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SYNTHESIS AND REACTIONS OF TRIORGANOTIN DIALKYLDITHIOPHOSPHATES

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Summary

Triorganotin dialkyldithiophosphates, $(RO)_2P(=S)SSnR'_3$ (R = Et, i-Pr, n-Pr or Ph and R' = Me, Et, Bu or Ph), have been synthesised by the interactions of triorganotin hydroxides, oxides and chlorides with dialkyldithiophosphoric acids, $(RO)_2P(=S)SH$, or their (Na, NH_4 or lead) salts in anhydrous benzene. An ester-type, structure is proposed, in which the diethyldithiophosphate moiety shows monodentate behaviour.

Introduction

Dialkyldithiophosphoric acids, $(RO)_2P(=S)SH$, are versatile ligands which show both bidentate (chelating or bridging [1—3]) and monodentate [4] behaviour and form chelates or salts with various metals, mainly of the transition series. Main group metal derivatives of these ligands are almost unexplored [5,6].

We have carried out a study on organotin(IV) derivatives of various dialkyldithiophosphoric acids, $(RO)_2P(=S)SH$, (R = Et, i-Pr, n-Pr, Ph). A few uncharacterized organotin dialkyldithiophosphates have been reported in the patent literature [7] to possess pesticidal activity. The corresponding dialkyldithiophosphinates, on the other hand, are well characterized [8,9]. The present paper describes the synthesis and reactions of triorganotin dialkyldithiophosphates.

Experimental

Molecular weights were determined ebulliometrically. IR spectra were recorded in the ranges 4000—400 and 4000—200 cm^{-1} on Perkin—Elmer 337 and 621 spectrometers, respectively, as neat liquids or Nujol mulls between KBr cells or KBr pellets. PMR spectra were recorded in carbon tetrachloride at room

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temperature on a Perkin—Elmer R12B instrument. Electronic spectra were recorded for a few compounds on a Toshniwal Spectrometer RL 02/01 using concentrations of 0.04—0.10 × 10^{-3} M. Conductance measurements were carried out on 10^{-3} M solutions in nitrobenzene with a Tesla RLC Bridge, Bombay (India).

The dipole moment of the compound was determined with the help of Toshniwal Dipolemeter type RL-09/01 at 300 KHz using Higasi's equation:

$$\mu^2 = \frac{27\,KTM_2(a_0 - a_\infty)}{4\,\pi Nd(E_1 + 2)^2}$$

where M_2 is the molecular weight of the compound and the other symbols have their usual meaning.

Carbon and hydrogen analyses were carried out at the CDRI, Lucknow. Phosphorus was analysed volumetrically: the compound (0.15—0.22 g) was digested with fuming nitric acid (15 ml) in a Kjeldahl flask, diluted up to 250 ml and treated with freshly prepared ammonium molybdate solution for precipitation as ammonium phosphomolybdate, which was treated with excess 0.1 N NaOH and back titrated with 0.1 N HCl. The percentage of phosphorus can be calculated by using the expression: 1 ml 1 N NaOH $\triangleq$ 0.001349 g phosphorus.

Tin was estimated by digesting the compound (0.3—0.35 g) with fuming H_2SO_4 and HNO_3 acids (5—10 ml each), diluting upto 250 ml and precipitating the hydrated tin oxide by concentrated ammonia (with ammonium nitrate to coagulate the precipitate) and finally igniting the precipitate to SnO_2.

Sulphur was estimated by Messenger's method by refluxing the compound for about 6 h with $KMnO_4$ (2 g) solid + KOH (2 pellets) + 30% H_2O_2 (25 ml) and distilled water (50 ml) and precipitation of the sulphate which formed by addition of a freshly prepared 10% solution of $BaCl_2$, the sulphate was estimated as $BaSO_4$.

Ligands and their salts. Dialkyldithiophosphoric acids and their (Na, NH_4, Pb) salts were prepared as previously described [10—13] and stored under nitrogen. The acids and their salts were handled with caution since they are potentially biologically active [14].

Preparation. Typical methods of making some triorganotin dialkyldithiophosphates are as below:

(i) To a benzene solution (40 ml) of triphenyltin hydroxide (3.66 g, 0.01 mol) was added a solution of diethyldithiophosphoric acid (1.86 g, 0.01 mol) in benzene (20 ml). The mixture was refluxed (100°C oil bath) and the water liberated was fractionated off slowly as the binary azeotrope with benzene. The excess of solvent was removed under reduced pressure yielding a colourless or white solid (5.42 g, 98%) which was recrystallized from dry petroleum ether in a yield of 70%, m.p. 104—106°C.

(ii) Interaction between bis(tributyltin) oxide (5.95 g, 0.01 mol) and diethyldithiophosphoric acid (3.72 g, 0.02 mol) in benzene (50 ml) was carried out as in (i) to give tributyltin diethyldithiophosphate (9.50 g, 90%) as a pale oily liquid (b.p. 135—138°C/0.01 mmHg).

(iii) A mixture of diethyldithiophosphoric acid (1.86 g, 0.01 mol) and trimethyltin chloride (1.98 g, 0.01 mol) in benzene (50 ml) was refluxed for about 4 h until the evolution of hydrogen chloride ceased. The solvent was removed in vacuo. A colourless liquid (3.42 g, 85%; b.p. 93—95°C/0.3 mmHg) was obtained.

(iv) To the sodium salt of diethyldithiophosphoric acid (2.08 g, 0.01 mol) was added trimethyltin chloride in benzene (60 ml). An immediate reaction occurred with precipitation of sodium chloride. The mixture was refluxed for about 30 min and then filtered. Removal of the benzene in vacuo gave a colourless liquid (3.40 g), which distilled at 82—83°C/0.01 mmHg, yield 92%.

The analytical and other relevant data for all the compounds are given in Table 1.

Results and discussion

Triorganotin dialkyldithiophosphates have been prepared by the three methods in excellent yields:

1. $R'_3SnCl + (RO)_2P(=S)SH \rightarrow R'_3SnS(=S)P(RO)_2 + HCl\uparrow$
2. $(R'_3Sn)_2O + 2(RO)_2P(=S)SH \rightarrow 2\,R'_3SnS(=S)P(RO)_2 + H_2O\uparrow$
3. $R'_3SnCl + (RO)_2P(S)SM \rightarrow R'_3SnS(S)P(RO)_2 + MCl\downarrow$

Where M = Na, NH_4, $Pb_{0.5}$; R' = Me, Et, Bu, Ph; R = Et, i-Pr, n-Pr, Ph.

Reactions of triorganotin chloride with dialkyldithiophosphoric acids appear to be easier than the reactions of organotin halides with thiols. On mixing the reactants, the evolution of hydrogen chloride starts immediately at room temperature and the reactions are completed in about 4—5 h in refluxing benzene. In the corresponding reactions of organotin oxides and hydroxides in refluxing benzene, the water liberated has to be removed azeotropically. With acid salts, the reactions of triorganotin chlorides take place readily to give quantitative yields. It may be mentioned that the sodium, ammonium and lead salts of dialkyldithiophosphoric acids, are more stable than that and the ionic solids can be stored for indefinite period and even handled without exclusion of atmospheric moisture.

Except for the triphenyltin derivatives and diphenyldithiophosphoric acid derivatives, which are solids with sharp melting points, the compounds are pale yellow or colourless liquids which can be distilled under reduced pressure. All these derivatives are soluble in common organic solvents such as CCl_4, $CHCl_3$ and C_6H_6 and insoluble in water, and are not susceptible to hydrolysis. The derivatives appear to be more stable than the parent acids even towards atmospheric oxidation. All the derivatives are monomeric in refluxing benzene.

Infrared spectra

The bands shown by the parent acids in the region 2300—2600 cm^{-1}, due to the ν(S—H) stretching vibration [15], are absent for the triorganotin dialkyldithiophosphate derivatives indicating that tin is bonded to the sulphur atom of the ligands. The spectra of all the acids and their organotin derivatives show a sharp, intense peak in the 650—685 cm^{-1} region which can be assigned to ν(P=S) vibrations [16]. The spectra of acids and their triorganotin derivatives in the region 4000—200 cm^{-1} are almost indentical except for peaks due to the organo-

TABLE 1. SYNTHESES OF TRIALKYLTIN DIALKYLDITHIOPHOSPHATES

Compounds	Compound	B.p. (°C/mmHg) (m.p.)	Method of preparation	Yield of distilled product (%)	Analysis (Found (Calcd.) (%))				
					P	S	Sn	C	H
I	$(EtO)_2P(S)SSnMe_3$	90—91/0.3	1	90	8.72	18.49	33.91	24.03	5.51
		88—90/0.3	3	93	8.68	18.38	33.84	24.12	5.62
					(8.91)	(18.40)	(34.08)	(24.10)	(5.45)
II	$(EtO)_2P(S)SSnEt_3$	118—120/0.5	3	92	7.76	16.52	30.52	—	—
					(7.94)	(16.41)	(30.42)		
III	$(EtO)_2P(S)SSnBu_3$	135—138/0.01	3	88	6.30	13.58	25.02	40.48	7.82
					(6.23)	(13.49)	(24.94)	(40.42)	(7.79)
IV	$(EtO)_2P(S)SSnPh_3$	(104—106)	(1)	96	5.62	12.03	22.42	48.91	4.53
					(5.80)	(11.99)	(22.21)	(48.97)	(4.63)
V	$(i\text{-}PrO)_2P(S)SSnMe_3$	80—83/0.1	1	91	8.05	16.89	31.40		
		82—84/0.1	3	94	7.94	16.92	31.58	—	—
					(8.26)	(16.98)	(31.50)		
VI	$(i\text{-}PrO)_2P(S)SSnEt_3$	104—106/0.5	1	90	7.07	15.52	28.21	34.38	6.80
					(7.39)	(15.28)	(28.33)	(34.68)	(6.90)
VII	$(i\text{-}PrO)_2P(S)SSnBu_3$	125—130/0.05	2	93	6.16	12.89	23.45		
		128—129/0.05	3	89	6.03	12.92	23.52	—	—
					(6.17)	(12.75)	(23.62)		
VIII	$(i\text{-}PrO)_2P(S)SnPh_3$	(62—63)	1	98	5.59	11.48	21.40	51.30	5.09
					(5.51)	(11.39)	(21.21)	(51.24)	(5.16)
IX	$(n\text{-}PrO)_2P(S)SSnMe_3$	98—99/0.1	1	94	8.10	16.82	31.60		
		96—97/0.1	3	90	8.02	16.88	31.66	—	—
					(8.26)	(16.98)	(31.50)		
X	$(n\text{-}PrO)_2P(S)SSnEt_3$	122—124/0.2	1	96	7.21	15.34	28.28	—	—
					(7.39)	(15.28)	(28.33)		
XI	$(n\text{-}PrO)_2P(S)SSnBu_3$	140—143/0.01	2	92	6.08	12.93	23.58		
		141—142/0.01	3	88	6.01	12.90	23.69	—	—
					(6.17)	(12.75)	(23.62)		
XII	$(n\text{-}PrO)_2P(S)SSnPh_3$	(111—113)	1	98	5.34	11.48	21.30	—	—
					(5.51)	(11.39)	(21.21)		
XIII	$(PhO)_2P(S)SSnMe_3$	—^{a}	3	99	6.82	14.26	26.61	40.53	4.20
					(6.98)	(14.10)	(26.58)	(40.54)	(4.27)
XIV	$(PhO)_2P(S)SSnEt_3$	—^{a}	1	98	6.21	13.32	24.30	—	—
					(6.37)	(13.17)	(24.28)		
XV	$(PhO)_2P(S)SSnBu_3$	—^{a}	2	99	5.18	11.48	20.83	—	—
					(5.44)	(11.22)	(20.70)		

[a] White sticky solid. Methods 1, 2 and 3 correspond to the equations given in the discussions.

TABLE 2

SOME RELEVANT IR FREQUENCIES (cm^{-1})^{a} IN $R'_3SnS_2P(OR)_2$

Compound	ν((P)—O—C)	ν(P—O—(C))	ν(P=S)	ν(P—S)	ν(Sn—C)	ν(Sn—S)
I	1043vs	852m	658vs	512m	543s	390m
III	1040vs	851m	657vs	511m	544s	395m
IV	1042s	858m	651vs	538s	448s	385m
V	1000vs	788 (sh)	651vs	514m	548s	—
VI	1015 (sh)	774s	651vs	511m	550	—
VII	1020s	774s	650vs	520m	548s	—
VIII	1020m	790s	650m	520m	450s	—
IX	1000 (sh)	846m	660vs	512m	540s	—
XIII	1188vs	1028m	690vs	504m	537s	375m
XIV	1192vs	1023m	688vs	507m	526s	370m

^{a} Compound numbers refer to those in Table 1; m, medium; s, strong; vs, very strong; (sh), shoulder.

tin moiety. The ν(Sn—C)$_{asym.}$ vibration may be assigned to the peaks in the region 550—515 cm^{-1} [17]. These peaks usually overlap the peaks due to ν(P—S). The acids and the salts show no absorption between 350—400 cm^{-1}, while the spectra of organotin compounds show medium intensity peaks in the region 380—75, which can be assigned to the ν(Sn—S) stretching vibration [18]. Some important IR spectral bands are assigned in Table 2.

Proton magnetic resonance spectra

The sharp singlet at τ 5.81—6.50 ppm characteristic of the S—H proton in dialkyldithiophosphoric acids is absent from the PMR spectra of the organotin compounds. Complex multiplets due to the protons of phenyl, butyl or ethyl

TABLE 3

PMR SPECTRAL DATA FOR A FEW TRIORGANOTIN DIALKYLDITHIOPHOSPHATES $R'_3SnS_2P(OR)_2$

Compounds	R	R′	Chemical shifts (τ, ppm)
I	C_2H_5	CH_3	5.68, m, 4 H(OCH$_2$); 8.49, t, 6 H, J 7 (CH$_3$); 9.10, s, 9 H (Sn—CH$_3$); J(^{117}Sn—CH$_3$) 55 Hz, J(^{119}Sn—CH$_3$) 58.5 Hz
III	C_2H_5	C_4H_9	5.82, m, 4 H (OCH$_2$); 8.45—8.98; m, 33 H (CH$_3$) + (Sn—C$_4$H$_9$)
IV	C_2H_5	C_6H_5	6.08, m, 4 H (OCH$_2$); 8.93, t, 6 H, J 7 Hz (CH$_3$); 2.17—2.74, m, 15 H (Sn—C$_6$H$_5$)
V	i-C_3H_7	CH_3	5.02, m, 2 H, J 6 Hz (OCH<), 8.42, d, 12 H, J 7 (CH$_3$); 9.09, s, 9 H (Sn—CH$_3$); J(^{117}Sn—CH$_3$) 55 Hz, J(^{119}Sn—CH$_3$) 58 Hz.
VI	i-C_3H_7	C_2H_5	5.17, m, 2 H, J 6 Hz (OCH<), 8.52—8.63, m, 27 H (CH$_3$) + (Sn—C$_2$H$_5$)
VII	i-C_3H_7	C_4H_9	5.22, m, 2 H, J 6 Hz (OCH<); 8.58—9.00, m, 39 H (CH$_3$) + (Sn—C$_4$H$_9$)
VIII	i-C_3H_7	C_6H_5	5.32, m, 2 H, J 6 Hz (OCH<); 8.80, d, 12 H, J 6 Hz (CH$_3$); 2.23—2.73, m, 15 H (Sn—C$_6$H$_5$).
IX	n-C_3H_7	CH_3	5.86, m, 4 H (OCH$_2$); 8.07, q, 4 H, J 7 Hz (CH$_2$); 8.78, t, 6 H, J 7 Hz (CH$_3$); 9.18, s, 9 H (Sn—Me); J(^{117}Sn—CH$_3$) 5.55 Hz, J(^{119}Sn—CH$_3$) 60 Hz.
XIII	C_6H_5	CH_3	2.70, d, 10 H (C$_6$H$_5$O); 9.35, s, 9 H (Sn—Me); J(^{117}Sn—CH$_3$) 55 Hz, J(^{119}Sn—CH$_3$) 59 Hz

TABLE 4

SOME PHYSICO-CHEMICAL DATA FOR $R'_3Sn(S_2P(OR)_3$

Compound	Molecular weight (Found (calcd.))	Refractive index (30°C)	Dipole moments (D) (Higasse's Method)	Electronic spectra	
				λ_{max}(nm)	(log ε)
I	351 (348)	1.5210	3.62	228	4.33
II	399 (390)	1.5224	—	278	3.02
III	486 (475)	1.5266	—	—	—
IV	545 (534)	—	3.72	—	—
V	381 (376)	1.5221	3.78	230 280	4.35 3.06
VI VII	425 (418)	1.5240	—	—	—
VII	510 (502)	1.5273	—	—	—
VIII	580 (562)	—	3.64	—	—
IX	385 (376)	1.5301	—	—	—
X	429 (418)	1.5328	3.68	229 279	4.36 3.08
XI	513 (502)	1.5346	—	—	—
XII	578 (562)	—	—	—	—
XIII	499 (444)	—	—	—	—
XIV	493 (486)	—	—	—	—
XV	586 (570)	—	—	—	—

groups attached to the tin atom are observed in the region τ 2.41, 8.78, 8.50 ppm, respectively. Sn—CH_3 protons appear as a sharp singlet with double satellite resonances of relative intensity of 4—5% on the sides of the main peak (singlet); these are due to the coupling of methyl protons with ^{117}Sn and ^{119}Sn isotopes having coupling constants $J(^{117}Sn—CH_3)$ 55—56 Hz and $J(^{119}Sn—CH_3)$ 58—60 Hz.

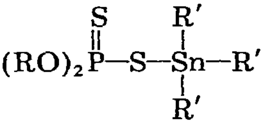
Electronic spectra

All the triorganotin dialkyldithiophosphates absorb strongly in the region 229 ± 1 mm, corresponding to a $\pi \rightarrow \pi^*$ transition. Other rather weak absorptions occur at 279 ± 1 nm, which may be due to $n \rightarrow \pi^*$ transition. The dialkyldithiophosphoric acids also absorb in these regions.

Conductance measurements

The molar conductance of the organotin derivatives in nitrobenzene were found to be in the range 1.80—2.45 ohm^{-1} cm^2 mol^{-1}, showing them to be non-electrolytes.

Since the triorganotin dialkyldithiophosphates are monomeric they could have either a tetrahedral or trigonal bipyramidal structure depending on whether the dialkyldithiophosphate moiety behaves as a mono- or a bi-dentate ligand. The absorptions due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions occur at approximately the same positions in the electronic spectra of the acids and triorganotin derivatives indicating no involvement of the lone pair electrons on the sulphur atom in coordination. The values of tin—proton coupling constants have been suggested to be closely related to the coordination number of tin in organotin compounds [19] and the values of the coupling constants $J(^{119}Sn—CH_3)$ and $J(^{117}Sn—CH_3)$ in the new derivatives are rather similar to those already reported for trimethyltin chloride. Further, the bands in the 650—685 cm^{-1} region due to the $\nu(P{=}S)$ stretching mode appear at the same position in the organotin derivatives as in the free ligands. This confirms that the ligand is bonded to organotin through only one sulphur atom, and that the compounds possess an ester type structure, having tin in the tetracoordinate state, with the dialkyldithiophosphate moiety behaving as a monodentate ligand. The related triorganotin dithiocarboxylates and dithiocarbamates have also been recently reported to possess an ester type tetrahedral structure [20,21].



$$(RO)_2\overset{\overset{S}{\|}}{P}—S—\underset{\underset{R'}{|}}{\overset{\overset{R'}{|}}{Sn}}—R'$$

Preliminary results indicate the compounds to be excellent fungicides.

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