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OXY-AND THIO PHOSPHORUS ACID DERIVATIVES OF TIN. IX. DI- AND TR--ETC(U)

JUL 81 K C MOLLOY, F A NASSER, J J ZUCKERMAN   N00014-77-C-0432

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Six triorgano- and five diorganotin(IV) diphenylphosphates, $R_3SnO_2(OC_6H_5)_2$ where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5 and cyclo-C_6H_{11}, and $R_2Sn[O_2P(C_6H_5)_2]_2$ where R = CH_3, C_2H_5, n-C_4H_9, C_6H_5 and n-C_8H_{17}, are synthesized by five routes: elimination of water by condensation of diphenylphosphoric acid with triorganotin(IV) hydroxides (R = CH_3, C_6H_5 and cyclo-C_6H_{11}), bis-[triorganotin (IV)]oxide (R = n-C_3H_7, n-C_4H_9), or diorganotin(IV) oxides (R = CH_3, n-C_4H_9, n-C_8H_{17}, C_6H_5) where the released water is removed azeotropically to drive the reactions forward, or by precipitation of sodium chloride from the reaction of

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OXY- AND THIO PHOSPHORUS ACID DERIVATIVES OF TIN. IX. DI- AND TRIORGANOTIN(IV) DIPHENYLPHOSPHATE ESTERS[1]

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Prepared for Publication
in
Inorganic Chemistry

ABSTRACT

Six triorgano- and five diorganotin(IV) diphenylphosphates, $R_3SnO_2P(OC_6H_5)_2$ where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5 and cyclo-C_6H_{11}, and $R_2Sn[O_2P(C_6H_5)_2]_2$ where R = CH_3, C_2H_5, n-C_4H_9, C_6H_5 and n-C_8H_{17}, are synthesized by five routes: elimination of water by condensation of diphenylphosphoric acid with triorganotin(IV) hydroxides (R = CH_3, C_6H_5 and cyclo-C_6H_{11}), bis-{triorganotin(IV)}oxide (R = n-C_3H_7, n-C_4H_9), or diorganotin(IV) oxides (R = CH_3, n-C_4H_9, n-C_8H_{17}, C_6H_5) where the released water is removed azeotropically to drive the reactions forward, or by precipitation of sodium chloride from the reaction of sodium diphenylphosphate with tri- (R = C_6H_5) or diorganotin(IV) (R = C_2H_5) chlorides. The products are crystalline solids, soluble in polar and non-polar solvents, except for the triorganotin(IV) derivatives below R = CH_3 which are oils. An NMR $|^2J(^{119}Sn\text{-}C\text{-}^1H)|$ coupling constant of 73.0Hz is consistent with a five-coordinated structure for the trimethyltin(IV) derivative in solution. In none of the mass spectra are there parent molecular ions, ions of mass higher than the parent, or any di- or polytin-bearing species, thus ruling out association in the gas phase. The highest mass fragments derive from the loss of one organic group from tin from the tri- and from the loss of one ligand moiety from the diorganotin derivatives. Successive loss of phenyl groups can be seen in the phenyltin spectra. The tin-119m Mössbauer isomer shift (IS) values (1.26 - 1.74 mm s^{-1}), ρ [ratio of quadrupole splitting (QS) to IS] (2.60 - 3.54) and QS values (3.54 - 4.91 mm s^{-1}) specify higher coordination for the triorganotin(IV) complexes and six-coordinated, trans-diorganotin(IV) octahedral geometries with nearly linear C-Sn-C moieties for the diorganotin(IV) complexes.

In the early 1960's Kubo synthesized triphenyltin(IV) diphenylphosphate and demonstrated its fungi-, insect- and phytotoxicity.[3] The importance of organotins in biology and the environment is now well-known,[4-6] and in previous portions of this series of papers we have reported on the synthesis of organotin(IV) derivatives of the phosphorus acids.[7-8] We now report the preparation by several different methods and spectroscopic properties of a series of di- and triorganotin(IV) derivatives of diphenylphosphate, and draw conclusions concerning the structures of these species.

Experimental Section

Organotin starting materials and diphenylphosphate were of commercial grade and were used without further purification. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra were recorded on a Beckman 4250 Spectrometer as Nujol mulls on CsI plates. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectrometer at an exciting voltage of 70eV. Tin-119m Mössbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with an NaI scintillation counter and using $Ca^{119m}SnO_3$ as standard reference material for zero velocity. Velocity calibration was based upon β-tin and natural iron. Standard, nonlinear, least-squares techniques were used to fit the data to Lorentzian curves. Raman data were recorded on a Spex Ramalog 5 laser Raman spectrometer. Nmr spectra were recorded on a Varian T-60 spectrometer using deuterochloroform as solvent.

Five different methods of preparing the organotin derivatives of diphenylphosphate were used. Details of a typical example of each method are given below. All compounds studied are listed with the preparatory method used and their yields, melting points, and microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table II.

Diphenylphosphatotriphenyltin(IV), $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$.[3]

To a toluene solution (150mL) of triphenyltin(IV) hydroxide (3.67 g, 0.01 mol) diphenylphosphate (2.50g, 0.01 mol) was added and the mixture refluxed. The water formed in the reaction was removed azeotropically with toluene, and the mixture filtered. The filtrate, after cooling overnight gave the product as colorless crystals (3.0g, 50.1%), m.p. 178-180° C. (lit. 170° C.[3]).

Diphenylphosphatotri-n-propyltin(IV), $(n\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$.

To a benzene (a suspected carcinogen) solution (150mL) of bis-[tri-n-propyltin(IV)] oxide (2.56g, 0.005 mol) diphenylphosphate (2.50g, 0.5 mol) was added and the mixture refluxed. The water formed in the reaction was removed azeotropically. Excess solvent was removed under reduced pressure yielding a pale, oily product (4.25g, 85.51%).

Bis-(diphenylphosphato)dimethyltin(IV), $(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$.

To a toluene solution (150mL) of dimethyltin(IV) oxide (0.998g, 0.006 mol) diphenylphosphate (3.00g, 0.006 mol) was added and the mixture refluxed. The water formed in the reaction was removed azeotropically. The insoluble product was isolated by filtration and dried *in vacuo* (3.70g, 95.3%) m.p. > 250° C.

Diphenylphosphatotriethyltin(IV), $(C_2H_5)_2SnOP(O)(OC_6H_5)_2$.

To a solution of freshly prepared sodium ethoxide (0.01 mol) in dry ethanol (100mL) diphenylphosphate (2.5g, 0.01 mol) was added and the mixture stirred at room temperature for 10 minutes. Triethyltin(IV) chloride (1.68mL, 0.01 mol) was then added, and a white precipitate formed immediately. After refluxing for 1 hour, the mixture was allowed to cool, the precipitate separated by filtration, and the filtrate concentrated under reduced pressure to give the product as an oil (3.75g, 92%).

Bis-(diphenylphosphato)diethyltin(IV), $(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$.

To a solution of freshly prepared sodium ethoxide (0.01 mol) in dry ethanol (150mL) diphenylphosphate (5.00g, 0.01 mol) was added and the mixture stirred at room temperature for 30 minutes. Diethyltin(IV) dichloride (2.47g, 0.01 mol) was then added, and a white precipitate formed immediately. After refluxing for 1 hour, the mixture was allowed to cool, the precipitate separated by filtration, and the filtrate concentrated under pressure to give the product as a white solid (5.26g, 77.9%), m.p. > 250° C.

Results and Discussion

The di- and triorganotin(IV) derivatives of diphenylphosphate were synthesized by five routes, elimination of water by condensation of diphenylphosphoric acid with triorganotin(IV) hydroxides:

$$R_3SnOH + HOP(O)(OC_6H_5)_2 \xrightarrow{C_6H_6 \text{ or } C_6H_5CH_3} R_3SnOP(O)(OC_6H_5)_2 + H_2O \quad (1)$$

$R = CH_3$, Cyclo-C_6H_{11}, C_6H_5

with bis-[triorganotin(IV)] oxides:

$$(R_3Sn)_2O + 2\ HOP(O)(OC_6H_5)_2 \xrightarrow{C_6H_6 \text{ or } C_6H_5CH_3} 2R_3SnOP(O)(OC_6H_5)_2 + H_2O \qquad (2)$$

$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9$

or with diorganotin(IV) oxides:

$$R_2SnO + 2\ HOP(O)(OC_6H_5)_2 \xrightarrow{C_6H_6 \text{ or } C_6H_5CH_3} R_2Sn[OP(O)(OC_6H_5)_2]_2 + H_2O \qquad (3)$$

$R = CH_3,\ n\text{-}C_4H_9,\ n\text{-}C_8H_{17},\ C_6H_5$

where the released water is distilled azeotropically to drive the reactions forward, or by precipitation of sodium chloride from an ethanol solution of sodium diphenylphosphate with a triorganotin(IV) chloride:

$$R_3SnCl + NaOP(O)(OC_6H_5)_2 \xrightarrow{C_2H_5OH} R_3SnOP(O)(OC_6H_5)_2 + NaCl \qquad (4)$$

$R = C_2H_5$

or with a diorganotin(IV) chlorides:

$$R_2SnCl_2 + 2\ NaOP(O)(OC_6H_5)_2 \xrightarrow{C_2H_5OH} R_2Sn[OP(O)(OC_6H_5)_2]_2 + 2\ NaCl \qquad (5)$$

$R = C_2H_5$

The organotin diphenylphosphates listed in Table I are colorless, crystalline solids, soluble in polar and non-polar solvents, except for the trialkyltin(IV) derivatives which are oils. The compounds do not yield conducting solutions in either acetonitrile or nitrobenzene. Limited solubility precluded molecular weight determination, and the recording of nmr data for the diorganotin compounds.

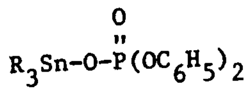
For the triorganotin(IV) derivatives three covalent structures are in principle possible. The monodentate form (A) is extremely unlikely for the diphenylphosphate ligand, although we have recently reported an analogous sulfur-containing example in O,O'-diethyldithiophosphatotriphenyltin(IV).[9] Oxygenated derivatives have a greater propensity for employing the bidentate phosphorus ligand fully, and moreover, in the bridging form (B) rather than in the chelated form (C) which are favored by their sulfur analogues. For each of the latter two, the question of whether the connections in the oxygen-tin-oxygen systems are equivalent or skewed (anisobidentate) is relevant, but spectroscopic evidence alone will not be able to decide, and X-ray diffraction data will be the final arbiter. Purely ionic forms (D) are also possible, but unlikely given the good solubility in non-polar organic solvents. On the other hand, in the related α-phenylphosphonatotrimethyltin(IV) we have discovered a unique, more complex ionic formulation,

$$\{[(CH_3)_3Sn]^+[C_6H_5\overset{O}{\overset{\|}{P}}(OH)OSn(CH_3)_3O\overset{O}{\overset{\|}{P}}(OH)C_6H_5]^-\}_n.$$ [11]

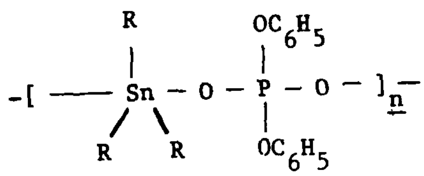
For the diorganotin(IV) derivatives both a four-coordinated, $R_2Sn[O\overset{O}{\overset{\|}{P}}(OC_6H_5)_2]_2$ configuration containing monodentate diphenylphosphate groups and an ionic, $[R_2Sn]^{2+}[O_2P(OC_6H_5)_2]^{2-}$, form are unlikely, given the availability of the ubiquitous trans-diorgano, octahedral geometry with bidentate diphenylphosphate groups.[12] However, the propensity for bridging, rather than chelation cannot be ignored in these oxygen derivatives, and a structure consisting of sheet-like polymers has been proposed for the simplest analogues, the hypophosphites, $R_2Sn(O_2PH_2)_2$.[13]

Infrared Spectra

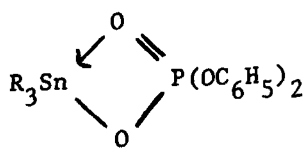
The tin-carbon frequencies in the two methyltin derivatives can yield important information bearing upon the structures of our compounds, and a guide to the positions of the absorptions can be found in work on the analogous di- and trimethyltin(IV) hypophosphites[13] and diorganophosphinates.[14] However, bands in the parent diphenylphosphate are found at 560, 524 and 508 cm^{-1} and at 538, 514 and



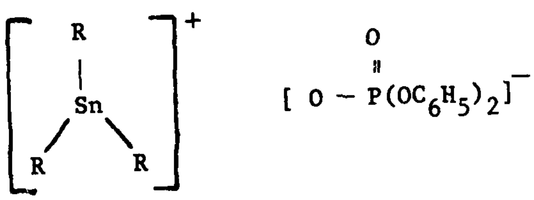
A



B



C



D

500 cm^{-1} in the Raman, obscuring region of interest, and ruling out the use of evidence from the ν(SnC) modes to draw conclusions concerning the planarity of the SnC_3 or the linearity of the SnC_2 groupings.

In addition, $\nu_{asym}(PO_4)$ and $\nu_{sym}(PO_4)$ modes appear as strong absorptions at 1016 and 971 cm^{-1} in the infrared spectrum of tin(II) orthophosphate,[15] $SnHPO_4$, and in the 1150 - 950 cm^{-1} region in dimethyltin(IV) orthophosphate,[13] $[(CH_3)_2Sn]_3PO_4$, and we have scanned the infrared spectra of our derivatives for features separated by ca. 100 cm^{-1} in these regions. A consistent set is found listed in Table VII for the ν_{asym} and $\nu_{sym}(PO_4)$ modes. We judge the strong absorption at 950 - 925 cm^{-1} in each spectrum to be too low in energy to arise from the $\nu_{sym}(PO_4)$ mode.

NMR Spectra

The spectra exhibit the expected resonances arising from the organotin and phenyl group moieties, for example, in trimethyltin(IV) diphenylphosphate the ten phenyl protons fall in the range 6.8 - 7.7 ppm with the nine methyltin protons at 0.33 ppm. The methyltin coupling constants can yield important structural information, and the magnitude of $|^2J(^{119}Sn\text{-}C\text{-}^1H)|$ = 73.0 Hz is consistent with a five-coordinated tin atom[16] in the dilute $CDCl_3$ solution in which the spectrum was recorded.

Mass Spectra

In none of the spectra are there detectable parent molecular ions, fragments of mass higher than the parent or any di- or polytin-bearing species, thus ruling out any gas phase association of the compounds in the spectrometer. As we have seen before in studying the di-[8] and triorganotin(IV)[7] dithiophosphate esters, the highest mass fragments derive from the loss of one organic group from tin in the tri- and from the loss of one phosphorus ligand moiety in the diorganotin derivatives. In the triorganotin series the former is frequently the most abundant peak in the spectrum, with $[SnO_2P(OC_6H_5)_2]^+$(m/e = 369), $[SnO_2POC_6H_5-H]^+$ (275) and $[SnO_2P]^+$ (183) fragments prevalent. Tin ions are found in each spectrum at m/e=120. Successive loss of phenyl groups can be seen in the phenyltin spectra. The spectrum of the diphenyltin derivative exhibits an abundant $(C_6H_5)_3Sn^+$ fragment, presumably arising from a gas phase rearrangement of phenyl groups. In the syntheses of the related O,O'-diisopropyldithiophosphatetriphenyltin(IV) we also observed phenyl group rearrangements.[7] The fragments at m/e = 213 in the tri- and diorganotin derivatives could in each case be assigned as $C_6H_5SnO^+$, also formed through a phenyl group rearrangement from the ligand. Most of the high abundance ions are even-electron species.

Mössbauer Spectra

The tin-119m Mössbauer data listed in Table II are consistent with organotin(IV) species in a higher than four-coordination geometry. The magnitudes of the isomer shift (IS) values (1.26 - 1.74 mm s^{-1}) confirm a tin(IV) oxidation state,[17] the magnitudes of the ρ values, the ratio of the quadrupole splitting (QS) to the IS (2.60 - 3.54), reflect a higher coordination at tin, while the extremely high QS values in the diorganotin series specify a trans-diorganotin configuration in an octahedral geometry for those systems.

We have previously used a treatment based upon a point charge model[18] to link the magnitude of the QS values with the C-Sn-C angle in six-coordinated diorganotin(IV) compounds.[8,19] This treatment assumes that the partial QS values for the ligands will be small compared to those for the R groups, and that the magnitude of the QS will reach ca. 4.0 mm s^{-1} when the R_2Sn system becomes linear in a trans-octahedral geometry. We have lately, however, examined several series of diorganotin(IV) derivatives which exhibit QS values much above 4.0 mm s^{-1}, including the $R_2Sn[OP(O)(C_6H_5)OH]_2$[20] and $R_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$[21] systems analogous to the compounds reported here. In these cases the partial QS values for the ligands obviously cannot be ignored, and the model breaks down. We surmise that in these examples the trans-diorganotin(IV) octahedra contain nearly linear R_2Sn systems.

Our diphenyltin(IV) derivative, on the other hand exhibits a QS value of only 3.84 mms^{-1}. Although the structural data for these phenyl systems are much more sparse than for the dimethyl analogues,[12] a correlation between doublet splitting and bond angle can be drawn,[8] and used to calculate a phenyl-tin-phenyl angle of 175.2° for our compound.

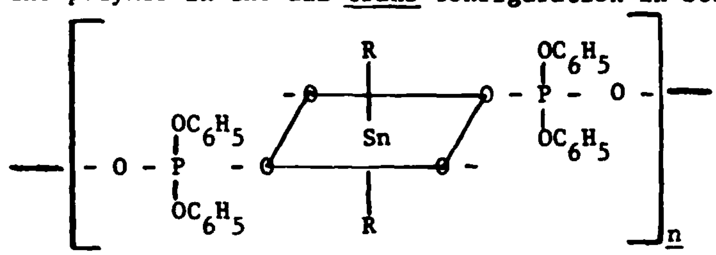
The dimethyltin(IV) derivative exhibits quite a strong Mössbauer spectrum at room temperature. While spectra can be recorded at these temperatures for several monomeric molecular solids of known structure,[22] we interpret this observation in terms of a lattice consisting of intermolecularly associated units propagating in at least one dimension.[17]

The trimethyl- and triphenyltin(IV) derivatives, on the other hand, fail to yield resolvable spectra at ambient temperatures, even after long counting times. We interpret this negative evidence as ruling out an intermolecularly associated polymeric lattice.

Structural Conclusions

While the vibrational spectra for the dimethyltin(IV) derivative fail to provide evidence which can be used to decide the question of the linearity of the carbon-tin-carbon skeleton, the magnitude of the Mössbauer QS and ρ values specify a trans-diorganotin, octahedral geometry. The question of bridging vs.

chelation is decided, at least tentatively, by the ambient temperature spectrum, and we depict the polymer in the all trans-configuration in structure E:



E

A similar, sheet-like polymeric structure has been proposed for the hypophosphite analogues, $R_2Sn(O_2PH_2)_2$.[13]

Again, for the triorganotin(IV) derivatives, the $\nu(SnC_3)$ region is obscured but the magnitudes of the Mössbauer QS and ρ values specify a higher than four-coordinated situation at tin, although the absence of resolvable ambient temperature spectra suggest that the value of n in structure B is finite. We have recently solved the structure of diphenylphosphatotriphenyltin(IV), which forms a solid composed of cyclic hexamers,[23] $[(C_6H_5)_3SnO_2P(OC_6H_5)_2]_6$. The related compound, α-phenylphosphonatotrimethyltin(IV), which is capable of hydrogen bonding, forms a helical polymer in the solid.[11] Model studies show that the smallest cyclic oligomer capable of incorporating linear O-Sn-O units is the pentamer (n = 5 in structure B) whose O-P-O angles would average 108°. In our cyclic triphenyltin(IV) solid, one phenyl group on each tin atom is thrust into the center of the oligomeric ring, which must expand to the hexamer in order to accomodate them.

Acknowledgements

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TABLE I. Physical Data for the Organotin(IV) Diphenylphosphates, $R_{\underline{n}}Sn[OP(O)(OC_6H_5)_2]_{4-\underline{n}}$ ($\underline{n}$=2,3)

Compound	Preparation	M.P.(°C)	%C Found[a]	%H Found[a]	Yield,%
$(CH_3)_3SnOP(O)(OC_6H_5)_2$	1	79-80	43.86(43.62)	4.76(4.63)	24.2
$(C_2H_5)_3SnOP(O)(OC_6H_5)_2$	4	-	46.15(47.50)	5.46(5.55)	92.4
$(n\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$	2	-	50.95(50.73)	6.36(6.28)	85.5
$(n\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$	2	-	53.76(53.40)	6.90(6.91)	39.1
$(C_6H_5)_3SnOP(O)(OC_6H_5)_2$	1	178-180[b]	60.85(60.13)	4.39(4.21)	50.1
$(Cyclo\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$	1	> 250°	58.77(58.37)	7.31(7.01)	80.2
$(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$	3	> 250°	48.05(48.25)	4.02(4.04)	95.3
$(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	5	> 250°	49.90(49.84)	4.81(4.47)	77.9
$(n\text{-}C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$	3	> 250°	52.77(52.55)	5.36(5.23)	98.6
$(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	3	> 250°	52.89(56.05)	3.81(3.91)	84.3
$(n\text{-}C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$	3	> 250°	56.92(56.95)	6.55(6.45)	80.8

[a] Calculated values in parentheses.

[b] Reported as 170° in ref. 3.

TABLE II. Tin-119m Mössbauer Data for the Organotin(IV) Diphenylphosphates, $R_nSn[OP(O)(OC_6H_5)_2]_{4-n}$ (n=2,3), at 77K

Compound	I.S.±0.03	Q.S.±0.06	Γ±0.03[a]	ρ=Q.S./I.S.
$(CH_3)_3SnOP(O)(OC_6H_5)_2$	1.36	4.10	1.65	3.01
$(n\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$	1.50	4.12	1.06	2.75
$(n\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$	1.49	4.09	0.97	2.74
$(C_6H_5)_3SnOP(O)(OC_6H_5)_2$	1.26	3.54	1.93	2.81
$(Cyclo\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$	1.60	4.15	1.63	2.59
$(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.38	4.91	1.73	3.56
	1.15[b]	4.93[b]	1.14[b]	4.29[b]
$(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.50	4.86	2.82	3.24
$(n\text{-}C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.54	4.58	2.56	2.97
$(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.46	3.84	1.44	2.63
$(n\text{-}C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$	1.74	4.78	0.98	2.75

[a] The fitting program constrained both wings of the doublet to equal linewidths.

[b] Data recorded at ambient temperatures.

TABLE III. Mass Spectral Data for the Triorganotin(IV) Diphenylphosphate, $R_3SnOP(O)(OC_6H_5)_2$, Derivatives

m/e	$(CH_3)_3SnOP(O)(OC_6H_5)_2$ [a]	$(C_2H_5)_3SnOP(O)(OC_6H_5)_2$ [a]	$(\underline{n}-C_3H_7)_3SnOP(O)(OC_7H_6)_2$ [a]
535			
523			
483			
455			$[(C_3H_7)_2SnOP(O)(OC_6H_5)_2]^+$(100.0)
445			
427		$[(C_2H_5)_2SnOP(O)(OC_6H_5)_2]^+$(100.0)	
399	$[(CH_3)_2SnOP(O)(OC_6H_5)_2]^+$(100.0)		
369	$[SnOP(O)(OC_6H_5)_2]^+$(11.2)	$[SnOP(O)(OC_6H_5)_2]^+$(55.7)	$[SnOP(O)(OC_6H_5)_2]^+$(50.0)
351			
275	$[SnOP(O)(OC_6H_5)-H]^+$(14.5)	$[SnOP(O)(OC_6H_5)-H]^+$(23.9)	$[SnOP(O)(OC_6H_5)-H]^+$(34.2)
273			
213	$[(CH_3)_2SnOP(O)]^+$ or $[C_6H_5SnO]^+$ (19.9)	$[(C_2H_5)SnOP(O)H]^+$ or $[C_6H_5SnO]^+$(74.6)	$[C_6H_5SnO]^+$(28.2)
183		$[SnOP(O)]^+$(17.6)	$[SnOP(O)]^+$(11.2)
165	$[(CH_3)_3Sn]^+$(28.7)		
150	$[(CH_3)_2Sn]^{+\cdot}$(7.9)	$[(C_2H_5)SnH]^{+\cdot}$(34.2)	
120	$Sn^{+\cdot}$(5.8)	$Sn^{+\cdot}$(21.9)	

[a] % Relative abundance values in parentheses; masses are based upon ^{120}Sn, ^{31}P, ^{16}O, ^{12}C and ^{1}H.

$(\underline{n}\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$[a]	$(cyclo\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$[a]	$(C_6H_5)_3SnOP(O)(OC_6H_5)_2$[a]	
	$[(C_6H_{11})_2SnOP(O)(OC_6H_5)_2]^+$(47.9)		535
		$[(C_6H_5)_2SnOP(O)(OC_6H_5)_2]^+$(93.7)	523
$[(C_4H_9)_2SnOP(O)(OC_6H_5)_2]^+$(100.0)			483
		$[C_6H_5SnOP(O)(OC_6H_5)_2\text{-}H]^+$(84.1)	445
$[SnOP(O)(OC_6H_5)_2]^+$(50.5)	$[(C_6H_{11})_3Sn]^+$ or $[SnOP(O)(OC_6H_5)_2]^+$(100.0)	$[SnOP(O)(OC_6H_5)_2]^+$(16.3)	369
		$[(C_6H_5)_3Sn]^+$(43.4)	351
$[SnOP(O)(OC_6H_5)\text{-}H]^+$(34.6)	$[SnOP(O)(OC_6H_5)_2\text{-}H]^+$(39.8)		275
		$[(C_6H_5)_2Sn\text{-}H]^+$(35.3)	273
$[C_6H_5SnO]^+$(34.9)	$[C_6H_5SnO]^+$(44.4)	$[C_6H_5SnO]^+$(51.1)	213
		$[C_6H_5Sn]^+$(100.0)	197
	$[SnOP(O)]^+$(10.5)	$[SnOP(O)]^+$(14.5)	183
$Sn^{+\cdot}$(8.8)	$Sn^{+\cdot}$(11.2)	$Sn^{+\cdot}$(52.8)	120

TABLE IV. Mass Spectral Data for the Diorganotin(IV) Diphenylphosphate, $R_2Sn[OP(O)(OC_6H_5)_2]_2$, Derivatives.

m/e	$(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$ [a,b]	$(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$ [a,c]	$(n\text{-}C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$ [a,c]
555	$[P-OC_6H_5]^+$(13.6)		
399	$[P-OP(O)(OC_6H_5)_2]^+$(23.7)		
369	$[SnOP(O)(OC_6H_5)_2]^+$(9.5)	$[SnOP(O)(OC_6H_5)_2]^+$(45.8)	$[SnOP(O)(OC_6H_5)_2]^+$(69.9)
351			
275	$[SnOP(O)(C_6H_5)-H]^+$(15.3)	$[SnOP(O)(OC_6H_5)-H]^+$(45.8)	$[SnOP(O)(OC_6H_5)-H]^+$(38.6)
213	$[(CH_3)_2SnOP(O)]^+$ or $[C_6H_5SnO]^+$(33.1)	$[C_2H_5SnOP(O)H]^+$ or $[C_6H_5SnO]^+$(70.75)	$[C_6H_5SnO]^+$(44.4)
197			
120	$Sn^{+\cdot}$(9.8)	$Sn^{+\cdot}$(14.6)	$Sn^{+\cdot}$(7.3)

$(n\text{-}C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$ [a,b]	$(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$ [a,b]	
	$[(C_6H_5)_2SnOP(O)(OC_6H_5)_2]^+$(54.3)	523
	$[C_6H_5SnOP(O)(OC_6H_5)-H]^+$(46.1)	445
$[SnOP(O)(OC_6H_5)_2]^+$(45.8)		369
	$[(C_6H_5)_3Sn]^+$(44.5)	351
$[SnOP(O)(OC_6H_5)-H]^+$(32.8)	$[(C_6H_5)_2SnH]^+$(29.0)	275
$[C_6H_5SnO]^+$ (46.3)	$[C_6H_5SnO]^+$ or $[SnOP(O)(OC_6H_5)-H]^+$(41.2)	213
	$[C_6H_5Sn]^+$(92.7)	197
$Sn^{+\cdot}$(6.3)	$Sn^{+\cdot}$(84.1)	120

a % Relative abundance values in parentheses; masses are based upon ^{120}Sn, ^{31}P, ^{16}O, ^{12}C and ^{1}H.

b The most abundant ion is at m/e = 77, $[C_6H_5]^+$.

c The most abundant ions is at m/e = 94, $[OC_6H_5 + H]^+$.

TABLE V. Infrared Spectral Frequencies of $HOP(O)(OC_6H_5)_2$ and the Triorganotin(IV) Diphenylphosphate, $R_3SnOP(O)(OC_6H_5)_2$, Derivatives

COMPOUND	INFRARED ABSORPTIONS (in cm^{-1})[a]
$HOP(O)(OC_6H_5)_2$	1486s, 1466sh, 1458s, 1378w, 1365sh, 1310vw, 1221s, 1200vs, 1197vs, 1169s, 1154s, 1072vw, 1005s, 962vs, 925s, 908w, 780s, 720sh, 755s, 690m, 686m, 616vw, 609vw, 650vw, 560vw, 524w, 508w, 498sh, 470vw, 380w, 378m, 345w, 335vw, 308vw
$(CH_3)_3SnOP(O)(OC_6H_5)_2$[b]	1492s, 1485s, 1468s, 1460s, 1454w, 1434s, 1380m, 1375vw, 1338vw, 1308vw, 1288vw, 1268vw, 1236m, 1221vs, 1197vs, 1093vs, 1024w, 1002vw, 934s, 930s, 902vw, 772s, 748m, 688w, 550vw, 523w
$(C_2H_5)_3SnOP(O)(OC_6H_5)_2$	1596m, 1491s, 1421vw, 1376vw, 1244s, 1222vs, 1202vs, 1161w, 1102vs, 1004vw, 926s, 896w, 776m, 748m, 680s, 526m, 386m, 344m, 328vw, 310vw
$(\underline{n}\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$	1594s, 1490vs, 1452w, 1415vw, 1370vw, 1332vw, 1233sh, 1225vs, 1204vs, 1162w, 1102vs, 1006w, 996w, 925vs, 898w, 774s, 748m, 708w, 686s, 674sh, 526m, 386m, 375w, 344m, 336sh, 328vw, 308vw
$(\underline{n}\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$	1598m, 1494s, 1468w, 1458w, 1378w, 1342vw, 1336vw, 1225vs, 1205vs, 1164w, 1103vs, 1009w, 930s, 900w, 880w, 868w, 778m, 750m, 690s, 610vw, 578vw, 522m, 396m, 379sh, 348m, 310vw
$(C_6H_5)_3SnOP(O)(OC_6H_5)_2$	1224sh, 1210vs, 1204vs, 1167w, 1110vs, 946s, 932s, 900vw, 776m, 758m, 728s, 690s, 520w, 445vw
$(cyclo\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$	1595m, 1492s, 1456m, 1446m, 1378vw, 1222vw, 1214sh, 1174m, 1108s, 1106s, 1081m, 1080m, 995w, 944s, 925s, 895vw, 840vw, 750m, 735sh, 685w, 660vw, 615vw, 585vw, 565vw, 520vw, 485vw, 378w, 345vw, 336vw, 328vw, 310vw

[a] s = strong, v = very, m = medium, w = weak, sh = shoulder.

[b] Raman bands are found at 555(sh), 554(m) and 518(vs) cm^{-1}.

TABLE VI. Infrared Spectral Frequencies of the Diorganotin(IV) Diphenylphosphate, $R_2Sn[OP(O)(OC_6H_5)_2]_2$, Derivatives below 1600 cm^{-1}.

COMPOUND	INFRARED ABSORPTIONS (in cm^{-1}) [a]
$(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$	1490s, 1455m, 1375w, 1220s, 1198s, 1170sh, 1152sh, 1008vw, 945s, 935sh, 900w, 792w, 775m, 680w, 668sh, 650sh, 585vw, 530vw, 515vw, 378vw, 342vw.
$(\underline{n}-C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	1592m, 1488m, 1406s, 1350m, 1368sh, 1234s, 1200s, 1120s, 968vw, 945s, 936m, 908vw, 900vw, 780m, 756m, 680m, 535w, 392w, 382w, 348w.
$(\underline{n}-C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$	1590m, 1488s, 1458w, 1374w, 1231vs, 1202vs, 1115vw, 1084vw, 940s, 900vw, 875vw, 755m, 750m, 725vw, 685vw, 650vw, 585vw, 550vw, 530w, 388vw, 376vw, 342w, 332vw, 308vw.
$(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	1590w, 1490m, 1460m, 1376m, 1266m, 1214vs, 1112vs, 1068vw, 1008vw, 950s, 935m, 900vw, 780w, 762w, 750vw, 735w, 698w, 686w, 668vw, 655vw, 525w, 455vw, 390vw, 382vw, 369vw, 348w, 336vw.
$(\underline{n}-C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$	1596m, 1490s, 4160vw, 1380s, 1368sh, 1290vw, 1226vs, 1203vs, 1164w, 1115vw, 1105vs, 1008w, 941vs, 934vs, 906w, 780s, 754s, 725vw, 690s, 610vw, 566vw, 535m, 500vw, 390m, 380m, 348m, 310vw.

[a] s = strong, v = very, m = medium, sh = shoulder, w = weak.

[b] A Raman band is found at 524(m) cm^{-1}.

TABLE VII. Selected Assignments in the Infrared Spectra of $R_nSn[OP(O)(OC_6H_5)_2]_{4-n}$ (n=2,3) (cm^{-1})

	n = 3						n = 2					
R =	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9	cyclo-C_6H_{11}	C_6H_5	CH_3	C_2H_5	n-C_4H_9	n-C_8H_{17}	C_6H_5	
	1093vs	1102vs	1102vs	1103vs	1108s	1110vs	1152sh	1120s	1115vs	1105s	1112vs	$\nu_{asym}(PO_4)$
	1024w	1004vs	1006w	1009w	995w	-	1008vw	968vw	-	1008w	1008vw	$\nu_{sym}(PO_4)$

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