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THE SYNTHESIS AND INFRARED SPECTRA OF ORGANOTIN(IV) MERCAPTOESTER CHLORIDES

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Summary

We have prepared several butyltin mercaptoesters and butyltin mercaptoester chlorides of the general formula $Bu_nSn(S(CH_2)_{1-2}CO_2R)_mCl_{4-(n+m)}$ ($n = 1$, $m = 1$-3; $n = 2$, $m = 1$-2) and we have studied, in some detail, their infrared spectra in the carbonyl region. The butyltin mercaptoester chlorides exist not as pure compounds but as mixtures in equilibrium with the respective butyltin mercaptoesters and butyltin chlorides. Our results suggest that anhydrous reactions between butyltin chlorides and isooctylthioglycolate give almost entirely butyltin isooctylthioglycolate chlorides in contrast to the findings of Herber and Stapfer [J. Organometal. Chem., 66 (1974) 425] who concluded that these reagents gave *trans* isomers of butyltin isooctylthioglycolates.

Introduction

Despite the importance of organotin mercaptoesters $R_nSn[S(CH_2)_mCO_2R']_{4-n}$ {$n = 1, 2$; $m = 1, 2$; R = Me, Bu, Oct; R' = alkyl (SCH_2CO_2-i-C_8H_{17}) ≡ (IOTG); ($SCH_2CH_2CO_2C_7H_{15}$) ≡ (HβMP)} as stabilisers for PVC relatively little attention has been paid to the determination of their structures. Likewise, even less well documented are the organotin mercaptoester chlorides the intermediate species in the degradation of the organotin mercaptoesters to the chlorides (R_nSnCl_{4-n}) ($n = 1, 2$). However, Stapfer and Herber have reported infrared and Mössbauer data for a number of these compounds [1]. These workers suggested that the structures of $R_nSn(IOTG)_{4-n}$ ($n = 1, 2$) are dependent upon the mode of preparation: '*cis*' isomers arising from aqueous hydrolyses of R_nSnCl_{4-n} in the presence of the appropriate quantities of isooctylthioglycolate and '*trans*' isomers arising from anhydrous reactions between R_nSnCl_{4-n} and isooctylthioglycolate alone. This work prompts us to submit the present paper which relates similarly to organotin mercaptoesters and organotin mercaptoester chlorides.

TABLE 1

ANALYTICAL AND INFRARED DATA FOR BUTYLTIN(IV) MERCAPTOESTERS

Compound	Found (calcd.) (%)			ν(cm^{-1}) (main peaks)
	S	Sn	Cl	
$Bu_2Sn(IOTG)_2$ [a]	10.07	18.37	—	2975vs, 2953vs, 2890s, 1735s, 1710s, 1465s
	(10.01)	(18.59)	(—)	1373m, 1291s, 1184s, 1146s, 1122s,
$Bu_2Sn(IOTG)Cl$	6.94	24.85	7.31	2997vs, 2950vs, 2906s, 1735wk, 1677s,
	(6.80)	(25.20)	(7.54)	1466m, 1405m, 1382m, 1320s, 1196s, 1154m
$Bu_2Sn(H\beta MP)_2$ [b]	9.89	18.25	—	2949vs, 2931vs, 2862s, 1740vs, 1458m,
	(10.01)	(18.59)	(—)	1342m, 1236s, 1183s, 1169s, 1143s
$Bu_2Sn(H\beta MP)Cl$	6.74	25.13	7.66	2966vs, 2930vs, 2865s, 1742m, 1692s,
	(6.80)	(25.20)	(7.54)	1457m, 1393m, 1347m, 1273m, 1230s, 1192s, 1150m
$BuSn(IOTG)_3$	12.30	14.93	—	2978vs, 2954vs, 2896s, 1740vs, 1457m, 1376m
	(12.23)	(15.12)	(—)	1287s, 1182s, 1144s, 1123m
$BuSn(IOTG)_2Cl$	10.46	19.23	6.01	2975vs, 2950vs, 2989s, 1737s, 1666s, 1460m,
	(10.37)	(19.23)	(5.75)	1398m, 1378m, 1321s, 1288s, 1197s, 1151s,
$BuSn(IOTG)Cl_2$	7.21	26.01	15.67	2990vs, 2965vs, 2905s, 1735w, 1667vs, 1468s,
	(7.12)	(26.40)	(15.80)	1406s, 1329s, 1210s, 1156m
$BuSn(H\beta MP)_3$	12.37	15.40	—	2945vs, 2909vs, 2843s, 1736vs, 1454m, 1342m,
	(12.23)	(15.12)	(—)	1230s, 1188s, 1167s, 1142s
$BuSn(H\beta MP)_2Cl$	10.32	19.01	5.82	2990s, 2936s, 2875m, 1738s, 1686s, 1460m,
	(10.37)	(19.23)	(5.75)	1396m, 1354m, 1278m, 1239s, 1198s, 1146m
$BuSn(H\beta MP)Cl_2$	7.26	25.97	15.88	2958s, 2907s, 2863m, 1735w, 1675vs, 1460m,
	(7.12)	(26.40)	(15.80)	1400m, 1358m, 1281m, 1238s, 1196s, 1153m
$Bu_4Sn_2Cl_2O$	—	43.31	12.70	2940vs, 2871vs, 1462s, 1370m, 1154w,
	(—)	(42.96)	(12.84)	1078w, 1022w

[a] $IOTG \equiv SCH_2CO_2C_8H_{17}$. [b] $H\beta MP \equiv SCH_2CH_2CO_2C_7H_{15}$.

Experimental

The infrared spectra were recorded as neat liquids or as nujol mulls between 4000 and 670 cm^{-1} using a Perkin—Elmer model 137 Spectrometer. The determination of chlorine (by silver nitrate titration) in the presence of organotin mercaptoesters and/or free mercaptoesters is complicated by the simultaneous formation of silver salts of mercaptoesters as well as silver chloride. Samples containing chlorine and mercaptoesters were, therefore, first treated with alkaline hydrogen peroxide in order to convert the mercaptoesters to disulphides which did not interfere with the standard Volhard determination of chlorine.

Synthesis of butyltin mercaptoesters

Dibutyltin bis(isooctylthioglycolate): A solution of 40.8 g (0.2 mol) of isooctylthioglycolate in 100 ml of toluene was heated under reflux with 24.9 g (0.1 mol) of dibutyltin oxide. The solid slowly dissolved and 1.8 ml of water was collected. The solvent was then removed on a flash evaporator to leave 63.9 g (quantitative yield) of a clear colourless liquid, dibutyltin bis(isooctylthioglycolate).

Dibutyltin bis(n-heptyl-β-mercaptopropionate), butyltin tris(isooctylthioglycolate) and butyltin tris(n-heptyl-β-mercaptopropionate) were all prepared by exactly similar methods. Analytical results are presented in Table 1.

Synthesis of butyltin mercaptoester chlorides

Butyltin bis(n-heptyl-β-mercaptopropionate) chloride: 14.1 g (0.05 mol) of butyltin trichloride was added, dropwise, with stirring to 78.5 g (0.1 mol) of butyltin tris(n-heptyl-β-mercaptopropionate) over 10 min at room temperature. An exotherm was observed which suggested that reaction had occurred and the mixture represented a quantitative yield of product butyltin bis(n-heptyl-β-mercaptopropionate) chloride.

Butyltin n-heptyl-β-mercaptopropionate dichloride, butyltin isooctylthioglycolate dichloride, butyltin bis(isooctylthioglycolate) chloride, dibutyltin n-heptyl-β-mercaptopropionate chloride and dibutyltin isooctylthioglycolate chloride were all prepared by exactly similar methods.

Alternative methods for dibutyltin mercaptoester chlorides

Dibutyltin isooctylthioglycolate chloride.

(i) A solution of 30.4 g (0.1 mol) of dibutyltin dichloride in 100 ml of toluene was heated under reflux with 24.9 g (0.1 mol) of dibutyltin oxide for two hours. The solvent was removed on a flash evaporator to yield 55.3 g (quantitative yield) of a white crystalline product, $Bu_4Sn_2Cl_2O$ (dibutyltin oxychloride). 55.3 g (0.1 mol) of the oxychloride was heated with 40.8 g (0.2 mol) of isooctylthioglycolate in 100 ml of toluene. 1.8 ml of water was collected under reflux and the solvent was removed on a flash evaporator to leave 84.3 g (quantitative yield) of a colourless liquid, dibutyltin (isooctylthioglycolate) chloride. This method was also applied to the preparation of dibutyltin n-heptyl-β-mercaptopropionate chloride.

(ii) 20.4 g (0.1 mol) of isooctylthioglycolate and 30.4 g (0.1 mol) of dibutyltin dichloride were dissolved in 50 ml of toluene and treated with 8.4 g

(0.1 mol) of anhydrous sodium bicarbonate. The temperature was raised to 60°C until effervescence had ceased; sodium chloride was removed by filtration and the toluene solution was dried over anhydrous magnesium sulphate. The solvent was then removed on a flash evaporator to give 47.2 g (quantitative yield) of a colourless liquid - dibutyltin isooctylthioglycolate chloride. Attempts were made to prepare monobutyltin mercaptoester chlorides by a similar method but the water of reaction caused hydrolysis of the remaining chlorine atoms which are more reactive than the corresponding dibutyltin chlorine atom.

Results and discussion

Isooctylthioglycolate salts

Dibutyltin compounds: $Bu_2Sn(IOTG)_2$ was prepared as described in the experimental section from Bu_2SnO (dibutyltin oxide) and isooctylthioglycolate. The IR (infrared) spectrum in the carbonyl stretching region (1650 to 1750 cm^{-1}) is presented in Fig. 1a and shows two peaks at 1735 and 1710 cm^{-1} (unless otherwise stated references to IR spectra are specifically to the carbonyl stretching region).

The IR spectrum of $Bu_2Sn(IOTG)_2$ has been adequately interpreted previously by Herber and Stapfer [1] who suggested that the peak at 1710 cm^{-1} is due to a carbonyl group which is intramolecularly bound to the tin atom whilst

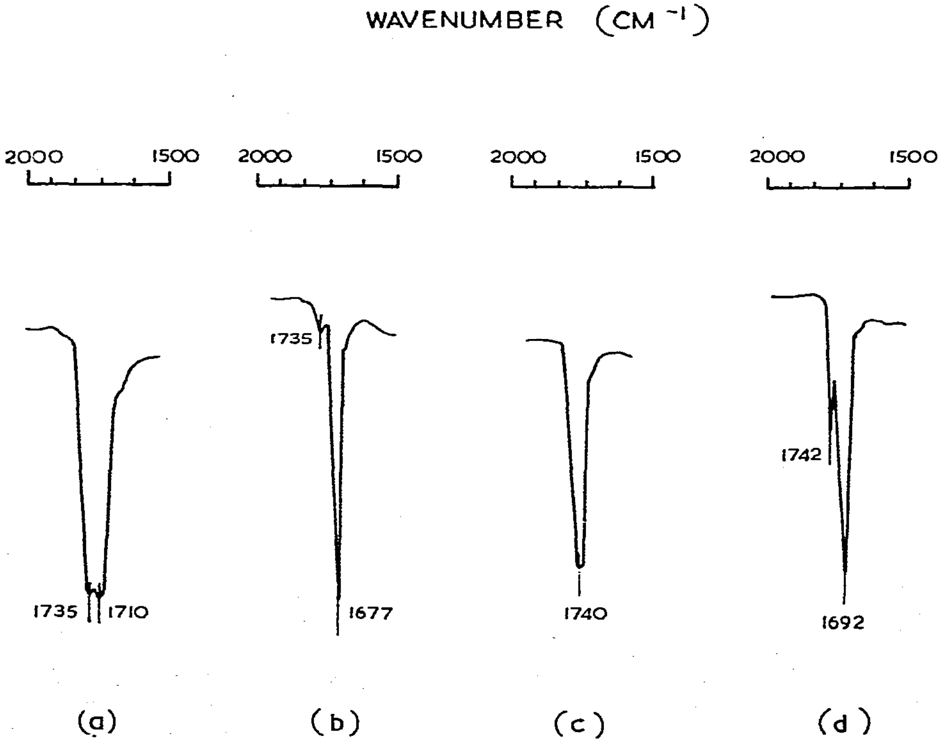
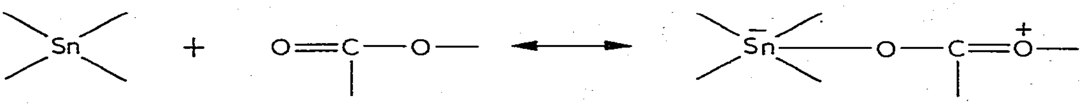


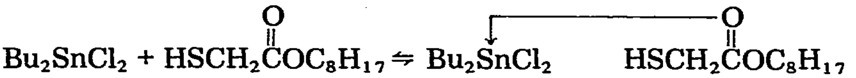
Fig. 1. The carbonyl region infrared spectra of dibutyltin mercaptoesters and dibutyltin mercaptoester chlorides: (a) $Bu_2Sn(IOTG)_2$; (b) $Bu_2SnCl(IOTG)$; (c) $Bu_2Sn(H\beta MP)_2$; (d) $Bu_2SnCl(H\beta MP)$.

the absorption peak at 1735 cm^{-1} is due to a carbonyl group which is 'free' or uncomplexed. The frequency of the coordinated carbonyl group is lower than that of the 'free' group since the bond order of the carbonyl group is lowered by the coordination viz.:



The interaction may be inter- or intramolecular in origin. Intramolecular coordination of this type is well documented for β-carbonylethyltin halides and the interaction is strong since the frequencies of the coordinated and 'free' carbonyl groups typically differ by some 70-80 cm^{-1} [2]. Intermolecular coordination can also be conveniently demonstrated since the IR spectrum of an equimolar mixture of $BuSnCl_3$ and methyl propionate ($CH_3CH_2CO_2CH_3$) shows two absorption maxima: one at 1734 cm^{-1} due to free methyl propionate, and one at 1700 cm^{-1} due to complexed molecules [3]. Dilution in a non-polar medium such as toluene causes the intensity of the higher frequency absorption to increase at the expense of the lower frequency absorption. Indeed the intramolecular interaction in $Bu_2Sn(IOTG)_2$ must be weak since the frequency difference of the two absorption maxima is relatively small (25 cm^{-1}).

In an attempt to prepare $Bu_2Sn(IOTG)_2$ from Bu_2SnCl_2 and isooctylthioglycolate via an anhydrous process Bu_2SnCl_2 (0.1 mol) and isooctylthioglycolate (0.2 mol) were stirred together at 100°C under a stream of dry N_2 for a total of nine days. The IR spectrum of the reaction mixture was monitored throughout the experiment and samples were taken intermittently and analysed for chlorine. Isooctylthioglycolate alone shows one sharp peak at 1735 cm^{-1}. The initial spectrum of the above reaction mixture also shows one absorption maximum at 1735 cm^{-1} but the peak is considerably broadened on the low frequency side and, since the chlorine content of the reaction mixture was within experimental error, equal to the theory chlorine content for a 2/1 mixture of isooctylthioglycolate and Bu_2SnCl_2 (found 9.93% calcd. 9.98%) the spectral modification must reflect intermolecular coordination as shown in eqn. 1.



$$Bu_2SnCl_2 + HSCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17} \rightleftharpoons Bu_2SnCl_2 \quad HSCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17} \qquad (1)$$

Not until two days had passed at 100°C was there a significant change in the IR spectrum of the reaction mixture whereupon a new shoulder appeared on the 1735 cm^{-1} absorption at 1680 cm^{-1} (Fig. 2b). After nine days reaction the new absorption had further increased in intensity until it was almost as intense as the original band (Fig. 2c). However, analysis of the reaction mixture at this point revealed that the chlorine content had dropped to only approximately 80% of its initial value.

When the final sample from this reaction was treated at 60°C with an amount of Na_2CO_3 just sufficient to neutralise the residual chlorine the IR spectrum reverted to that of Fig. 1a, consistent with the formation of $Bu_2Sn(IOTG)_2$.

Furthermore, we have prepared the organotin mercaptoester chloride, $Bu_2SnCl(IOTG)$, via the oxychloride [4] according to eqn. 2.

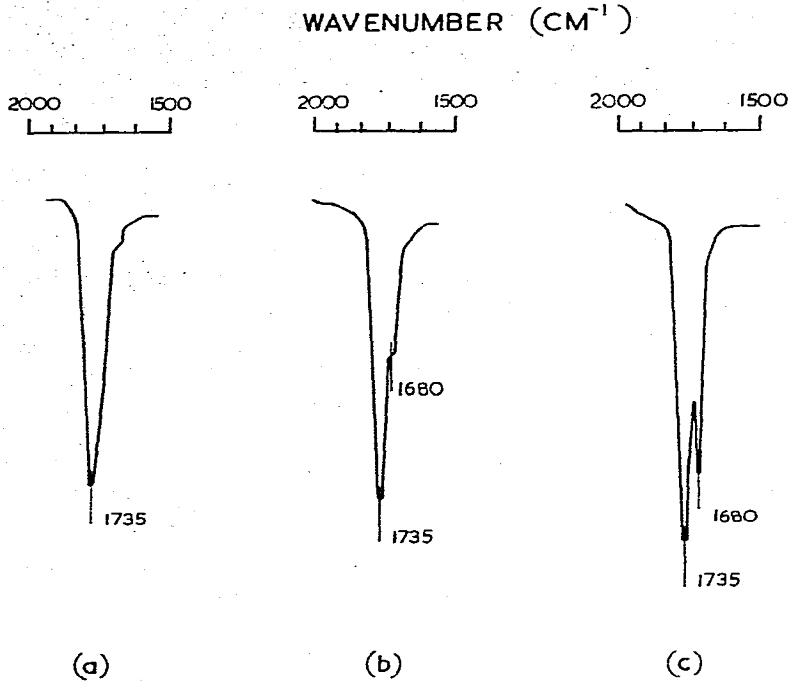
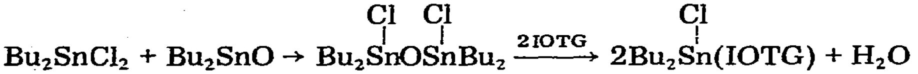


Fig. 2. The carbonyl region of the infrared spectrum of the reaction mixture of dibutyltin dichloride and two moles of isooctylthioglycolate at 100°C: (a) immediately after mixing; (b) recorded after 2 days; (c) recorded after 9 days.



$$Bu_2SnCl_2 + Bu_2SnO \rightarrow Bu_2\overset{Cl}{\overset{|}{Sn}}O\overset{Cl}{\overset{|}{Sn}}Bu_2 \xrightarrow{2\,IOTG} 2Bu_2\overset{Cl}{\overset{|}{Sn}}(IOTG) + H_2O \qquad (2)$$

The IR spectrum of $Bu_2SnCl(IOTG)$ shows one main peak at 1677 cm^{-1} and the peak is unaffected by dilution in toluene or ethereal solvents (see Table 2). The low frequency must be due to intramolecular coordination of the carbonyl group to the tin atom. We believe that the peak at 1680 cm^{-1} in the spectrum of the samples from the reaction between Bu_2SnCl_2 and two moles of isooctylthioglycolate is due to $Bu_2SnCl(IOTG)$. Indeed the results of Klemchuk's kinetic investigation of the stabilisation of PVC by Bu_2SnY_2 ($Y = SR'$, SCH_2CO_2R'', O_2CR''') [5] suggested that if Bu_2SnCl_2 was produced in the presence of Bu_2SnY_2 then a rapid equilibrium ensued to give Bu_2SnClY. Therefore, until the chlorine content of a mixture of Bu_2SnCl_2 and isooctylthioglycolate drops to less than approximately 50% of its initial value the concentration of $Bu_2Sn(IOTG)_2$ will be small and the major product will be $Bu_2SnCl(IOTG)$.

Of further interest are the synthetic possibilities of the reaction between Bu_2SnCl_2 and $Bu_2Sn(IOTG)_2$ which provides an alternative method for the preparation of $Bu_2SnCl(IOTG)$ (see experimental section). This compound can also be prepared in good yield from Bu_2SnCl_2 and one mole of isooctylthioglycolate in the presence of the requisite amount of an HCl abstractor (eg. Na_2CO_3).

$$Bu_2SnCl_2 + Bu_2Sn(IOTG)_2 \rightarrow 2Bu_2SnCl(IOTG) \qquad (3)$$

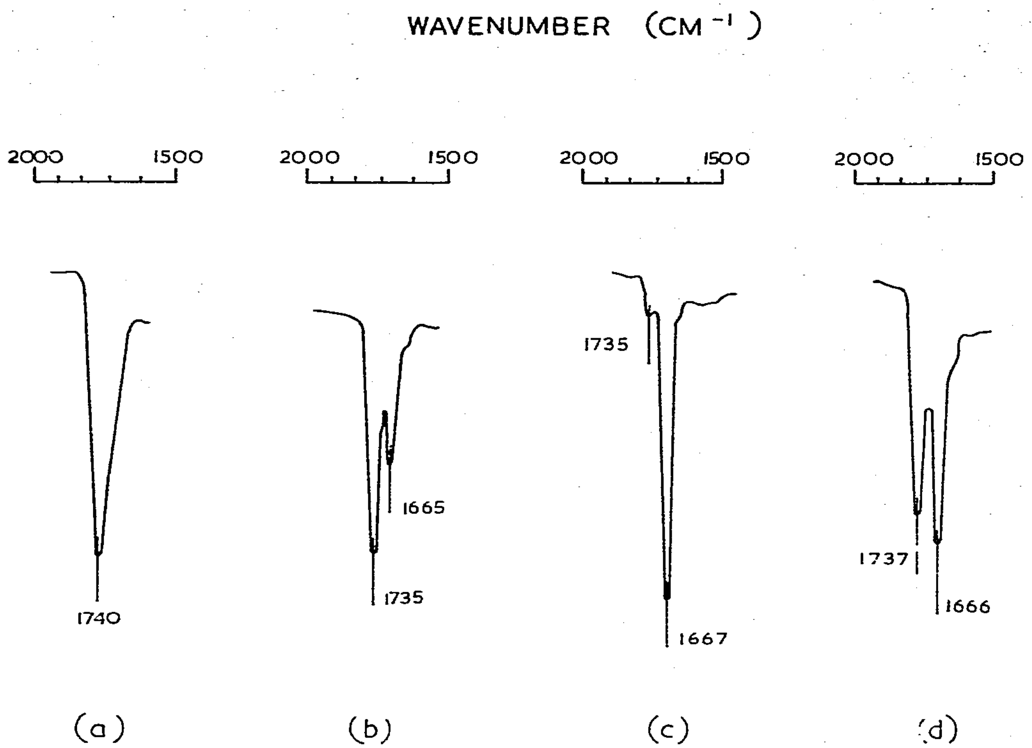
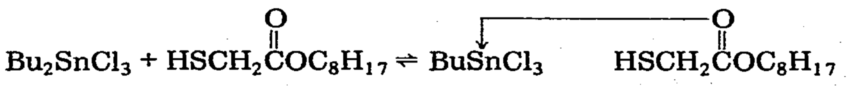


Fig. 3. The carbonyl region infrared spectra of monobutyltin isooctylthioglycolates and monobutyltin isooctylthioglycolate chlorides: (a) $BuSn(IOTG)_3$; (b) Initial mixture from the reaction between butyltin trichloride and 3 moles of isooctylthioglycolate at 95°C; (c) $BuSnCl_2(IOTG)$; (d) $BuSnCl(IOTG)_2$.

In each case the IR spectrum of the product is the same (Fig. 1b) and we believe that the occurrence of the small peak at 1735 cm^{-1} is significant. This point will be discussed later.

Monobutyltin compounds: $BuSn(IOTG)_3$ was prepared from $BuSnO_2H$ (butyltin oxide) and three moles of isooctylthioglycolate and gave the IR spectrum presented in Fig. 3a. We have again attempted to prepare $BuSn(IOTG)_3$ by an anhydrous route by stirring together $BuSnCl_3$ (0.1 mol) and isooctylthioglycolate (0.3 mol) at 95°C under a stream of dry N_2 for a total of four days. When the reagents were mixed some HCl was produced immediately suggesting that the chlorine atoms of $BuSnCl_3$ are much more reactive than those of Bu_2SnCl_2. Initially the IR spectrum showed a pronounced absorption at 1665 cm^{-1} (Fig. 3b), and since the intensity of this peak decreased when the spectrum was recorded in toluene, it must, at least in part, arise from intermolecular coordination viz.



$$Bu_2SnCl_3 + HSCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17} \rightleftharpoons BuSnCl_3 \quad HSCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17} \qquad (4)$$

After only four hours at 95°C the IR spectrum of the reaction mixture showed a strong peak at 1665 cm^{-1} although the chlorine content of the mixture was still approximately 65% of its initial value. Further heating caused little change in the spectrum and after four days the chlorine content of the mixture was still 50% of its initial theory value. As described in the experimental section we have prepared $BuSnCl_2(IOTG)$ and $BuSnCl(IOTG)_2$ from $BuSn(IOTG)_3$ and $BuSnCl_3$ according to eqns. 5 and 6.

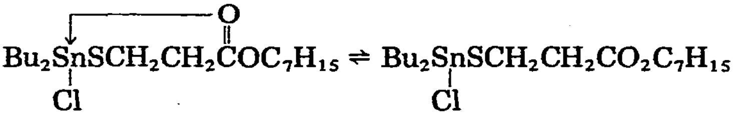
$$2BuSnCl_3 + BuSn(IOTG)_3 \rightarrow 3BuSnCl_2(IOTG) \quad (5)$$

$$BuSnCl_3 + 2BuSn(IOTG)_3 \rightarrow 3BuSnCl(IOTG)_2 \quad (6)$$

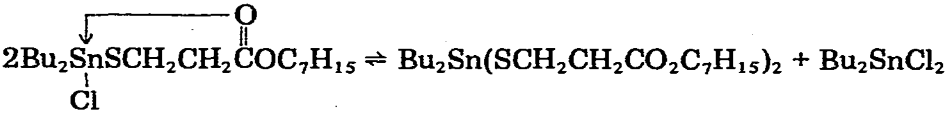
The IR spectra are presented in Figs. 3c and 3d and the spectra are insensitive to dilution in toluene or ethereal solvents. These spectra suggest that in $BuSnCl_2$-(IOTG) the carbonyl group is intramolecularly bound to the tin atom ($\nu(C{=}O) = 1667\ cm^{-1}$) whilst in $BuSnCl(IOTG)_2$ one carbonyl group is bound ($\nu(C{=}O) = 1666\ cm^{-1}$) and the other is free ($\nu(C{=}O) = 1737\ cm^{-1}$). On the basis of these observations the peak at 1665 cm^{-1} in the spectrum of the final mixture from $BuSnCl_3$ and three moles of isooctylthioglycolate must be due to either $BuSnCl_2$-(IOTG) or $BuSnCl(IOTG)_2$ or a mixture of both. Whilst the IR spectrum of $BuSnCl_2(IOTG)$ shows one peak at 1667 cm^{-1} there is again a small peak at 1735 cm^{-1}. The probable origin of this peak will be discussed in the next section which concerns n-heptyl-β-mercaptopropionate salts.

n-Heptyl-β-mercaptopropionate salts

Dibutyltin compounds: We have prepared $Bu_2Sn(H\beta MP)_2$ from Bu_2SnO and two moles of n-heptyl-β-mercaptopropionate and its IR spectrum is presented in Fig. 1c. The peak at 1740 cm^{-1} is much sharper than the absorption spectrum of $Bu_2Sn(IOTG)_2$ and presents little evidence for intramolecular coordination. We have also prepared $Bu_2SnCl(H\beta MP)$ from disproportionation of Bu_2SnCl_2 with $Bu_2Sn(H\beta MP)_2$ and via the oxychloride and n-heptyl-β-mercaptopropionate. The IR spectrum of $Bu_2SnCl(H\beta MP)$ was independent of the mode of synthesis and shows two peaks (Fig. 1d) a strong peak at 1692 cm^{-1} and a smaller but significant absorption at 1742 cm^{-1}. The spectrum was unaffected by dilution in toluene. The peak at 1742 cm^{-1} must be due to a significant fraction of uncoordinated carbonyl groups whilst the absorption at 1692 cm^{-1} must again represent intramolecularly coordinated carbonyl groups. There are two possible equilibria which might explain the origin of the uncoordinated carbonyl group: neither of which are concentration dependent.



$$Bu_2\underset{Cl}{Sn}SCH_2CH_2\overset{O}{\overset{\|}{C}}OC_7H_{15} \rightleftharpoons Bu_2\underset{Cl}{Sn}SCH_2CH_2CO_2C_7H_{15} \quad (7)$$



$$2Bu_2\underset{Cl}{Sn}SCH_2CH_2\overset{O}{\overset{\|}{C}}OC_7H_{15} \rightleftharpoons Bu_2Sn(SCH_2CH_2CO_2C_7H_{15})_2 + Bu_2SnCl_2 \quad (8)$$

Equilibrium 7 simply represents ring opening to relieve ringstrain. Equilibrium 8 represents the disproprotionation reaction for the production of $Bu_2SnCl(H\beta MP)$. The IR spectrum of $Bu_2Sn(H\beta MP)_2$ shows that its carbonyl groups are almost entirely 'free'.

TABLE 2

INFRARED DATA FOR BUTYLTIN(IV) ISOOCTYLTHIOGLYCOLATES

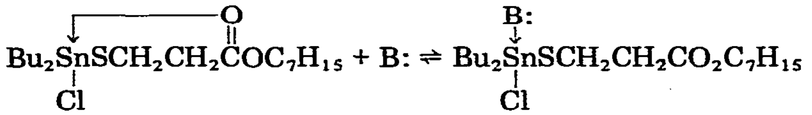
Compound	Solvent	ν(C=O) (cm^{-1}) (±3 cm^{-1})	ν(C=O→Sn) (cm^{-1}) (±3 cm^{-1})	Int. ν(C=O→Sn)/Int. ν(C=O) [a]
$Bu_2Sn(IOTG)_2$	—	1735	1710	1
$Bu_2SnCl(IOTG)$	—	1735	1677	14.5
$Bu_2SnCl(IOTG)$	Toluene	1735	1677	14.5
$Bu_2SnCl(IOTG)$	THF [b]	1735	1677	14.5
$Bu_2SnCl(IOTG)$	DME [c]	1735	1677	14.5
$BuSn(IOTG)_3$	—	1740		
$BuSnCl(IOTG)_2$	—	1737	1666	1.2
$BuSnCl(IOTG)_2$	Toluene	1737	1666	1.2
$BuSnCl(IOTG)_2$	THF	1737	1666	1.2
$BuSnCl(IOTG)_2$	DME	1737	1666	1.2
$BuSnCl_2(IOTG)$	—	1735	1667	14.0
$BuSnCl_2(IOTG)$	Toluene	1735	1667	14.0
$BuSnCl_2(IOTG)$	THF	1735	1667	14.0
$BuSnCl_2(IOTG)$	DME	1735	1667	14.0

[a] This value represents the ratio of the intensity of the intramolecularly coordinated carbonyl peak to the intensity of the 'free' carbonyl peak. [b] THF = tetrahydrofuran. [c] DME = 1,2-dimethoxyethane.

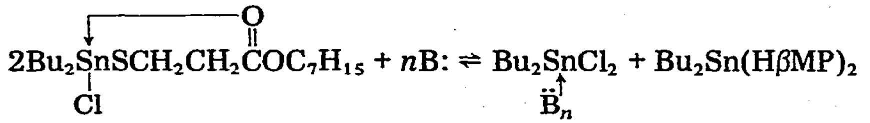
It is possible to differentiate between the two possible equilibrium since only eqn. 8 will be affected by the addition of excess Bu_2SnCl_2. Indeed when a sample of $Bu_2SnCl(H\beta MP)$ was mixed with an equimolar quantity of Bu_2SnCl_2 the peak at 1742 cm^{-1} was significantly diminished and a 4:1 molar excess of Bu_2SnCl_2 was almost sufficient to remove all the absorption at this frequency. The peak at 1742 is therefore due to $Bu_2Sn(H\beta MP)_2$ and equilibrium 8 prevails.

When the spectrum of $Bu_2SnCl(H\beta MP)$ was recorded in an ethereal solvent, (B:) the peak at 1742 cm^{-1} was significantly more intense. The results for a number of solvents are presented in Table 3, which also gives the ratio of the intensity of the absorption due to the intramolecularly coordinated carbonyl group to that of the 'free' carbonyl group (N.B. this value is presented to reflect the variation with solvent and does not represent relative numbers of the respective groups since the extinction coefficients are not known).

In order to rationalise the effect of solvents, two equilibria 9 and 10 might be suggested:



$$Bu_2\underset{Cl}{Sn}SCH_2CH_2\overset{O}{\overset{\|}{C}}OC_7H_{15} + B: \rightleftharpoons Bu_2\underset{Cl}{\overset{\overset{B:}{\downarrow}}{Sn}}SCH_2CH_2CO_2C_7H_{15} \qquad (9)$$



$$2Bu_2\underset{Cl}{Sn}SCH_2CH_2\overset{O}{\overset{\|}{C}}OC_7H_{15} + nB: \rightleftharpoons Bu_2\underset{\overset{\uparrow}{\ddot{B}_n}}{Sn}Cl_2 + Bu_2Sn(H\beta MP)_2 \qquad (10)$$

$(n = 1, 2)$

Equilibrium 9 represents carbonyl displacement by polar ether molecules. Solution of $Bu_2SnCl(H\beta MP)$ in ethereal solvents should favor the formation of $Bu_2Sn(H\beta MP)_2$ since Bu_2SnCl_2 has a greater affinity than $Bu_2SnCl(H\beta MP)$ for polar ether molecules due to its more electronegative tin atom. This process is represented by equilibrium 10. Whilst the latter equilibrium almost certainly still predominates in ethereal solvents the addition of a 9/1 excess of Bu_2SnCl_2 to a sample of $Bu_2SnCl(H\beta MP)$ in dioxan did not totally remove the absorption at 1742 cm^{-1} and hence the occurrence of equilibrium 9 can not be categorically ruled out.

Monobutyltin compounds: $BuSnCl_2(H\beta MP)$ and $BuSnCl(H\beta MP)_2$ were prepared from the appropriate quantities of $BuSn(H\beta MP)_3$ and $BuSnCl_3$ as described in the experimental section. Their IR spectra are similar to the corresponding isooctylthioglycolate salts except that the peaks at higher frequency are slightly more pronounced in the n-heptyl-β-mercaptopropionate salts and are presented in Table 3; neither spectrum is affected by dilution in toluene. When a 1 molar excess of $BuSnCl_3$ was added to a sample which was nominally $BuSnCl_2(H\beta MP)$ the higher frequency peak (1735 cm^{-1}) was diminished corresponding to a displacement of equilibrium 11 to the l.h.s.

$$\begin{array}{l} 3BuSnCl_2(H\beta MP) \rightleftharpoons BuSnCl_2(H\beta MP) + BuSnCl(H\beta MP)_2 + BuSnCl_3 \qquad (11) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 2BuSnCl_3 \overset{\upharpoonleft\downharpoonright}{+} BuSn(H\beta MP)_3 \end{array}$$

$BuSnCl(H\beta MP)_2$ is almost certainly responsible for the peak at 1735 cm^{-1} in the spectrum of $BuSnCl_2(H\beta MP)$. The above evidence suggests that species such as $BuSnCl_n(L)_{3-n}$ ($n = 1, 2$) and $Bu_2SnCl(L)$ (L = IOTG, HβMP) exist, not as pure compounds, but as mixtures in equilibrium with their respective butyltin mercaptoesters and butyltin chlorides. The n-heptyl-β-mercaptopropionate salts most noticeably show this effect but we believe that the high frequency peaks in the

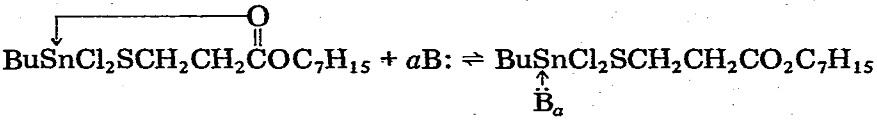
TABLE 3

INFRARED DATA FOR BUTYLTIN(IV) HEPTYL-β-MERCAPTOPROPIONATES

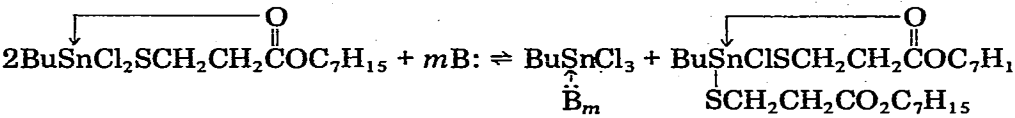
Compound	Solvent	ν(C=O) (cm^{-1}) (±3 cm^{-1})	ν(C=O→Sn) (cm^{-1}) (±3 cm^{-1})	Int. ν(C=O→Sn)/Int. ν(C=O)
$Bu_2Sn(H\beta MP)_2$	—	1740		—
$Bu_2SnCl(H\beta MP)$	—	1742	1692	2.5
$Bu_2SnCl(H\beta MP)$	Toluene	1742	1692	2.5
$Bu_2SnCl(H\beta MP)$	DME	1742	1692	1.7
$Bu_2SnCl(H\beta MP)$	Bu_2O	1741	1693	1.4
$Bu_2SnCl(H\beta MP)$	Dioxan	1739	1690	1.2
$Bu_2SnCl(H\beta MP)$	THF	1738	1690	1.1
$Bu_2SnCl(H\beta MP)$	Bu_2SnCl_2 [a]	1742	1692	4.1
$Bu_2SnCl(H\beta MP)$	Bu_2SnCl_2 [b]	1742	1692	9
$BuSn(H\beta MP)_3$	—	1736		—
$BuSnCl(H\beta MP)_2$	—	1738	1686	0.94
$BuSnCl(H\beta MP)_2$	Toluene	1738	1686	0.94
$BuSnCl(H\beta MP)_2$	DME	1739	1681	0.81
$BuSnCl(H\beta MP)_2$	THF	1740	1683	0.73
$BuSnCl_2(H\beta MP)$	—	1735	1675	5.0
$BuSnCl_2(H\beta MP)$	Toluene	1735	1675	5.0
$BuSnCl_2(H\beta MP)$	Bu_2O	1735	1676	3.1
$BuSnCl_2(H\beta MP)$	DME	1737	1674	1.7
$BuSnCl_2(H\beta MP)$	THF	1737	1675	1.4
$BuSnCl_2(H\beta MP)$	$BuSnCl_3$ [c]	1737	1675	12.0

[a] 50 mol% mixture of $Bu_2SnCl(H\beta MP)$ and Bu_2SnCl_2. [b] 20 mol% solution of $Bu_2SnCl(H\beta MP)$ in Bu_2SnCl_2.
[c] 50 mol% mixture of $BuSnCl_2(H\beta MP)$ and $BuSnCl_3$.

spectra of $\mathrm{Bu_2SnCl(IOTG)}$ and $\mathrm{BuSnCl_2(IOTG)}$ are due to low concentrations of $\mathrm{Bu_2Sn(IOTG)_2}$ and $\mathrm{BuSnCl(IOTG)_2}$ respectively. The IR spectra of both $\mathrm{BuSnCl_2(H\beta MP)}$ and $\mathrm{BuSnCl(H\beta MP)_2}$ are dramatically solvent sensitive (see Table 3) but unfortunately a rigorous interpretation of these effects is very difficult because of the greater number of species present. It is, however, envisaged that for example, in the case of $\mathrm{BuSnCl_2(H\beta MP)}$ the most prominent equilibria will be 12 and 13.



$$\mathrm{BuSnCl_2SCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OC_7H_{15}} + a\mathrm{B{:}} \rightleftharpoons \mathrm{Bu}\underset{\underset{\ddot{\mathrm{B}}_a}{\uparrow}}{\mathrm{S}}\mathrm{nCl_2SCH_2CH_2CO_2C_7H_{15}} \qquad (12)$$



$$2\mathrm{BuSnCl_2SCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OC_7H_{15}} + m\mathrm{B{:}} \rightleftharpoons \mathrm{Bu}\underset{\underset{\ddot{\mathrm{B}}_m}{\uparrow}}{\mathrm{S}}\mathrm{nCl_3} + \mathrm{Bu}\underset{\underset{\mathrm{SCH_2CH_2CO_2C_7H_{15}}}{|}}{\mathrm{S}}\mathrm{nClSCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OC_7H_{15}} \qquad (13)$$

Finally, our results suggest that anhydrous reactions between $\mathrm{Bu}_n\mathrm{SnCl}_{4-n}$ (n = 1, 2) and appropriate quantities of isooctylthioglycolate give only butyltin mercaptoester chlorides and not '*trans*' isomers of the respective butyltin mercaptoesters as suggested by Herber and Stapfer [1].

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