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β-SUBSTITUTED ALKYLTIN HALIDES

I. MONOALKYLTIN TRIHALIDES: SYNTHETIC, MECHANISTIC AND SPECTROSCOPIC ASPECTS

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Summary

$HSnCl_3(Et_2O)_2$ reacts with a variety of α,β-unsaturated carbonyl compounds to give high yields of β-substituted organotin compounds. The hydrostannation proceeds under a wide variety of conditions. Temperatures between approximately —30 and 120°C can be employed. Ethereal solvents can be used but are not essential, since monomer solvation of $HSnCl_3$ ($M \rightarrow HSnCl_3$) can occur in non-ethereal media. Intramolecular carbonyl coordination to tin occurs in these β-substituted organotin compounds.

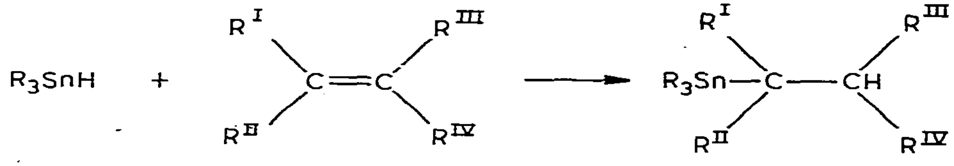
Introduction

Monoalkyltin trihalides ($RSnX_3$) (R = Me, Bu, Oct, X = Cl, Br) are commercially important as intermediates in the synthesis of organotin stabilisers for PVC. Whilst the synthesis either by disproportionation of R_4Sn with SnX_4 [1] or by reaction of RX with SnX_2 [2] is well known, complex catalyst systems are required in order to achieve high yields.

$$SnR_4 + 3\ SnX_4 \rightarrow 4\ RSnX_3 \qquad (1)$$

$$RX + SnX_2 \rightarrow RSnX_3 \qquad (2)$$

Alternatively, C—Sn bond formation can be effected by the insertion of an olefinic compound into an Sn—H bond [3] (hydrostannation). Hitherto, this reaction has only been applied to the synthesis of tetraalkyltin compounds and trialkyltin halides. Potentially, however, alkyltin halides may be synthesised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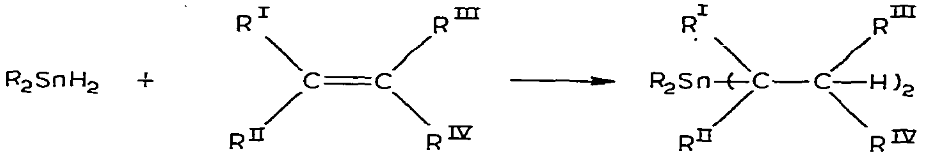
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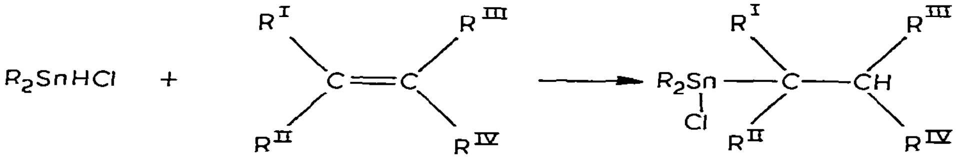
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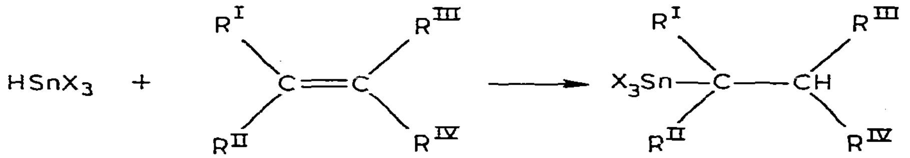
via hydrostannation of olefinic monomers with halogenostannane species (eq. 6 and 7). Amberger has suggested the participation of dichlorostannane (H_2Sn-Cl_2) in the decomposition of H_3SnCl, although there is little evidence for its existence [4]. Somewhat better characterized are $HSnX_3$ species (X = Cl, Br) which have been isolated as complexes with Et_2O (diethyl ether) or amines. These trihalogenostannane complexes have been prepared by reduction of SnX_4 with $LiAlH_4$ [5] and also by addition of SnX_2 to a solution of excess HX in Et_2O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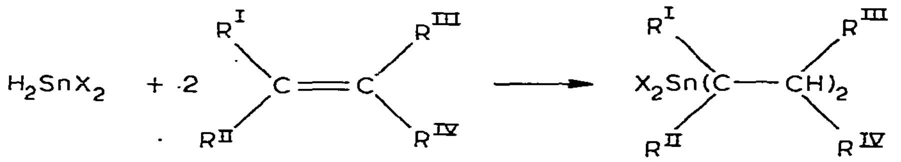
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(X = Cl, Br, I)

[6]. We have prepared $HSnCl_3(Et_2O)_2$ by a slight modification of the latter method, and tested its reaction with a variety of olefines [7,8].

Experimental

Spectroscopy

Infrared spectra were recorded as nujol mulls of liquid films on a Perkin—Elmer 577 grating spectrophotometer. 60 MHz nuclear magnetic resonance spectra were recorded as solutions in $CDCl_3$ on a Perkin—Elmer R12B spectrophotometer.

Synthesis

(i) Preparation of $Cl_3SnCH_2CH_2CO_2Me$

Method (a): To 80.0 g (0.42 mol) of anhydrous $SnCl_2$ suspended in 150 ml Et_2O was added 36.0 g (0.98 mol) of anhydrous HCl over a period of 1.0 h. An ice/water bath was used to keep the temperature at 25° C. $HSnCl_3 (Et_2O)_2$ separated as a dense lower layer and 36.3 g (0.42 mol) of MeAc (methyl acrylate) were added over a period of 2 h, stirring being continued for a further 1.5 h. Et_2O and $ClCH_2CH_2CO_2Me$ were removed on a rotary evaporator and the residue extracted with $CHCl_3$. This solution was then evaporated to leave 129.1 g (97.6%) of a pale yellow crystalline product, which was shown by spectroscopy and elemental analyses to be $Cl_3SnCH_2CH_2CO_2Me$ (b.p. 174° C/4 mmHg). The organotin products from compounds marked by ^{c} in Table 1 were prepared by this method.

Method (b): To 80.0 g (0.42 mol) of anhydrous $SnCl_2$ suspended in a solution of 36.3 g (0.42 mol) of MeAc in 200 ml hexane was added 19.9 g (0.55 mol) of anhydrous HCl. The exothermic reaction which ensued was controlled with the aid of an ice/water bath. The HCl addition was completed in 4 h and the solid was filtered off. It was dried and dissolved in $CHCl_3$, and the solution filtered to remove traces of residual $SnCl_2$. Evaporation of this solution then gave the required product (125.1 g (95%)), which was characterised as above. The organotin products from phenyl acrylate, methyl methacrylate, methyl crotonate, phorone, acrylamide and methyl propiolate were prepared by the same methods.

(ii) Preparation of $Cl_3SnCH_2CH_2CO_2Bu$

To 100 g (0.53 mol) of anhydrous $SnCl_2$ suspended in 74.4 g (0.58 mol) of $CH_2{=}CH \cdot CO_2Bu$ was added 29.5 g (0.81 mol) of anhydrous HCl during 2 h. The temperature was maintained at 20° C. After this time the mixture was stripped at 150° C/4 mmHg to remove residual $CH_2{=}CH \cdot CO_2Bu$ and $ClCH_2CH_2$-CO_2Bu. The warm residue (60° C) was filtered to remove residual $SnCl_2$, and crystallised on cooling. 171.9 g (90.6%) of $Cl_3SnCH_2CH_2CO_2Bu$ was obtained, and was characterised by spectroscopy and elemental analyses.

(iii) Preparation of $Cl_3SnCMe_2CH_2COMe$

To a stirred suspension of 100 g (0.53 mol) of anhydrous stannous chloride

TABLE 1

THE REACTION BETWEEN HCl, SnCl$_2$ AND α,β-UNSATURATED CARBONYL COMPOUNDS IN DIETHYL ETHER

Compound	Temperature (°C)	Reaction time (hours)	Conversion [a] of SnCl$_2$ (%)	Product analytical data (%)	
				Cl [b]	Sn
CH$_2$=CHCO$_2$Me	25	3.5	98	34.62 (34.11)	38.09 (38.02)
CH=CHCO$_2$Me (+ HSnBr$_3$)	20	1	72	52.91 (53.84) [d]	26.64 (26.62)
CH$_2$=CHCO$_2$Et [c]	15	1	79	32.29 (32.65)	37.51 (36.69)
CH$_2$=CHCO$_2$Bu	20	2	92	30.10 (30.08)	33.47 (33.61)
CH$_2$=CHCO$_2$Ph	20–25	5	89	28.31 (28.38)	37.53 (37.45)
CH=CMe · CO$_2$Me	25	3.5	62	32.71 (32.65)	36.33 (36.39)
MeCH=CHCO$_2$Me	20–25	4	30	31.78 (32.65)	36.60 (36.39)
MeCH=CHCO$_2$Me (+ DSnCl$_3$)	20	3	25	32.58 (32.56)	36.17 (36.29)
CH$_2$=CHCO$_2$H	25	4	99	35.37 (35.71)	39.82 (39.80)
MeCH=CHCO$_2$H	15	5	~40 [e]	[g] (34.11)	(38.02)
CH$_2$=CHCOMe [c]	15	2.5	70	35.78 (35.96)	40.19 (40.07)
Me$_2$C=CHCOMe	25	2	80 [f]	32.90 (32.83)	36.57 (36.60)
(Me$_2$C=CH)$_2$CO	20	4	30	29.07 (29.22)	31.79 (32.57)
MeCH=C(CO$_2$Et)$_2$ [c]	20–25	2.5	<20	[g] (25.84)	(28.80)
CH$_2$=CHCONH$_2$	20	10	<20	[g] (35.82)	(39.93)
CH≡CCO$_2$H [c]	20–25	2	~60 [e]	35.70 (35.95)	39.84 (40.07)
CH≡CCO$_2$Me	20	6	60	34.45 (34.33)	38.25 (38.27)

[a] Within the limits of experimental determination, SnCl$_2$ is quantitatively converted to organotin compound. [b] Values in parenthesis are the theoretical values for 1 : 1 addition products between HSnCl$_3$ and the monomers. [c] Monomer added to HSnCl$_3$(Et$_2$O)$_2$. [d] Theoretical Br analysis. [e] Accurate estimation of the SnCl$_2$ converted to organotin product was not possible due to HCl elimination. [f] The product was isolated by crystallisation from the reaction medium — the conversion of SnCl$_2$ is probably higher. [g] Purification of the product was difficult — characterisation was by NMR analysis of the crude reaction product.

in 51.9 g (0.53 mol) of mesityl oxide and 250 ml of Et_2O was added 25.1 g (0.69 mol) of anhydrous HCl. Discolouration occurred during the HCl addition. The mixture was kept at 15° C for 5 h, and filtered to give 68.4 g of an off-white crystalline product, which was washed with cold (—10° C) Et_2O. Analysis verified the absence of Sn^{II}, and spectroscopic data showed the product was pure $Cl_3SnCMe_2CH_2COMe$ (40%). (Undoubtedly the mother liquors contained more product, but this was not isolated).

(iv) Attempted reactions between $HSnCl_3$ and $Cl_3SnCMe_2CH_2COCH{=}CMe_2$

The reaction between $HSnCl_3$ and phorone in Et_2O at 20° C gave only $Cl_3SnCMe_2CH_2COCH{=}CMe_2$ after a period of 4 h. No evidence for the formation of the corresponding bis-$HSnCl_3$ addition product could be obtained even when the requisite amount of $HSnCl_3$ was used for a reaction time of 10 h. A six-fold excess of $HSnCl_3$ added to $Cl_3SnCMe_2CH_2COCH{=}CMe_2$ in dimethoxyethane gave no reaction after 10 h at 20° C. Raising the temperature to 80° C as further HCl was introduced had no effect. We conclude that the C=C bond in $Cl_3SnCMe_2CH_2COCH{=}CMe_2$ is unreactive.

(v) Preparation of $Cl_3SnCH_2CH_2CO_2H$

A slight excess of anhydrous HCl was slowly added to an equimolar mixture of anhydrous $SnCl_2$ and $CH{=}CHCO_2H$ in Et_2O. Et_2O and excess HCl were then removed under vacuum (4 mmHg) at 30—40° C. An amorphous off-white powder was obtained, which corresponded analytically and spectroscopically to $Cl_3SnCH_2CH_2CO_2H$. The product was also shown to contain <0.2% Sn^{II}. The yield was 99%.

Care must be taken in the isolation of $Cl_3SnCH_2CH_2CO_2H$ since attempts to remove the residual traces of $SnCl_2$ by solvent extraction or by recrystallisation result in partial dehydrochlorination. N.B.: Efficient dehydrochlorination of $Cl_3SnCH_2CH_2CO_2H$ can be effected by refluxing in *p*-xylene.

$$Cl_3SnCH_2CH_2CO_2H \xrightarrow[12\ h]{139^\circ C} Cl_2\overset{+}{Sn}CH_2CH_2CO_2^-$$

The product separates from hot *p*-xylene in which $Cl_3SnCH_2CH_2CO_2H$ is soluble. Characterisation was by elemental analyses and NMR spectroscopy. A similar elimination has been observed for the addition product from Ph_3SnH and acrylic acid. In this case benzene was eliminated, with formation of $Ph_2\overset{+}{Sn}CH_2CH_2CO_2^-$ [9].

Results and discussion

Addition of excess dry gaseous hydrogen chloride to a slurry of anhydrous $SnCl_2$ in Et_2O causes the separation of a pale yellow lower layer which has been previously characterised as $HSnCl_3(Et_2O)_2$ [6]. Above about 30° C this complex decomposes to regenerate HCl and $SnCl_2$, and the existence of an equilibrium (eq. 8) is suggested:

$$HCl + SnCl_2 + 2\ Et_2O \rightleftharpoons HSnCl_3(Et_2O)_2 \qquad (8)$$

Homogeneous solutions are produced from the reaction of HCl and $SnCl_2$ in

TABLE 2

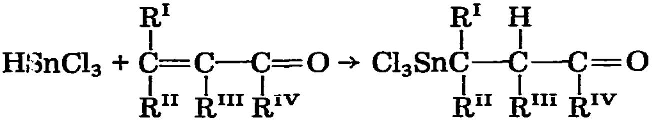
MELTING POINT AND SPECTROSCOPIC DATA FOR FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

Compound	M.p. (°C)	ν(C=O) [a] (±2 cm^{-1})	Chemical shifts (τ) [b]			Coupling constants [c] (Hz)	
			CH (α)	CH (β)	Others	J(Sn—H$_\alpha$)	J(Sn—H$_\beta$)
$Cl_3SnCH_2CH_2CO_2Me$	69	1660	7.73	7.01	6.03(OMe)	102	186
$CH_3CH_2CO_2Me$		1738			6.34(OMe)		
$Br_3SnCH_2CH_2CO_2Me$	75	1655	7.62	7.12	6.08(OMe)	92	192
$Cl_3SnCH_2CH_2CO_2Et$	68	1665	7.77	7.06	5.55(OCH$_2$) 8.63(Me)	[d]	
$Cl_3SnCH_2CH_2CO_2Bu$	46	1659	7.74	6.94	5.63(OCH$_2$)	ca. 118	ca. 209
$Cl_3SnCH_2CHMeCO_2Me$	86	1660	7.75	6.70	5.59(OMe) 8.44(CH$_\gamma$)	[d]	
$Cl_3SnCH_2CH_2CO_2Ph$	177	1686	7.64	6.67	2.63, 2.72(Ph)	112	221
$Cl_3SnCH_2CH_2COMe$	70	1659	8.12	6.84	7.52 (COMe)	ca. 85	177
CH_3CH_2COMe		1723			7.88 (COMe)		
$Cl_3SnCMe_2CH_2COMe$	123	1665		6.85 (CH$_2$) 8.77 (CMe)	7.43 (COMe)		210 (CH$_2$) 204 (Me)
$Cl_3SnCMe_2CH_2COCH{=}CMe_2$	77	1580					
$Cl_3SnCH_2CH_2CO_2H$	123—127	1665	7.80	6.92	−1.25 (CO$_2$H)	ca. 88	207
$Cl_2Sn^+CH_2CH_2CO_2^-$	234 (dec.)		8.55	7.65 [e]		ca. 120	ca. 120
$Cl_3SnCH{=}CHCO_2H$		1623	2.18	2.94		286	473
$Cl_3SnCH_2CH_2CONH_2$			8.29	6.96	1.84, 1.97(NH$_2$) [f]	119	207
$Cl_3SnCH{=}CHCO_2Me$			2.55	2.95	5.88 (OCH$_3$)	255	421
$Cl_3SnCHCH_3CHDCO_2Me$		1655	8.80	7.23	6.03 (OCH$_3$) 8.35 (Me)	[d]	

[a] Spectra recorded as nujol mulls. [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 the ^{119}Sn—H coupling constants. [d] The Sn—H satellite peaks are masked by the other signals. [e] Spectrum recorded in $(CD_3)_2SO$. [f] The NH_2 signal appears as a doublet.

THF (tetrahydrofuran), DME (dimethoxyethene), ethyl acetate, methanol and also upon dissolution of $SnCl_2$ is concentrated hydrochloric acid; presumably $HSnCl_3$ is formed in each case.

Addition of α-olefines such as oct-1-ene to $HSnCl_3(Et_2O)_2$ at 15° C gave little reaction but some 2-chloro octane was isolated, as were trace amounts (<1%) of sec-octyltin trichloride. Similar results were obtained with both propene and but-1-ene. However, strongly exothermic reactions ensued when α,β-unsaturated carbonyl compounds, such as methyl acrylate, were added to $HSnCl_3(Et_2O)_2$, and organotin compounds were formed. Table 1 summarises the successful reactions. The fastest conversion rates were obtained with simple acrylates and, as far as we can determine, the $SnCl_2$ consumed is quantitatively converted into organotin compound with any monomer. The products were characterised by elemental analyses (Cl and Sn) and IR (infrared) and NMR (nuclear magnetic resonance) spectroscopies: this data is presented in Table 2. In each case only the β-addition product was obtained as identified by NMR spectroscopy. The overall reaction can be simply represented by eq. 9.



$$HSnCl_3 + \underset{R^{II}}{\overset{R^{I}}{C}}{=}\underset{R^{III}}{C}{-}\underset{R^{IV}}{C}{=}O \rightarrow Cl_3Sn\underset{R^{II}}{\overset{R^{I}}{C}}{-}\underset{R^{III}}{\overset{H}{C}}{-}\underset{R^{IV}}{C}{=}O \qquad (9)$$

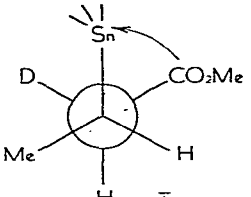
Not all α,β-unsaturated carbonyl compounds are active, however. Isophorone ($CMe_2CH_2COCH{=}CMeCH_2$) did not react with $HSnCl_3$ during 72 h in Et_2O at 20—25° C Its lack of reactivity is highly significant, as shown in the discussion of the mechanism below.

Reaction conditions

Addition of MeAc (methyl acrylate) to a suspension of $HSnCl_3(Et_2O)_2$ in Et_2O or solutions of $HSnCl_3$ in solvents such as THF, DME, EtOAc (ethyl acetate) or MeOH in each case gave good yields of $Cl_3SnCH_2CH_2CO_2Me$. However, when H_2O was utilized as solvent the organotin compound was produced in only low yield (based on the acrylate) due to hydrolysis and hydrohalogenation of the monomer. Attempts to prepare $HSnCl_3$ in hydrocarbon solvents (n-hexane, toluene or benzene) or dibutyl ether were unsuccessful due to the insolubility of $SnCl_2$ in these media. These solvents were, however, successfully employed in the synthesis of $Cl_3SnCH_2CO_2Me$ by an in-situ process in which HCl was introduced into a suspension of $SnCl_2$ in a solution of methyl acrylate in the appropriate solvent. In fact the solvent can be dispensed with if an excess of the acrylate is employed. We have performed this in-situ reaction with appropriate monomers at temperatures between approximately —30 and 120° C. The upper temperature limit is only governed by the boiling point of the solvent (or monomer) or by the onset of thermal polymerisation of the monomer. At the lower temperatures HCl addition to several monomers becomes important, e.g. in a reaction with methyl acrylate in Et_2O at —25° C approximately 50% hydrochlorination of the monomer was observed. The $HCl/SnCl_2$ couple has been successfully replaced by the corresponding bromide complex in conjuction with methyl acrylate. The data for the product are also included in Table 1.

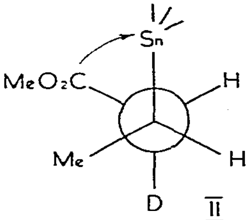
Reaction mechanism

In order to assist understanding of the mechanism of this hydrostannation we studied in some detail the product from the reaction between $DSnCl_3$ and methyl crotonate (MeCr) in ether at 15° C (see Tables 1 and 2). This compound, corresponding analytically to $Cl_3SnCHCH_3CHDCO_2Me$, showed a carbonyl absorption in the IR spectrum at 1655 cm^{-1} and a $J(H_\alpha—H_\beta)$ coupling constant of ca. 2 Hz. The NMR spectrum is consistent with the structure shown. Briefly, the $\nu(C{=}O)$ value is consistent with intramolecular carbonyl coordination to Sn (this phenomenon will be discussed in detail in a later section) and this interaction imparts structural rigidity to the molecule. In principle, $DSnCl_3$ might add "*cis*" or "*trans*" to the activated C=C double bond in methyl crotonate to give the possible products I—IV.

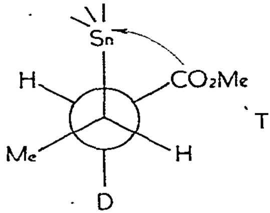


I

'CIS'

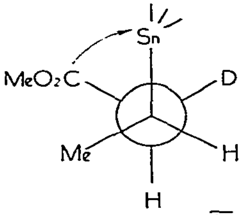


II



III

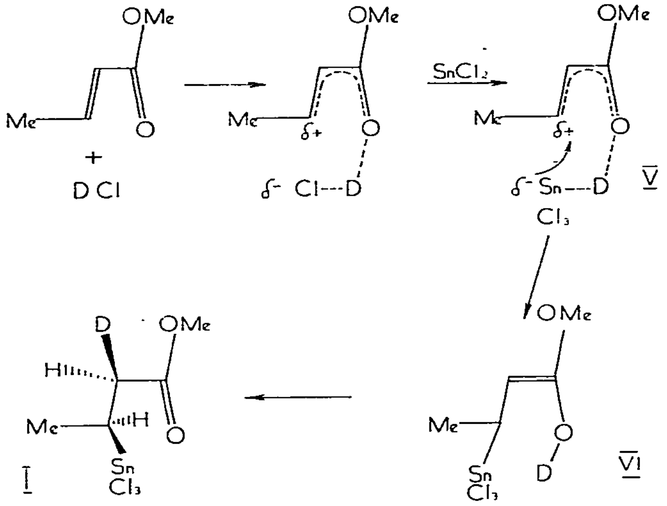
'TRANS'



IV

Structures II and IV are sterically unfavourable and thus will not be considered further. The small $J(H—H)$ coupling constant of 2 Hz observed for this compound is then consistent with structure I, since structure III would almost certainly give a much larger (ca. 10 Hz) $J(H—H)$ coupling constant [10]: "*cis*" addition of $DSnCl_3$ to MeCr is therefore suggested by these results. As in all other trichlorostannane additions to α,β-unsaturated carbonyl compounds, addition of $DSnCl_3$ to MeCr gives specifically the β-addition product. That these reactions can be performed in non polar media suggests that monomer solvation of trichlorostannane is an important feature of the mechanism. Finally, isophorone does not react with $HSnCl_3$, suggesting that only a "*cis*" monomer conformation can undergo reaction with $HSnCl_3$. (Phorone and mesityl oxide are both active, see Table 1.)

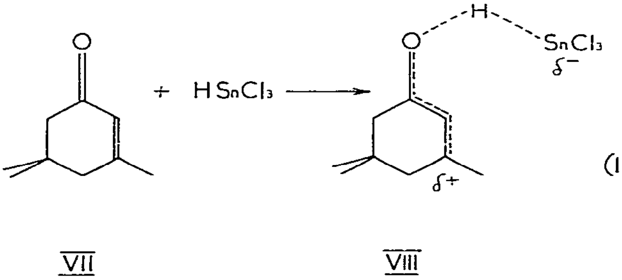
To explain the experimental observations, the following mechanism is proposed. The primary step in the in-situ reaction (at least in non-polar media and also probably in all solvents) must be monomer solvation of HCl. This complex then interacts with $SnCl_2$ to give a monomer: → $HSnCl_3$ aggregate (V). This intermediate complex then collapses by attack of $Cl_3Sn^{\delta-}$ at the carbon atom β to the ester group. The complete reaction sequence is shown below in eq. 10 for $DSnCl_3$ and MeCl. This mechanism represents a tin-hydride addition to a C=C double bond with the $Sn^{\delta-}$- - - -$H^{\delta+}$ polarisation of the tin—hydrogen bond. Thus $HSnCl_3$ provides a unique example of a tin-hydride species reacting in this fashion, since all previous tin-hydride additions have been shown to operate either by free radical mechanisms or with the $Sn^{\delta+}$- - - -$H^{\delta-}$ polarisation of the tin—hydrogen bond [3].



(10)

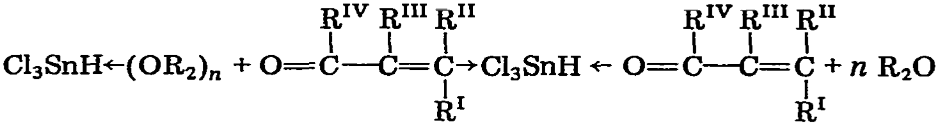
In order to achieve "*cis*" addition to the double bond, ketonisation of the enol intermediate (VI) must occur by an intra-, rather than an intermolecular process. The latter process would almost certainly result in "*trans*" addition, by analogy with the addition of DCl to α,β-unsaturated esters, in which the final ketonisation step is catalysed by other DCl molecules [11]. In the present case, the deuterium transfer may be assisted by a chlorine atom of the $SnCl_3$ group.

The inactivity of isophorone results from the unfavourable geometry of the complex, since the $SnCl_3^{\delta-}$ entity will be located too far from the active site, as shown in eq. 11.

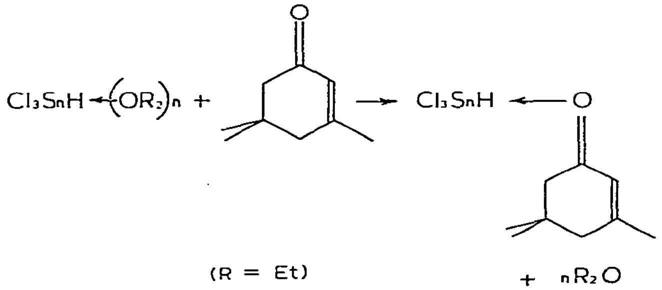


(11)

Isophorone does, however, solvate $HSnCl_3$, as demonstrated by the following observations. HCl does not react with $SnCl_2$ in n-hexane, but in the presence of 2 moles of isophorone (per mole of $SnCl_2$) a two phase system is produced, similar in appearance to that from HCl and $SnCl_2$ in Et_2O. The IR spectrum of the lower layer shows a carbonyl absorption at 1621 cm^{-1}, 56 cm^{-1} displaced to lower frequency from $\nu(C=O)$ of pure isophorone (1677 cm^{-1}). This effect is consistent with strong co-ordination, as would be expected for VIII. The solution produced from HCl, $SnCl_2$ and VII in n-hexane was stable for 72 h at 20° C, and addition of MeAc to the system resulted in the formation of $Cl_3SnCH_2CH_2CO_2Me$ and VII. The monomer: → $HSnCl_3$ complexes in hydrocarbon solutions are undoubtedly important, and it seems likely that similar complexes are also important in ethereal media (eq. 12) but, because of their immediate conversion to products, it is impossible to study these spectroscopically. VII, at least, preferentially solvates $HSnCl_3$ in Et_2O at 20° C, since the addition of VII to $HSnCl_3(Et_2O)_2$ again gave a solution with a low frequency carbonyl absorption (1625 cm^{-1}) consistent with carbonyl coordination (eq. 13).

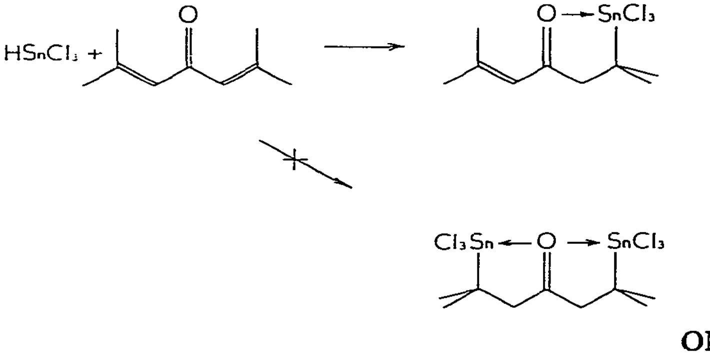


$$Cl_3SnH\leftarrow(OR_2)_n + O{=}\overset{R^{IV}}{C}-\overset{R^{III}}{C}{=}\underset{R^{I}}{\overset{R^{II}}{C}}\rightarrow Cl_3SnH \leftarrow O{=}\overset{R^{IV}}{C}-\overset{R^{III}}{C}{=}\underset{R^{I}}{\overset{R^{II}}{C}} + n\,R_2O \qquad (12)$$

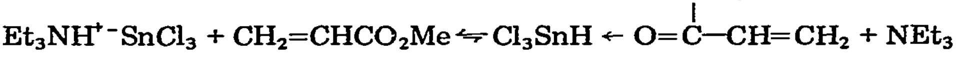


(13)

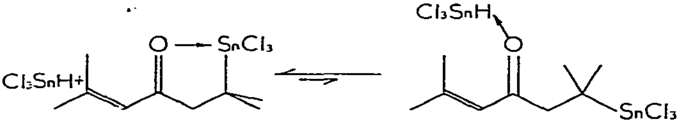
Also consistent with the concept of monomer solvation are the following observations: (i) $Et_3\overset{+}{N}H\overline{Sn}Cl_3$ is inactive towards MeAc; and (ii) only one of the C=C bonds in phorone is active towards $HSnCl_3$ under a variety of conditions (eq. 14).



(14)



$$Et_3NH^{+}\,{}^{-}SnCl_3 + CH_2{=}CHCO_2Me \rightleftharpoons Cl_3SnH \leftarrow O{=}\overset{OMe}{C}-CH{=}CH_2 + NEt_3 \qquad (15)$$



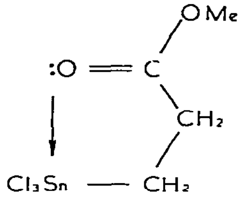
(16)

Presumably MeAc is sufficiently basic to displace ether molecules from the complex with $HSnCl_3$ but cannot effect a similar displacement of the more basic

NEt_3. The C=C bond in $Cl_3SnCMe_2CH_2COCH{=}CMe_2$ is inactive due to carbonyl coordination to Sn which is sufficiently strong (ν(C=O) = 1580 cm^{-1}) to prevent the vital coordination to $HSnCl_3$ (eq. 16).

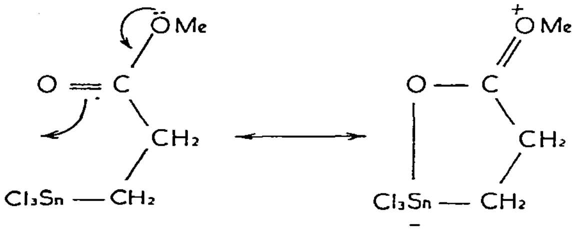
Structure and spectroscopy

Spectroscopic data (IR (ν(C=O) and NMR) for a number of new organotin compounds are presented in Table 2. With very few exceptions the carbonyl stretching frequencies in these compounds lie between 1655 and 1665 cm^{-1}, roughly 80 cm^{-1} in most cases to lower frequency than the saturated analogues of the parent α,β-unsaturated carbonyl eompound. The carbonyl frequencies for methyl propionate and butan-2-one are also included in Table 2 for comparison. Furthermore, the ester methyl signal in $Cl_3SnCH_2CH_2CO_2Me$ is situated downfield from the corresponding signal in $CH_3CH_2CO_2Me$, and a similar effect is observed for the methyl signals in $Cl_3SnCH_2CH_2COMe$ and CH_3CH_2-COMe. These spectroscopic effects are consistent with carbonyl coordination to Sn, since this phenomenon reduces the C=O bond order [12] (and hence the carbonyl stretching frequency) and also the perturbation of the electron distribution causes a deshielding effect on the relevant protons. Since the carbonyl stretching frequency for any compound in Table 2 is unaffected by dilution in toluene or ethereal solvents, the carbonyl coordination to Sn is almost certainly intramolecular in origin. For example the structure of β-carbomethoxyethyltin trichloride can be represented by IX.



IX

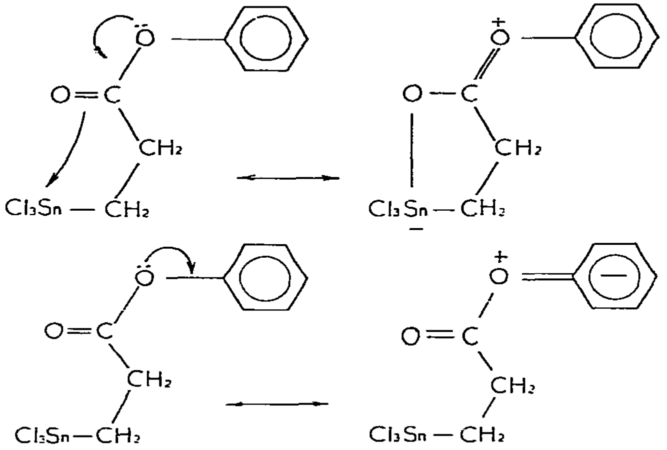
However, a closer examination of the IR spectra of $Cl_3SnCH_2CH_2CO_2Me$ and $CH_3CH_2CO_2Me$ shows that ν(C—O) for the ester group in $Cl_3SnCH_2CH_2CO_2Me$ lies some 63 cm^{-1} to higher frequency than the same vibration in $CH_3CH_2CO_2$-Me (1270 cm^{-1} vs. 1207 cm^{-1}). Possibly the methoxy oxygen lone-pair electrons are also involved in the delocalisation of the ester carbonyl electron density on to Sn. The intramolecular coordination may, therefore, be represented by X.



X

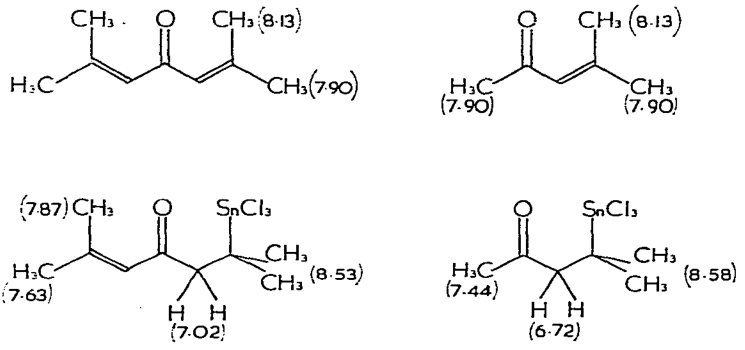
Intramolecular carbonyl coordination of the type described above is not novel, but it is significantly stronger in the esters and ketones described in Table 2 than that in the corresponding dialkyltin compounds described in a review by Omae [13].

The phenyl ester shows a relatively high frequency carbonyl absorption (1686 cm^{-1}) compared to the other ester substituted organotin compounds. In this case the phenyl group probably withdraws electron density from the ester function hence diminishing delocalisation on to Sn (XI).



XI

The organotin product obtained from phorone ($Cl_3SnCMe_2CH_2CO \cdot CH{=}CMe_2$) shows an extremely low frequency carbonyl absorption at 1580 cm^{-1} which suggests that carbonyl coordination to tin is extremely strong in this case and is assisted by the residual unsaturation. A close examination of the NMR spectra of this, and of related compounds, supports this theory.

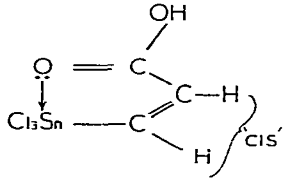


(τ VALUES)

Both mesityl oxide and phorone show exactly similar NMR spectra in the region of the olefine methyl signals. It was, therefore, somewhat surprising to find the analogous signals in $Cl_3SnCMe_2CH_2CO \cdot CH{=}CMe_2$ at distinctly lower field. The deshielding of these protons can be accounted for by electron delocalisation onto tin involving the C=C and the C=O groups as shown by XII.

XII

The IR spectrum of $Cl_3SnCH{=}CHCO_2H$ also shows a relatively low frequency carbonyl absorption (1623 cm^{-1}) probably as a consequence of carbonyl conjugation to C=C. The NMR spectrum is also interesting. The coupling $J(H_\alpha{-}H_\beta)$ is 9 Hz, a value suggesting that the C=C double bond assumes a "*cis*" structure. (This assignment was made by comparison with trialkylvinyl tin compounds [3]). This observation, however, suggests that the addition of $HSnCl_3$ to $HC{\equiv}C{-}CO_2H$ occurs in a "*trans*" fashion and not "*cis*" as occurs with $DSnCl_3$ and methyl crotonate (and almost certainly $HSnCl_3$ and most acrylic esters). Mechanistically, therefore, the reaction with propiolic acid is markedly different. It is possible that the reactions follow somewhat similar paths to the enol stage, but that in the case of propiolic acid the $-SnCl_3$ group, which possibly assists the intra molecular ketonisation in the case of $DSnCl_3$ and MeCr, is not suitably placed to effect a similar ketonisation. It is probable, therefore, that an intermolecular ketonisation process leads to the "*trans*" addition mode. Finally the Sn—H spin-spin coupling constants for $Cl_3SnCH{=}CHCO_2H$ are especially noteworthy, since the values, viz. 286 Hz ($J(Sn{-}H_\alpha)$) and 473 Hz ($J(Sn{-}H_\beta)$) are the largest indirect Sn—H coupling constants recorded.



Acknowledgement

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