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Synthesis, characterisation and halogen-cleavage reactions of Ph_3SnCH_2SR (R = benzothiazole, benzoxazole, 1-methylimidazole, pyrimidine)

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Abstract

The compounds Ph_3SnCH_2SR (R = benzothiazole (bth), benzoxazole (box), *N*-methylimidazole (Meim) and pyrimidine (pym)) and $(RSCH_2)_4Sn$ have been synthesised from RSNa and Ph_3SnCH_2I or $(ICH_2)_4Sn$, respectively. Subsequent reaction of Ph_3SnCH_2SR with one equivalent of X_2 (X = Cl, Br, I) leads exclusively to cleavage of the Sn–Ph bond. The structures of $Ph_2(X)SnCH_2R$ are discussed in terms of their ^1H, ^{13}C, ^{119}Sn NMR and ^{119}Sn Mössbauer spectra.

Introduction

We have been interested in the synthesis of compounds of general formula Ph_2RSnX, in which R is a heterocycle or heterocycle-containing group. This interest is based on the fact that triorganotin compounds are of biocidal interest, and combinations with biocidally active heterocycles may lead to compounds of enhanced activity. In order to maintain any potential synergy between the metal and heterocyclic centres under hydrolytic/aerobic conditions, we have sought to link the heterocycle to tin via an Sn–C bond, rather than Sn–N, O, S linkages which are less stable under these conditions. For example, we have reported a series of derivatives of 2-mercaptoheterocycles R'_3SnSR (R = benzothiazole, benzoxazole, benzimidazole), and although certain compounds are active, they are no better than, typically, R_3SnOH, plausibly because the Sn–S bond is easily hydrolysed under environmental conditions [1]. However, direct attachment of R_3Sn to the carbon of the same or similar heterocycles leads to compounds in which the heterocycle can again be easily cleaved [2]. We have found that this reactivity can be totally mitigated when the ligand is modified to generate a $SnCH_2CH_2R$ moiety, and we have recently reported the synthesis of a series of compounds of type Ph_2RSnX, where $R = CH_2CH_2$(heterocycle) (heterocycle = 2-pyridine, 4-pyridine, pyrollidin-2-one) and X = Ph, halogen, carboxylate, dithiocarbamate [3]. For comparison with both this latter series and the derivatives of 2-mercaptoheterocycles mentioned earlier, we have prepared compounds of the type

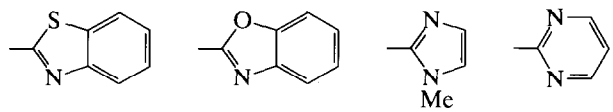
$Ph_2(X)SnCH_2SR$, where again the heterocycle R is separated by a two-atom linkage from the metal. The findings of this study are reported herein.

Previous reports on compounds of this general type are rather limited. Brassington and Poller have prepared $(RSCH_2)_4Sn$ (R = Bu, Ph) and $Bu_{4-n}Sn(CH_2SPh)_n$ ($n = 1, 2$) [4], while Wardell has reported $Ph_3SnCH_2SC_6H_4Me$-*p* [5]. More recently, the structures of $Cy_3SnCH_2SC_6H_4Cl$-*p* [6] and $Ph_2ClSn(CH_2)_3SC_6H_4Me$-*p* [7] have been determined. In addition to our own work on the biological activity of organotin derivatives of 2-mercaptoheterocycles [1], varying degrees of fungicidal activity have been noted for these species by others [8–10]. Two compounds in which the Me_3Sn moiety is bound directly to the C-5 atom of a 2,4-dialkoxy-substituted pyrimidine ring (OR = OMe, OCH_2Ph) have been reported [11].

Results and discussion

Tetraorganotin compounds of generic type Ph_3SnCH_2SR (R = benzothiazole (bth), benzoxazole (box), *N*-methylimidazole (Meim) and pyrimidine (pym)) have been synthesised by the reaction of NaSR and Ph_3SnCH_2I [12] (eq. 1):

$$Ph_3SnCH_2I + NaSR \longrightarrow NaI + Ph_3SnCH_2SR \qquad (1)$$

R = 

(1) **(2)** **(3)** **(4)**

$$(ICH_2)_4Sn + 4NaS(box) \longrightarrow 4NaI + Sn\left[CH_2S\text{-}(box)\right]_4 \qquad (2)$$

(10)

Similarly, $[(box)SCH_2]_4Sn$ has been synthesised for comparison from NaS(box) and $(ICH_2)_4Sn$ [12] (eq. 2).

In order to generate potentially active triorganotin species from **1–4**, one of the organic groups must be replaced by a conventional anion, e.g. halogen. In this respect, reaction of the tetraorganotin with X_2 (X = Cl, Br, I) results solely in the cleavage of the Sn–C(Ph) bond, with yields of product in excess of 60%. Thus, the CH_2S unit, as we have previously found for CH_2CH_2 [3], directs the reaction towards the more labile phenyl groups (eq. 3):

$$Ph_3SnCH_2SR + X_2 \longrightarrow PhX + Ph_2Sn(X)CH_2SR \qquad (3)$$

(R = bth, X = I (**5**), Br (**6**);
R = box, X = I (**7**), Br (**8**);
R = pym, X = Cl (**9**))

All the compounds reported in this study are stable under normal atmospheric conditions.

The four tetraorganotin compounds **1–4** all exhibit zero or small Mössbauer quadrupole splittings (QS: 0.00–0.49 mm s^{-1}) and ^{119}Sn NMR chemical shifts of ca. −120 ppm (Table 1). These are typical of tetrahedral species in which small

Table 1

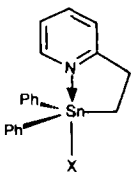
^{119}Sn NMR [a] and Mössbauer [b] spectroscopic data

Compound	$\delta(^{119}Sn)$	IS	QS	Γ [c]
1	−121.1	1.25	–	1.06
2	−118.6	1.25	0.22	0.87, 0.82
3	−126.5	1.24	–	1.12
4	−128.7	1.29	0.49	1.04, 0.92
5	−194.9	1.32	2.73	0.84, 0.83
6	−171.7	1.27	2.73	0.90, 0.85
7	−204.4	1.36	2.79	0.88, 0.88
8	−179.0	1.33	2.85	0.92, 0.92
9	−138.9	1.23	2.66	0.88, 0.85
10	−82.4	1.26	–	0.99
Ph_3SnCH_2I [d]	−121.7	1.25	–	
$(ICH_2)_4Sn$	−47.1	1.31	–	1.11
$Ph_3SnCH_2SC_6H_4Me$ [e]	−118.0	1.30	–	
Ph_3SnCH_3	−98 [f]	1.23 [g]	–	

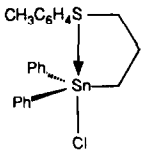
[a] Chemical shifts in ppm relative to Me_4Sn. [b] All parameters in mm s^{-1}; Isomer shift (IS) relative to $CaSnO_3$ at 78 K. [c] Full width at half-height. [d] Ref. 17. [e] Ref. 5. [f] Ref. 14. [g] Ref. 18.

differences in the Sn–CH_2 and Sn–C_6H_5 bonds may, under favourable circumstances, generate sufficient dipole at tin to produce a resolvable splitting in the Mössbauer spectra. Data for related four-coordinate species are also given in Table 1 for comparison. The four compounds also exhibit $^2J(^{117,119}Sn–^1H)$ (34–41 Hz) and $^1J(^{117,119}Sn–^{13}C)$ couplings (328–410 Hz) for the Sn–CH_2 moiety which can only reflect four-coordinate tin, though the ^2J couplings are smaller than previously noted for the related compound $Ph_3SnCH_2C_6H_4CH_3$-*p* (^2J 47.5, 50.0 Hz [5]), while the ^1J couplings are higher than others have noted for this coordination number (300–340 Hz [13]). The structure of $Cy_3SnCH_2SC_6H_4Cl$-*p* which has recently been reported [6] is a good structural model for the compounds reported here for the first time. The spectral data for $[(box)SCH_2]_4Sn$, to which compound we also assign a coordination number of four, are also comparable to those of the parent $(ICH_2)_4Sn$ (Table 1).

The four unsymmetrical triorganotin halides **5–8** all exhibit enhanced ^1J (473–529 Hz) and ^2J (60–69 Hz) couplings within the Sn–CH_2 unit, couplings which are normally associated with an Sn–C bond enriched in *s*-character, usually as part of sp^2 hybrids making up the equatorial plane of a five-coordinated, trigonal bipyramidal arrangement about tin. For example, ^1J(Sn–C) couplings for this coordination number at tin are reported to be typically 450–480 Hz [13]. An expanded coordination about the metal is also suggested by the observed upfield ^{119}Sn chemical shifts (−171 to −204 ppm) which are more shielded than similar four-coordinate systems e.g. Ph_3SnI −112.8, Me_3SnBr 128 ppm [14], though data for an appropriate mixed triorganotin halide (e.g. Ph_2MeSnX) do not appear to have been reported [14]. Intramolecular chelation by the CH_2SR group would seem the most reasonable mode for arriving at five-coordinate tin, in a manner analogous to derivatives of $Ph_2(X)SnCH_2CH_2C_5H_4N$-2 (I) [3] and $Ph_2(Cl)Sn(CH_2)_3SC_6H_4CH_3$-*p* (II) [7]. The Mössbauer QS values for the four compounds lie in the range 2.73–2.85 mm s^{-1}, slightly larger than normally associated with a four



(I)



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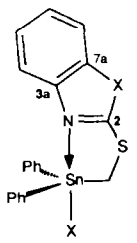
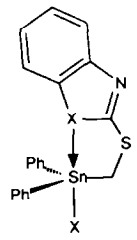


(IIIa)

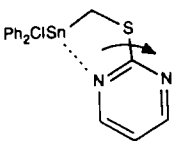


(IIIb)

coordinate tin (1.00–2.40 mm s^{-1}) but not as large a splitting as is expected for a regular *trans*-$XYSnR_2R'$ geometry (3.00–4.00 mm s^{-1}) [15]. The values observed are also less than in the structurally analogous species (I) (X = Br, I) (ca. 2.95 mm s^{-1} [3]). It would appear then that intramolecular chelation by the ligating atom of the heterocycle is weak, and that significant distortions are inherent in the coordination sphere. It is interesting to note that in $Ph_2(Cl)Sn(CH_2)_3SC_6H_4CH_3$-*p* the intramolecular S: → Sn bond is weak (319.5(4) pm), and the structure is estimated as being 63% displaced from tetrahedral to trigonal bipyramidal [7]. For comparison, the non-bonding Sn–S separation in tetrahedral $Cy_3SnCH_2C_6H_4Cl$-*p* is 326–329 pm [6].

For both bth (**5**,**6**) and box (**7**,**8**) pairs of compounds, two donor atoms are available within the heterocycle, either N (IIIa) or X (IIIb), X = S or O respectively. In principle, such situations can be distinguished by changes in the ^{13}C chemical shifts of the atoms surrounding the donor centres. In these cases, however, the three carbon atoms in question (C2, C3a, C7a, see IIIa) all appear (if at all) as very weak signals (as expected for quaternary carbon atoms), and unambiguous distinctions from the *ipso*-carbon of the Ph(Sn) moieties are not always possible, particularly since the signal from this nucleus is also weak, and ^1J(Sn–C) couplings, which could be taken as a diagnostic identifier, are not visible. To our knowledge, though, there have been no reports of chelation by S and X in the coordination chemistry of mercaptobenzoxazoles and mercaptobenzothiazoles, which can be taken as a guide to the donor capacity of X. On the other hand, chelation by S and N in such ligands is common, suggesting that in the four organotin compounds under discussion it is more likely to be the nitrogen of the heterocycle which coordinates to tin [1, and references therein].

The pyrimidine derivative **9** presents a more ambiguous set of spectral data. The ^1J(Sn–C) couplings (340.9, 348.6 Hz), as in its parent **4** (367.1, 348.6 Hz), are suggestive of a four-coordinate tin, as is the similarity in ^{119}Sn NMR chemical shift for the two species (−138.9, −128.7 ppm, respectively). In the solid state, the Mössbauer QS (2.66 mm s^{-1}) is similar to the five-coordinate compounds **5**–**8** (2.73–2.85 mm s^{-1}), though the presence of the electronegative chlorine might anyway be expected to enhance the electric field gradient within a tetrahedral geometry. The evidence here for a strong coordination between the metal and a nitrogen of the pyrimidine ring is not compelling. On the other hand, ^2J(Sn–H) for the Sn–CH_2 linkage is large (ca. 70 Hz), larger than for any of the five-coordinate halides already discussed. Moreover, while the ^1H NMR spectrum for **4** contains a



(IV)

doublet, triplet pattern for the three pyrimidine protons, as expected for a symmetrical, non-coordinating pyrimidine group, in **9** the NC-H protons adjacent to the nitrogens appear as a broad singlet. The explanation that we prefer for this collective data is that both nitrogen atoms of the heterocycle participate in turn in the bonding to tin, the two situations being interconverted via a four-coordinate species which enables the heterocycle to rotate about the S–C(heterocycle) bond (IV). This equilibrium would effectively reduce the coordination number about tin, and explain the broadened NC-H proton resonance in the ^{1}H NMR spectrum of **9**. In addition, the Mössbauer QS value would reflect a weak N: → Sn interaction, one which is maintained at the temperature of the Mössbauer experiment (78 K), but weak enough to be easily broken at room temperature, as observed in the NMR spectra.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^{1}H, ^{13}C NMR), JEOL GX400 (^{119}Sn NMR). Details of our Mössbauer spectrometer and related procedures are given elsewhere [16]. NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature. Microanalyses were carried out by the Analytical Services Unit, University of Bath.

Triphenyl(iodomethyl)tin and tetrakis(iodomethyl)tin were prepared by published methods [12]. The mercaptoheterocycles were of commercial origin (Aldrich) and were used without further purification.

Synthesis of (benzothiazolyl-2-thiomethyl)triphenyltin (1)

Sodium metal (0.21 g, 9 mmol) was dissolved in absolute ethanol (50 ml) and the solution was stirred for 15 min at room temperature.

2-Mercaptobenzothiazole (1.51 g, 9 mmol) was added in portions and the mixture was stirred for 15 min to form a pale-yellow solution. Triphenyl(iodomethyl)tin (4.41 g, 9 mmol) was added and the mixture refluxed for 12 h. After cooling, the solvent was removed *in vacuo* and the solid residue taken up in ether (50 ml). The extract was filtered to remove inorganic salts and the solvent again evaporated. Recrystallisation of the residue from ethanol yielded the product as white needles (3.43 g, 72%, m.p. 103°C). Analysis, Found (calculated for $C_{26}H_{21}NS_2Sn$): C, 58.90 (58.90); H, 3.95 (4.00); N, 2.47 (2.64)%. Selected NMR data: ^{1}H 3.09s (2H, $SnCH_2$), $^{2}J(^{117,119}Sn-^{1}H)$ 37.1, 39.4 Hz; ^{13}C 12.13 ($SnCH_2$), $^{1}J(^{117,119}Sn-^{13}C)$ 328.5, 344.2 Hz.

Also prepared by the same method were:

(Benzoxazolyl-2-thiomethyl)triphenyltin (2). Brown oil, recrystallised from petroleum ether (80–100°C) to give white florets (38%, m.p. 60°C). Analysis,

Found (calculated for $C_{26}H_{21}NOSSn$): C, 60.60 (60.73); H, 4.12 (4.12); N, 2.71 (2.72)%. Selected NMR data: ^1H 3.09s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 36.6, 38.2 Hz; ^{13}C 10.54 ($SnCH_2$), $^1J(^{117,119}Sn-^{13}C)$ 389.4, 410.7 Hz.

(1-Methylimidazolyl-2-thiomethyl)triphenyltin (3). Mixture refluxed for 24 h; product recrystallised from petroleum ether (80–100°C) as white florets (65%, m.p. 72°C). Analysis, Found (calculated for $C_{23}H_{22}N_2SSn$): C, 57.10 (57.89); H, 4.52 (4.66); N, 5.77 (5.87)%. Selected NMR data: ^1H 2.93s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 34.8, 38.0 Hz, 3.20s (2H, CH_3N); ^{13}C 20.36 ($SnCH_2$) (weak spectrum, no couplings observed), 32.88 (CH_3N).

(Pyrimidinyl-2-thiomethyl)triphenyltin (4). Mixture refluxed for 24 h; product recrystallised from petroleum ether (60–80°C) as white florets (76%, m.p. 81–82°C). Analysis, Found (calculated for $C_{23}H_{20}N_2SSn$): C, 58.60 (58.13); H, 4.19 (4.25); N, 5.80 (5.89)%. Selected NMR data: ^1H 2.83s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 39.0, 40.5 Hz, 6.70t (1H, NCC*H* pyrimidine), 8.16d (2H, NC*H* pyrimidine); ^{13}C 10.50 ($SnCH_2$), $^1J(^{117,119}Sn-^{13}C)$ 367.1, 385.1 Hz.

Tetrakis(benzoxazoyl-2-thiomethyl)tin (10). From sodium (0.13 g, 5.86 mmol), mercaptobenzoxazole (0.88 g, 5.86 mmol) and tetrakis(iodomethyl)tin (1.00 g, 1.46 mmol). Recrystallisation from petroleum ether (60–80°C) yields white florets of **10** (0.71 g, 62%, m.p. 89°C). Analysis, Found (calculated for $C_{32}H_{24}N_4O_4S_4Sn$): C, 50.10 (49.37); H, 3.31 (3.11); N, 7.06 (7.19)%. Selected NMR data: ^1H 2.74s (8H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 34.9, 37.1 Hz; ^{13}C 12.13 ($SnCH_2$), $^1J(^{117,119}Sn-^{13}C)$ 412.7, 433.8 Hz.

Synthesis of (benzothiazolyl-2-thiomethyl)diphenyltin iodide (5)

To a solution of **1** (0.60 g, 1.1 mmol) in $CHCl_3$ (20 ml) one of iodine (0.29 g, 1.1 mmol) in the same solvent (30 ml) was added during 30 min with stirring. After this period the iodine colour had disappeared. The solvent was evaporated under reduced pressure to leave a brown oil, which was recrystallised from petroleum ether (60–80°C)/ethyl acetate (10/1) as white needles (0.41 g, 64%, m.p. 166°C). Analysis, Found (calculated for $C_{20}H_{16}INS_2Sn$): C, 41.20 (41.41); H, 2.80 (2.79); N, 2.41 (2.41)%. Selected NMR data: ^1H 3.27s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 60.8, 64.1 Hz; ^{13}C 17.83 ($SnCH_2$) (weak spectrum, no couplings observed).

Also prepared by the same procedure were:

(Benzothiazolyl-2-thiomethyl)diphenyltin bromide (6). From **1** and bromine; recrystallised from petroleum ether (80–100°C) as white needles (79%, m.p. 169–170°C). Analysis, Found (calculated for $C_{20}H_{16}BrNS_2Sn$): C, 45.36 (45.06); H, 3.04 (3.03); N, 2.58 (2.63)%. Selected NMR data: ^1H 3.17 s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 64.1, 68.6 Hz; ^{13}C 16.41 ($SnCH_2$) (weak spectrum, no couplings observed).

(Benzoxazolyl-2-thiomethyl)diphenyltin iodide (7). From **2** and iodine; recrystallisation from petroleum ether (60–80°C) yielded white prisms (92%, m.p. 159°C). Analysis, Found (calculated for $C_{20}H_{16}INOSSn$): C, 42.80 (42.58); H, 2.78 (2.87); N, 2.48 (2.48)%. Selected NMR data: ^1H 3.36s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 60.2, 63.0 Hz; ^{13}C 19.64 ($SnCH_2$), $^1J(^{117,119}Sn-^{13}C)$ 473.6, 492.5 Hz.

(Benzoxazolyl-2-thiomethyl)diphenyltin bromide (8). From **2** and bromine; recrystallisation from petroleum ether (60–80°C) yields white needles (81%, m.p. 153°C). Analysis, Found (calculated for $C_{20}H_{16}BrNOSSn$): C, 46.60 (46.46); H, 3.10 (3.13); N, 2.70 (2.71)%. Selected NMR data: ^1H 3.27s (2H, $SnCH_2$), $^2J(^{117,119}Sn-^1H)$ 64.1, 67.5 Hz; ^{13}C 18.00 ($SnCH_2$), $^1J(^{117,119}Sn-^{13}C)$ 505.6, 528.6 Hz.

Synthesis of (pyrimidinyl-2-thiomethyl)diphenyltin chloride (9)

Chlorine gas was passed through CCl_4 until the solution was saturated. The concentration of Cl_2 was determined from density measurements. **4** (2.09 g, 4.4 mmol) was dissolved in CCl_4 (30 ml) and the required amount of chlorine-saturated solution added dropwise with stirring during 30 min. The precipitate was filtered off and recrystallised from petroleum ether (60–80°C) to give the product as white prisms (1.73 g, 90%, m.p. 150–151°C). Analysis, Found (calculated for $C_{17}H_{15}ClN_2SSn$): C, 47.00 (47.10); H, 3.46 (3.49); N, 6.44 (6.46)%. Selected NMR data: ^{1}H 2.94s (2H, SnCH_2), $^2J(^{117,119}Sn-^1H)$ 70.5, 72.5 Hz, 6.91t (1H, NCC*H* pyrimidine), 8.25br s (2H, NC*H* pyrimidine); ^{13}C 12.77 (Sn*C*H$_2$), $^1J(^{117,119}Sn-^{13}C)$ 340.9, 348.6 Hz.

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