Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

TIN–OXYGEN–PHOSPHORUS COMPOUNDS

R. E. RIDENOUR AND E. E. FLAGG
Chemicals Laboratory, The Dow Chemical Company, Midland, Michigan 48640 (U.S.A.)

(Received September 19th, 1968)

SUMMARY

Four types of tin–oxygen–phosphorus compounds are described and characterized. All of the compounds are oligomeric and incorporate either phosphinato or phosphonato bridging. Physical data are consistent with 5-coordinate tin for triorganotin diorganophosphinates, (I); both 4- and 5-coordinate tin for bis(triorganotin) organophosphonates, (II); 5-coordinate tin for poly(diorganotin organophosphonates), (III); and 6-coordinate tin for diorganotin bis(diorganophosphinates), (IV). Structures are proposed on the basis of molecularity, infrared, NMR, and Mössbauer data.

INTRODUCTION

Recent publications[1–5] attest to the current interest in tin–oxygen–phosphorus compounds. This interest is attributable in part to the successful characterization of other organotin oxo-bridging compounds[6–9] and the rapidly expanding field of metal–oxygen–phosphorus polymers[10–17]. Two factors enhance the interest in Sn–O–P compounds: (1) the expansion of the inner coordination sphere of tin by utilizing *d* orbitals; and (2) the ability of phosphoryl (P=O) moieties to form stable bridge bonds. This paper describes the preparation and properties of four distinct types of Sn–O–P compounds: $R_3SnOP(O)R'_2$, (I); $(R_3SnO)_2P(O)R'$, (II); $[-R_2SnO(R')P(O)O-]_n$, (III); and $R_2Sn[OP(O)R'_2]_2$, (IV). Organotin hydrides and either phosphinic or phosphonic acids reacted in stoichiometric ratios of 1/1 or 2/1 to give the desired products and hydrogen.

EXPERIMENTAL

Elemental analyses were performed in our laboratories. Molecular weights were obtained using either a Mechrolab Model 501 membrane osmometer or by using a differential ebulliometer with thermopiles reproducible to 0.005°. Infrared spectra were obtained on a Beckman IR 9 or IR 11. Fluorolube mulls were used for the 3800–1330 cm^{-1} region; Nujol mulls were used below 1330 cm^{-1}. Raman spectra were run on a Perkin–Elmer Model LR1 modified to use a Spectrophysics Model 125 He/Ne continuous gas laser. Nuclear magnetic resonance spectra were obtained on an instrument described by Baker and Burd[18]. The instrumentation

TABLE I

PROPERTIES AND ANALYSES OF TIN–OXYGEN–PHOSPHORUS COMPOUNDS

Type-number	Compound[a]	Analyses, found (calcd.) (%) C	H	P	Sn	M.p.[b] (°C)	Molecularity[c] d.p.	Solubility[d]
(I-1)	$(CH_3)_3SnOP(O)(CH_3)_2$	23.58 (23.65)	5.89 (5.93)	12.06 (11.74)	46.21 (45.85)	120	4.6[e]	A, Ar, Et
(I-2)	$(C_4H_9)_3SnOP(O)(CH_3)_2$	44.30 (43.90)	8.68 (8.69)	8.02 (8.08)	30.65 (30.98)	Liq.	6.6	A, Ar, Et
(I-3)	$(C_4H_9)_3SnOP(O)(C_6H_{13})_2$	54.35 (55.08)	9.77 (10.21)	5.96 (5.92)	22.55 (22.68)	Liq.	3.6	A, Ar, Et
(I-4)	$(C_4H_9)_3SnOP(O)(C_6H_5)_2$	56.85 (56.60)	7.42 (7.71)	6.08 (6.08)	23.20 (23.30)	220	1.8	Ar,
(I-5)	$(C_6H_5)_3SnOP(O)(CH_2C_6H_5)_2$	63.40 (64.60)	4.66 (4.91)	19.90 (19.90)	5.26 (5.20)	Inf.	3.2[f]	Ar
(II-6)	$[(C_4H_9)_3SnO]_2P(O)(CH_3)$	44.60 (44.55)	8.54 (8.52)	4.75 (4.59)	34.85 (35.21)	Liq.	4.0	A, Ar, Et
(II-7)	$[(C_4H_9)_3SnO]_2P(O)(C_8H_{17})$	49.90 (49.77)	9.34 (9.27)	4.18 (4.01)	30.50 (30.74)	Liq.	2.6[g]	A, Ar, Et
(II-8)	$[(C_4H_9)_3SnO]_2P(O)(CH_2C_6H_5)$	49.70 (49.63)	8.10 (8.20)	4.15 (4.13)	31.45 (31.64)	Liq.	2.7	A, Ar, Et
(III-9)	$-(C_4H_9)_2SnOP(O)(C_6H_{13})O-$	42.20 (42.35)	7.79 (7.87)	7.85 (7.80)	29.80 (29.89)	310	37[12][h]	A, Ar, Et
(III-10)	$-(C_4H_9)_2SnOP(O)(CH_2C_6H_5)O-$	44.40 (44.70)	6.12 (6.25)	7.70 (7.68)	29.27 (29.44)	290	20.8[10][i]	Ar
(III-11)	$-(C_4H_9)_2SnOP(O)(C_8H_{17})O-$	43.37 (45.20)	7.89 (8.29)	7.60 (7.28)	28.50 (27.91)	290	8[5][i]	A, Ar, Et
(IV-12)	$(C_4H_9)_2Sn[OP(O)(C_5H_{11})_2]_2$	52.30 (52.27)	9.58 (9.74)	9.40 (9.63)	18.36 (18.45)	310	1.9	A, Ar, Et
(IV-13)	$(C_4H_9)_2Sn[OP(O)(C_6H_{13})_2]_2$	54.05 (54.94)	9.84 (10.08)	8.75 (8.85)	16.75 (16.96)	250	2.0	A, Ar, Et
(IV-14)	$(C_4H_9)_2Sn[OP(O)(C_6H_{13})(CH_2C_6H_5)]_2$	57.50 (57.40)	8.10 (8.22)	8.50 (8.71)	16.62 (16.68)	230	1.9	Ar

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[a] Formula for monomer or repeating unit. All alkyl groups are unbranched. [b] Liq., liquid; Inf., infusible. Glass phases were observed during melting. Liquids decomposed before boiling. [c] Multiples of the monomer or repeating unit; d.p. (degree of polymerization or association). Conc. range: 0.02–0.005 g/cc. [d] A, alkanes; Ar, aromatics; Et, ethers. [e] Ebulliometric in benzene unless indicated otherwise. [f] Ebulliometric mol. wts. were the same in benzene and tetrahydrofuran (THF). [g] Some concentration dependency was observed in THF [*i.e.*, 0.0185 g/cc (1990, d.p., 2.6); 0.00924 (1230, d.p., 1.6)]. [h] Osmometric mol. wt. in THF reported first; brackets indicate ebulliometric mol. wt. in benzene. [i] Osmometric mol. wt. in toluene and ebulliometric mol. wt. in benzene.

used to obtain the Mössbauer spectra has been described by Ruegg *et al.*[19]. The spectrometer utilized an approximately 7 MHz ^{119}Sn source in a Pd matrix (nominally Pd_3Sn), with a constant acceleration mode and the data were accumulated by a Nuclear Data 180 FM 512 Channel scaler. The samples were scanned at liquid nitrogen temperature. Thermogravimetric analyses (TGA) were performed on a quartz spring thermo-balance. A heating rate of 10°/min was used with either nitrogen or air.

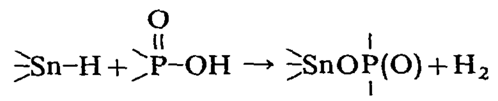
Phosphinic and phosphonic acids were prepared by known procedures[15,20]. The acids were purified by repeated recrystallization from appropriate organic solvents. Organotin hydrides were prepared by reacting organotin halides with lithium aluminum hydride, and isolating the products by careful distillation[21]. Fresh distillate was always used in the tin–oxygen–phosphorus reaction.

All solvents were distilled over sodium or metal hydrides, and stored under anhydrous conditions. Stoichiometric ratios of reactants were dissolved in suitable solvents, usually tetrahydrofuran or cyclohexane, and mixed in an inert atmosphere dry box at ambient temperature. The solutions were heated approximately 12 to 24 h under refluxing solvent and a stream of high purity nitrogen.

The preparation of tri-n-butyltin di-n-hexylphosphinate (Type I) is the only example given because of the similarity of the reactions. Tri-n-butyltin hydride (5.9414 g, 0.02041 mole) was placed in a one-liter flask containing 500 ml of cyclohexane and di-n-hexylphosphinic acid (4.7825 g, 0.02041 mole) was added. A slow evolution of hydrogen was observed immediately after the acid addition. The reaction flask was removed from the dry box, attached to a reflux condenser with a dry nitrogen source, then heated under refluxing solvent for 16 h. The nonsolvated product, a viscous liquid, was isolated by removing the solvent under reduced pressure. Analytical data are reported in Table 1 for all of the products.

RESULTS AND DISCUSSION

Organotin hydrides reacted to completion with either phosphinic or phosphonic acids to form Sn–O–P bonds exclusively; *i.e.**, no tin–tin bonds were observed[22]. The reaction has the obvious advantage of giving a gaseous by-product,



$$\geqslant\mathrm{Sn{-}H} + {>}\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{{-}OH} \rightarrow \geqslant\mathrm{SnO}\overset{|}{\underset{|}{\mathrm{P}}}\mathrm{(O)} + \mathrm{H_2}$$

and virtually pure materials in quantitative yields. Types (I) and (IV) may be classified as organotin derivatives of phosphinic acids; similarly, Types (II) and (III) are derivatives of phosphonic acids. Such classifications are misleading because the structures of the molecules obviously depend upon the number of primary and coordinate covalent bonds (*i.e.*, phosphoryl moieties) per tin atom. Table 1 indicates that physical properties depend upon the type of compound and the organic substituents. It should be noted that viscous liquids are observed for Types (I) and (II) when the alkyl content is high and the oxygen content is low.

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* Tin–tin bond formation was reported[22] for the 1/1 mole reaction of an organotin dihydride and a carboxylic acid.

Without exception, compounds of all types exhibit good hydrolytic stability. Compounds (I-3), (II-7), (III-11), and (IV-13) give no detectable signs of hydrolysis after immersion in boiling water for 72 hours. The compounds are normally insoluble in aqueous solution and resistant to attack by acids and bases. The organic substituents apparently shield the intersphere coordinate sites of tin from attack; the Sn–C and P–C bonds are relatively nonpolar, and evidence will be presented for extensive intersphere bonding by the phosphoryl moieties. As expected, the compounds are soluble in most organic solvents, especially when the number and chain length of alkyl groups are large.

The thermal stabilities are lower than those reported for most metal–oxygen–phosphorus compounds[11–17]. Thermogravimetric curves indicate that decomposition begins between 210° and 300° in either air or nitrogen. Two distinct breaks are usually observed in the TGA curve (Fig. 1). The first break is characteristic of the organotin moieties rather than the type of compound; therefore, this break is assigned to the rupture of the tin–carbon bond. The relative stabilities of the organotin moieties are phenyltin > n-butyltin > methyltin. The second break is more difficult to characterize but a similar correlation is observed for the phosphorus substituents. In general, the thermal stabilities are consistent with resonance interaction between the phenyl–tin bonds[23] and the relative bond energies[24] of tin–carbon, tin–oxygen, phosphorus–carbon, and phosphorus–oxygen bonds*. Preliminary attempts to observe the cracking patterns by mass spectrometry gave ambiguous results because of instrumental difficulties.

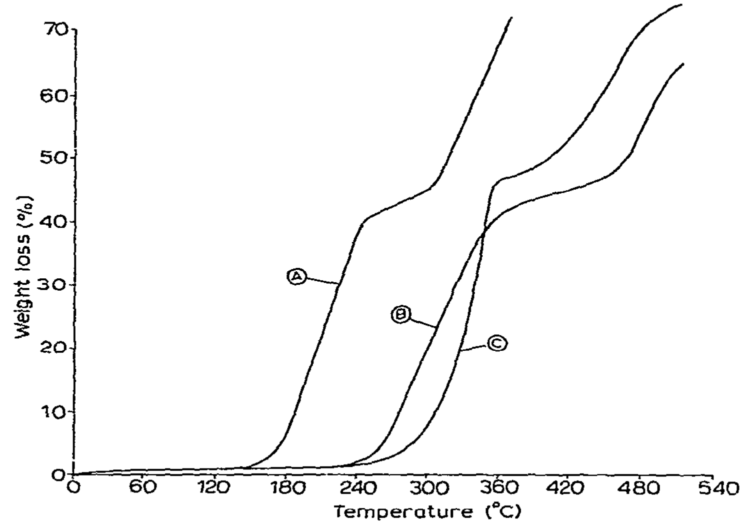

Fig. 1. Typical thermogravimetric analysis curves for Sn–O–P compound. A, $CH_3Sn\leq$(I-1); B, n-$C_4H_9Sn\leq$ (I-3), (IV-14); C, $C_6H_5Sn\leq$(I-5).

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* Approximate bond energies are[24]: E(C–Sn), 54 kcal; E(C–P), 63 kcal; E(P–O) bridged, 80 kcal; E(P–O) phosphoryl, 120 kcal; and E(Sn–O), 134 kcal.

Triorganotin diorganophosphinates, (I)

Previous reports of Type (I), $R_3SnOP(O)R'_2$, preparations have involved metathesis reactions with organotin salts[4], the oxidation of organotin phosphines or, basically, hydride exchange reactions between dialkylphosphine oxides and bis(trialkyltin) oxides[2]. Using the Brönsted acid–base reaction of this report, compounds have been prepared with methyl, n-butyl, and phenyl moieties on tin, and methyl, benzyl, n-hexyl, and phenyl moieties on phosphorus [Table 1, compounds (I-1), (I-2), (I-3), (I-4), and (I-5)]. The properties of (I-4), $(C_4H_9)_3SnOP(O)(C_6H_5)_2$ are consistent with data reported in the literature[2,4].

Molecularity data (Table 1) indicate that Type (I) compounds are oligomers at low concentration in solution. Degrees of association range from 6.6 for $(C_4H_9)_3SnOP(O)(CH_3)_2$, (I-2), to 1.8 for $(C_4H_9)_3SnOP(O)(C_6H_5)_2$, (I-4). These compounds differ only in phosphorus substitutents which suggest that the bulk and inductive effect of the $-PR'_2$ moieties influences the extent of association. Limited infrared and ebulliometric data for (I-5), $(C_6H_5)_3SnOP(O)(CH_2C_6H_5)_2$, also suggest that the bridging link is sufficiently strong to be independent of the solvents, THF or benzene. The bridging unit must be the phosphoryl–tin bond, where the inner coordinate sphere of tin has increased to five. It is reasonable to conclude that the tin atom has a

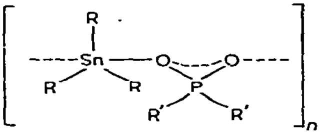

Fig. 2. Proposed structure for Type (I).

TABLE 2

TYPE (I), $R_3SnOP(O)R'_2$, SELECTED INFRARED BANDS (CM^{-1})

antisym, antisymmetric; sym, symmetric; def, deformation; v, very; s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Assignments	$R = CH_3$ $R' = CH_3$	$R = C_4H_9$ $R' = CH_3$	$R = C_4H_9$ $R' = C_6H_{13}$
ν antisym PO_2	1137 vs	1141 vs	1134 vs
ν sym PO_2	1061 vs	1067 vs	1056 vs
ν PC_2	740 s	738 s	747 vw
	701 vw	700 s	699 m
ν antisym C_3Sn	552 s		
	544 s	~540 vwsh	545 sh
ν sym C_3Sn	[a]	515 m	525 w–m
PO_2 scissor	470 sh		452 sh
SnO (ν, sym)	307 m		
	279 m		
C_3Sn def	152 vs		

[a] Raman active, 500 cm^{-1}.

5-coordinate, trigonal bipyramid configuration as suggested by other work in the literature[1,2,5,7] (see Fig. 2). Infrared, nuclear magnetic resonance (NMR), and Mössbauer data were valuable in substantiating this conclusion.

Extensive infrared studies[6,8,25] of trimethyltin esters, $(CH_3)_3SnOC(O)R$, confirm symmetry considerations for the stretching modes of C_3Sn moieties in the trigonal bipyramidal configuration. Fundamentally, the in-plane C_3Sn symmetrical stretching mode is infrared inactive and Raman active. Table 2 presents selected infrared bands for three Type (I) compounds*. An examination of data for $(CH_3)_3SnOP(O)(CH_3)_2$ indicates that the C_3Sn symmetrical stretching mode (band at ~520 cm^{-1}) is inactive in the infrared spectrum, but a strong band does appear at 500 cm^{-1} in the Raman spectrum. This is interpreted as strong evidence for equatorial methyl moieties in the trigonal bipyramid plane. It should be noted that the C_3Sn symmetrical stretching bands are observed in the tributyltin compounds. This does not exclude the possibility of three equatorial butyl moieties, but it is consistent with the loss of site symmetry because of C_3Sn coupling with C–C stretching modes within butyl moieties. The absence of an infrared band near 1200 cm^{-1} for the phosphoryl moiety and the strong bands near 1140 and 1060 cm^{-1} indicate the PO bonds are approximately equivalent. Thus, these data are consistent with the trigonal bipyramid structure with phosphinate bridges.

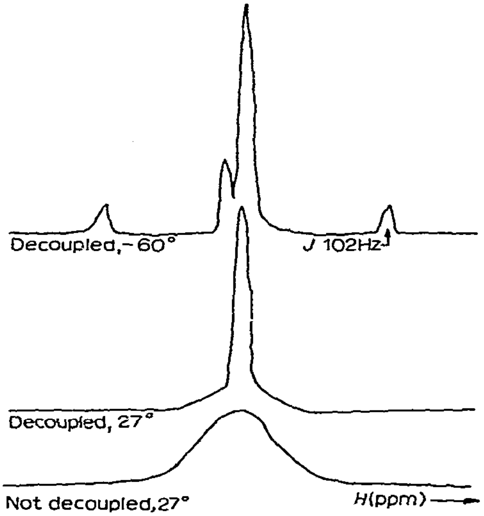

Fig. 3. ^{31}P NMR spectra of $(CH_3)_3SnOP(O)(CH_3)_2$ (Type I). (Solvent, THF; c 50%).

The ^{31}P NMR study of $(CH_3)_3SnOP(O)(CH_3)_2$ is considered representative of Type (I) compounds (see Fig. 3)**. At ambient temperature, the ^{31}P spectrum consists of a single broad (~25 Hz) signal. Upon decoupling the protons by the double resonance technique[18], only a narrower signal (~3 Hz) remains. When the temperature is lowered to −60°, a weaker, slightly less shielded signal is observed in

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* Bands above 1200 cm^{-1} are not characteristic of molecular structures, but are very typical of the individual alkyl or aryl substituents.

** This work was performed by Dr. E. B. Baker of The Dow Chemical Company.

addition to the strong main signal (~2 Hz). The weaker signal may be attributed to less mobile terminal phosphinato moieties at −60°. Unresolved ^{117}Sn and ^{119}Sn satellites are also observed; the coupling constant, J(Sn–P), is 102 Hz.

Table 3 includes the Mössbauer* spectra for two Type (I) compounds. Only one kind of tin atom (two peaks) is observed which suggests that there are no terminal (end blocking) phosphinato moieties in the crystalline state at −196°. Although the compounds have different molecularities in solution, the spectra are almost identical at the lower temperature.

TABLE 3

SUMMARY OF MÖSSBAUER DATA

Compound	Type designation	Quadrupole splitting (mm/sec)	Isomer[a] shift (mm/sec)
$(C_4H_9)_3SnOP(O)(C_6H_{13})_2$	(I-3)	3.72±0.01	−0.11±0.01
$(C_4H_9)_3SnOP(O)(CH_3)_2$	(I-2)	3.73±0.01	−0.13±0.01
$[(C_4H_9)_3SnO]_2P(O)CH_3$	(II-6)	3.62±0.03[b]	−0.11±0.03
		2.63±0.03[c]	−0.11±0.03
$[-(C_4H_9)_2SnOP(O)(C_8H_{17})O-]$	(III-11)	3.12±0.02[d]	−0.37±0.02
$(C_4H_9)_2Sn[OP(O)(C_6H_{13})_2]_2$	(IV-13)	4.00±0.02	−0.15±0.02

[a] The reference is a Pd_3Sn source at room temperature. To convert to white tin (β-tin), subtract 1.04±0.01 mm/sec. [b] Outer lines. [c] Inner lines. [d] The data can be fitted to four curves by the computer if the second set (2.2±0.2 mm/sec.) constitutes 16% of the total area. This interpretation would be consistent with an end block.

The physical data support the proposed structure. Apparently, a rapid equilibrium exists at ambient temperatures between bridging phosphinato moieties. At −60°, the equilibrium is slow, and both bridging and nonbridging moieties are observable by NMR. At −196°, the compounds are in a crystalline state, and Mössbauer spectroscopy detects only one type of tin atom.

Bis(triorganotin) organophosphonates, (II)

Type (II) compounds, $[R_3SnO]_2P(O)R'$, are analogous to triorganotin phosphinates, (I), with the important exception that only one phosphoryl moiety is available for two potential bridging tin sites. Although the phosphoryl moieties should be more electron deficient in the phosphonates, oligomeric structures are suggested with one bridging tin per monomer unit (Fig. 4). Molecularity data for (II-6), (II-7), and (II-8) give degrees of association greater than two; thus, structural differences between triorganostannoxyl moieties should be experimentally observable. Infrared data in Table 4 are less helpful because the nonbridging C_3SnO moieties should have tetrahedral C_{3v} site symmetry and give infrared active bands near 520 cm^{-1}. The interpretative value is further diminished by the use of tributyltin moieties. Nevertheless, the data clearly indicate bridging Sn–O–P bonds, *i.e.*, the absence of the phosphoryl bands and the $-PO_3$ bands near 1050, 972, and 495 cm^{-1}.

Compound (II-6), $[(C_4H_9)_3SnO]_2P(O)CH_3$, was chosen as representative of

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* The Mossbauer spectra were obtained by Dr. C. W. Kocher of The Dow Chemical Company.

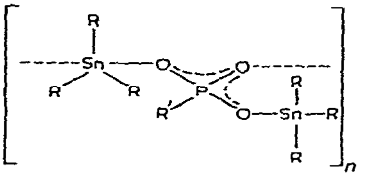

Fig. 4. Proposed structure for Type (II). One trigonal bipyramidal tin atom with approximately planar $C_3Sn\langle$ groups and phosphonate bridges. There is one tetrahedral tin atom.

Type (II) NMR data. A single signal (15 Hz) is observed at ambient temperature, which becomes narrower (7 Hz) at +50°. At −50°, the main signal (8 Hz) is accompanied by two sets of tin satellites with average coupling constants of 83 Hz and 110 Hz (Fig. 5)*. This means that phosphorus is coupled in two different ways to tin, *i.e.*, the phosphorus is in the environment of three tin atoms of which two are equivalent. This is consistent with the proposed structure when the bridging P–O bonds are equivalent. Finally, there is no evidence for chemically shifted phosphoryl end groups.

TABLE 4

TYPE (II), $[R_3SnO]_2P(O)R'$, SELECTED INFRARED BANDS (CM^{-1})

Tentative assignments	$R = C_4H_9$ $R' = CH_3$	$R = C_4H_9$ $R' = C_8H_{17}$	$R = C_4H_9$ $R' = CH_2C_6H_5$
ν antisym $-PO_3$	1056 vs	1051 vs	1050 s
ν sym $-PO_3$	973 vs	972 vs	977 s
ν P–C	758 vs	(778 w) 748 vw	780 m
ν antisym C_3Sn	558 m	545 w–m(b)	548 sh
ν sym C_3Sn		515 w(b)	525 m
δ antisym $-PO_3$	496 s	~498 bsh	492 w

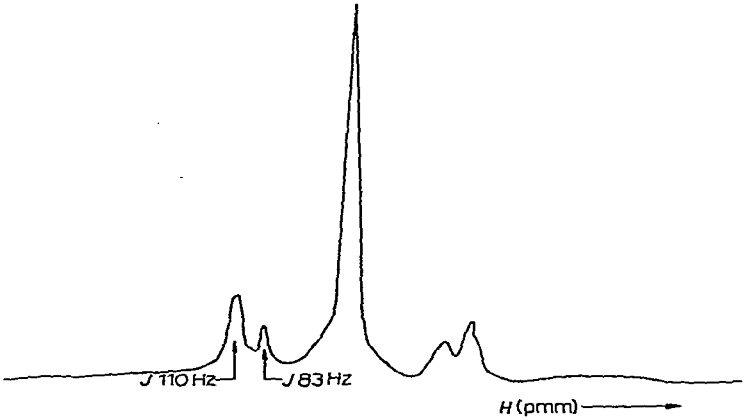

Fig. 5. ^{31}P NMR spectrum of $[(n\text{-}C_4H_9)_3SnO]_2P(O)CH_3$ (Type II). (Solvent, THF; *c* 50%), at −50°, protons decoupled.

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* Each set of satellites is the average of both ^{117}Sn and ^{119}Sn couplings with phosphorus.

The Mössbauer data for (II-6) (Table 3) gave more definitive data for two nonequivalent tin atoms. Only two peaks are observed for Types (I), (III), and (IV), but four peaks are observed for (II-6). These data, coupled with the absence of chemically shifted phosphoryl end groups in the NMR spectra, strongly suggest the presence of two types of tin atoms. The relative areas of the peaks are 2.9 ± 0.2 for the outer set, and 2.0 ± 0.2 for the inner pair.

Poly(diorganotin organophosphonates), (III)

Type III compounds $\{-R_2SnOP(R')(O)O-\}_n$, have two primary Sn–O valencies, [Sn–O–P(O)O–], therefore, coordinate bonds by the phosphoryl moieties are not essential for oligomeric structures*. Molecularity data (Table 1) indicate that the degrees of association are the largest for this type of compound (37, 21, and 8 by membrane osmometry). Phosphoryl bands are not observed in the infrared spectrum. A structure is proposed with trigonal bipyramidal tin atoms, approximately planar $OC_2Sn\langle$ moieties, and phosphonate bridges (Fig. 6).

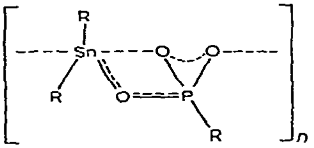

Fig. 6. Proposed structure for Type (III). Trigonal bipyramidal tin with approximately planar $OC_2Sn\langle$ groups and phosphonate bridges.

TABLE 5

TYPE (III), $[-R_2SnOP(O)(R')O-]$, SELECTED INFRARED BANDS (CM^{-1})

Tentative assignments	$R = C_4H_9$ $R' = C_6H_{13}$	$R = C_4H_9$ $R' = C_8H_{17}$	$R = C_4H_9$ $R' = CH_2C_6H_5$
ν antisym $-PO_3$	1075 vs	1075 vs sh	1075 s sh
ν sym $-PO_3$	990 s	~995 sh	995 s sh
ν PC	750 vw	750 vw	(749 vw)
	695 vw	702 vwsh	
ν antisym C_2Sn	559 w	583 m	582 vwsh
ν sym C_2Sn	509 w–m	523 w	528 m–s
δ antisym PO_3	(~490 vwsh)		(~490 wsh)

The Mössbauer and NMR data for poly(dibutyltin n-octylphosphonate), (III-11), give valuable structural information. Only one major type of tin atom (two peaks) is observed in the Mössbauer spectrum (Table 3). When the protons are decoupled for ^{31}P NMR (Fig. 7), the main signal is flanked by two pairs of tin satellite signals. The two different couplings, 144 Hz and 172 Hz, are from unresolved tin isotopes and correspond to tin–phosphorus coupling in two ways. This is consistent with the proposed structure when Sn–O–P exchange is slow. Essentially, the phosphorus nuclei observed tin nuclei from the local environment of one and two oxygen

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* This does not exclude the formation of a "chelated" monomer, $R_2SnO_2P(O)R$, but suggests that it is not favored.

atoms, respectively. When both Mössbauer and NMR data* are considered, strong phosphoryl bridging is essential to explain the difference between approximately equivalent tin and phosphorus atoms.

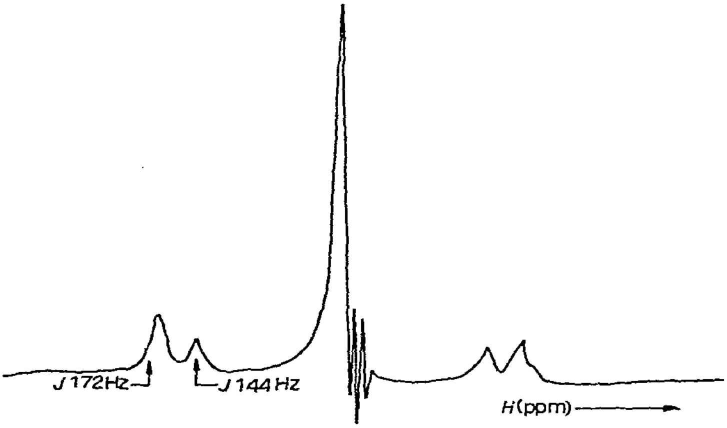

Fig. 7. ^{31}P NMR spectrum of [–(n-C_4H_9)$_2$SnOP(O)(n-C_8H_{17})O–]$_n$ (Solvent, THF; c 50%), at 27°, protons decoupled.

Diorganotin bis(diorganophosphinates), (IV)

Six-coordinate tin is expected for type (IV) compounds, $R_2Sn[OP(O)R'_2]_2$, if both phosphoryl moieties form coordinate bonds. Three basic structures must be considered: (1) two intramolecular (chelate) phosphoryl bonds; (2) one intramolecular and one intermolecular bridging moiety; and (3) two intermolecular bridging moieties. The first structure would be monomeric; the second, dimeric or polymeric; and the third, clearly polymeric. Molecularity data indicate that (IV-12), (IV-13), and (IV-14) are primarily dimeric. Fig. 8 gives a proposed structure with 6-coordinate tin, and intramolecular and intermolecular phosphinato moieties. Infrared data (Table 6) do not have free phosphoryl bands, but strong bands near 1130 and 1050 cm^{-1} are consistent with $\rangle PO_2$ stretching modes. The bands near 515 cm^{-1} are very weak which suggest the alkyl groups are in axial positions. The Mössbauer spectrum of $(C_4H_9)_2Sn[OP(C_6H_{13})_2(O)]_2$ [Table 3, (IV-13)] indicates one type of tin atom.

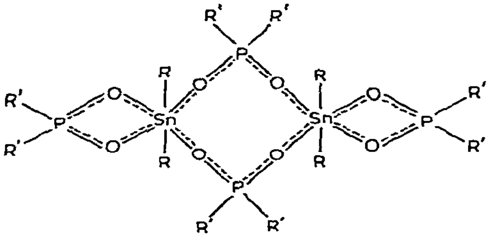

Fig. 8. Proposed structure for Type (IV).

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* The temperature difference between NMR and Mössbauer data should not detract from the salient features of this interpretation.

TABLE 6

TYPE (IV), $R_2Sn[OP(O)R'R'']_2$, SELECTED INFRARED BANDS (cm^{-1})

Tentative assignments	$R = C_4H_9$ $R' = R'' = C_5H_{11}$	$R = C_4H_9$ $R' = R'' = C_6H_{13}$	$R = C_4H_9$ $R' = C_6H_{13}$ $R'' = CH_2C_6H_5$
ν antisym PO_2	1125 vs	1140 vs	1130 vs 1119 vs
ν sym PO_2	1042 s	1071 vs	1042 vs
ν PC_2	750 w–m (695 w)	(742 vwsh) (690 w)	750 vw
ν antisym C_2Sn	594 w	(~590 vw)	582 m
ν sym C_2Sn	(518 vwsh)	(513 vwsh)	(513 wsh)
PO_2 scissor	483 w	483 vw	490 s

The ^{31}P NMR spectrum of (IV-13) was difficult to obtain because of broad signals and the low percentage of phosphorus in solution. A spectrum was obtained by using fast passage dispersion mode, time averaging, and proton decoupling. The spectrum (Fig. 9) shows two nonequivalent phosphorus atoms with chemical shifts of −41.8 ppm and −52.0 ppm relative to 85% orthophosphoric acid. The shift difference is too large to be a coupling. The broadness of the peaks is partly due to the dispersion mode at high RF field, but there is probably some contribution from tin and phosphorus couplings. These data support the proposed structure.

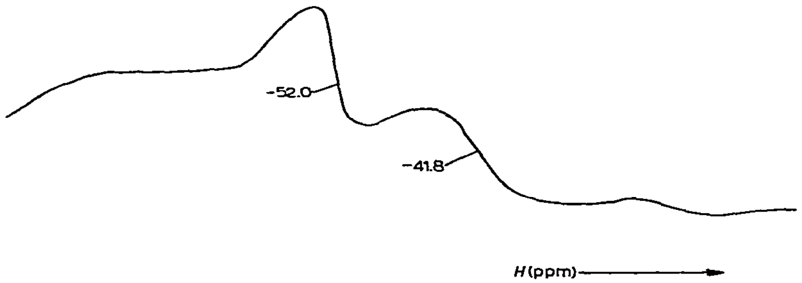

Fig. 9. ^{31}P NMR spectrum of $(n\text{-}C_4H_9)_2Sn[OP(O)(n\text{-}C_6H_{13})_2]_2$ (Type IV). (Solvent, C_6H_6; c sat. 27°), at 50°, reference H_3PO_4; protons decoupled, time averaging, fast passage dispersion.

ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research. We are very grateful to Dr. E. B. BAKER for the NMR data and Dr. C. W. KOCHER for the Mössbauer data. We are also grateful to R. A. NYQUIST for his assistance with infrared and Raman data. We wish to thank R. B. NUNEMAKER, E. T. WAGONER, and L. E. SWIM for their assistance with analytical and thermal data.

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