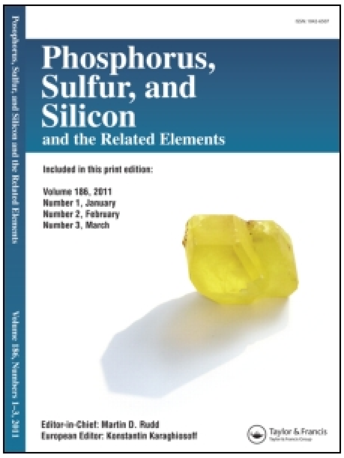

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DIALKYL THIOPHOSPHONATE DERIVATIVES OF TRIORGANOTIN(IV)

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The reaction of triorganotin chlorides with sodium dialkyl thiophosphites proceeds to completion on refluxing the reactants in a 1:1 molar ratio for about ten hours. Similar reactions of triorganotin chloride with dialkyl thiophosphonate do not give comparable yields in the presence of triethylamine. The products formed are colorless volatile liquids having pungent odour, are miscible with common organic solvents and are found to be monomeric. Exposure of these compounds to atmospheric oxygen the thiophosphite [Sn-S-P] linkage was oxidized to a thiophosphate [Sn-O-P(S)] linkage. These complexes have been characterized by elemental analyses, molecular weight determination, IR, ^{1}H NMR and ^{31}P NMR spectral data.

Key words: Dialkyl thiophosphonate; 2-thiono-1,3,2-dioxa-4,4′,6-trimethyl-phosphorinane; triorganotin dialkyl thiophosphite

INTRODUCTION

Dialkyl phosphonates[1,2] and dialkyl thiophosphonates[3,4] are versatile ambidentate ligands and form a wide variety of complexes with transition[5–7] and main group elements.[8–13] A survey of literature reveals that no work appears to have been carried out on organotin dialkyl thiophosphites. The work carried out on dialkyl phosphonate[9,10] and dialkyl thiophosphonate[11] derivatives of arsenic(III) have also been extended to organotin moieties.

RESULTS AND DISCUSSION

Reaction of dialkyl phosphinouschloride with dry hydrogen sulphide gas in the presence of triethylamine in a nitrogen atmosphere has been found to be a most suitable method for the synthesis of dialkyl thiophosphonates[3,4]:

$$(RO)_2PCl + H_2S + Et_3N \xrightarrow{N_2\,atm.} (RO)_2P(S)H + Et_3N.HCl\downarrow$$

The above method has been extended to the synthesis of a new, 2-thiono-1,3,2-dioxa-4,4′,6-trimethyl-phosphorinane:*

$$G(OH)_2 + PCl_3 + 2Et_3N \xrightarrow[0\text{–}5^\circ C]{N_2\,atm.} \overline{OGOP}Cl + 2Et_3N.HCl\downarrow$$

$$\overline{OGOP}Cl + H_2S + Et_3N \xrightarrow[0\text{–}5^\circ C]{N_2\,atm.} \overline{OGOP}(S)H + Et_3N.HCl\downarrow$$

$$(\text{where } G = Me_2\underset{|}{C}CH_2\underset{|}{C}HMe^* \;\&\; \underset{|}{C}H_2CMe_2\underset{|}{C}H_2)$$

TABLE I

Synthesis and properties of triorganotin dialkyl thiophosphites

S. No.	Reactants (g) R_3SnCl R	Reactants (g) >P(S)H R or G		Product (g) physical state	NaCl or $Et_3N{\cdot}HCl$ (g) found (calcd)	b.p. °C/mm (% yield)	% Analyses Found Sn	% Analyses (Calcd) S	Mol. Wt. found (calcd) &
1.	Me 3.70	Et 2.87	Et_3N 2.07	$Me_3SnSP(OEt)_2$ 5.36, transparent liquid	2.22 (2.56)	65–70/3 (67)	36.98 (37.47)	9.85 (10.10)	—
2.	Et 4.16	Et 2.66	Na 0.58	$Et_3SnSP(OEt)_2$ 5.57, light yellow liquid	1.20 (1.01)	90/4.2 (65)	33.94 (33.08)	9.05 (8.92)	354 (358.7)
3.	Me 1.20	$—OCH_2CMe_2CH_2O—$ 1.0	Et_3N 1.66	$Me_3SnSPOCH_2CMe_2CH_2O$ 2.16, white viscous liquid	0.74 (0.83)	80/0.5 (45)	36.01 (36.11)	9.51 (9.79)	—
4.	Et 1.28	$—OCH_2CMe_2CH_2O—$ 0.88	Et_3N 0.59	$Et_3SnSPOCH_2CMe_2CH_2O$ 2.38, transparent liquid	0.53 (0.73)	85–90/0.25 (43)	31.56 (32.01)	8.52 (8.63)	365 (370.0)
5.	Et 1.25	$—OCMe_2CH_2CHMeO—$ 0.94	Na 0.12	$Et_3SnSPOCMe_2CH_2CHMeO$ 1.45, transparent liquid	0.46 (0.25)	85/0.05 (67)	30.62 (30.85)	8.19 (8.31)	—
6.	Pr^n 1.12	$—OCMe_2CH_2CHMeO—$ 0.70	Na 0.09	$Pr^n_3SnSPOCMe_2CHMeO$ 1.96, transparent liquid	0.22 (0.22)	93–98/0.05 (72)	27.62 (27.81)	7.34 (7.49)	—

2-Thiono-1,3,2-dioxa-4,4,'6-trimethyl-phosphorinane is a colorless volatile liquid (b.p., 160°C/0.7 mm) miscible with common organic solvents. The IR spectrum shows characteristic absorption at 2375 (ν P-H) and 690 (ν P = S) cm^{-1}. The PMR spectrum is quite complicated in the region 1.1–1.3 ppm. However, some of the sharp peaks which can be assigned appear at δ 1.1d(CH_3), 1.2s(CH_3—C—CH_3), 1.3d(CH_2), 4.5m(CHO) and 4.9s P-H proton). Sodium salts of dialkyl and alkylene thiophosphonates were prepared by refluxing these with sodium in benzene for 4–6 hours:

$$(RO)_2P(S)H + Na \xrightarrow{N_2\,atm.} (RO)_2PSNa + \tfrac{1}{2}H_2\uparrow$$

$$\overline{OGOP}(S)H + Na \xrightarrow{N_2\,atm.} \overline{OGOP}SNa + \tfrac{1}{2}H_2\uparrow$$

$$\text{(where } R = Et,\ G = \underline{C}H_2CMe_2\underline{C}H_2,\ Me_2\underline{C}CH_2\underline{C}HMe)$$

For the reaction with triorganotin chlorides, sodium salts were prepared in situ, as these cannot be stored for a long time. Triorganotin dialkyl thiophosphites have been synthesized by the methods described below:

$$R_3SnCl + (EtO)_2PSNa \rightarrow R_3SnSP(OEt)_2 + NaCl\downarrow$$

$$R_3SnCl + (EtO)_2P(S)H + Et_3N \rightarrow R_3SnSP(OEt)_2 + Et_3N.HCl\downarrow$$

$$R_3SnCl + \overline{OGOP}SNa \rightarrow R_3SnS\overline{POGO} + NaCl\downarrow$$

$$R_3SnCl + \overline{OGOP}(S)H + Et_3N \rightarrow R_3SnS\overline{POGO} + Et_3N.HCl\downarrow$$

$$\text{(where } R = Me,\ Et,\ Pr^n,\ G = \underline{C}H_2CMe_2\underline{C}H_2,\ Me_2\underline{C}CH_2\underline{C}HMe)$$

The reactions of triorganotin chlorides with sodium salts proceed to completion on refluxing the reactants in 1:1 molar ratio for ~10 hrs. while similar reactions in the presence of triethylamine gives lower yields. The products, isolated after filtering off the sodium chloride or triethylamine hydrochloride and removal of the solvent in *vacuo,* are colorless volatile liquids having a pungent odor. These are miscible with common organic solvents and are found to be monomeric in refluxing benzene (Table I). In all the derivatives the mode of bonding with tin appears to occur through the sulfur atom of the thiophosphite group [P-S-Sn], as concluded from a study of their spectroscopic properties.

IR Spectra

A comparison of the IR spectra of triorganotin dialkyl thiophosphites with the starting materials shows the following characteristic features:

1. The disappearance of ν P-H and ν Sn-Cl bands present at 2400 ± 10 cm^{-1} and 350 cm^{-1}.
2. The disappearance of strong and sharp thiophosphoryl (P = S) band present at 630 cm^{-1}.
3. Appearance of a new, sharp and strong band at 680-650 cm^{-1} which is tentatively assigned to ν Sn-S-P band.

TABLE II

Some relevant IR spectral data for triorganotin dialkyl thiophosphites

Compound	ν(P)—O—C	νP—O—(C)	νSn—S—P	νSn—C
$Me_3SnSP(OEt)_2$	1125 s	875 m	770 vs	450 m
$Et_3SnSP(OEt)_2$	1080	990 s	660 vs	510 s
$Me_3SnSPOCH_2CMe_2CH_2O$	1060 vs	1000 s	770 s	470 m
$Et_3SnSPOCH_2CMe_2CH_2O$	1065 vs	965 s	673 vs & br	503 vs
$Et_3SnSPOCH_2CMe_2CHMeO$	1080 vs	970 s	670 vs & br	503 s
$Pr^nSnSPOCH_2CMe_2CHMeO$	1110 vs	895 s	675 vs	580 vs

s = strong, vs = very strong, m = medium, br = broad.

The (P)-O-C and P-O-(C) absorption bands are retained in the products and are present in the same range as in dialkyl thiophosphonates (875–1125 cm^{-1}). The position of Sn-S-P band was assigned on the basis that there is no IR absorption band in the region 630–750 cm^{-1} in the reactants. The IR spectrum of triethyltin diethyl thiophosphite exposed to atmospheric moisture shows the appearance of ν P-H absorption band at 2420 cm^{-1} which was absent initially in the distilled product. On exposing these compounds to atmospheric oxygen at ambient temperatures, a broad and diffuse band of low intensity also appeared in the thiophosphoryl region at 630 cm^{-1}. It was presumed that the appearance of this band in the thiophosphoryl(P = S) region indicates sensitivity of these complexes towards atmospheric oxygen and shows conversion of the -thiophosphite [P-S-Sn] linkage to the -thiophosphate [Sn-O-P(S)] linkage. Other important IR absorption frequencies are listed in Table II.

NMR Spectra

The ^1H NMR spectra of these complexes show characteristic resonance of the corresponding alkyl groups present on tin and alkoxy and glycoxy groups on phosphorus atom respectively. The P-H proton NMR signal was absent in these complexes. A complex multiplet was present for the CH_2OP and CHOP protons

TABLE III

^1H NMR spectral data for triorganotin dialkyl thiophosphites

Compound	^1H chemical shift in δ ppm (in CCl_4)
$Me_3SnSP(OEt)_2$	0.56 s, (CH_3Sn), 1.44 t(CH_3), 4.11 dq (CH_2OP)
$Et_3SnSP(OEt)_2$	1.1 m(CH_3, CH_3CH_2Sn), 4.1 m(CH_2OP)
$Me_3SnSPOCH_2CMe_2CH_2O$	0.56 s(CH_3Sn), 0.55 d, 1.0 d, 1.33 d $(CH_3)_2C$, 2.89–4.22 m (CH_2OP)
$Et_3SnSPOCH_2CMe_2CH_2O$	1.22 t($(CH_3)_2C$, CH_3), 2.0 q (CH_2Sn), 2.9–4.3 m (CH_2OP)
$Et_3SnSPOCMe_2CH_2CHMeO$	1.0–1.7 m, 1.2s $(CH_3)_2C$, & (CH_2C, C_2H_5Sn) 4.6 m (CHOP)
$Pr^n_3SnSPOCMe_2CH_2CHMeO$	1.0 s $(CH_3)_2C$, 1.1 d (CH_3), 1.3–1.6 m (—CH_2—), 4.8 m (CHOP)

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

due to the coupling with phosphorus atom. The ^1H NMR spectral data of these compounds are listed in Table III.

The ^{31}P NMR spectra of these compounds present a complicated pattern of resonance peaks. In the proton coupled spectrum of $\overline{OCH_2CMe_2CH_2OP}SSnR_3$ (R = Me & Et) pentet are present in the region for a tricovalent phosphorus atom (109–116.01 ppm). This value for the phosphorus chemical shift indicates preferential formation of Sn-S-P linkage rather than a Sn-P(S) linkage. The ^{31}P NMR chemical shift value for $(Pr^iO)_2PSSiPh_3$ have also been observed at 104.7 ppm[14] which is also in agreement with the current results.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture and oxygen during experimental manipulations. Dialkyl thiophosphonates (open chain & cyclic)[3,4] were prepared by already reported methods. Sulphur and tin were estimated gravimetrically as barium sulphate (Messenger's method) and tin oxide respectively. Molecular weights were determined ebulloscopically in refluxing benzene. IR spectra were recorded as neat liquids on a Perkin-Elmer 577 spectrometer in the range 4000–200 cm^{-1} using CsI cells. ^1H NMR spectra were recorded in carbon tetrachloride on a Perkin-Elmer R-12B spectrometer (60 MHz) using TMS as an external standard. ^{31}P NMR spectra were recorded in carbon tetrahcloride on JEOL FX 90Q spectrometer using H_3PO_4 as an external standard.

Methods of Preparation

(a) Reaction of triethyltin chloride and diethyl thiophosphonate in 1:1 molar ratio

To a calculated quantity of sodium wire (0.58 g, 0.02 moles) in toluene (~50 ml) was added drop-wise a toluene solution of diethyl thiophosphonate (2.66 g, 0.017 moles) in nitrogen atmosphere. The contents were refluxed for 2–3 hours until the reaction of sodium wire with diethyl thiophosphonate was complete. To this solution was added drop-wise a toluene solution (~10 ml) of triethyltin chloride (4.16 g, 0.017 moles) within one hour. The contents were refluxed for ~10 hours to ensure completion of the reaction. Sodium chloride was precipitated. Sodium chloride (Found 1.2 g, calcd. 1.01 g) was filtered off under anhydrous reaction conditions and the solvent was removed under reduced pressure. The product triethyltin diethyl thiophosphite (5.57 g) was obtained as a light colored transparent liquid with a pungent smell. The product was finally distilled under reduced pressure (90°C/4.2 mm, 67%). A viscous liquid (1.07 g) was left as a residue. Found: S, 9.05; Sn, 33.94; Calcd. for $C_{10}H_{25}O_2PSSn$: S, 8.92%; Sn, 33.09%.

(b) Reaction between triethyltin chloride and 2-thiono-5,5′-dimethyl-1,3,2-dioxa-phosphorinane in a 1:1 molar ratio

To a benzene (~30 ml) solution of 2-thiono-5,5′-dimethyl-1,3,2-dioxa-phosphorinane (0.88 g, 0.005 mole) and triethylamine (0.59 g, 0.006 mole) in a nitrogen atmosphere was added drop-wise a benzene solution (~10 ml) of triethyltin chloride (1.28 g, 0.005 mole). A small amount of white solid was precipitated. The reaction mixture was refluxed for eight hours to ensure completion of the reaction. Triethylamine hydrochloride (Found 0.53 g, Calcd. 0.73 g) precipitated was filtered off, and the excess of solvent was removed under reduced pressure. The product (2.38 g) was obtained as a transparent viscous liquid, which on distillation under reduced pressure (85–90°/0.25 mm) yields a colorless liquid (1.02 g, 43%). Found: S, 8.52; Sn, 31.56; Calcd. for $C_{11}H_{25}O_2PSSn$: S, 8.62; Sn, 32.01%.

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

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