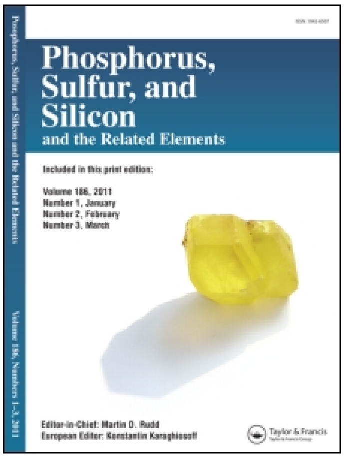

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O-Alkyl Trithiophosphate Derivatives of Triorganotin(IV) and S-Alkyl Trithiophosphate Derivatives of Diorganotin(IV) Chloride

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O-ALKYL TRITHIOPHOSPHATE DERIVATIVES OF TRIORGANOTIN(IV) AND S-ALKYL TRITHIOPHOSPHATE DERIVATIVES OF DIORGANOTIN(IV) CHLORIDE

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Reactions of triorganotin chlorides with potassium salt of O-alkyl trithiophosphate $[ROP(S)(SK)_2; R = Me, Pr^i, Ph]$ *in 2:1 molar ratio in anhydrous benzene yield triorganotin O-alkyl trithiophosphate of the type* $ROP(S)\ [SSnR'_3]_2\ R = Me, Pr^i; Ph, R' = Pr^n, Bu^n, Ph]$ *which are found to be monomeric in nature. These complexes are soluble in common organic solvents. Similar reactions of diorganotin chloride with dipotassium salt of* S-*alkyl trithiophosphate yield diorganotin*-S-*alkyl trithiophosphate of the type* $[(RS)P(O)S_2]_2SnR'_2; R = Me, Pr^i; R' = Me,$ *Et, Ph, which also are found to be monomeric in nature and are soluble in common organic solvents. The newly synthesized derivatives have been characterized by physicochemical and spectroscopic techniques, IR, NMR (*^1H, ^{31}P, *and* ^{119}Sn*).*

Keywords: Diorganotin(IV)-*S*-alkyltrithiophosphates; *O*-alkyltrithiophosphate; *S*-alkyl trithiophosphate; triorganotin(IV)-*O*-alkyltrithiophosphates

In continuation to our earlier investigations on metal, organometal, and organic derivatives of phosphonate and dithiophosphate (open chain and cyclic) esters,[1–14] it was considered of interest to extend the investigations to trithiophosphate ligands.[15–18]

Potassium salts of *O*-alkyltrithiophosphates $[(RO)P(S)(SK)_2]$ show the tendency of isomerization and there exists an equilibrium between thiono $\geqslant P{=}S$ and thiolo $\geqslant P{=}O$ which can show interesting chemical bonding modes in metal and organometal derivatives. Thus it was considered of interest to investigate these reactions.

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RESULTS AND DISCUSSION

Reaction of triorganotin chloride with potassium salt of *O*-alkyl-trithiophosphates in 2:1 molar ratio in anhydrous benzene yield triorganotin *O*-alkyl trithiophosphate.

$$\mathrm{ROP(S)(SK)_2 + 2R'_3SnCl \xrightarrow[\sim 8\,hrs.]{C_6H_6} ROP(S)[SSnR'_3]_2 + 2\,KCl\downarrow}$$

(where R = Me, Pr^i, Ph; R′ = Pr^n, Bu^n, Ph)

These reactions are quite facile but to ensure completion of the reaction, the reaction mixture was refluxed for ~8 h. The products were isolated as viscous liquids.

These complexes are soluble in common organic solvents (benzene, chloroform, carbontetrachloride, dichloromethane) and are found to be monomeric in nature. No change has been observed in the molecularity of these complexes even in the concentrated solutions. In comparison to the hydrolytically stable triorganotin dialkyl and alkylene dithiophosphate, the above derivatives are highly sensitive toward moisture; however, they do not show any aging phenomenon on storage over time.

Diorganotin dichloride reacts with dipotassium salt of *S*-alkyl trithiophosphates in refluxing anhydrous benzene in 1:1 molar ratio to yield diorganotin *S*-alkyl trithiophosphates.

$$\mathrm{(RS)P(O)(SK)_2 + R'_2SnCl_2 \xrightarrow[\sim 6\,hrs.]{C_6H_6} (RS)P(O)S_2SnR'_2 + 2\,KCl\downarrow}$$

(where R = Me, Pr^i; R′ = Me, Et, Ph)

These derivatives are white coloured amorphous solids, soluble in common organic solvents, monomeric in nature, and melt with decomposition at 130°C.

IR SPECTRA

Sharp bands present in the region 635–595 $\mathrm{cm^{-1}}$ are due to νSn—C asymmetric and symmetric vibrations.[9] The absorption band in the region 405–305 $\mathrm{cm^{-1}}$, which is assigned to νSn-S vibrations, clearly indicates the formation of tin-sulphur chemical bond in the triorganotin(IV) derivatives (Table I). In diorganotin, an analogous characteristic is the absorption band in the region of 1190–1150 $\mathrm{cm^{-1}}$ which has been assigned to phosphoryl group coordinated to tin atom which also has been reported in the addition complexes of dialkyl phosphonates with tin (IV) and organotin(**IV**) cholorides[19] as well as in tin(IV) derivatives of

TABLE I IR Spectra of Triorganotin *O*-alkyltrithiophosphates and Diorganotin *S*-alkyltrithiophosphates

S. No.	Compound	ν(P)—O—C	νP—O—(C)	νP=S	νP—S	νSn—C	νSn—S
1	$CH_3OP(S)[SSn(C_3H_7^n)_3]_2$	1010s	880s	700s	545s	625s	395m
2	$CH_3OP(S)[SSn(C_4H_9^n)_3]_2$	1015s	865s	705s	540s	635m	380m
3	$^iC_3H_7OP(S)[SSn(C_4H_9^n)_3]_2$	980s	850s	670vs	530s	595m	365w
4	$C_6H_5OP(S)[SSn(C_4H_9^n)_3]_2$	1020s	865s	710s	545s	610m	405m
5	$C_6H_5OP(S)[SSn(C_6H_5^n)_3]_2$	1015vs	860s	695vs	540s	615s	400w

S. No.	Compound	ν(P)=O	νP—S	νSn—C	νSn—S
6	$CH_3SP(O)[S_2Sn(CH_3)_2]$	1180s	680s	630s	345w
7	$CH_3SP(O)[S_2Sn(C_2H_5)_2]$	1165s	675s	640s	340m
8	$CH_3SP(O)[S_2Sn(C_6H_5)_2]$	1165s	675m	640s	350m
9	$C_3H_7SP(O)[S_2Sn(CH_3)_2]$	1150s	650m	635m	360w
10	$C_3H_7SP(O)[S_2Sn(C_2H_5)_2]$	1155s	670s	620m	365w

mono thiophosphotes.[20] The extent of shifting of phosphoryl absorptions toward lower wavenumbers indicates strong intermolecular coordination with tin atom.

^{1}H NMR SPECTRA

The ^{1}H NMR spectra of triorganotin(IV) derivatives show the characteristic resonances for trialkyl and aryl protons present on tin moiety and show a singlet at δ 3.61–3.88 ppm which is due to the methoxy protons present on phosphorus (Table II). However, an interesting difference is observed in the spectra of derivatives of diorganotin chloride in that the resonance signal for protons present on phosphorous atom get shifted toward downfield. It appears that there is isomerisation from *O*-alkyl to *S*-alkyl in these complexes.[21]

^{31}P NMR SPECTRA

The ^{31}P NMR spectra of triorganotin(IV) derivatives show only one signal in the range of δ 94.63–103.97 ppm which in shifted downfield compared to *O*-alkyl-trithiophosphate (δ 24.32 ppm). This unexpected shift may be due to isomerization of *S*-alkyl trithiophosphate into *O*-alkyl-trithiophosphate. This type of isomerization also has been postulated by C. Glidewell et al. in triorganotin(IV) dialkyl

TABLE II NMR ^{1}H, ^{31}P and ^{119}Sn Spectral Data of Triorganotin *O*-alkyl trithiophosphate and Diorganotin *S*-alkyltrithiophosphates

S. No.	Compound	Chemical shift (δ ppm)	Chemical Shift (d .. ppm)	
			^{31}P	^{119}Sn
1	$CH_3OP(S)[SSn(C_3H_7^n)_3]_2$	1.03–1.75, m, 42H (Sn-$C_3H_7^n$) 3.61, d, 3H (OCH_3)	103.47	138.09
2	$C_3H_7OP(S)[SSn(C_4H_9^n)_3]_2$	0.84, t, 18H (CH_3); 1.09–1.72, m, 42H [Sn-$(CH_2)_3$, CH_3]; 4.71–4.87, m, 1 (OCH)	94.63	141.70
3	$^iC_3H_7OP(S)[SSn(C_4H_9^n)_3]_2$	0.82, t, 18H (CH_3); 1.05–1.51, m, 42H [Sn-$(CH_2)_3$, CH_3^a]; 4.53–4.61, m, 1 (OCH)	97.90	139.51
4	$C_6H_5OP(S)[SSn(C_4H_9^n)_3]_2$	0.81, t, 18H (CH_3); 1.09–1.66, m, 36H [Sn-$(CH_2)_3$]; 7.28, s, 5H (OC_6H_5)	102.17	152.34
5	$C_6H_5OP(S)[SSn(C_6H_5^n)_3]_2$	7.25–7.59, m, 35H (C_6H_5; OC_6H_5)	98.74	—
6	$CH_3SP(O)[S_2Sn(CH_3)_2]$	1.10, s, 6H (CH_3); 3.78, d, 3H (SCH_3)	69.73	121.4
7	$CH_3SP(O)[S_2Sn(C_2H_5)_2]$	1.44, t, 6H (CH_3); 2.00–2.35, m, 4H (CH_2); 3.73, d, 3H (SCH_3)	66.85	87.90
8	$CH_3SP(O)[S_2Sn(C_6H_5)_2]$	3.79, d, 3H (SCH_3); 7.28–7.59, m, 10H (C_6H_5)	65.87	128.16
9	$C_3H_7SP(O)[S_2Sn(CH_3)_2]$	0.91, d, 6H (CH_3); 1.28, s, 6H (Sn-CH_3); 4.6–4.83, m, 1H (SCH)	68.11	126.58
10	$C_3H_7SP(O)[S_2Sn(C_2H_5)_2]$	1.30, d, 6H (CH_3); 1.63–1.88, m, 16H (S-C_2H_5); 4.55–4.77, m, 1H (SCH)	64.36	

[a] Methyl protons of isopropoxy group.

monothiophosphates

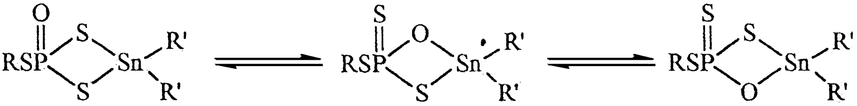
$$(RS)P[O][SSnR'_3]_2 \rightleftharpoons (RO)P(S)[SSnR'_3]_2$$

$$(RO)_2P[O]SSnR'_3 \rightleftharpoons (RO)_2P(S)OSnR'_3$$

On the other hand the diorganotin *S*-alkyl trithiophosphate show only one signal for each derivative in the region δ 64.36–69.73 ppm, which show an upfield shift in contrast to triorganotin derivatives. This indicates the chelation tendency of trithiophosphate ligand and formation of heterocyclic rings with tin atom (Table II).

^{119}Sn NMR SPECTRA

The resonance signals in the range of δ 136.67–152.34 ppm indicates the formation of S—Sn$\lessdot$ chemical bond in compounds of the type $(RO)P(S)[SSnR'_3]_2$. It first has been observed that while in the compounds of the type $(RS)P(O)S_2SnR'_2$, the signal present in the range of δ 87.90 to 128.58 ppm indicates that there a tendency of isomerization as well as may be a formation of a four-membered hetrocyclic ring through sulphur with the tin atom as postulated below (Table II).



EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the course of reactions. Potassium salts of *O*-alkyl and *S*-alkyl trithiophosphates were obtained by the method of Kotwich *et al.*[10] Sulphur was estimated gravimetrically as barium sulphate (Messenger's Method)[22] and tin was estimated through decomposing it by sulphuric acid (A.R.) and nitric acid. Molecular weights were determined by the "Knauer vapour pressure osmometer" using chloroform solution at 45°C. IR spectra were recorded in nujol mull (4000–200 cm^{-1}) on Perkin-Elmer 577 spectrophotometer. Carbon and hydrogen analyses were performed on a Perkin-Elmer CHN/O analyser. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a 90 MHz JEOL FX 90 spectrometer using TMS as an internal reference. ^{31}P NMR were recorded in $CHCl_3$ using H_3PO_4 as an external reference. ^{119}Sn NMR were recorded in benzene (~50–70% concentration) at 33.35 MHz using Me_4Sn as entrance reference. The experimental details of a representative complex is being described below. Analytical results are summarized in Table III.

Preparation of $CH_3OP(S)[SSn(C_3H_7^n)_3]_2$

Tri-n-propyltin (2.00 g) and dipotassium-*O*-methylphosphori-trithioate (0.83 g) were taken in refluxing dry benzene (~40 ml). This reaction mixture was refluxed for about 8 h. The desired product, a powdered solid was obtained after removal of solvent under reduced pressure. The above procedure was adopted for all other preparations. Relevant data are given in Table III.

TABLE III Synthetic and Analytical Data of Triorganotin O-alkyltrithiophosphates and Diorganotin S-alkyltrithiophosphates

	Reactants (g)		Product	Analyses Found (Calcd.)		M. Wt. Found (Calcd.)
	$ROPS_3\dot{K}_2$	R'_3SnCl	$ROPS[SSnR'_3]_2$			
S. No.	R = ….	R′ = …	…….. g; ……..	S	Sn %	
1	Me	Pr^n	$MeOPS(SSnPr^n_3)_2$	14.53	36.51	631.51
	0.83 (3.51)	2.00 (7.06)	1.42 83	(14.69)	(36.33)	(653.38)
2	Pr^I	Bu^n	$Pr^iOPS(SSnBu^n_3)_2$	12.32	31.17	711.04
	1.24 (4.69)	3.04 (9.34)	3.19 89	(12.54)	(31.01)	(765.38)
3	Pr	Bu^n	$PrOPS(SSnBu^n_3)_2$	12.32	31.17	711.04
	1.24 (4.69)	3.04 (9.34)	3.19 89	(12.54)	(31.01)	(765.38)
4	Ph	Bu^n	$PhOPS(SSnBu^n_3)_2$	12.78	29.87	—
	1.24 (4.16)	2.71 (8.32)	2.89 87	(12.00)	(29.69)	
5	Ph	Ph	$PhOPS(SSnPh_3)_2$	10.21	25.53	—
	1.31 (4.55)	3.51 (9.11)	3.92 93	(10.44)	(25.82)	

S. No.	$ROPS_3K_2$	R'_2SnCl	$RSP(O)S_2SnR_2$	S	Sn %	M. Wt. Found (Calcd.)
6	Me	Me	$MeSP(O)S_2SnMe_2$	31.08	38.92	293.18
	1.32 (5.59)	1.23 (5.59)	1.63 95	(31.30)	(38.70)	(306.69)
7	Me	Et	$MeSP(O)S_2SnEt_2$	28.61	35.52	—
	1.45 (6.14)	1.52 (6.13)	2.04 97	(28.68)	(35.46)	
8	Me	Ph	$MeSP(O)S_2SnPh_2$	22.18	27.44	—
	1.31 (5.55)	1.90 (5.52)	2.18 91	(22.28)	(27.55)	
9	Pr^i	Me	$Pr^iSP(O)S_2SnMe_2$	28.57	35.61	314.51
	1.31 (4.96)	1.08 (4.91)	1.58 95	(28.68)	(35.46)	(334.69)
10	Pr	Et	$Pr^iSP(O)S_2SnEt_2$	28.57	35.61	—
	1.31 (4.96)	1.52 (6.13)	1.58 95	(28.68)	(35.46)	

Preparation of $CH_3SP(O)[SSn(CH_3)_2]_2$

Dimethyltin dichloride (1.23 g) and dipotassium *O*-methyl trithiophosphates (1.32 g) were taken in benzene (40 ml) and refluxed for ~6 h. After complete dissolution of trithiophosphate potassium chloride (0.88 g, calcd. 0.89 g) was removed by filtration. It was a white coloured sticky solid. The above procedure was adopted for all other preparations.

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