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TRIORGANOTIN(IV) *O,O*-ALKYLENE DITHIOPHOSPHATES

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Summary

The *O,O*-alkylene dithiophosphates of triorganotin(IV) of the general formula $R_3SnS_2PO_2G$ (where $R = C_6H_5$, n-C_4H_9, n-C_3H_7, C_2H_5 and CH_3; $G = CH_2C(CH_3)_2CH_2$, $C(CH_3)_2C(CH_3)_2$ and $C(CH_3)_2CH_2CHCH_3$) have been synthesized by treatment of triorganotin(IV) chlorides with ammonium *O,O*-alkylene dithiophosphates in 1/1 molar ratio in benzene. These novel complexes are either white crystalline solids or distillable liquids; all are soluble in common organic solvents and are monomeric in refluxing benzene. Like dialkyldithiophosphate derivatives of triorganotin(IV), these cyclic chain derivatives appear to be tetrahedral, the ligands behaving as unidentates.

Introduction

Dialkyldithiophosphates of transition metals have been extensively studied and the studies have been extended more recently to derivatives of non-transition metals, including organotin(IV) moieties [1–4], which are known to have biocidal properties [5,6]. In contrast to the bidentate behaviour of dialkyldithiophosphates as chelating ligands towards transition metals and diorganotin(IV) moieties [7], it has been shown recently on the basis of their Mössbauer spectra, confirmed by the crystal structure of triphenyltin(IV) diethyldithiophosphate [8], that these ligands behave as unidentates towards trialkyl(aryl)tin moieties. Metal derivatives of cyclic *O,O*-alkylene dithiophosphoric acids, (a facile synthesis of which was recently described [9,10]) do not appear to have received much attention except for the determination of some stability constants and spectrophotometric studies of some of the nickel, cobalt, copper and zinc derivatives [11–13]. In view of the exceptional bonding characteristics of simple dialkyldithiophosphates towards triorganotin(IV) moieties, a study of the corresponding cyclic derivatives should be of considerable interest, and the synthesis and properties of a few triorganotin(IV) *O,O*-alkylene dithiophosphates are described below.

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TABLE 1

REACTIONS OF TRIORGANOTIN(IV) CHLORIDES WITH AMMONIUM *O,O*-ALKYLENE DITHIOPHOSPHATES IN 1/1 MOLAR RATIO

Reactants		Ammonium chloride (g) (Found (Calcd.))	Yield (%)	Physical state m.p./b.p. (°C/mmHg)	Analysis (Found (calcd.) (%))		Molecular weight Found (Calcd.)
R_3SnCl R (g)	$H_4NS_2PO_2G$ G (g) (Found (Calcd.))				Sn	S	
C_6H_5 1.23	$(CH_3)_2CCH_2CHCH_3$ 0.75 (0.73)	0.17 (0.18)	98	White solid 145–147	21.08 (21.17)	11.25 (11.42)	–
n-C_4H_9 1.29	$(CH_3)_2CCH_2CHCH_3$ 0.96 (0.91)	0.20 (0.21)	95	Colourless liquid 145/.01	23.45 (23.70)	12.59 (12.78)	–
n-C_3H_7 2.38	$(CH_3)_2CCH_2CHCH_3$ 2.33 (2.30)	0.53 (0.53)	99	Colourless liquid 156/.05	25.80 (25.86)	13.89 (13.94)	–
C_2H_5 2.04	$(CH_3)_2CCH_2CHCH_3$ 1.97 (1.93)	0.42 (0.43)	97	Colourless liquid 162/.01	28.40 (28.48)	15.28 (15.35)	–
CH_3 1.96	$(CH_3)_2CCH_2CHCH_3$ 2.29 (2.26)	0.51 (0.52)	97	White solid 125	31.50 (31.68)	17.24 (17.08)	341 (374)
C_6H_5 2.12	$(CH_3)_2CC(CH_3)_2$ 1.32 (1.26)	0.29 (0.29)	98	White solid 115–116	21.54 (21.17)	11.57 (11.42)	517 (560)
n-C_4H_9 1.79	$C(CH_3)_2C(CH_3)_2$ 1.33	0.22 (0.29)	97	Colourless liquid 162–163/.01	23.70 (23.70)	12.70 (12.78)	–

n-C_3H_7 1.38	$(CH_3)_2CC(CH_3)_2$ 1.19 (1.19)	0.24 (0.26)	94	Colourless liquid 130–132/.05	25.81 (25.86)	13.87 (13.94)	–
C_2H_5 1.23	$C(CH_3)_2C(CH_3)_2$ 1.83 (1.83)	0.39 (0.43)	93	Colourless liquid 141–144/.01	28.46 (28.48)	15.27 (15.35)	–
CH_3 1.26	$C(CH_3)_2C(CH_3)_2$ 1.45 (1.45)	0.40 (0.44)		White solid 65–68	31.64 (31.68)	17.02 (17.08)	333 (374)
C_6H_5 1.69	$CH_2C(CH_3)_2CH_2$ 0.94 (0.94)	0.23 (0.24)	95	White solid 65	21.10 (21.71)	11.67 (11.70)	544 (546)
n-C_4H_9 2.19	$CH_2C(CH_3)_2CH_2$ 11.48 (1.43)	0.34 (0.36)	98	Colourless liquid 170/.05	24.28 (24.39)	13.54 (13.15)	–
n-C_3H_7 2.29	$CH_2C(CH_3)_2CH_2$ 1.99 (1.75)	0.51 (0.53)	68	Colourless liquid 160/.1	26.60 (26.69)	14.09 (14.39)	–
C_2H_5 1.25	$CH_2C(CH_3)_2CH_2$ 1.22 (1.09)	0.28 (0.30)	94	Colourless liquid 145/.1	25.62 (25.68)	13.78 (13.84)	–
CH_3 2.41	$CH_2C(CH_3)_2CH_2$ 2.61(2.60)	0.55 (0.64)	89	Sticky solid	32.73 (32.91)	17.94 (17.74)	–

Results and discussion

Triorganotin(IV) *O,O*-alkylene dithiophosphates were prepared by treatment of ammonium *O,O*-alkylene dithiophosphates with triorganotin(IV) chlorides in 1/1 molar ratio in benzene.

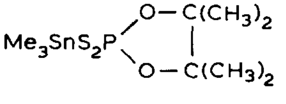
(R = C_6H_5, n-C_4H_9, n-C_3H_7, C_2H_5 and CH_3 ;
G = $-CH_2C(CH_3)_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$ and $-C(CH_3)_2CH_2CHCH_3$)

The reactions occur readily and are completed within 2–3 h when the reactants solution is stirred at room temperature. The products are soluble in common organic solvents such as benzene, chloroform, carbon tetrachloride and carbon disulfide. The triphenyltin(IV) and trimethyltin(IV) derivatives are white crystalline solids while the others are liquids. The solid products were crystallized from a benzene/petroleum ether (40–60°C) mixture, and the liquid products were purified by distillation under reduced pressure. All the compounds were shown to be monomeric in refluxing benzene.

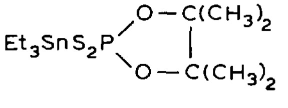
In the IR spectra of these derivatives (Table 2), the bands present in the regions 1000–1050 and 810–870 cm^{-1} are assigned [1,14–17] to ν((P)–O–C) and ν(P–O–(C)) stretching vibrations, respectively. A sharp band in the region 650–720 cm^{-1} appears to be due to ν(P=S) [18] stretching vibrations, and this overlaps with Sn-C_6H_5 vibrations in triphenyltin compounds. The bands present in the region 490–600 cm^{-1} are due to ν(P–S) [1,14] symmetric and asymmetric vibrations. The bands present in the region 908–950 cm^{-1} are due to dioxaphospholane and dioxaphosphorinane ring vibrations [19,20]. The ν(Sn–C) vibrations appear in the range 490–545 cm^{-1} [1,21].

The ^1H NMR spectra (Table 3) show the characteristic proton resonances of the corresponding alkylene protons as well as those of the alkyl(aryl)tin groups. The sharp singlet in the range δ 3.1–3.7 ppm, characteristic of the S–H protons in *O,O*-alkylene dithiophosphoric acids, is absent from the ^1H NMR spectra of the organotin(IV) derivatives. The complex multiplet due to the protons of phenyl groups attached to the tin atom was present at δ 7.0–8.1 ppm. The Sn–CH_3 protons appear give a sharp singlet with double satellite resonances of relative intensity of 4–5% on both sides of the main peak (singlet); due to the coupling of the protons with ^{119}Sn and ^{117}Sn isotopes the coupling constant being 52–56 Hz. The similarity of the coupling constant to that reported for simple trimethyltin(IV) dialkyldithiophosphates [1] indicates that the ligands are also monodentate in the cyclic derivatives.

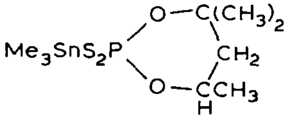
The ^{31}P NMR resonances were observed at δ 85.5 and δ 87.2 ppm for I and II,



(I)



(II)



(III)

TABLE 2

SOME RELEVANT INFRARED SPECTRAL DATA (Nujol mulls) FOR TRIORGANOTIN(IV) *O,O*-ALKYLENE DITHIOPHOSPHATES AND ALKYLENE DITHIOPHOSPHORIC ACIDS

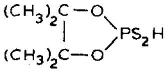
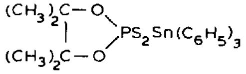
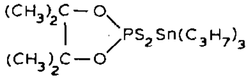
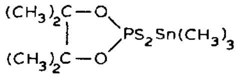
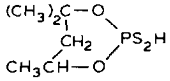
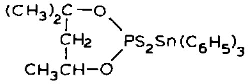
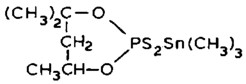
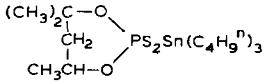
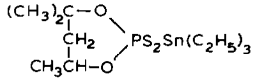
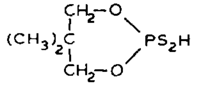
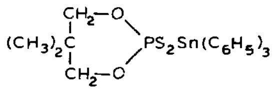
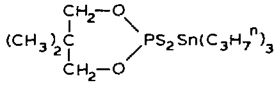
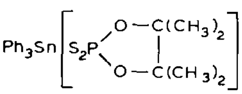
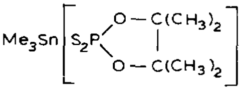
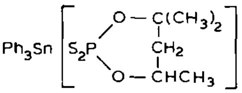
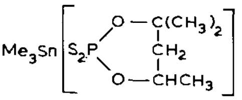
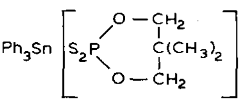
Compound	ν(S–H) cm^{-1}	ν(P)–O–C cm^{-1}	νP–O–(C) cm^{-1}	Ring vibration cm^{-1}	ν(P=S) cm^{-1}	ν(P–S) cm^{-1}	ν(Sn–C cm^{-1}
	2550–2450	1010	860	930	690	585	–
	–	1010	860	920	710	600	500
	–	1010	850	915	700	600	520
	–	1020	868	925	698	602	490
	2450	1060	855	930	650	575	–
	–	1050	810	950	720	590	515
	–	1045	810	940	702	590	513
	–	1050	787	920	708	590	515
	–	1050	780	820	580	590	520
	2450	1000	840	950	670	538	–
	–	1005	860	995	685	570	545
	–	988	850	908	690	598	508

TABLE 3

PMR SPECTRAL DATA FOR A FEW TRIORGANOTIN(IV) *O,O*-ALKYLENE DITHIOPHOSPHATES

Compound	Chemical shift, δ(ppm) [a]
	7.0–7.8, m (Sn–C_6H_5) 15H 1.5, s (CH_3) 12H
	0.7, s (Sn–CH_3) 9H 1.5, s (CH_3) 12H.
	7.2–8.1, m (Sn–C_6H_5) 15H 4.5–5.0, m (–CHO) 1H 1.0–2.0, m (CH_3,CH_2) 11H
	0.7, s (Sn–CH_3) 9H 6.0–5.7, m (–CHO) 1.8–1.3, m (CH_3,CH_2) 11H
	7.2–7.8, m (Sn–C_6H_5) 15H 3.3–3.8, d (–OCH_2) 4H 0.5–1.0, s (–CH_3) 6H

[a] s = singlet, d = doublet, m = multiplet.

respectively. These indicate the unidentate behaviour of the ligands since the resonances for the free ligands appear at a similar position, viz. δ 93.0 ppm.

The ^{13}C NMR spectra of two representative compounds, I and III show sharp singlet at −1.3 and −1.7 ppm, respectively; these are attributed to tin-methyl carbons. The $J(Sn^{119}–C^{13})$ values for these derivatives are 370 and 374 Hz, respectively, in the range expected for four coordinate tin species [22–24], and this confirms the unidentate behaviour of the ligands in these derivatives.

Finally, the tetracoordinated nature of tin in these derivatives was confirmed [25,26] by the ^{119}Sn chemical shifts (relative to tetramethyltin) for two representative compounds I and III, which appear at δ 102.8 and 103.4 ppm, respectively.

Experimental

The *O,O*-alkylene dithiophosphoric acids and their ammonium salts were prepared as recently reported [9]. Sulfur was estimated as barium sulphate and tin as the oxide.

Molecular weights were determined ebullioscopically. ^1H, ^{13}C and ^{31}P NMR spectra in $CDCl_3$ were recorded using TMS and H_3PO_4 as internal standards. ^{119}Sn NMR spectra were recorded in $CDCl_3$ with tetramethyltin as reference. IR spectra (4000–400 cm^{-1}) were recorded as Nujol mulls.

Reaction of triphenyltin(IV) chloride with ammonium O,O-hexylene dithiophosphate in 1/1 molar ratio

A solution of triphenyltin(IV) chloride (1.23 g) was added to a suspension of ammonium *O,O*-hexylene dithiophosphate (0.75 g) in benzene. The mixture was stirred for 3–4 h than the solid was allowed to settle. After filtration the solvent was evaporated under reduced pressure to leave a white crystalline solid (1.77 g), which was recrystallised from a benzene/petroleum ether (40–60°C) mixture.

Details for similar syntheses of the other compounds are given in Table 1.

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