also the precursor to II when hydrogen chloride is absent) reacts with hydrogen chloride to reform $RSnCl_3$ (eq. 11) or (b) their precursor is not even produced with hydrogen chloride present. Consequently it is unlikely that eq. 10 gives rise to II in the presence of hydrogen chloride and an alternative explanation is offered for the signal at τ 6.21 in these experiments. It is suggested that in the presence of hydrogen chloride [HSnCl] is produced which reduces β-carbomethoxyethyltin trichloride (I) to $[RHSnCl_2]$ (R = $CH_2CH_2CO_2Me$), this then reacts with butyl acrylate to give $Cl_2SnCH_2CH_2CO_2Me$ · $CH_2CH_2CO_2Bu$ (V) according to eq. 12. We have already demonstrated that a reaction similar to (eq. 12, ii) does occur (eq. 7, ii).

$$2[RSnCl_2^-] + 2\ HCl \rightarrow 2\ RSnCl_3 + H_2 \tag{11}$$

$$(R = CH_2CH_2CO_2Me)$$

$$RSnCl_3 + HCl/Sn\ ([HSnCl]) \rightarrow [RHSnCl_2] + SnCl_2 \qquad (i)$$

$$[RHSnCl_2] + CH_2 = CHCO_2Bu \rightarrow RSnCl_2CH_2CH_2CO_2Bu\ (ii) \tag{12}$$
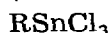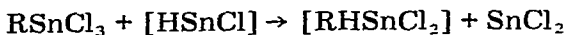$$(V)$$

In view of the experimental observations recorded above it now appears that the most feasible mechanism for the formation of $Cl_2Sn(CH_2CH_2CO_2Me)_2$ from the interaction of hydrogen chloride, tin and methyl acrylate is as follows. Initially the monoalkyltin trichloride ($Cl_3SnCH_2CH_2CO_2Me$) is formed and is then largely converted to the dialkyltin compound via the halogenostannane intermediate $[Cl_2SnHCH_2CH_2CO_2Me]$ It appears possible that this step involves the intermediate formation of [HSnCl] which is effective in the reduction: see eq. 13.

$$HCl + Sn \rightarrow [HSnCl] \xrightarrow{HCl} H_2 + SnCl_2$$

$$CH_2{=}CHCO_2Me : HCl + SnCl_2 \rightarrow [CH_2{=}CHCO_2Me : HSnCl_3]$$
$$\downarrow$$
$$RSnCl_3 \tag{13}$$

$$RSnCl_3 + [HSnCl] \rightarrow [RHSnCl_2] + SnCl_2$$

$$[RHSnCl_2] + CH_2 = CHCO_2Me \rightarrow R_2SnCl_2$$

$$(R = CH_2CH_2CO_2Me)$$

Further experimental work is underway in an attempt to verify these tentative proposals.

Experimental

Spectroscopy. Infrared spectra were recorded as nujol mulls or liquid films on a Perkin—Elmer 577 grating spectrophotometer. 60 MHz nuclear magnetic resonance spectra were recorded on a Perkin—Elmer R12B spectrophotometer.

Synthesis. The synthesis of mixtures of substituted mono- and di-alkyltin halides has already been described [4]. The purification of the bis(β-substituted alkyl)tin dihalides is described in the footnotes to Table 1.

Mechanistic studies

(i) The reaction between hydrogen chloride, tin and excess butyl acrylate. To a stirred suspension of 400 g (3.37 mol) of powdered tin in 1965 g (15.33 mol) of butyl acrylate was charged hydrogen chloride gas at a rate of 0.937 mol/hour/ mol tin. The temperature was maintained at 60°C (±0.5°C) throughout the experiment. The concentrations of $Cl_3SnCH_2CH_2CO_2Bu$ and $Cl_2Sn(CH_2CH_2CO_2Bu)_2$ were determined by NMR spectroscopy on 1 g sample withdrawn periodically from the reaction mixture. These values were then plotted as a function of time to give rise to Fig. 1.

(ii) The reaction between hydrogen chloride, an excess of tin and methyl acrylate in dimethoxymethane. To a stirred suspension of 12.82 g (0.108 mol) of powdered tin in 2.32 g (0.027 mol) of methyl acrylate and 25 ml of dimethoxy methane was added hydrogen chloride gas at a rate of 1.20 mol/hour/mol tin. The temperature was maintained at 40°C with the aid of a thermostated bath. 0.5 ml samples were withdrawn periodically from the reaction mixture and their NMR spectra were recorded. Naphthalene was utilized as an internal standard for determination of the concentrations of $Cl_3SnCH_2CH_2CO_2Me$ and Cl_2Sn-$(CH_2CH_2CO_2Me)_2$. The concentrations of these compounds as a function of time are presented in Fig. 3.

(iii) (a) Reactions between $Cl_3SnCH_2CH_2CO_2Me$ and tin in butyl acrylate. In these experiments roughly 0.1 mol (31.2 g) of $Cl_3SnCH_2CH_2CO_2Me$ was treated with the appropriate amount of powdered tin in butyl acrylate (100 g). Reactions were performed under nitrogen at 60°C and 1 ml samples were removed periodically for examination by NMR spectroscopy. In these experiments the solvent, butyl acrylate, served as an internal standard.

In a typical experiment 31.22 g (0.10 mol) of $Cl_3SnCH_2CH_2CO_2Me$ was added to 11.87 g (0.10 mol) of powdered tin in 100 g (0.78 mol) butyl acrylate. Stirring was commenced and the temperature was quickly (approximately 5 min) raised to 60°C. The first sample was then taken and the temperature maintained at 60°C (±0.5°) throughout the experiment. NMR spectra were recorded immediately or samples were stored at 0°C until the spectra could be recorded.

In experiments where hydrogen chloride was added the addition was commenced when 60°C was reached.

(b) Reactions between $Cl_3SnCH_2CH_2CO_2R$ and tin in various solvents. These reactions were all performed with powdered tin and carried out under dry nitrogen. The details and results of these experiments are presented in Table 4.

(iv) The reaction between Cl₃SnCH₂CH₂CO₂Me and Bu₃SnH in methyl acryl- $Cl_3SnCH_2CH_2CO_2Me$ and Bu_3SnH
ate. To a solution of 1.0 g (3.20 mmol) of $Cl_3SnCH_2CH_2CO_2Me$ in methyl acryl-ate (4.77 g, 3.18 mmol) at 20°C under dry N_2 was added dropwise 0.0926 g (3.18 mmol) of Bu_3SnH with stirring. The reaction mixture was allowed to stand overnight and 30 ml of n-hexane was added. Filtration yielded 1.20 g of a white solid which was recrystallised from methanol to yield 0.60 g (52%) of Cl_2Sn-$(CH_2CH_2CO_2Me)_2$. Bu_3SnH was prepared according to the method of Van der Kerk et al. [14].

$ClSn(CH_2CH_2CO_2Me)_3$ was prepared according to the method of Van der Kerk and Noltes [19].

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