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ORGANOTIN CHEMISTRY

XII*. THE STRUCTURE AND REACTIONS OF SOME MONO-ORGANOTIN(IV) COMPOUNDS

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SUMMARY

The preparation, ^{119m}Sn Mössbauer spectra, and ^{119}Sn NMR spectra, of a series of mono-organotin(IV) compounds, $RSnX_3$ (X=S, Cl, or O), are reported. The organostannatranes, $RSn(OCH_2CH_2)_3N$, constitute a new family of readily accessible organotin trialkoxides.

INTRODUCTION

Mössbauer spectroscopy and tin-119 heteronuclear double magnetic resonance have supplemented the more common spectroscopic techniques in elucidating the structure of organotin(IV) compounds. Most of this work, however, has been concerned with dialkyl- and trialkyltin(IV) compounds, and the amount of information available on monoalkyltin(IV) derivatives is relatively small: a few Mössbauer parameters[2-5] and tin-119 NMR chemical shifts[6-9] have been reported, and the only X-ray investigations are those on methyltin sesquisulphide[10], and methyltin trinitrate[11].

We now report the results of studies on a variety of monoalkyltin(IV) compounds, namely (*a*) organotin sesquisulphides $(RSnS_{1.5})_4$, (*b*) organotin trichlorides, $RSnCl_3$, (*c*) organostannonic acids, $[RSn(O)OH]_n$, and (*d*) organotin trialkoxides, $RSn(OR)_3$, and organic stannatranes, $RSn(OCH_2CH_2)_3N$.

RESULTS AND DISCUSSION

(*a*). *Organotin sesquisulphides*, $(RSnS_{1.5})_4$

These compounds were prepared by treating the appropriate organotin trichloride with an aqueous solution of sodium sulphide[12,13]. They are all white powders

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[*] For part XI, see ref. 1.

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TABLE 1

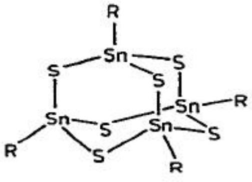
ANALYTICAL DATA AND MÖSSBAUER PARAMETERS FOR ORGANOTIN SESQUISULPHIDES

Compound	*Yield* (%)	*M.p.*[a] (°C)	*Analyses found (calcd.) (%)* C	H	S	δ (*mm/sec*)	ΔE_Q (*mm/sec*)
$(MeSnS_{1.5})_4$	95	230(d)	6.0 (6.6)	1.7 (1.7)	26.2 (26.4)	1.38	1.40
$(EtSnS_{1.5})_4$	90	Decomp.	12.4 (12.3)	2.7 (2.6)	24.7 (24.6)	1.40	1.49
$(BuSnS_{1.5})_4$	81	120[b] 230(d)	21.5 (21.5)	3.9 (4.1)	21.4[c] (21.5)	1.42	1.40
$(C_8H_{17}SnS_{1.5})_4$	86	108–128[b]	33.8 (34.3)	6.0 (6.1)	17.0 (17.2)	1.39	1.37
$(PhSnS_{1.5})_4$	99	230(d)	28.9 (29.6)	2.2 (2.1)	19.5 (19.7)	1.34	1.17
$(ClSnS_{1.5})_4$[d]						1.30	0

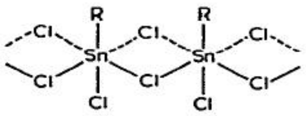
[a] Literature values: Me compound 250° (d)[12], 200° (d)[13]; Bu compound 150° (d)[12], 135–6° (d)[13]; Ph compound 255° (d)[13]. [b] Changes form from white powder to transparent glassy material. [c] Sn 52.9 (53.0%). [d] Ref. 17.

which decompose over a range of temperatures, and which are insoluble in the most common organic solvents, and this precluded studies of the tin-119 NMR spectra. The yields, analytical data, and Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters for the products where R=methyl, ethyl, n-butyl, n-octyl, and phenyl, are recorded in Table 1; n-octyltin sesquisulphide appears to be a new compound.

A recent X-ray study of methyltin sesquisulphide showed it to have an adamantane type of structure (I)[10], and the butyl compound has been reported to be tetrameric in benzene[12].



(I)



(II)

The Mössbauer parameters for the sesquisulphides are all very similar, with the phenyl compound showing slightly smaller values because of the electron withdrawal by the phenyl group. This suggests that all these compounds are isostructural with the methyl compound (I), and indeed the alkyltin sesquisulphides appear to be one of the very few classes of organotin(IV) compounds which are tetrahedral and unassociated in the solid state. The quadrupole splittings ($\Delta E_Q = 1.2$–1.5 mm/sec) are small and in accord with the range of values expected[4,14] for a tetrahedral $RSnX_3$ environment.

The polymeric phenyltin sulphide, $(Ph_2Sn_2S_3)_n$, m.p. 250°, reported by Schmidt and Schumann[15], the ethyltin sulphide, $(EtSnS_{1.5})_n$, described by Luijten[16], and also the compound stannic chloride sulphide, $Cl_2Sn_2S_3$, recently prepared by Stapfer[17] from dibutyltin sulphide and stannic chloride, probably all have the same structure (I). Data for stannic chloride sulphide are given in Table 1. The lower isomer shift when R=Cl (1.30 mm/sec) than when R=alkyl (ca. 1.4 mm/sec) is consistent with the electron-releasing character of the alkyl group, and the zero quadrupole splitting is expected for the environment $SnClS_3$ where the tin atom is surrounded by four inorganic ligands.

(*b*). *Organotin trichlorides, $RSnCl_3$*

The presence of three electron-withdrawing halogen atoms in the $RSnCl_3$ molecule would be expected to reduce the electron density at the tin and to promote an increase in co-ordination number by intermolecular association. This is supported by the IR and Raman spectra in which solid methyltin trichloride shows lower stretching and higher bending frequencies than does the pure liquid or its solutions[18–20]. Dialkyltin dichlorides and alkyltin trichlorides show a similar effect.

The Mössbauer quadrupole splitting values of the organotin trichlorides fall in the narrow range 1.8–2.0 mm/sec[2,4,21], and are rather uninformative since associated structures, such as the linear polymer (II), are expected[4] to show similar values to those of the tetrahedral unassociated $RSnCl_3$ compounds. On the other hand, the association of dimethyltin dichloride[22], and of trimethyltin chloride[23] results in a large change in the ΔE_Q values which are expected for the tetrahedral monomers.

Since most of the organotin trichlorides are liquids or soluble solids, their tin-119 NMR chemical shifts were measured to provide further information regarding the species present in solution; the results are given in Table 2.

TABLE 2

TIN-119 CHEMICAL SHIFT DATA FOR ORGANOTIN TRICHLORIDES

Compound	*Temp. (°C)*	*Conditions*	$\delta(^{119}Sn)^a$ *(ppm)*
$MeSnCl_3$[b]	25	3 mole % soln in C_6H_6	-20.03 ± 0.47
	25	8 mole % soln in C_6H_6	-16.23 ± 0.09
	25	41 mole % soln in C_6H_6	-18.73 ± 0.04
	74	Molten sample	-6.03 ± 1.2
$EtSnCl_3$	−5	Neat liq.+3 drops CH_2Cl_2[c]	-2.0 ± 1.5
	25	Neat liq.+3 drops CH_2Cl_2	-3.0 ± 2.0[d]
	50	Neat liq.+3 drops CH_2Cl_2	-2.0 ± 2.0
$BuSnCl_3$[e]	25	Neat liq.	$+1.4 \pm 0.2$
n-$C_8H_{17}SnCl_3$	25	Neat liq.	-0.5 ± 2.0
$PhSnCl_3$	25	Neat liq.	$+60.5 \pm 0.5$

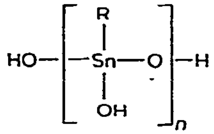
[a] Relative to tetramethyltin. [b] Lit.[9] −21 ppm (3–20% soln in C_6H_6 or $CHCl_3$). [c] CH_2Cl_2 added to prevent freezing of pure sample. [d] Lit.[24] -6.5 ± 1.2 ppm. [e] Lit.[6] $+3 \pm 1$ ppm.

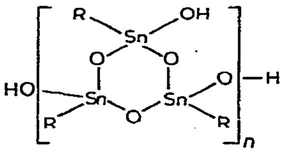
The tin-119 chemical shifts lie in the range −20 to +2 ppm with respect to tetramethyltin. As the length of the alkyl chain increases in the sequence methyl, ethyl, n-butyl, and n-octyl, the chemical shifts move slightly to higher field. Dialkyltin dichlorides behave similarly, and this may reflect the increase of shielding of the tin by the large alkyl group. The higher chemical shift of phenyltin trichloride is in accord with that of other phenyltin compounds[8].

Methyltin trichloride has been reported to be monomeric in benzene solution[3]. The chemical shift values for methyltin trichloride vary little with concentration, and those for ethyltin trichloride are independent of temperature (−5° to +55°). Intermolecular association in the alkyltin trichlorides therefore appears to be negligible in solution. Molten methyltin trichloride shows a slightly higher chemical shift, probably indicating the onset of the weak association which exists in the crystal.

(c). *Organostannonic acids*, $[RSn(O)OH]_n$

Complete hydrolysis of the alkyltin trichlorides gives the stannonic acids with the approximate compositions $[RSn(O)OH]_n$[16]. These compounds are infusible white powders, for which the polymeric structure (III) has been proposed[16,25]. The structure (IV) has been suggested for a partially dehydrated material[26]. In both (III) and (IV), the tin atoms are four-coordinate in a tetrahedral environment of the type $RSnX_3$.


(III)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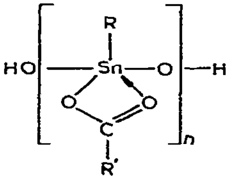

(V)

Analytical data and Mössbauer parameters for five stannonic acids are shown in Table 3.

TABLE 3

ANALYTICAL DATA AND MÖSSBAUER PARAMETERS FOR ORGANOSTANNONIC ACIDS

C H

Compound	*Analyses found (calcd.) (%)* C	*Analyses found (calcd.) (%)* H	δ (*mm/sec*)	ΔE_Q (*mm/sec*)
$[MeSn(O)OH]_n$	7.7	2.0	0.40	1.29
	(7.2)	(2.4)		
$[EtSn(O)OH]_n$	13.5	3.3	0.76	1.61
	(13.3)	(3.3)	0.70	1.70[a]
$[BuSn(O)OH]_n$	22.1	4.3	0.68	1.52
	(23.0)	(4.8)	0.70	1.65[a]
$[C_8H_{17}Sn(O)OH]_n$	35.9	6.6	0.66	1.62
	(36.2)	(6.8)		
$[PhSn(O)OH]_n$	30.9	2.8	0.78	1.83
	(31.4)	(2.6)		

[a] Ref. 27.

The low observed quadrupole splittings ($\Delta E_Q = 1.29$–1.83 mm/sec) are consistent with a tetrahedral geometry about the tin atom, but do not exclude the possibility of association. The isomer shift values ($\delta = 0.40$–0.78 mm/sec) are very small because of the low *s*-electron density at the tin resulting from electron attraction by the surrounding oxygens. The carboxylic acid derivatives of the stannonic acid, $[RSn(O)O \cdot COR']_n$, show larger quadrupole splitting values (2.00–2.64 mm/sec)[28,29], and a structure such as (V) seems most likely, in which the tin atoms occupy a trigonal bipyramidal *e.g.*, $RSnX_4$ configuration, and which would be expected[4] to show a quadrupole splitting of about 2.25 mm/sec. Infrared studies confirm the chelating nature of the carboxylate groups[28].

(*d*). *Organotin trialkoxides* $[RSn(OR')_3]$

Simple trialkyltin alkoxides, R_3SnOR', and dialkyltin dialkoxides, $R_2Sn(OR')_2$, can be prepared by treating the appropriate organotin chloride with a sodium alkoxide. The same reaction with the alkyltin trichlorides, however, gives only partial substitution even under forcing conditions, leading to a new class of compounds, the alkyltin alkoxide dichlorides, $RSn(OR')Cl_2$. These are very readily hydrolysed [probably to products of the type $RSn(OH)Cl_2$[16]], and were difficult to purify, but butyltin methoxide dichloride was obtained in a pure form. Dialkyltin alkoxide halides, $R_2Sn(OR')X$, have been prepared previously in these laboratories[30].

The only simple alkyltin trialkoxides, $RSn(OR')_3$, which have been reported were obtained by Lorberth and Kula[31] by the alcoholysis of the appropriate alkyltin tris(dialkylamide), $RSn(NR'_2)_3$. The three oxygen ligands might be expected to promote intermolecular association, and this is supported by our preliminary tin-119 NMR studies, and by the intensity of the Mössbauer spectra [*e.g.* $BuSn(OMe)_3$, δ 0.64, ΔE_Q 1.52 mm/sec].

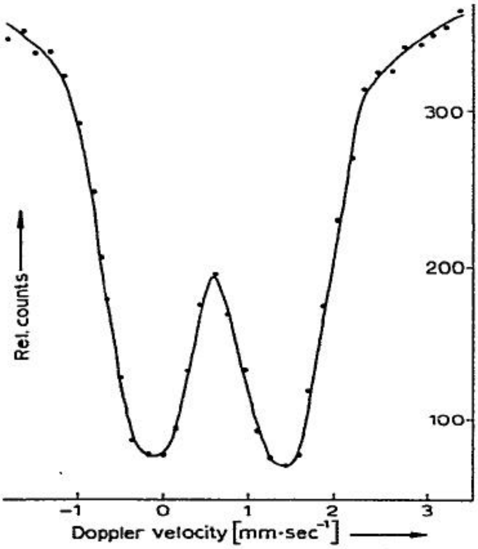


Fig. 1. Mössbauer spectrum of $BuSn(OMe)_3$.

The cyclic dialkoxides from diols can be prepared particularly easily, and, once prepared, are surprisingly hydrolytically stable. In line with this, we find that the sodium derivative of triethanolamine will react with alkyltin trichlorides to give a new class of compounds, the stannatranes, $RSn(OCH_2CH_2)_3N$ (R = Et, Bu, C_8H_{17}, and Ph).

The same compounds can be obtained by co-dehydrating equimolar amounts of the organostannonic acid and triethanolamine in toluene by azeotropic distillation.

$$[RSn(O)OH]_n + n\,(HOCH_2CH_2)_3N \rightarrow n\,RSn(OCH_2CH_2)_3N + 2n\,H_2O$$

Analytical data, and Mössbauer parameters, for these compounds are given in Table 4. Unfortunately, measurements of molecular weights or of tin-119 NMR spectra were precluded by insolubility. Some related compounds, the alkoxystannatranes, $ROSn(OCH_2CH_2)_3N$ (R = Me[32], i-Pr[33], and t-Bu[33]) have been reported in the literature.

TABLE 4

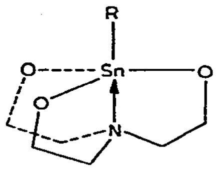
ANALYTICAL DATA AND MÖSSBAUER PARAMETERS FOR STANNATRANE COMPOUNDS

Compound	*Yield* (%)	*M.p.* (°C)	*Analyses found (calcd.)* (%)			*δ* (*mm/sec*)	*ΔE_Q* (*mm/sec*)
			C	*H*	*N*		
$EtSn(OCH_2CH_2)_3N$	41[a]	172–8(d)	32.6 (32.6)	6.6 (5.8)	4.6 (4.8)	0.76	1.92
$BuSn(OCH_2CH_2)_3N$	90[b]	158–9	37.3 (37.3)	6.7 (6.6)	4.2 (4.4)	0.79	2.00
$n\text{-}C_8H_{17}Sn(OCH_2CH_2)_3N$	85[b]	112–122	44.7 (44.5)	7.8 (7.7)	3.8 (3.7)	0.70	1.99
$PhSn(OCH_2CH_2)_3N$	79[b]	220(d)	42.4 (42.1)	5.0 (5.0)	3.3 (4.1)	0.43	1.18
$MeOSn(OCH_2CH_2)_3N$[c]	99	232–8(d)				0.22	0.54

[a] Preparation method 1. [b] Preparation method 2. [c] Data from ref. 32.

Phenylstannatrane shows a quadrupole splitting value (1.18 mm/sec) close to that of phenyltin sesquisulphide (1.17 mm/sec), and is probably similarly tetrahedral. The alkylstannatranes are less susceptible to hydrolysis, and the difference between their values of ΔE_Q (1.9–2.0 mm/sec) and that for the phenyl compound is larger than is usual when phenyl group is replaced by an alkyl group. This may indicate an increase in the coordination number in the alkyltin compounds by an intramolecular N→Sn interaction, as shown in structure (VI). Simple point charge calculations predict a quadrupole splitting for this configuration approximately equal to that for *cis*-octahedral R_2SnX_4 compounds (ca. 2.0 mm/sec [34]), in agreement with our observed values. The small splitting observed for the methoxy stannatrane is as expected from a trigonal bipyramidal SnX_5 structure (VI; R = MeO), *e.g.* Et_4NSnCl_5, $\Delta E_Q = 0.77$ mm/sec[14].

The analogous silicon compounds are similarly thought to be five-coordinate[32].


(VI) R = Et, Bu, n-C_8H_{17}

EXPERIMENTAL

Spectra

Mössbauer spectra were obtained using a constant velocity cam-driven instrument, with both absorber and $^{119m}SnO_2$ source cooled to liquid nitrogen temperature. Samples were sealed in polyethylene cells. All isomer shift (δ) values are quoted relative to SnO_2 at 77° K and are considered accurate to within ±0.08 mm/sec.

Tin-119 *chemical shifts* were determined by heteronuclear double resonance using a JEOL C-60-H instrument operating at a proton frequency of 60 MHz, and containing an extra coil within the probe. The ^{119}Sn frequency (ca. 22.37 MHz) was provided by a Schlumberger frequency synthesizer model FS30. Proton spectra were recorded in the field-sweep mode throughout.

Organotin trichlorides

Methyltin trichloride (m.p. 47°) was prepared by the Kocheshkov exchange reaction of tetramethyltin with stannic chloride in a 1/3 molar ratio. The product was purified by vacuum sublimation.

Ethyltin trichloride (b.p. 94°/13 mm) was prepared similarly from tetraethyltin and stannic chloride and purified by vacuum distillation. Butyltin trichloride (b.p. 98°/11 mm) was a gift from Albright and Wilson (Mfg.) Ltd.

Octyltin trichloride (b.p. 100°/0.2 mm) was a gift from Schering A.G.

Phenyltin trichloride (b.p. 90°/0.7 mm) was prepared from tetraphenyltin and stannic chloride.

Organotin sesquisulphides, $(RSnS_{1.5})_4$

The appropriate organotin trichloride, $RSnCl_3$ (R = Me, Et, Bu, C_8H_{17} and Ph) was slowly added to an aqueous solution containing the equivalent amount of sodium sulphide dihydrate. During the addition the mixture was stirred continuously and an off-white precipitate of the sesquisulphide was produced with the liberation of heat. The precipitate was filtered off and washed with water until the washings gave no reaction with silver nitrate solution. The product was then dried under reduced pressure at 20° for several hours.

The sesquisulphides are sparingly soluble in benzene. They are more soluble in dimethyl sulphoxide, but attempts to recrystallise the products from this solvent were unsuccessful and the sesquisulphide usually had to be reprecipitated with water. Analytical data and melting points are shown in Table 1.

Organostannonic acids, $[RSn(O)OH]_n$

Methyl-[35], ethyl-[16], butyl-[16] and octylstannonic[16] acids were prepared using literature methods.

Phenylstannonic acid was prepared by the addition of water to phenyltin trichloride. The resulting white precipitate was washed with water and dried at 120° for several hours. Analytical data for the organostannonic acids are shown in Table 3.

n-Butyltin methoxide dichloride, $BuSn(OMe)Cl_2$

Butyltin trichloride (37.9 g, 0.13 mole) was added slowly to a stirred solution of sodium methoxide (from sodium, 3.1 g, 0.3 mole, and dry methanol) in a centrifuge bottle placed inside a nitrogen-filled glove-box. A vigorous exothermic reaction occurred and a white precipitate of sodium chloride was formed. The resulting suspension was centrifuged (2000 rpm, 15 min) and the supernatant liquid decanted off into a dry flask inside the glove-box. The yield of dry sodium chloride was 7.9 g (100%).

Solvent was then removed under vacuum, leaving a white crystalline solid, which was dried at 0.1 mm for 6 h at room temperature. The crude product was recrystallised from anhydrous methanol or ether and dried *in vacuo*, leaving butyltin methoxide dichloride, m.p. 58–63° (34 g, 91%). (Found: C, 22.5; H, 4.4; Cl, 25.4. $C_5H_{12}Cl_2OSn$ calcd.: C, 21.6; H, 4.4; Cl, 25.6%.) This compound has not been reported previously in the literature.

The product is soluble in benzene, ether, methanol and, to a lesser extent, in light petroleum. It is readily hydrolysed in the atmosphere and must be handled under anhydrous conditions.

Attempts to obtain analytically pure samples of alkoxide dichlorides from the other organotin trichloride were unsuccessful due to contamination by small amounts of hydrolysis products, such as $RSn(OH)Cl_2$[16].

n-Butyltin trimethoxide, $BuSn(OMe)_3$

In a dry glove-box, anhydrous methanol (0.98 g, 0.03 mole) was added slowly to butyltin tris(dimethylamide)[36] (3.15 g, 0.01 mole) in dry benzene (15 ml). An exothermic reaction occurred and, after 30 min, all volatile material was removed at 0.1 mm, leaving the trialkoxide as a white, hydrolytically unstable solid, m.p. 140–154° (lit.[37] ca. 250°). (Found: C, 31.6; H, 6.6. $C_7H_{18}O_3Sn$ calcd.: C, 31.2; H, 6.7%.)

Organic stannatranes, $RSn(OCH_2CH_2)_3N$

Method 1. From the corresponding organostannonic acid (R = Et, Bu). Stoichiometric quantities of triethanolamine and the appropriate organostannonic acid, together with potassium hydroxide (0.1 g), were suspended in toluene and the mixture heated under a Dean and Stark separator. When the theoretical amount of water had been removed (up to 4 h), the hot solution was filtered and concentrated to a small bulk using a rotary evaporator. The stannatrane separated as a white solid, which could be recovered with difficulty from hot benzene or light petroleum as an amorphous solid.

Like the corresponding alkoxide dichlorides, the stannatranes are slowly hydrolysed on standing (especially when R = Ph), probably forming products of the type $RSn(OH)(OCH_2CH_2)_2NCH_2CH_2OH$, and separation from these products is very difficult. Melting points and analytical data are given in Table 4.

Method 2. From the corresponding trichloride (R = Et, Bu, n-C_8H_{17} and Ph). This method is somewhat quicker, and easier to use under moisture-free conditions.

Sodium methoxide solution (3 mole) was added to a methanol solution of triethanolamine (1 mole) in a nitrogen-filled glove-box, and the mixture shaken for

5 min. A solution of the appropriate organotin trichloride (1 mole) in sodium-dried benzene was then slowly added, when an exothermic reaction occurred and sodium chloride separated. The clear supernatant solution was decanted off and all volatile material removed using a rotary evaporator. The resulting impure stannatrane was dried for several hours at 0.1 mm and purified as above.

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