SYNTHESIS AND CHARACTERIZATION OF 1,3–BIS(O,O-DIALKYL AND ALKYLENE DITHIOPHOSPHATO)TETRABUTYLDISTANNOXANES

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ABSTRACT

O,O-Dialkyl and alkylene dithiophosphoric acids react with 1,3–(diacetato)tetrabutyldistannoxane in 1:2 molar ratio in refluxing benzene to yield $[(RO)_2PS_2SnBu_2]_2O$, R = Et, Pr-n, Pr-i, Bu-i and Ph, and $[OGOPS_2SnBu_2]_2O$ where G = – $CH_2CMe_2CH_2$–, – $CH_2CEt_2CH_2$– and – CMe_2CMe_2 –. The complexes are white solids or colorless viscous liquids, soluble in common organic solvents and monomeric in nature. These have been characterized on the bases of elemental analyses, molecular weight determinations, IR and NMR (^1H, ^{13}C, ^{31}P and ^{119}Sn NMR).

INTRODUCTION

Distannoxane derivatives have been prepared by same methods as for other distannoxanes compounds(1-3). These distannoxanes are several times as effective as the usual catalysts(4), such as dibutyltin dilaurate and tertiary amines in polyurethane formation(5).

As an alternative route for synthesis of 1,3–bis(dithiophosphato)tetrabutyldistannoxanes is the reaction 1,3–(diacetato)tetrabutyldistannoxanes with dialkyl and alkylene dithiophosphoric acids in 1:2 mole. It was thought worthwhile to extend our studies on the synthesis of the above compounds and to study their structural feature. It was also envisaged that replacement reactions of 1,3–(diacetato)tetrabutyldistannoxanes should constitute convenient route for such complexes.

RESULTS AND DISCUSSION

The reactions of 1,3–(diacetato)tetrabutyldistannoxanes with two moles of dialkyl and alkylene dithiophosphoric acids in refluxing benzene with constant stirring and removal acetic acid under vacuum, yield 1,3–bis(dithiophosphato)tetrabutyldistannoxane derivatives.

$$[CH_3OCOSnBu_2]_2O \quad + \quad 2HS_2P(OR)_2 \longrightarrow [(RO)_2PS_2SnBu_2]_2O \quad + \quad 2CH_3COOH$$
R = Et, Pr–n, Pr–i, Bu–i and Ph.

$$[CH_3OCOSnBu_2]_2O \quad + \quad 2HS_2\overline{POGO} \longrightarrow [\overline{OGOP}S_2SnBu_2]_2O \quad + \quad 2CH_3COOH$$
G = –$CH_2CMe_2CH_2$–, –$CH_2CEt_2CH_2$– and –CMe_2CMe_2–.

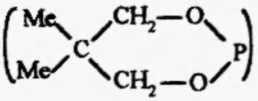
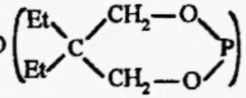
These distannoxane derivatives Table (I) are white solids or viscous liquids soluble in common organic solvents such as chloroform, dichloromethane and benzene. The solid compounds are insoluble in n-hexane and can be purified by washing with the same. However, attempts to crystallize the solid compounds from benzene/n-hexane mixture were unsuccessful. The solubility of all these compounds decrease on storing for long period.

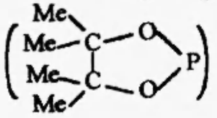
Molecular Weight

It was expected that such complexes will give dimer structure, but the molecular weights of these complexes determined in chloroform show monomer structure. This unexpected behavior has been noted before in the case of $(R'OCO)R_2SnOSnR_2(OH)$, $[Me_2SnOOCH_3]_2O$ and $[Bu_2SnOOCCl_3]_2O$ by changing solvent(6).

Table (I) Synthesis and physical properties of 1,3–bis(O,O-dialkyl and alkylene dithiophosphato)tetrabutyldistannoxanes (1:2 Molar Ratio).

Sl. No.	Reactants g (mmol)		Product g (mmol)	Yield %	M. P. °C	Mol Wt. Found (Calc)	Elemental analysis	
	1,3–(diacetato)tetra-butyldistannoxanes	dithiophosphoric acid					% Sn Found / (Calc)	% S
1.	0.543 (0.905)	$HS_2P(OEt)_2$ 0.337 (1.80)	$[(EtO)_2PS_2SnBu_2]_2O$0.725 (0.851)	94.0	---	865 (852.292)	28.22 (27.85)	14.43 (15.05)
2.	0.672 (1.120)	$HS_2P(OPr\text{-}n)_2$ 0.480 (2.240)	$[(n\text{-}PrO)_2PS_2SnBu_2]_2O$ 0.951 (1.047)	93.5	---	899 (908.400)	25.46 (26.13)	13.23 (14.12)
3.	0.598 (0.997)	$HS_2P(OPr\text{-}i)_2$ 0.427 (1.993)	$[(i\text{-}PrO)_2PS_2SnBu_2]_2O$ 0.853 (0.939)	94.2	---	901 (908.400)	25.22 (26.13)	13.50 (14.12)
4.	0.653 (1.088)	$HS_2P(OBu\text{-}i)_2$ 0.528 (2.177)	$[(i\text{-}BuO)_2PS_2SnBu_2]_2O$ 0.950 (0.985)	90.5	---	955 (964.508)	23.77 (24.61)	14.00 (13.30)
5.	0.721 (1.202)	$HS_2P(OPh)_2$ 0.679 (2.404)	$[(PhO)_2PS_2SnBu_2]_2O$ 1.151 (1.102)	91.7	106	10430 (1044.472)	23.04 (22.73)	11.54 (12.28)
6.	0.833 (1.388)	$HS_2POCH_2CMe_2CH_2O$ 0.550 (2.777)	$[OCH_2CMe_2CH_2OPS_2SnBu_2]_2O$ 1.092 (1.247)	89.8	159	888 (876.128)	27.00 (27.09)	13.77 (14.64)
7.	0.779 (1.298)	$HS_2POCH_2CEt_2CH_2O$ 0.587 (2.597)	$[OCH_2CEt_2CH_2OPS_2SnBu_2]_2O$ 1.089 (1.169)	90.0	163	921 (932.228)	24.45 (25.46)	13.99 (13.76)
8.	0.688 (1.147)	$HS_2POCMe_2CMe_2O$ 0.487 (2.293)	$[OCMe_2CMe_2OPS_2SnBu_2]_2O$ 0.918 (1.015)	88.5	182	920 (904.188)	25.34 (26.25)	15.11 (14.19)

The POGO fragment may be six member ring such as $POCH_2CMe_2CH_2O$  and $POCH_2CEt_2CH_2O$ 

or five member ring such as $POCMe_2CMe_2O$ 

IR Spectra

The IR spectral data for 1,3-bis(dithiophosphato)tetrabutyldistannoxanes are given in Table (II). The absorption bands due to νS–H in the region 2400 – 2550 cm^{-1} in the parent dialkyl and alkylene dithiophosphoric acids(7) are obviously absent in the spectra of the corresponding complexes. New bands appeared in the region 330 – 390 cm^{-1} which are probably due to νSn–S(8) and the bands due to Sn–O–Sn(9) are found in the region 530 – 560 cm^{-1}. The bands presence in the regions 1020 – 1150 and 780 – 920 cm^{-1} may be assigned to ν(P)–O–C and νP–O–(C) respectively(10,11). The sharp bands present in the region 961 – 999 cm^{-1} may be ascribed to dioxaphospholane and dioxaphosphorinane ring vibration(12,13). The bands presence in the regions 610 – 690 cm^{-1} can be assigned to νP=S vibrations(14-16). This shows notable shifting (Δ ~13 cm^{-1}) towards higher shift with respect to its position in the free acids. This shifting is probably due to coordination of sulfur of the P=S group to tin atom. The bands in medium intensities in the region 580 – 611 cm^{-1} may be attributed to νP–S asymmetric and symmetric vibrations(15,16).

Table (II) The spectral data for 1,3–bis(O,O-dialkyl and alkylene dithiophosphato)tetrabutyldistannoxanes.

Sl. No.	Compound	ν(P)–O–C	νP–O–(C)	νP=S	νP–S	νSn–O	νSn–S
1.	$[(EtO)_2PS_2SnBu_2]_2O$	1120 s	822 s	668m	604m	540 w	377 w
1.	$[(n\text{–}PrO)_2PS_2SnBu_2]_2O$	1151 s	779 s	666s	606m	543 m	382 w
1.	$[(i\text{–}PrO)_2PS_2SnBu_2]_2O$	1116 s	780 s	684m	608m	550 m	389 w
1.	$[(i\text{–}BuO)_2PS_2SnBu_2]_2O$	1022 s	863 s	685s	610m	559 w	390 w
1.	$[(PhO)_2PS_2SnBu_2]_2O$	1148 m	848 s	663s	602m	538 m	350 w
1.	$[OCH_2CMe_2CH_2OPS_2SnBu_2]_2O$	1049 m	819 m	692m	583m	544 m	345 m
1.	$[OCH_2CEt_2CH_2OPS_2SnBu_2]_2O$	1078 m	809 s	688m	591m	---	335 w
1.	$[OCMe_2CMe_2OPS_2SnBu_2]_2O$	1087 m	920 s	612m	611m	533 w	---

s = strong, m = medium, w = weak and b = broaden absorption bands

^{1}H NMR Spectra

The ^{1}H NMR Spectra Table (III) recorded in $CDCl_3$ shows the characteristic resonances due to alkoxy and glycoxy protons. The signal due to the SH present in the region (δ 3.02 – 3.69 ppm), in the parent dithiophosphoric acids(7), expected disappears in complexes. There is considerable overlapping of peaks due to the protons of dibutyltin group and those for methylene and methyl groups of alkoxy or glycoxy moieties.

Table (III) The ^{1}H, ^{31}P and ^{119}Sn NMR spectral data for 1,3–bis(O,O-dialkyl and alkylene dithiophosphato) tetrabutyldistannoxanes.

Sl. No.	Compound	^{1}H chemical shift (δ ppm)	^{31}P (δ ppm) (Parent acid)	^{119}Sn (δ ppm) (Bu_2Sndtp_2)
1.	$[(EtO)_2PS_2SnBu_2]_2O$	1.19 – 2.21, m, 56H (CH_3, CH_2)* 4.69 – 4.82, m, 8H (CH_2O)	94.21 (85.80)	----
1.	$[(n\text{–}PrO)_2PS_2SnBu_2]_2O$	0.85 – 2.18, m, 76H (CH_3, CH_2) 4.50 – 4.79, m, 8H (CH_2O)	95.05 (86.10)	–177.09 (–178.50)
1.	$[(i\text{–}PrO)_2PS_2SnBu_2]_2O$	0.83 – 2.33, m, 60H (CH_3, CH_2) 4.56 – 5.15, m, 4H (CHO)	93.17 (82.30)	–179.44 (–179.90)
1.	$[(i\text{–}BuO)_2PS_2SnBu_2]_2O$	0.83–2.24,m,64H(CH_3,CH_2, CH) 3.72 – 3.99, m, 8H (CH_2O)	96.67 (85.70)	–178.33 (–181.10)
1.	$[(PhO)_2PS_2SnBu_2]_2O$	0.90, t, (J = 7.2 Hz), 12H (CH_3) 1.25 – 1.87, m, 24H (CH_2) 7.12 – 8.60, m, 20H (C_6H_5O)	95.76 (79.90)	–199.91 (–196.90)
1.	$[OCH_2CMe_2CH_2OPS_2SnBu_2]_2O$	0.91 – 1.02, m, 48H(CH_3, CH_2) 4.03, d, (J= 16.3 Hz), 8H (CH_2O)	93.28 (77.30)	–137.98 (–137.50)
1.	$[OCH_2CEt_2CH_2OPS_2SnBu_2]_2O$	0.89 – 1.97, m, 56H(CH_3, CH_2) 4.15, d, (J= 16.2 Hz), 8H (CH_2O)	94.67 (78.50)	---
1.	$[OCMe_2CMe_2OPS_2SnBu_2]_2O$	0.90, t, (J = 7.2 Hz), 24H (CH_3) 1.26 – 1.66, m, 36H(CH_3, CH_2)	111.17 (93.10)	–215.45 (–214.98)

s = singlet, d = doublet, t = triplet, m = multiplet and J = $^3J(^1H–^{31}P)$.

- The chemical shift included both protons of $SnBu_2$ and $(RO)_2P$ or OGOP.

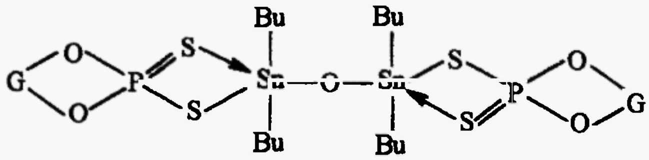


Fig. (1) Suggested structures of 1,3–bis(O,O-dialkyl and alkylene dithiophosphato)tetrabutyldistannoxanes.

^{13}C NMR Spectra

The ^{13}C NMR chemical shifts Table (IV) of 1,3–bis(dialkyl and alkylene dithiophosphato)tetrabutyl-distannoxanes were recorded in $CHCl_3$. The spectra do not show any notable change from those of the corresponding dithiophosphoric acids.

Table (IV) The ^{13}C NMR spectral data for 1,3 – bis(O,O-dialkyl and alkylene dithiophosphato)tetrabutyl – distannoxanes.

Sl. No.	Compound	Sn – Bu carbons $^{*}C_1$	C_2	C_3	C_4	Dialkyl and alkylene carbons
1.	$[(n–PrO)_2PS_2SnBu_2]_2O$	29.1	23.6	22.6	13.6	14.12, s, (CH_3) 20.50, s, (CH_2) 78.23, d, (J = 6.21 Hz), (CH_2O)
1.	$[(i–BuO)_2PS_2SnBu_2]_2O$	29.0	26.3	26.6	13.7	18.88, s, (CH_3) 28.21, d, (J = 8.51 Hz), (CH) 73.53, d, (J = 7.42 Hz), (CH_2O)
1.	$[OCH_2CMe_2CH_2OPS_2SnBu_2]_2O$	28.9	27.0	26.4	13.8	22.00, s, (CH_3) 32.99, d, (J = 6.98 Hz), (C) 77.01, s, (CH_2O)

* $^{1}J(^{13}C – ^{119}Sn)$

^{31}P NMR Spectra

The proton decoupled ^{31}P NMR spectra of 1,3–bis(dialkyl and alkylene dithiophosphato)tetrabutyl-distannoxanes have been recorded in $CHCl_3$ Table (III) it shows only one signal for each compound in the region (δ 93 – 111 ppm). There is relatively large shifting of the signal towards lower field by (11.22 ppm) from its position in the corresponding acids. According Glidewell's(17) observations, a shift of this magnitude indicates bidentate behavior of these ligands.

^{119}Sn NMR Spectra

The ^{119}Sn NMR chemical shifts for six representative 1,3–bis(dialkyl and alkylene dithiophosphato) tetrabutyldistannoxanes are given in Table (III). Thus, the ^{119}Sn chemical shifts of these compounds occur in the range –137 to –216 ppm. It may be mentioned that there are no ^{119}Sn NMR spectral studies of sulfur bonded distannoxane moieties in the literature with which meaningful comparison could be made. However, the ^{119}Sn signals in distannoxanes appear at lower frequencies than observed for four coordinated compounds and the shifts are in the same range as those for the corresponding dibutyltin bis(dialkyl and alkylene dithiophosphates) with the small differences(18). This indicates that these derivatives contain 6–coordinated tin as those in dibutyltin bis(dialkyl and alkylene dithiophosphates). But it was found that there are small differences on ^{119}Sn chemical shift between 5– and 6–coordinated tin compounds due to the weak chelation of dithiophosphate ligand(19).

Structural Elucidation

A perusal of all the evidence, suggest that the ligands are bonded to distannoxane moiety through two sulfur atoms. So the presence of penta– coordinated tin atom may be inferred. In view of the above and the monomeric nature of these compounds, the following structures are suggested for these, Fig. (1):

EXPERIMENTAL

Moisture was carefully excluded throughout the experimental manipulations. Dialkyl(20) and alkylene(21) dithiophosphoric acids were prepared by standard methods. Glycol was distilled before use, 1,3–(diacetato) tetrabutyl distannoxane (Merck) was used as such. Sulfur was determined by Messenger's method as barium sulfate. Tin was determined by gravimetrically as tin oxide.

IR spectra were recorded as Nujol mulls using CsI cells in region 4000 – 200 cm^{-1} on a FT-IR 8201 PC spectrometer. ^{1}H, ^{13}C, ^{31}P and ^{119}Sn spectra were recorded on a Jeol – FT – NMR spectrometer – LA300 using TMS as internal reference (for ^{1}H and ^{13}C), H_3PO_4 (for ^{31}P) as external reference and tetramethyltin (for ^{119}Sn) as standard reference.

The following synthetic details for one specific 1:2 represent the procedure used to synthesize all compounds:

Reaction between 1,3–(Diacetato)tetrabutyldistannoxane with Dialkyl (OPr-i) and Alkylene Dithiophosphoric Acid in 1:2 Molar Ratio:

To solution of 1,3–(diacetato)tetrabutyldistannoxanes (0.598 g, 0.997 mmol) in benzene (~ 20 ml), $HS_2P(OPr\text{-}i)_2$ (0.427 g, 1.993 mmol) in the same solvent (~ 20 ml) was added droppwise with constant stirring. The reaction mixture was refluxed for over night. The excess solvent and acetic acid were removed under vacuum to yield a white solids or colorless viscous liquid and the product washed many times by n-hexane and the resulted product was finally dried under reduced pressure.

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