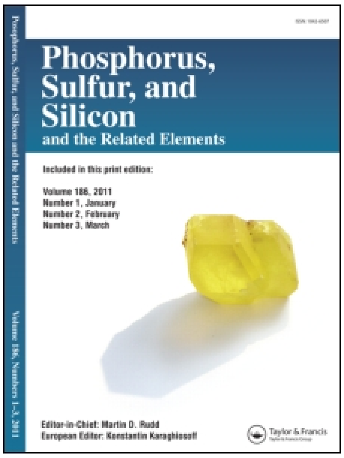

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REACTIONS OF MONOBUTYLTIN OXIDE WITH DIALKYL AND ALKYLENE DITHIOPHOSPHORIC ACIDS: SYNTHESIS AND SPECTRAL STUDIES

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Monobutyltin(IV) dialkyl and alkylene dithiophosphates, $[OSnBuS_2P(OR)_2]_2$, $HOSnBu[S_2P(OR)_2]_2$, (R = Pr^n, Pr^i, Bu^i and Ph), $[OSnBuS_2\overline{POCH_2CMe_2CH_2O}]_n$, $HOSnBu[S_2\overline{POCH_2CMe_2CH_2O}]_2$, $BuSn[S_2P(OR)_2]_3$ (R = Ph and Bu^i) and $BuSn[S_2\overline{POCH_2CH_2CH(Me)O}]_3$ have been synthesized by the reactions of monobutyltin oxide with dialkyl and alkylene dithiophosphoric acids, in 1:1, 1:2 and 1:3 molar ratios in refluxing benzene. These products have been characterized by molecular weight determinations, NMR (^1H, ^{13}C, ^{31}P and ^{119}Sn), IR and elemental analyses. Plausible structures have been suggested.

Key words: Monobutyltin(IV) dialkyl and alkylene dithiophosphates.

INTRODUCTION

The only published work so far, in the field of monoorganotin dithiophosphates is the synthesis of a few tris(dithiophosphato), and mixed chloride dithiophosphato derivatives of BuSn(IV) and PhSn(IV).[1–3] It may be pointed out that the reactions of monobutyltin oxide with O,O′-dialkyl phosphoric acid and diorganophosphoric acids have already been studied.[4–6] The salient differences in the coordination mode of dialkyl phosphato and dithiophosphato groups are well known.[7–11] In view of this, it was thought worthwhile to study the reactions of monobutyltin oxide with dialkyl and alkylene dithiophosphoric acids in various molar ratios and to characterize the isolated products spectroscopically.

RESULTS AND DISCUSSION

Monobutyltin(IV) dialkyl and alkylene dithiophosphates have been synthesized by the reactions of monobutyltin oxide with dialkyl and alkylene dithiophosphoric acids in different stoichiometric ratios in refluxing benzene. The reactions proceed with liberation of water:

(i) $BuSnO_{1.5} + HS_2P(OR)_2 \rightarrow \frac{1}{2}[OSnBuS_2P(OR)_2]_2 + \frac{1}{2}H_2O$
$R = Pr^n, Pr^i, Bu^i, Ph$
$BuSnO_{1.5} + HS_2\overline{POCH_2CMe_2CH_2O} \rightarrow \frac{1}{2}[OSnBuS_2\overline{POCH_2CMe_2CH_2O}]_2 + \frac{1}{2}H_2O$

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(ii) $BuSnO_{1.5} + 2HS_2P(OR)_2 \rightarrow HOSnBu[S_2P(OR)_2]_2 + \frac{1}{2}H_2O$
$R = Pr^n, Pr^i, Bu^i, Ph$
$BuSnO_{1.5} + 2HS_2\overline{POCH_2CMe_2CH_2O} \rightarrow HOSnBu[S_2\overline{POCH_2CMe_2CH_2O}]_2$
$+ \frac{1}{2}H_2O$

(iii) $BuSnO_{1.5} + 3HS_2P(OR)_2 \rightarrow BuSn[S_2P(OR)_2]_3 + 1\frac{1}{2}\,H_2O$
$R = Bu^i, Ph$
$BuSnO_{1.5} + 3HS_2\overline{POCH_2CH_2CH(Me)O} \rightarrow BuSn[S_2\overline{POCH_2CH_2CH(Me)O}]_3$
$+ 1\frac{1}{2}\,H_2O$

The above derivatives are solids or viscous liquids which are soluble in common organic solvents. These are resistant to atmospheric moisture and oxygen and are nonvolatile even under reduced pressure. The molecular weight determination of these derivatives in chloroform indicate their monomeric nature (Tables I and V), except in the case of dithiophosphato monobutyltin oxides which are dimeric (except neopentylene dithiophosphate derivative which is an insoluble solid probably owing to its polymeric nature).

IR SPECTRA

The IR bands (Table II) in the region 1230–1080 cm^{-1} and 930–770 cm^{-1} may be ascribed to the (P)—O—C and P—O—(C) stretching modes respectively.[12]

The P═S and P—S stretching vibrations are observed in the region 685–640 cm^{-1} and 590–520 cm^{-1}, respectively, which are almost in the same range as in the corresponding acids.[13,14]

The band present at 970 cm^{-1} may be assigned to the ring vibration in the cyclic

TABLE I

Molecular weights* of some dithiophosphatomonobutyltin oxides $[OSnBuS_2P(OR)_2]_n$

S.No.	Compound	Conc. g/kg	Mol. wt.	Value of n
1.	$[OSnBuS_2P(OPr^n))]_n$	39.37 47.07	809.1 806.3	2.00 1.99
2.	$[OSnBuS_2P(OPr^i)_2]_n$	69.88 76.30	733.90 744.10	1.81 1.84
3.	$[OSnBuS_2P(OBu^i)_2]_n$	36.15 43.15	871.10 889.10	2.01 2.05
4.	$[OSnBuS_2P(OPh)_2]_n$	91.17 125.84	940.38 1030.30	1.99 2.18

* In chloroform

TABLE II

IR spectra of monobutyltin dithiophosphates

S.No.	Compound	(P)-O-C	P-O-(C)	Ring vibrations	P=S	P-S	Sn-S	HO
1.	$[OSnBuS_2P(OPr^n)_2]_2$	1230m	830s	-	640s	520s	360m	-
2.	$[OSnBuS_2P(OPr^i)_2]_2$	1170s	770s	-	645s	560m	370m	-
3.	$[OSnBuS_2P(OBu^i)_2]_2$	1220bw	830bs	-	640s	570s	350m	-
4.	$[OSnBuS_2P(OPh)_2]_2$	1180s	930s	-	685s	590w	350w	-
5.	$[OSnBuS_2\overline{POCH_2CMe_2CH_2O}]_2$	1080m	815m	970s	660w	525m	370w	
6.	$HOSnBu[S_2P(OPr^n)_2]_2$	1220s	830s	-	650s	520s	360w	3190s
7.	$HOSnBu[S_2P(OPr^i)_2]_2$	1170s	770s	-	650s	650m	340m	3400b
8.	$HOSnBu[S_2P(OBu^i)_2]_2$	1230s	810bs	-	635s	520s	350w	3120b
9.	$HOSnBu[S_2P(OPh)_2]_2$	1180s	925s	-	690s	590m	370m	3300b
10.	$HOSnBu[S_2\overline{POCH_2CMe_2CH_2O}]_2$	1160s	860s	970m	660s	550w	360w	3300b
11.	$BuSn[S_2P(OBu^i)_2]_3$	1230s	830s	-	650s	530s	360w	-
12.	$BuSn[S_2P(OPh)_2]_3$	1160m	920s	-	680s	520s	320w	-
13.	$BuSn[S_2\overline{POCH_2CH_2CH(Me)O}]_3$	1140s	870s	960s	665s	590s	385w	-

s = strong, m = medium, bw= broad weak, w = weak; b = broad

TABLE III

^{31}P, ^{119}Sn and ^{1}H NMR chemical shifts in $CHCl_3$ and $CDCl_3$ respectively of monobutyltin dithiophosphates

S.No.	Compound	^{31}P (ppm)	^{119}Sn (ppm)	^{1}H NMR Chemical shift (ppm)
1.	$(OSnBuS_2P(OPr^n)_2]_2$	91.8	-68.5	(0.9-1.9),m,(Me and CH_2) (3.7-4.33),m,(CH_2O).
2.	$[OSnBuS_2P(OPr^i)_2]_2$	88.5	-78.9	(0.9-1.4),m,(Me and CH_2) (4.6-5.2),m,(CHO)
3.	$[OSnBuS_2P(OBu^i)_2]_2$	92.0	-80.2	(0.9-2.19),m,(Me,CH_2 & CH) (3.66-4.06),m,(CH_2O)
4.	$[OSnBuS_2P(OPh)_2]_2$	88.0	-	0.98,t,(J=7Hz) 6HMe (1.25-1.83),m,12H CH_2 7.74-7.35,m,20H(OPh)
5.	$HOSnBu[S_2P(OPr^n)_2]_2$	91.81	-225.0	(0.90-1.83),m,(Me & CH_2) of Pr^n and Bu (3.71-4.15),m,8H(CH_2O)
6.	$HOSnBu[S_2P(OPr^i)_2]_2$	89.90	-252.6	(0.90-1.43),m,(Me & CH_2) of Pr^i and Bu (4.73-5.22),m,4H(CHO)
7.	$HOSnBu[S_2P(OBu^i)_2]_2$	92.08	-232.49	(0.90-2.23),m,(Me & CH_2,CH) of Bu and Bu^i and OH (3.66-4.11),m,4H(CH_2O)
8.	$HOSnBu[S_2P(OPh)_2]_2$	88.0	—	0.89,t,(J=7Hz),3HMe (1.11-1.65),m,7H(-CH_2) (7.24-7.50),m,20H(OPh)
9.	$HOSnBu[S_2\overline{POCH_2CMe_2CH_2O}]_2$	84.6	—	(1.11-1.90),m,(Me and CH_2) of Bu and ligand 4.15,d(J=16Hz),8H(OCH_2)
10.	$BuSn[S_2P(OBu^i)_2]_3$	92.0	-235	(0.90-2.23),m,(Me,CH_2 and CH) of OBu^i and BuSn (3.84-4.15),m,12H(OCH_2)
11.	$BuSn[S_2P(OPh)_2]_3$	88.5		0.98,t,3H(Me) (1.92-1.56),m,6H(CH_2) (7.77-7.33),m,30H(OPh)
12.	$BuSn[S_2\overline{POCH_2CH_2CH(Me)O}]_3$	84.9	-132.8	(0.80-2.14),m,(Me,CH_2) (2.57-2.90),m,(OCH) (3.12-3.39),m,(OCH_2)

derivatives.[12] The bands in the region 2550 cm^{-1} due to (SH) vibration disappear in these complexes, confirming deprotonation of ligands and metal-sulphur bond formation. The Sn—S stretching bands are assigned in the region 370–350 cm^{-1}.

In case of hydroxomonobutyltin bis(dialkyl and alkylene dithiophosphates) broad bands related to OH are present in the region 3380–3100 cm^{-1}.[17]

NMR SPECTRA

The ^1H NMR spectral data (Table III) of these complexes were recorded in $CDCl_3$. The spectra show characteristic proton resonances of corresponding glycoxy, alkoxy and tinbutyl groups. The spectra are similar to those of the corresponding dialkyl and alkylene dithiophosphoric acids except for the absence of the peak due to the SH proton which indicates the formation of Sn—S bond by deprotonation and presence of a multiplet due to butyl protons, overlapping with alkoxy and glycoxy proton signals.

The signal due to OH proton in hydroxomonobutyltin bis(dialkyl and alkylene) dithiophosphates is not visible and is probably overlapping with the complex multiplet due to Sn—Bu protons.

The ^{13}C NMR spectral data (Table IV) were obtained for some representative derivatives. The spectra show the same chemical shifts for alkoxy carbons as the parent dithio acids. The tin butyl carbons show four signals at the usual positions. The satellites due to $^{13}C—^{119}Sn$ coupling, however, could not be observed. From these data therefore, no useful information about the tin coordination is obtained.

The ^{31}P NMR spectra (Table III) of these complexes recorded in $CHCl_3$ show signals in the range 92.08–84.60 ppm, which indicate the bidentate behaviour of the ligands towards tin.[18,19]

The ^{119}Sn NMR spectral data for some representative compounds are recorded in Table III. The spectra show only one signal for each compound:

(i) In case of dialkyl dithiophosphato monobutyltin oxides the observed chemical

TABLE IV

^{13}C Chemical shifts of monobutyltin dithiophosphates in $CHCl_3$

S.No.	Compound	BuSn Carbons $CH_3CH_2CH_2CH_2Sn$				Alkoxy carbons
		C_1	C_2	C_3	C_4	
1.	$[OSnBuS_2P(OPr^n)_2]_2$	28.33	25.78	24.10	13.70	70.1,(J=7.33Hz)(OCH_2) 35.9,s,(CH_2); 23.4,t,(J=3.7 Hz)Me
2.	$[OSnBuS_2P(OPr^i)_2]_2$	28.70	25.67	23.51	13.70	73.78,d,(J=7.30Hz)(OCH) 23.5,t,(J=3.66Hz)Me
3.	$[OSnBuS_2P(OBu^i)_2]_2$	29.57	27.57	25.78	13.75	74.1,d,(J=7.32Hz)(OCH_2) 18.85,s,(CH_3), 29.25,s,CH
4.	$HOSnBu[S_2P(OPr^i)_2]_2$	28.70	28.20	26.03	13.37	74.78,d,(J=6Hz)OCH 23.36,d,(J=4.88Hz)Me
5.	$HOSnBu[S_2P(OBu^i)_2]_2$	28.70	28.30	-	13.38	74.0,d,(J=7.32Hz)(OCH_2) 18.63,s,(CH_3) 28.22,d,(J=8.21Hz)CH

shifts are in the range (-68 to -80 ppm) which indicate five coordinated environment around the tin atoms.[2]

(ii) The ^{119}Sn NMR chemical shifts of three representative compounds of hydroxomonobutyltin bis(dialkyl dithiophosphates) have been found to be in the range (-252.67 to -225.0 ppm). These values fit well with the presence of six-coordinated tin atoms.[2]

(iii) The ^{119}Sn chemical shifts for monobutyltin tris(dialkyl and alkylene) dithiophosphates are observed in the range -254 to -235 ppm for open chain and -132 ppm for the cyclic derivative, respectively.

From ^{119}Sn NMR studies we can conclude that the ^{119}Sn NMR shifts in the dithiophosphate derivatives are highly influenced by the nature of alkoxy and glycoxy groups attached to phosphorus. Thus, open chain moieties shield the tin atom more effectively than cyclic dithiophosphato moieties.

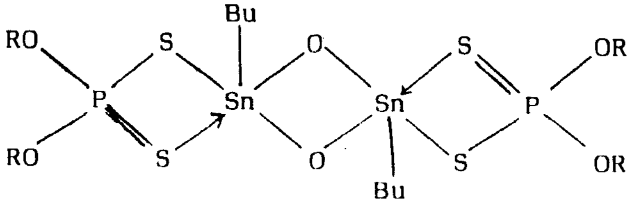
The dramatic change in chemical shifts observed on going from tributyltin dithiophosphate to dibutyltin bis(dithiophosphate) does not repeat itself on going from dibutyltin derivatives to monobutyltin derivatives. In fact, in cyclic dithiophosphates, there is no change at all. In open chain dithiophosphate there is substantial change (60 to 100 ppm) and the tin atom is much more shielded in butyltin tris(dithiophosphates).

From tin NMR data it can be concluded that butyltin tris(dithiophosphates) derived from open chain dithiophosphoric acids possess 7-coordinated environment around tin atom, similar to corresponding dithiocarbamates.[20,21]

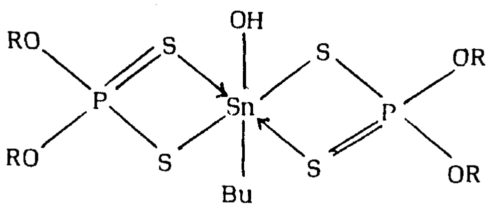
The data for butyltin tris(alkylene) derivatives can be correlated with a 6-coordinated structure for these compounds. In such a case, two dithiophosphato moieties will be bidenate and one will be monodentate. This is, however, not supported by the ^{31}P NMR spectra which shows only one signal for each compound. Thus, it may be concluded that tris(alkylene dithiophosphates) are either 6-coordinated with fast exchange between the bidentate and monodentate or all the dithiophosphates moieties are bidentate but the chelation is very weak.

STRUCTURAL ELUCIDATION

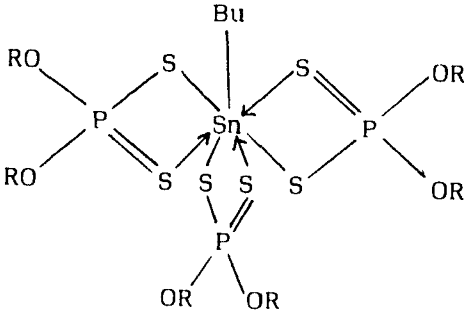
In keeping with the trend of the dialkyl and alkylene dithiophosphate ligands behaving as mono- and bidentate with tri and diorganotin moieties, respectively, their bidentate nature could also be expected in monoorganotin derivatives.



(I)



(II)



(III)

In the light of the molecular weight and spectroscopic studies structure (I) (II) and (III) are proposed for dialkyldithiophosphato monobutyltin oxides, hydroxomonobutyltin bis(alkyl) dithiophosphates and butyltin tris(dialkyl)dithiophosphates, respectively.

Similar structures may be proposed for cyclic derivatives also.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture from the experimental set-up. The dialkyl and alkylene dithiophosphoric acids were prepared by literature methods.[8] Sulphur and tin were estimated gravimetrically as barium sulphate (Messenger's method) and tin oxide, respectively. Molecular weights were determined cryoscopically in chloroform. IR spectra (4000–200 cm^{-1}) were recorded in Nujol on a Perkin-Elmer 577 spectrometer. NMR spectra were recorded on a Jeol FX 90Q MHz spectrometer using TMS (for ^{1}H and ^{13}C) as the internal reference, H_3PO_4 (for ^{31}P) and Me_4Sn (for ^{119}Sn) as external references.

METHODS OF PREPARATION

Mixtures of dialkyl or alkylene dithiophosphoric acid and monobutyltin oxide in appropriate ratios in benzene were refluxed on a fractionating column for ~3 hrs. The liberated water was removed azeotropically, with subsequent removal of excess benzene. The products were obtained by drying under reduced pressure.

Analytical and other relevant data for these experiments are given in Table V.

TABLE V

Reactions of monobutyltin oxide with dithiophosphoric acids in different molar ratios

S.No.	Reactants		Molar ratio	Products g/(mmol)	Yield %	Physical state (M.P.°C)	Molecular weight* Found (Calcd.)	Analyses	
	$BuSnO_{1.5}$ g/(mmol)	Dialkyl and alkylene dithiophosphoric acid g/(mmol)						Sn Found (Calcd.)	S
1	2	3	4	5	6	7	8	9	10
1.	1.51 (7.56)	$HS_2P(OPr^n)_2$ 1.62 (7.57)	1:1	$[OSn(Bu)S_2P(OPr^n)_2]_2$ 2.98 (7.36)	97.3	Yellow liquid	-	29.51 (29.33)	15.47 (15.81)
2.	2.48 (12.41)	$HS_2P(OPr^i)_2$ 2.66 (12.42)	1:1	$[OSn(Bu)S_2P(OPr^i)_2]_2$ 4.88 (12.05)	97.2	Yellow liquid	-	29.63 (29.33)	15.23 (15.81)
3.	0.89 (4.45)	$HS_2P(OBu^i)_2$ 1.08 (4.46)	1:1	$[OSn(Bu)S_2P(OBu^i)_2]_2$ 1.82 (4.20)	94.7	Yellow viscous liquid	-	27.55 (27.43)	14.83 (14.79)
4.	1.16 (5.80)	$HS_2P(OPh)_2$ 1.64 (5.81)	1:1	$[OSn(Bu) S_2P(OPh)_2]_2$ 2.63 (5.56)	95.9	White solid (98)	—	25.63 (25.11)	13.24 (13.50)
5.	1.23 (6.15)	$HS_2\overline{POCH_2CMe_2CH_2O}$ 1.21 (6.11)	1:1	$[OSn(Bu)S_2\overline{POCH_2CMe_2CH_2O}]_2$ 2.11 (5.42)	88.2	White solid (128)	—	30.86 (30.53)	16.27 (16.47)
6.	0.83 (4.15)	$HS_2P(OPr^n)_2$ 1.77 (8.27)	1:2	$HOSn(Bu)[S_2P(OPr^n)_2]_2$ 2.52 (4.07)	98.0	Yellow viscous liquid	615.1 (618.7)	19.36 (19.18)	20.44 (20.68)
7.	1.10 (5.50)	$HS_2P(OPr^i)_2$ 2.36 (11.02)	1:2	$HOSn(Bu)[S_2P(OPr^i)_2]_2$ 3.31 (5.34)	97.3	Yellow viscous liquid	630.4 (618.7)	19.74 (19.18)	20.73 (20.68)
8.	0.91 (4.55)	$HS_2P(OBu^i)_2$ 2.20 (9.09)	1:2	$HOSn(Bu)[S_2P(OBu^i)_2]_2$ 2.93 (4.34)	95.1	Yellow viscous liquid	678.9 (674.7)	17.83 (17.59)	28.91 (28.45)
9.	0.37 (1.85)	$HS_2P(OPh)_2$ 1.05 (3.72)	1:2	$HOSn(Bu)[S_2P(OPh)_2]_2$ 1.31 (1.73)	94.2	Yellow viscous liquid	740.7 (754.7)	16.20 (15.91)	17.62 (17.16)
10.	1.14 (5.70)	$HS_2\overline{POCH_2CMe_2CH_2O}$ 2.27 (11.46)	1:2	$HOSn(Bu)[S_2\overline{POCH_2CMe_2CH_2O}]_2$ 3.22 (5.48)	96.4	Sticky yellow semi-solid	647.3 (586.7)	21.04 (20.54)	22.30 (22.15)
11.	0.47 (2.35)	$HS_2P(OBu^i)_2$ 1.71 (7.06)	1:3	$BuSn[S_2P(OBu^i)_2]_3$ 1.98 (2.20)	93.8	Orange viscous liquid	891.1 (898.7)	13.26 (13.20)	21.64 (21.36)
12.	0.50 (2.50)	$HS_2P(OPh)_2$ 2.11 (7.48)	1:3	$BuSn[S_2P(OPh)_2]_3$ 2.36 (2.31)	94.5	Yellow viscous liquid	1016.0 (1018.7)	11.88 (11.65)	18.69 (18.84)
13.	2.32 (11.65)	$HS_2\overline{POCH_2CH_2CH(CMe)O}$ 6.41 (34.83)	1:3	$BuSn[S_2\overline{POCH_2CH_2CH(Me)O}]_3$ 7.99 (11.03)	95.0	Brown viscous liquid	729.4 (724.7)	16.57 (16.37)	26.85 (26.49)

* In chloroform

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