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## THE STEREOCHEMISTRY OF ORGANOTIN(IV) OXINATES IN SOLUTION: TIN-119 NUCLEAR MAGNETIC RESONANCE STUDY OF TRIORGANOTIN(IV) OXINATES

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### Summary

Contrary to the previously proposed fluxional trigonal bipyramidal structure for triorganotin(IV) oxinates, the  $^{119}\text{Sn}$  NMR chemical shifts of these compounds are consistent with tetrahedral, 4 coordinate tin. No fluxional processes could be detected in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{Me}_3\text{SnOx}$  down to  $-90^\circ\text{C}$ .

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### Introduction

Although the bidentate behaviour of the oxine ligand has been well established in monoorganotin tris(oxinates) [1,2] and in diorganotin bis(oxinates) [3–5], the behaviour of oxine in triorganotin oxinates is the subject of conflicting interpretations. Triorganotin oxinates have been considered by some authors [6–9] to contain chelating oxine while others have suggested that these compounds are four-coordinate with unidentate oxine [10–12].

Tin-119 chemical shifts have been found to be sensitive to the coordination number of the tin atom; as the coordination number increases from four to five, six or seven, the tin signal is shifted by up to several hundred ppm to lower frequency [13,14]. In view of this we have studied the  $^{119}\text{Sn}$  NMR spectra of a series of triorganotin(IV) oxinates.

### Results and discussion

Triorganotin(IV) oxinates were prepared by the literature method involving reaction of triorganotin chlorides with sodium oxinate in anhydrous benzene [7]. Tribenzyltin oxinate is reported for the first time. Dimethyltin bis(oxinate) was

prepared from the reaction of dimethyltin oxide with 8-hydroxyquinoline in a ratio of 1/2 in refluxing benzene.

The  $^1\text{H}$  NMR spectra of  $\text{Me}_3\text{SnOx}$  and  $\text{Me}_2\text{Sn}(\text{Ox})_2$  ( $\text{OxH} = 8\text{-hydroxyquinoline}$ ) were in agreement with those reported [7,8]. The  $^{13}\text{C}$  NMR spectrum of  $\text{Me}_3\text{SnOx}$  showed a single peak for the methyl carbon atoms at  $\delta$  2.11 ppm ( $J(^{117,119}\text{Sn}-^{13}\text{C})$  417.7 Hz) [15] while the spectrum of  $\text{Et}_3\text{SnOx}$  showed a peak for the methyl carbon atoms at  $\delta$  10.11 ppm and a peak for methylene carbon atoms at  $\delta$  11.26 ppm ( $J(^{117,119}\text{Sn}-^{13}\text{C})$  391.0 Hz) [15]. These results are consistent with the complexes having either a static tetrahedral structure or a trigonal bipyramidal structure in which rapid interconversion of the non-equivalent alkyl groups is occurring. Kawakami and Okawara [7] have suggested that  $\text{Me}_3\text{SnOx}$  has a monomeric trigonal bipyramidal structure and that the single peak observed for the methyl protons in the  $^1\text{H}$  NMR spectrum of this compound is the result of either accidental coincidence of the two types of methyl protons or rapid interconversion of the methyl environments. Our attempts to freeze out any fluxional process by observing the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{Me}_3\text{SnOx}$  at  $-85^\circ\text{C}$  in dichloromethane were unsuccessful as the spectra were unaffected by lowering the temperature. The  $^{13}\text{C}$  NMR spectrum of  $\text{Me}_2\text{Sn}(\text{Ox})_2$  showed a peak for the methyl carbon atoms at  $\delta$  6.93 ppm ( $J(^{117,119}\text{Sn}-^{13}\text{C})$  617.8 Hz) [15].

TABLE I  
TIN-119 NMR CHEMICAL SHIFTS OF SOME ORGANOTIN COMPOUNDS

Compound	Coordination number	Solvent	$\delta(^{119}\text{Sn})^a$	Reference
$\text{Me}_3\text{SnOx}$		neat	47.8	<sup>b</sup>
		$\text{CD}_2\text{Cl}_2$	50.5	<sup>b</sup>
		$\text{CDCl}_3$	50.9	<sup>b</sup>
		$\text{C}_6\text{D}_6$	47.8	<sup>b</sup>
		$\text{CD}_3\text{OD}$	42.8 <sup>c</sup>	<sup>b</sup>
$\text{Et}_3\text{SnOx}$		$\text{CDCl}_3$	28.5	<sup>b</sup>
$\text{Pr}_3^n\text{SnOx}^d$		$\text{CDCl}_3$	34.9	<sup>b</sup>
$\text{Bu}_3^n\text{SnOx}^d$		neat	30.1	<sup>b</sup>
		$\text{CDCl}_3$	36.3	<sup>b</sup>
$\text{Bz}_3\text{SnOx}^d$		$\text{CD}_2\text{Cl}_2$	-98.2	<sup>b</sup>
$\text{Ph}_3\text{SnOx}$		$\text{CDCl}_3$	-190.5	<sup>b</sup>
$\text{Me}_2\text{Sn}(\text{Ox})_2$	6	$\text{CDCl}_3$	-235.8	<sup>b</sup>
			-237	5
$\text{Me}_3\text{SnCl}$	4	$\text{CDCl}_3$	159 - 171 <sup>e</sup>	14
$\text{Me}_3\text{SnOH}$	4	$\text{CH}_2\text{Cl}_2$	118	16
$\text{Me}_3\text{SnOPh}$	4	$\text{C}_6\text{H}_6$	131.8	17
$\text{Me}_3\text{SnCl} \cdot \text{pyridine}$	5	pyridine/ $\text{CCl}_4$	-9.5	14
$\text{Me}_3\text{SnCl} \cdot \text{DMSO}$	5	DMSO	-3	18
$\text{Me}_2\text{SnCl}_2(\text{DMSO})_2$	6	$\text{CCl}_4$	-246	18
$\text{Et}_3\text{SnCl}$	4	neat	155	19
$\text{Bu}_3^n\text{SnCl}$	4	neat	143	20
$\text{Ph}_3\text{SnCl}$	4	$\text{CH}_2\text{Cl}_2$	-48	21
$\text{Bz}_3\text{SnCl}$	4	$\text{CDCl}_3$	52	14
$\text{Bu}_3^n\text{SnOPh}$	4	neat	105	22

<sup>a</sup> In ppm downfield from external  $\text{Me}_4\text{Sn}$  (neat liquid). <sup>b</sup> This work. <sup>c</sup> Second broad signal observed at  $\delta$  65.8 ppm. <sup>d</sup> Traces of  $(\text{R}_3\text{Sn})_2\text{O}$  observed in spectrum. <sup>e</sup> Chemical shifts depends on concentration.

Tin-119 NMR data for triorganotin oxinates are given in Table 1. The  $^{119}\text{Sn}$  chemical shifts of trialkyltin oxinates occur in the range  $\delta$  50 to 28 ppm. Substitution by  $\text{Bu}^n$ ,  $\text{Pr}^n$  or Et groups for Me results in increased shielding of the tin nucleus as has been observed for other trialkyltin compounds [13,14]. The chemical shifts of  $\text{Me}_3\text{SnOx}$  and  $\text{Bu}_3\text{SnOx}$  as neat liquids do not differ significantly from those obtained in solution, suggesting that the compounds are monomeric as neat liquids as has been established for the compounds in solution by molecular weight measurements [7]. In agreement with this the mass spectrum of  $\text{Me}_3\text{SnOx}$  shows a molecular ion peak,  $m/e$  309. The chemical shift observed for  $\text{Bu}_3\text{SnOx}$  as a neat liquid agrees with the previously reported value [13,14]. The spectrum of  $\text{Me}_3\text{SnOx}$  in  $\text{CD}_3\text{OD}$  shows an additional broad resonance at  $\delta$  65.8 ppm which could be due to hydrolysis of the compound in methanol solution to give  $\text{Me}_3\text{SnOH}$ .

The chemical shifts of the trialkyltin oxinates may be best interpreted in terms of the compounds containing four coordinate tin. As is apparent from Table 1, which cites literature values of  $^{119}\text{Sn}$  chemical shifts of some organotin compounds, increasing the coordination number of tin from four to five or six results in a shift of the tin signal to lower frequency. Furthermore, substitution of Cl by groups such as OMe and OPh also results in a shift to lower frequency. Thus, the chemical shift of  $\text{Me}_3\text{SnOx}$ , if it were five coordinate, should be to lower frequency from those of the known five coordinate compounds  $\text{Me}_3\text{SnCl} \cdot \text{Py}$  and  $\text{Me}_3\text{SnCl} \cdot \text{DMSO}$ . In contrast, the chemical shift of  $\text{Me}_3\text{SnOx}$  is  $\delta$  47.8 ppm which is consistent with the compound being four coordinate. Comparison of the chemical shift of  $\text{Me}_3\text{SnOx}$  with that of the six coordinate compounds  $\text{Me}_2\text{SnOx}_2$  and  $\text{Me}_2\text{SnCl}_2(\text{DMSO})_2$  also suggests that  $\text{Me}_3\text{SnOx}$  is four coordinate.

The other trialkyltin oxinates are also most likely four coordinate as the observed shifts to lower frequency (Table 1) on replacement of the methyl groups for higher alkyl groups are consistent with that reported in the literature (e.g.  $\text{R}_3\text{SnCl}$  see Table 1).

The phenyl substituted compound,  $\text{Ph}_3\text{SnOx}$ , shows a  $^{119}\text{Sn}$  signal at  $\delta$  190 ppm which is 237 ppm to lower frequency than that observed for  $\text{Me}_3\text{SnOx}$ . The substitution of phenyl for methyl in triorganotin compounds usually results in a considerable shift of the tin signal to lower frequency by 150–250 ppm depending on the nature of the ligand, e.g. about 205 ppm for  $\text{R}_3\text{SnCl}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) (Table 1) [13,14]. The observed shielding of 237 ppm for  $\text{Ph}_3\text{SnOx}$  compared with  $\text{Me}_3\text{SnOx}$  is consistent with four coordinate tin.

The benzyl compound,  $\text{Bz}_3\text{SnOx}$ , has a chemical shift of  $\delta$  –98.2 ppm which is at lower frequency than that of  $\text{Me}_3\text{SnOx}$ , consistent with trends observed for other tribenzyl compounds [14]. The  $^1\text{H}$  NMR spectrum of  $\text{Bz}_3\text{SnOx}$  shows a singlet at  $\delta$  2.50 ppm for the methylene protons with  $^2J(^{119}\text{Sn}-^1\text{H})$  68 Hz and  $^2J(^{117}\text{Sn}-^1\text{H})$  66 Hz.

In conclusion, the  $^{119}\text{Sn}$  chemical shifts of triorganotin oxinates suggest that these compounds contain four coordinate tin with unidentate oxine and that any Sn–N interaction, if present, must be very weak.

## Experimental

The  $^{119}\text{Sn}$  NMR spectra were recorded at 149.2 MHz on the Brüker WH-400 NMR spectrometer of the South-Western Ontario NMR facility. Chemical shifts are

reported in ppm downfield from external  $\text{Me}_4\text{Sn}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra at room temperature were recorded on a Brüker WP-60 instrument at 60 and 15.1 MHz, respectively. Low temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on the Brüker WH-400 instrument at 400 and 100.6 MHz, respectively. Chemical shifts are reported downfield from  $\text{Me}_4\text{Si}$ . Mass spectra were recorded on a CH7 Varian Mat spectrometer.

Solvents were dried and distilled prior to use. Analyses were performed by Guelph Chemical Laboratories and the Department of Chemistry, University of Rajasthan. The compounds,  $\text{Me}_3\text{SnOx}$ ,  $\text{Et}_3\text{SnOx}$ ,  $\text{Pr}^n\text{SnOx}$  and  $\text{Bu}^n\text{SnOx}$  were prepared by literature methods [7] and distilled immediately prior to obtaining the spectra. Even so, the  $\text{Pr}^n$  and  $\text{Bu}^n$  compounds contained traces of trialkyltin oxides.

#### *Preparation of dimethyltin bis(oxinate)*

A mixture of dimethyltin oxide (2.56 g) and 8-hydroxyquinoline (4.56 g) in the ratio of 1/2 was heated under reflux in benzene for 4 h. Water which formed during the reaction was removed azeotropically. The remaining benzene was removed under vacuum leaving a yellow solid residue which was recrystallized from hot benzene to give yellow crystals (5.0 g, 75%) m.p. 232–234°C,  $M^+ m/e = 423$ . Found: C, 55.00; H, 3.95,  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{Sn}$  calcd.: C, 54.92; H, 4.12%.

#### *Preparation of triphenyltin oxinate*

8-Hydroxyquinoline (1.13 g) was added to a solution of sodium methoxide formed from 0.18 g sodium in methanol (25 ml).  $\text{Ph}_3\text{SnCl}$  (3 g) was then added and the reaction mixture stirred at 65°C for 2 h. The methanol was then removed in vacuo and the residue extracted with benzene and filtered. The benzene solution was then evaporated to dryness and the yellow solid obtained was recrystallized from hot, dry ethanol (Yield 2.1 g, 55%). Found: C, 65.48; H, 4.05; N, 2.86,  $\text{C}_{27}\text{H}_{21}\text{NOSn}$  calcd.: C, 65.62; H, 4.28; N, 2.84%.  $\text{Bz}_3\text{SnOx}$  was prepared similarly but was not recrystallized from ethanol. Found: C, 66.99; H, 5.15.  $\text{C}_{30}\text{H}_{27}\text{NOSn}$  calcd.: C, 67.19; H, 5.08%.

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