

Mixed triorganotin compounds, $R_3Sn-X-SnR'_3$: ^{119}Sn NMR evidence for their formation in solution

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Abstract

^{119}Sn NMR spectroscopy has been used to demonstrate the existence, for the first time, of mixed triorganotin compounds, $R_3Sn-X-SnR'_3$, where R or $R' = Bu, Ph$ or $cyclo-C_6H_{11}$ and $X = O$ or S . These species exist in solution in equilibrium with the corresponding symmetrical species $R_3Sn-X-SnR_3$ and $R'_3Sn-X-SnR'_3$. ^{119}Sn NMR chemical shifts and $J(^{119}Sn-X-^{117/119}Sn)$ coupling constants for these compounds are reported. In some cases, significant 2nd order effects were observed in the ^{119}Sn NMR spectra of the mixed triorganotin compounds.

Introduction

Triorganotin compounds, R_3SnX , are known to possess biocidal activity [1], although the species towards which the compound is most active is very much dependent upon the nature of the organic group, R (Table 1). Such species specificity has enabled certain triorganotin compounds to gain commercial accep-

Table 1

Species specificity of triorganotin compounds, R_3SnX (ref. 2)

Species	R in most active R_3SnX compound
Insects	CH_3
Mammals	C_2H_5
Gram.-neg bacteria	$n-C_3H_7$
Gram.-pos. bacteria, fish, fungi, molluscs, plants	$n-C_4H_9$
Fish, fungi, molluscs	C_6H_5
Fish, mites	$\begin{cases} cyclo-C_6H_{11} \\ C_6H_5(CH_3)_2CCH_2 \end{cases}$

tance in a number of biocidal applications [3]. In some areas, however, a broader spectrum of activity would be beneficial, e.g. a single compound which possesses both fungicidal and acaricidal activity, and this could possibly be achieved by combining two different triorganotin moieties in the same molecule. To our knowledge, there have been no previous reports of organotin compounds of this type. In this work, however, we describe evidence, obtained by ^{119}Sn NMR spectroscopy, for the existence in solution of mixed triorganotin compounds, $\text{R}_3\text{Sn-X-SnR}'_3$, where $\text{R} = \text{Bu}$, Ph or $\text{cyclo-C}_6\text{H}_{11}$ (Cy) and $\text{X} = \text{O}$ or S .

Experimental

^{119}Sn NMR spectra were recorded on a JEOL FX60Q spectrometer at 22.24 MHz, under nuclear Overhauser suppressed conditions, and with field frequency lock to external D_2O . ^{119}Sn chemical shifts ($\delta(^{119}\text{Sn})$) are relative to Me_4Sn and are accurate to ± 0.2 ppm. Coupling constants are accurate to ± 5 Hz. All spectra were recorded with toluene solutions.

The triorganotin oxygen compounds, $(\text{Bu}_3\text{Sn})_2\text{O}$, Cy_3SnOH and Ph_3SnOH , were commercial products and were used without further purification.

The triorganotin sulphides, $(\text{R}_3\text{Sn})_2\text{S}$ ($\text{R} = \text{Bu}$, Cy , Ph) were prepared by previously published procedures [4].

The reactions were studied by mixing the appropriate mole ratio (1/1 or 1/2) of the reactants in toluene (200 cm^3) followed by heating under reflux for 2 h. Solutions were prepared such that the total Sn concentration was approximately 0.1 M. When the reactants involved hydroxides, water was removed using a Dean and Stark trap. After reflux, solutions were concentrated to approximately 25 cm^3 on a rotary evaporator, prior to NMR investigation.

Results and discussion

^{119}Sn NMR parameters for toluene solutions of the reactants and resultant reaction mixtures are given in Tables 2 and 3 respectively. From Table 2 it may be seen that ^{119}Sn chemical shifts clearly distinguish between either Bu, Ph or Cy groups attached to the Sn atom. Additionally, the ^{119}Sn NMR spectra of the symmetric oxides and sulphides, $\text{R}_3\text{Sn-X-SnR}_3$, contain as well as the main peak, satellites of approximately 4% intensity resulting from $J(^{119}\text{Sn-X-}^{117}\text{Sn})$ coupling. With regard to reactions 1–6 (Table 3) it was found that the ^{119}Sn NMR spectra

Table 2

^{119}Sn NMR parameters for the reactants

Compound	$\delta(^{119}\text{Sn})$ (ppm)	$J(^{119}\text{Sn-X-}^{117}\text{Sn})$ (Hz)
$(\text{Bu}_3\text{Sn})_2\text{O}$ (A)	82.7	458
$(\text{Bu}_3\text{Sn})_2\text{S}$ (B)	81.6	205
Cy_3SnOH (C)	1.5	—
$(\text{Cy}_3\text{Sn})_2\text{O}$ (D)	−7.6	620
$(\text{Cy}_3\text{Sn})_2\text{S}$ (E)	21.1	225
$(\text{Ph}_3\text{Sn})_2\text{O}$ (F)	−82.7	420
$(\text{Ph}_3\text{Sn})_2\text{S}$ (G)	−51.0	215

Table 3
 ^{119}Sn NMR parameters for the reaction solutions

Reaction no.	Reactants	Products present	$\delta(^{119}\text{Sn})$ (ppm)	$J(^{119}\text{Sn}-\text{X}-^{117}\text{Sn})$ (Hz)	$J(^{119}\text{Sn}-\text{X}-^{119}\text{Sn})$ (Hz)
1	A + 2C	A	82.9	458	—
		D	— 7.4	618	—
		$\text{Bu}_3\text{Sn}-\text{O}-\text{SnCy}_3$	79.9	539	563
		$\text{Bu}_3\text{Sn}-\text{O}-\text{SnPh}_3$	— 3.4	541	566
2	A + F	A	83.1	454	—
		F	— 82.8	420	—
		$\text{Bu}_3\text{Sn}-\text{O}-\text{SnPh}_3$	100.4	437	459
		$\text{Bu}_3\text{Sn}-\text{O}-\text{SnPh}_3$	— 91.2	436	459
3	2C + F	D	— 6.9	618	—
		F	— 82.7	420	—
		$\text{Cy}_3\text{Sn}-\text{O}-\text{SnPh}_3$	9.3	525	548
		$\text{Cy}_3\text{Sn}-\text{O}-\text{SnPh}_3$	— 92.6	524	548
4	B + E	B	81.2	205	—
		E	20.9	224	—
		$\text{Bu}_3\text{Sn}-\text{S}-\text{SnCy}_3$	80.0	216	227
		$\text{Bu}_3\text{Sn}-\text{S}-\text{SnCy}_3$	24.9	215	227
5	B + G	B	81.2	204	—
		G	— 51.3	214	—
		$\text{Bu}_3\text{Sn}-\text{S}-\text{SnPh}_3$	89.5	205	216
		$\text{Bu}_3\text{Sn}-\text{S}-\text{SnPh}_3$	— 49.8	205	217
6	E + G	E	21.4	226	—
		G	— 50.9	214	—
		$\text{Cy}_3\text{Sn}-\text{S}-\text{SnPh}_3$	26.3	210	—
		$\text{Cy}_3\text{Sn}-\text{S}-\text{SnPh}_3$	— 49.3	208	220
7	A + G	A	82.9	^a	—
		B	81.3	^a	—
		F	— 82.9	^a	—
		G	— 51.2	^a	—
		$\text{Bu}_3\text{Sn}-\text{O}-\text{SnPh}_3$	100.4	^a	^a
		$\text{Bu}_3\text{Sn}-\text{O}-\text{SnPh}_3$	— 91.4	^a	^a
		$\text{Bu}_3\text{Sn}-\text{S}-\text{SnPh}_3$	89.5	205	216
		$\text{Bu}_3\text{Sn}-\text{S}-\text{SnPh}_3$	— 49.8	205	214

^a Not observed.

showed four main resonances. Of these, two were attributable to the presence of the symmetric oxide or sulphide $\text{R}_3\text{Sn}-\text{X}-\text{SnR}_3$ ($\text{X} = \text{O}$ or S), by comparison with chemical shift and $J(^{119}\text{Sn}-\text{X}-^{117}\text{Sn})$ coupling parameters of the authentic compound. Thus, it is apparent that where the initial reaction involved the triorganotin hydroxide, dehydration occurs under reflux conditions to form the appropriate bis(triorganotin) oxide. In fact, it was found that dissolution of Ph_3SnOH in toluene resulted in the immediate formation of $(\text{Ph}_3\text{Sn})_2\text{O}$, as evidenced by the appearance of ^{117}Sn satellites in the ^{119}Sn NMR spectrum. With regard to the remaining two resonances in the ^{119}Sn NMR spectra of the refluxed solutions (reactions 1–6), the chemical shift information shows that these were due to different R_3Sn moieties, where R was either Bu, Ph or Cy, depending on the appropriate combination of

Table 4

Ratio of the frequency separation ($\Delta\delta$), measured at 22.24 MHz, between the two ^{119}Sn resonances for compounds $\text{R}_3\text{Sn-X-SnR}'_3$ to the $J(^{119}\text{Sn-X-}^{119}\text{Sn})$ coupling

Compound	$\Delta\delta$ (Hz) ^a	$J(^{119}\text{Sn-X-}^{119}\text{Sn})$ (Hz)	$\Delta\delta/J$
$\text{Bu}_3\text{Sn-O-SnCy}_3$	1852	566	3.3
$\text{Bu}_3\text{Sn-O-SnPh}_3$	4261	458	9.3
$\text{Cy}_3\text{Sn-O-SnPh}_3$	2266	550	4.1
$\text{Bu}_3\text{Sn-S-SnCy}_3$	1200	227	5.4
$\text{Bu}_3\text{Sn-S-SnPh}_3$	3098	216	14.3
$\text{Cy}_3\text{Sn-S-SnPh}_3$	1681	220	7.6

^a $\Delta\delta$ = chemical shift separation in ppm $\times$ 22.24.

reactants. On both of these resonances, in addition to the central feature two sets of satellites, both of approximately 4% intensity, were present, resulting from $J(^{119}\text{Sn-X-}^{117}\text{Sn})$ and $J(^{119}\text{Sn-X-}^{119}\text{Sn})$ coupling. It was further noted that the magnitudes of these couplings were, within experimental error, identical on both resonances. These observations lead to the conclusion that coupling is occurring between inequivalent Sn atoms contained in the same molecule, i.e. a species of the type $\text{R}_3\text{Sn-X-SnR}'_3$.

It should be mentioned at this point that for the $J(^{119}\text{Sn-X-}^{119}\text{Sn})$ satellites associated with the two ^{119}Sn resonances from the $\text{R}_3\text{Sn-X-SnR}'_3$ molecule, in some cases significant 2nd order effects were observed, i.e. the $J(^{119}\text{Sn-X-}^{119}\text{Sn})$

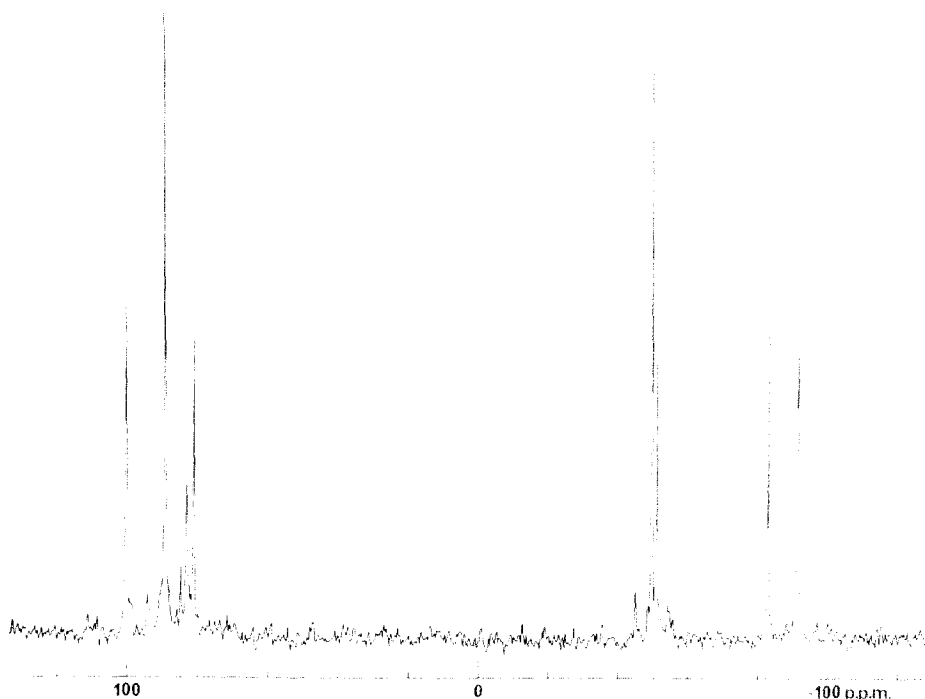


Fig. 1. ^{119}Sn NMR spectrum of the products of reaction 7.

satellites were typical of an AB system. Hence, the inner satellites showed increased intensity at the expense of the outer and the chemical shift position was not at the mid-point of the doublet but lay approximately at the 'centre-of-gravity' of the doublet. Since the ^{119}Sn NMR spectra were recorded at 22.24 MHz, the frequency separation ($\Delta\delta$) between the two resonances given by the $\text{R}_3\text{Sn-X-SnR}'_3$ compound is generally of the same order of magnitude as the $J(^{119}\text{Sn-X-}^{119}\text{Sn})$ coupling. (Table 4). Unperturbed coupling is generally observed when $\Delta\delta \gg J$. In the present investigation, the coupling shown by $\text{Bu}_3\text{Sn-O-SnCy}_3$, for which $\Delta\delta/J = 3.3$, was offset from the chemical shift position by 42 Hz, whilst even $\text{Bu}_3\text{Sn-S-SnPh}_3$ ($\Delta\delta/J = 14.3$) showed doublets offset by 2 Hz.

From these studies it is apparent that compounds of the type $\text{R}_3\text{Sn-X-SnR}'_3$ exist in solution. However, it should be remembered that the two symmetric triorganotin compounds were also present in the reaction mixture and the mole ratio of these to the mixed triorganotin species was in all cases approximately 1/1/2. Consequently, we believe that the mixed and symmetric triorganotin compounds are present in solution in equilibrium, and that the ratio reflects total scrambling of the R_3Sn moieties between O or S atoms as appropriate. In line with this, it was noted that crystallisation of $(\text{Ph}_3\text{Sn})_2\text{O}$ from the reaction solution 2 resulted in the reformation of both symmetric triorganotins at the expense of the mixed species. Since the mixed triorganotin compound exists as a result of scrambling of the R_3Sn moieties, reaction of $(\text{Bu}_3\text{Sn})_2\text{O}$ with $(\text{Ph}_3\text{Sn})_2\text{S}$ (reaction 7) was found, as expected, to yield all possible combinations of $\text{R}_3\text{Sn-X-SnR}'_3$ species, where R or R' = Bu or Ph and X = O or S (Table 3 and Fig. 1).

Conclusion

^{119}Sn NMR evidence has been obtained for the existence of mixed triorganotin compounds, $\text{R}_3\text{Sn-X-SnR}'_3$. Unfortunately, since these species are in equilibrium with their symmetrical analogues, $\text{R}_3\text{Sn-X-SnR}_3$ and $\text{R}'_3\text{Sn-X-SnR}'_3$, we believe that it is not possible to isolate the mixed triorganotin species alone.

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