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Synthesis and spectroscopic studies on dibutyl-, tributyl- and triphenyltin esters of *p*-methoxy *trans*-cinnamic acid

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Abstract

One triphenyl, one tributyl, and two dibutyl esters of *p*-methoxy *trans*-cinnamic acid have been synthesized and characterized by IR, NMR (^1H, ^{13}C, ^{119}Sn) and ^{119}Sn Mössbauer spectral data. Spectroscopic data suggest that the carboxy-dibutyl distannoxane adopts a ladder structure containing five-coordinate tin atoms, while the dibutyltin bis(cinnamate) ester has a distorted six-coordinate *trans*-R_2SnO_4 structure. The tributyltin ester is a five-coordinated polymer in the solid state and is a four-coordinate monomer in solution. The corresponding triphenyltin ester is four-coordinate in the solid and in solution.

Introduction

Organotin carboxylate esters have attracted interest in studies of relationships between biocidal activity and structure [1–4]. In consequence, in recent years there has been a large increase in reports of the synthesis and structural elucidation of various organotin caboxylates, and each report has revealed a new structural possibility [5–8]. However, diorganotin esters, particularly carboxy-distannoxanes, have received comparatively little attention, and have shown different structural features [9–11]. In this paper we describe the synthesis and structural characterisation of some di- and tri-organotin esters of *p*-methoxy *trans*-cinnamic acid.

Experimental

Infrared spectra were recorded as either KBr pellets or $CHCl_3$ solutions on a Beckman IR-4220 spectrophotometer. The ^{13}C and ^{119}Sn NMR spectra were recorded on a JEOL FX 60Q spectrometer and the ^1H NMR spectra on a Perkin–Elmer

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R12B spectrometer. The chemical shifts were determined relative to internal $(CH_3)_4Si$ for ^1H and ^{13}C, and to external $(CH_3)_4Sn$ for ^{119}Sn NMR, respectively. ^{119}Sn Mössbauer spectra were obtained with a constant acceleration, microprocessor controlled spectrometer (Cryophysics Ltd., Oxford, UK); barium stannate source was used at room temperature, and samples were packed in Perspex discs and cooled to 80 K in a liquid nitrogen cryostat. Isomer shift data are relative to SnO_2.

p-Methoxy *trans*-cinnamic acid was recrystallized from ethanol (m.p. 172–173° C). The synthesis of organotin esters is illustrated by the following example.

Synthesis of μ-dioxo-tetrakis(dibutyltin p-methoxy trans-cinnamate)

Dibutyltin oxide (2.49 g, 10 mmol) was suspended in 50 ml of benzene and a solution of *p*-methoxy *trans*-cinnamic acid (1.78 g, 10 mmol) in 30 ml of benzene was added. The mixture was refluxed for 4 h and water was removed continuously by use of a Dean and Stark trap. The solvent was evaporated and the residue extracted with petroleum ether (40–60° C). Evaporation of the extract left a white solid, which was recrystallized from an ether/petroleum ether mixture.

All other compounds were recrystallized from an ether/petroleum ether mixture or dichloromethane.

Results and discussion

μ-Dioxo-tetrakis(dibutyltin *p*-methoxy *trans*-cinnamate) (I), tributyltin *p*-methoxy *trans*-cinnamate (III) and triphenyltin *p*-methoxy *trans*-cinnamate (IV) have been prepared by treatment of Bu_2SnO, $(Bu_3Sn)_2O$, or Ph_3SnOH with a one molar proportion of *p*-methoxy *trans*-cinnamic acid and dibutyltin bis[*p*-methoxy *trans*-cinnamate] (II), by reaction of dibutyltin oxide with a 2 molar proportion of the acid. Reactions were carried out in benzene with azeotropic removal of water.

Physical and analytical data for the products are given in Table 1. The white crystalline compounds are soluble in common organic solvents except petroleum ether. Cryoscopic molecular weight determinations in benzene suggest that I is dimeric and the others are monomeric.

Table 1

Physical and analytical data for organotin esters

Compound	M.p. (° C)	Analysis (Found (calc)(%))			Molecular wt. Found (calc)
		C	H	Sn	
$[\{(C_4H_9)_2SnO_2CCH{=}CHC_6H_4OCH_3\text{-}p\}_2O]_2$ (I)	140	51.41 (51.67)	6.57 (6.46)	28.62 (28.46)	1658 (1672)
$(C_4H_9)_2Sn\{O_2CCH{=}CHC_6H_4OCH_3\text{-}p\}_2$ (II)	84	57.26 (57.24)	6.18 (6.13)	20.61 (20.27)	569 (587)
$(C_4H_9)_3SnO_2CCH{=}CHC_6H_4OCH_3\text{-}p$ (III)	60	56.28 (56.53)	7.62 (7.70)	25.61 (25.48)	458 (467)
$(C_6H_5)_3SnO_2CCH{=}CHC_6H_4OCH_3\text{-}p$ (IV)	142	63.23 (63.75)	4.80 (4.55)	22.36 (22.58)	512 (527)

Table 2

Selected infrared data for organotin esters [a] (cm^{-1})

Compound	$\nu_{asym}CO_2$	$\nu_{sym}CO_2$	ν(SnOSn)	ν(Sn–C)	ν(Sn–O)
p-$CH_3OC_6H_4CH{=}CHCO_2H$	1690s	1450m	–	–	–
p-$CH_3OC_6H_4CH{=}CHCO_2Na$	1600s	1400m	–	–	–
I	1630s, 1520sh (1630s), (1535br)	1390s, 1340s (1390m), (1300br)	665s	550m	395m
II	1670s, 1590m (1670s), (1595m)	1380s, 1340m (1380s), (1355br)	–	565s	430w
III	1585m (1625s)	1410s (1375s)	–	600s	425m
IV	1620br (1620m)	1375s (1350m)	–	265w	350w

[a] Solution spectra ($CHCl_3$) in parentheses.

Infrared spectral data for the compounds are useful in comparing solid and solution state structures, and important infrared bands are shown in Table 2. Assignments of the bands associated with $\nu_{asym}(CO_2)$ mode are ambiguous owing to the presence of stretching vibrations of both C=C and the phenyl ring in the same region of the spectrum. For I the solid state spectrum shows $\nu_{asym}(CO_2)$ at 1630 cm^{-1}, a higher frequency than the corresponding band from the sodium salt of *p*-methoxy *trans*-cinnamic acid; this indicates a unidentate carboxylate group bonded to tin [12]. An additional band appears as a shoulder at 1520 cm^{-1}, suggesting the presence of a bidentate bridging carboxylate group in the compound [13]. The positions of the $\nu_{asym}CO_2$ bands are essentially unchanged for solution indicating that there is no change in structure on going from the solid state. A very sharp band at 665 cm^{-1} is characteristic of an $\overline{SnOSnO}$ ring in the compound [14,15].

The infrared spectrum of II shows two $\nu_{asym}(CO_2)$ absorptions, at 1670 and 1590 cm^{-1}. The former is assigned to a unidentate carboxylate group while the latter is associated with bidentate chelating carboxylate group [16]. The solution spectrum again shows little difference, indicating that the structure persists in solution. However, Lockhart [17] has commented on the presence of multiple $\nu(CO_2)$ stretches in the infrared spectrum of $Me_2Sn(O_2CMe)_2$ which arise from hydrolysis by moisture from the air. Since the band at 1670 cm^{-1} is at an extremely high wavenumber for a tin-carboxylate, a similar explanation may hold for II, and this would mean that only bidentate carboxylate groups are present.

In compound III, the $\nu_{asym}(CO_2)$ band is observed at 1585 cm^{-1}, suggesting a bridging bidentate nature for the carboxylate group [13,16] but in solution this band is shifted to 1625 cm^{-1}, indicating the cleavage of weak intermolecular bridges on dissolution. IV shows $\nu_{asym}(CO_2)$ frequency at 1620 cm^{-1} for solid and solution, and this is associated with a unidentate carboxylate group.

^1H NMR spectra of *p*-methoxy *trans*-cinnamic acid and related organotin esters are given in Table 3. The ^1H NMR spectra are consistent with the assumed compositions of the compounds. Chemical shift data from the ^{13}C NMR spectra are listed in Table 4, and are consistent with the suggested formulations, they are in agreement with data for other organotin esters [18,19].

The ^{119}Sn NMR spectra along with the Mössbauer spectral data (Tables 5 and 6, respectively) proved to be useful in determining the coordination number, geometry

Table 3

^{1}H NMR data for organotin esters [a]

Compound	Aromatic protons	β-CH	α-CH	-OCH_3	-$(CH_2)_3$	-CH_3
p-$CH_3OC_6H_4$=$CHCO_2H$ [b]	7.0(2H,d) 6.4(2H,d)	7.6(1H,d)	5.5(1H,d)	(3.8(3H,s)		
I	7.55(2H,d,*J* 8.6) 6.94(2H,d,*J* 8.4)	7.62(1H,d,*J* 15.7)	6.38(1H,d,*J* 15.7)	3.82(3H,s)	1.77(4H,m) 1.63(4H,m) 1.42(4H,m) (*J* 7.33)	0.93 (6H,t,*J* 6.96)
II	7.37(4H,d,*J* 8.6) 6.78(4H,d,*J* 8.79)	7.63(2H,d,*J* 15.94)	6.32(2H,d,*J* 15.93)	3.70(6H,s)	1.64(8H,m) 1.32(4H,m) (*J* 7.33)	0.81 (6H,t,*J* 7.33)
III	7.46(2H,d,*J* 8.79) 6.88(2H,d,*J* 8.8)	7.60(1H,d,*J* 15.93)	6.40(1H,d,*J* 15.9)	3.78(3H,s)	1.62(12H,m) 1.30(6H,m) (*J* 7.33)	0.92 (9H,t,*J* 7.33)
IV	7.80(7H,m) 7.41(10H,m) 6.83(2H,d,*J* 8.79)	7.40(1H,m)	6.46(1H,d,*J* 15.94)	3.70(3H,s)	–	–

[a] Shifts relative to Me_4Si (ppm); coupling constants in Hz. Data are for $CDCl_3$ solutions, unless otherwise stated. [b] DMSO-d_6 solution.

Table 4

^{13}C NMR data for organotin esters [a,b]

Compound	COO	C(1)	C(2,6)	C(3,5)	C(4)	α-C	β-C	OCH_3	C(1′)	C(2′)	C(3′)	C(4′)
I	172.75	127.56	129.35	114.13	160.87	118.9	143.03	55.10	28.34	27.63	26.72	13.55
II	176.34	126.95	129.64	114.13	161.26	114.98	145.76	55.10	26.17	26.49	25.03	13.39
III	172.23	127.59	129.25	114.04	160.81	117.38	143.33	55.04	27.56	27.73	26.88	13.45
IV [c]	195.22	128.31	128.76	114.17	161.20	115.37	145.50	55.10				

[a] Chemical shifts in ppm. [b] C(1′)–C(4′) correspond to the carbon atoms of the butyl groups. [c] Chemical shifts of the phenyl carbons in $(C_6H_5)_3Sn$ are: C_i 137.13, C_o 136.77, C_m 129.96, C_p 129.61 ppm.

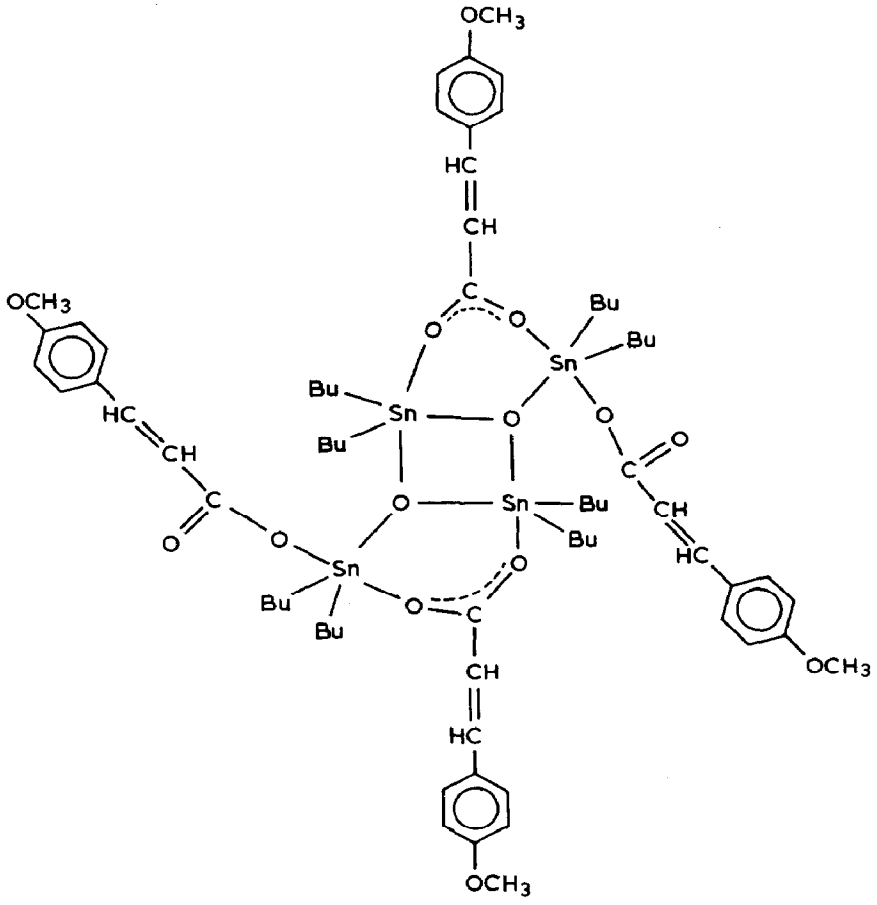
Table 5

^{119}Sn NMR data for organotin esters

Compound	Chemical shift (ppm) [a]
I	−205.1, −217.8
II	−154.6
III	104.7
IV	−116.9

[a] Relative to Me_4Sn.

and stereochemistry about the tin atom. The ^{119}Sn NMR spectrum of I shows two signals, at −205.1 and −217.8 ppm, owing to the presence of two non-equivalent tin sites, the ^{119}Sn NMR chemical shifts (−202.2 and −218.4) of the analogous 1,3-diacetoxy-tetrabutyldistannoxane [20] are in good agreement with those reported here. These signals show chemical shifts in the region associated with five-coordinate tin, supporting the ladder structure for the distannoxane shown below [20]:



(I)

μ-dioxo-tetrakis (dibutyltin *p*-methoxy *trans*-cinnamate)

Table 6

^{119}Sn Mössbauer spectroscopic data (80 K) for organotin esters [a]

Compound	*IS* [b]	*QS* [c]	Γ_1	Γ_2	ρ
I	1.26	3.26	0.99	0.99	2.58
II	1.35	3.32	0.90	0.95	2.46
III	1.44	3.54	1.01	1.03	2.45
IV	1.21	2.44	1.00	0.98	2.01

[a] All values in mm s^{-1}. [b] ±0.02 mm s^{-1}. [c] ±0.04 mm s^{-1}.

The ^{119}Sn Mössbauer quadrupole splitting (*QS*) parameter (3.26 mm s^{-1}) in distannoxane (I) is consistent with the presence of two tin atoms having trigonal bipyramidal geometry with *cis*-SnR_2O_3 stereochemisty [21].

Diorganotin(IV) carboxylates represent five-coordinate tin compounds that have chemical shifts varying from −110.5 to −161.1 ppm [18]. The ^{119}Sn NMR spectrum of II shows a peak at −154.6 ppm which is assignable to five coordinate tin. At the same time, the quadrupole splitting in diorganotin compounds is a function of the coordination environment at tin, but often fails to provide unequivocal evidence for coordination number at the metal since it is largely determined by the C–Sn–C angle irrespective of coordination number. Thus, distorted five- or six-coordinated tin species can often exhibit similar Mössbauer spectra. Using the model of Sham and Bancroft [22], we calculate the C–Sn–C angle in II to be ca. 137°; this is close to the calculated equivalent angle in $Me_2Sn(O_2CCH_3)_2$ (140°; [17]), which is believed to be a distorted *trans*-R_2SnO_4 octahedron at tin. Such a structure is most likely for II, the relatively low ^{119}Sn NMR chemical shift value for a six-coordinated tin atom reflecting the anisobidentate nature of the chelating carboxylate groups.

Compound III shows a ^{119}Sn NMR signal at 104.7 ppm. Holoček et al. [19] have suggested that chemical shifts for four-coordinate tin compounds fall between 40 and −120 ppm. The Mössbauer spectrum of III shows a quadrupole splitting value of 3.54 mm s^{-1}. Recently Holmes et al. [7] have shown that the quadrupole splitting parameter falls in the range 2.30–2.55 mm s^{-1} for monomeric triorganotin esters having trigonal bipyramidal geometry and a chelating bidentate carboxylate group, while those having five coordinate chain structures formed by bridging carboxylate groups give quadrupole splitting parameters in the range 3.59–3.70 mm s^{-1}. The *QS* value of 3.54 mm s^{-1} for III is consistent with a five-coordinate tin with *trans*-O_2SnR_3 stereochemistry having a weakly bridged chain polymeric structure. The solution state ^{119}Sn NMR data thus reflects a breakdown of the coordination polymer into its constituent monomeric fragments, common behaviour with this type of compound.

The ^{119}Sn chemical shift of IV (−116.9 ppm) is consistent with reported values −96.2 to −124.5 ppm for a series of triphenyltin-substituted benzoates [6], which have been judged to contain four-coordinate tin. This assignment is corroborated by the relatively small Mössbauer *QS* (2.44 mm s^{-1}) and $\rho < 2.1$ ($\rho = IS/QS$ [23]), which is also similar to those data for the triphenyltin benzoates [6].

Conclusion

We conclude that I is a carboxy-distannoxane having a ladder structure, with two five-coordinated tin atoms bonded via two bridging carboxylate groups and two

unidentate carboxylate groups. The solid state structure is retained in solution. II is a *trans*-R_2SnO_4 octahedron, with a very distorted geometry arising from weakly chelating carboxylate ligands, again the structure is unaltered in the solution. III is a five-coordinate *trans*-R_3SnO_2 polymeric chain structure with weak intermolecular bridges through the oxygen of carboxylate groups; these bridges are cleaved in solution, and the resulting monomer contains four-coordinate tin. IV is a four-coordinate monomer in the solid and in solution, with a unidentate carboxylate group.

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