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DIORGANOTIN(IV) DIALKYL DITHIOPHOSPHATES: SYNTHESIS AND SPECTRAL STUDIES OF DIORGANO(HYDROXO)TIN(IV) DIALKYLDITHIOPHOSPHATES

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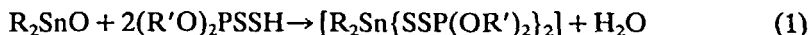
Complexes of the type $[R_2Sn(OH)\{SSP(OR')_2\}]$ ($R = Et, Pr^i, Bu^i$; $R' = Et, Pr^i, Pr^t$) have been prepared and characterized by elemental analyses and IR and NMR spectroscopy. These complexes are associated in the solid state probably through hydroxo-bridges whereas in solution they exist in equilibrium with monomeric species.

Key words: Diorganotin(IV) dialkyldithiophosphates; hydroxo bridges; NMR; IR

INTRODUCTION

Reactions of diorganotin oxides with protic ligands (LH) afford a variety of products, such as R_2SnL_2 , $(R_2SnL)_2O$, etc., depending on the nature of the ligand, R group attached to tin, stoichiometry of the reactants and the reaction conditions.^{1,2} Reactions in 1:1 stoichiometry employing bidentate ligands with small bite, like carboxylic acids, result in the formation of tetra-organodistannoxanes.¹⁻³ On the other hand hydroxo complexes, $[R_2Sn(OH)L]$, are formed with monodentate protic ligands in some cases.^{4,5} These complexes can be considered to be the partial hydrolysis products of R_2SnL_2 ; when R is a bulky group like Bu^i , *tert*-pentyl or 2-phenoxyphenyl, such compounds have been isolated in the solid state.⁶⁻⁸ In spite of the extensive work on organotin compounds only a few compounds of this class are known till now. Among these $[R_2Sn(OH)(NO_3)]^9$ and $[Ph_2Sn(OH)\{OP(S)(OPh)_2\}]^{10}$ have been fully characterised.

The biocidal activity of organotin(IV) dialkyldithiophosphates has attracted much attention in recent years.¹¹ Diorganotin(IV) bis(dialkyldithiophosphates) have been prepared^{12,13} in nearly quantitative yields by the following reaction (Equation 1).



The ability of the monothiophosphate ligand $[(PhO)_2P(S)O]^-$ to form the hydroxo-complex¹⁰ suggested that dithiophosphate ligands could be likely candidates for the formation of such complexes, or may as well form tetra-

organodistannoxanes considering their potentially small bite. In the present work the reaction between R_2SnO and $(R'O)_2PSSH$ was carried out in 1:1 stoichiometry with a view to obtain tetraorganodistannoxanes/hydroxo-complexes. The compounds formed were found to be diorgano(hydroxo)tin(IV) complexes.

EXPERIMENTAL

Dialkylthiophosphoric acids, $(R'O)_2PSSH$ ($R' = Et, Pr^n, Pr^i$),¹³ and R_2SnO ($R = Me, Et, Pr^n, Bu^n, Ph$)² were prepared according to literature methods. Analytical grade solvents were dried and distilled under nitrogen atmosphere, and were used throughout. Infrared spectra were recorded as nujol mulls between CsI optics on a Perkin-Elmer 577 spectrometer. A few IR spectra were recorded in benzene or CCl_4 on Mattson FT-IR spectrometer using NaCl cell. The 1H and ^{31}P NMR spectra were recorded on Varian FT-80A spectrometer at 79.54 and 32.20 MHz, respectively in deuterated chloroform or benzene. Chemical shifts are relative to internal benzene peak (δ 7.15 ppm) or chloroform peak (δ 7.26 ppm) for 1H and external 85% H_3PO_4 for ^{31}P . All the compounds were prepared by analogous methods; a typical preparative method is given below.

Preparation of $[Bu_2Sn(OH)\{SSP(OEt)_2\}]$ To a benzene (20 ml) suspension of Bu_2SnO (1.04 g; 4.18 mmole), a benzene solution (25 ml) of $HSSP(OEt)_2$ (0.78 g; 4.19 mmole) was added under nitrogen atmosphere and stirred vigorously for 2 h at room temperature ($30 \pm 3^\circ C$), during which considerable amount of Bu_2SnO had dissolved. Contents were filtered in open atmosphere through a fine filter paper or sintered funnel to give a clear, colourless solution. The solvent was removed under vacuum to give a pasty mass which was stirred with hexane (15 ml) when a white solid was obtained. This was cooled at $0^\circ C$ for 2 h, the solid was filtered out, washed with hexane and again dissolved in 2 ml benzene. To this solution 15 ml hexane was added and cooled in a freezer for 10 h to give a white solid which was filtered, washed with hexane and dried under vacuum. $[Bu_2Sn(OH)\{SSP(OEt)_2\}]$ was obtained as white solid in 25% yield (0.46 g). Hexane washings on evaporation gave $[R_2Sn\{SSP(OR')_2\}]$. Pertinent data for the complexes are given in Table I.

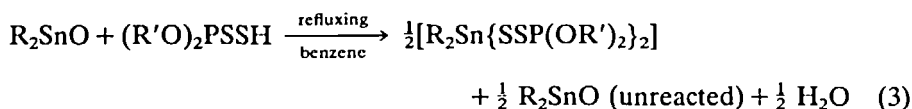
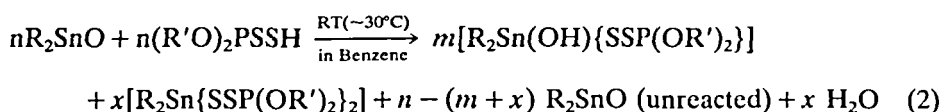
TABLE I
Physical, analytical data for $[R_2Sn(OH)\{SSP(OR')_2\}]$

Complex	% yield*	m.p. $^\circ C$	% Analyses	Found (Calculated)			
			C	H	P	S	Sn
$[Et_2Sn(OH)\{SSP(OEt)_2\}]$	10	127–129	25.00 (25.36)	5.30 (5.58)	8.21 (8.17)	16.27 (16.92)	30.55 (31.31)
$[Et_2Sn(OH)\{SSP(OPr^n)_2\}]$	8	105	29.68 (29.50)	6.17 (6.19)	7.55 (7.61)	—	28.42 (29.15)
$[Et_2Sn(OH)\{SSP(OPr^i)_2\}]$	13	115	29.63 (29.50)	6.10 (6.19)	7.71 (7.61)	—	28.54 (29.15)
$[Pr_2Sn(OH)\{SSP(OEt)_2\}]$	9	115	29.30 (29.50)	6.10 (6.19)	7.76 (7.61)	15.21 (15.75)	28.94 (29.15)
$[Pr_2Sn(OH)\{SSP(OPr^n)_2\}]$	20	117	33.12 (33.12)	6.80 (6.72)	7.21 (7.12)	14.18 (14.74)	26.84 (27.27)
$[Pr_2Sn(OH)\{SSP(OPr^i)_2\}]$	10	138–139	33.07 (33.12)	6.67 (6.72)	6.63 (7.12)	14.29 (14.74)	26.56 (27.27)
$[Bu_2Sn(OH)\{SSP(OEt)_2\}]$	25	120	34.12 (33.12)	6.92 (6.72)	6.75 (7.12)	14.27 (14.74)	28.06 (27.27)
$[Bu_2Sn(OH)\{SSP(OPr^n)_2\}]$	36	129	36.37 (36.30)	7.28 (7.18)	6.13 (6.69)	13.97 (13.84)	25.23 (25.62)
$[Bu_2Sn(OH)\{SSP(OPr^i)_2\}]$	22	129	36.81 (36.30)	6.94 (7.18)	6.75 (6.69)	13.42 (13.84)	24.98 (25.62)

* Based on the quantity of R_2SnO taken for the reaction

RESULTS AND DISCUSSION

Treatment of R_2SnO in benzene with an equimolar quantity of $(R'O)_2PSSH$ at room temperature affords $[R_2Sn(OH)\{SSP(OR')_2\}]$ **I** together with $[R_2Sn\{SSP(OR')_2\}_2]$ **II** (Equation 2). However, this reaction in refluxing benzene gives **II** and water leaving 50% unreacted R_2SnO (Equation 3). **I** on heating in benzene for a few minutes (2–10 minutes) converts to the corresponding **II** as revealed by ^{31}P NMR data, and R_2SnO . The yields of hydroxo complexes **I** were influenced by the R group on tin and were in the order $Bu^n > Pr^n > Et >> Me > Ph$; no detectable quantities of **I** being formed with the latter two R groups. The hydroxo complexes **I** are white amorphous solids, soluble in benzene and chloroform but insoluble in hexane.



The infrared spectra of these complexes displayed a characteristic broad band at $3360\text{--}3470\text{ cm}^{-1}$ which was neither present in the parent R_2SnO nor in the free dithiophosphoric acids. This has been assigned to $\nu(Sn)\text{—O—H}$ vibration. This band sharpens and shifts to higher wave number in benzene or CCl_4 solution (Figure 1) indicating the associated nature of these compounds in the solid state. A band in the region $880\text{--}940\text{ cm}^{-1}$ may be attributed to OH deformation mode.¹⁴

The $\nu P=S$ ($625\text{--}705\text{ cm}^{-1}$),^{13,15-17} $\nu P-S$ ($480\text{--}585\text{ cm}^{-1}$),^{13,15-17} $\nu Sn-S$ ($360\text{--}375\text{ cm}^{-1}$),^{15,18} $\nu Sn-O$ ($460\text{--}530\text{ cm}^{-1}$)^{19,20} and $\nu Sn-C$ ($530\text{--}650\text{ cm}^{-1}$)²¹⁻²³ absorption bands have been reported in the region $350\text{--}700\text{ cm}^{-1}$ for various organotin compounds. Assignment of such bands would provide valuable information about the stereochemistry of the molecule. However, in the case of our complexes richness of the spectra in this region and the coupled nature of

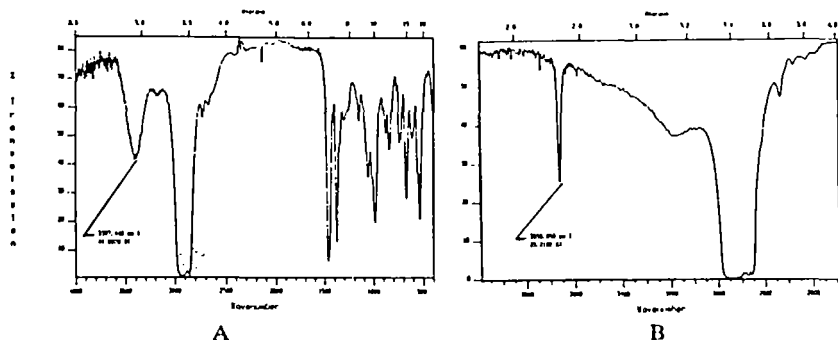


FIGURE 1 IR spectra of $[Bu_2Sn(OH)\{SSP(OPr')_2\}]$ recorded on Mattson FT-IR spectrometer. (A) in nujol (B) in CCl_4 .

TABLE II
 $^{31}\text{P}\{^1\text{H}\}$ NMR and IR data for $[\text{R}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OR}')_2)]$

Complex	Solvent	$^{31}\text{P}\{^1\text{H}\}$ NMR data			IR data†	
		$\delta^{31}\text{P}$ in ppm	Δ in Hz	ν OH‡	Vibrations in the region 1100–280 cm^{-1}	
$[\text{Et}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OEt})_2)]$	C_6D_6	98.4	69	3380–3420	1088 vs, 1010 vs(br), 940 vs, 775 vs(br), 710 m, 655 vs, 595–610 vs(br), 550 vs(br), 535 vs, 400 s, 380, s, 280 s.	
$[\text{Et}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OPr}')_2)]$	C_6D_6	100.1 97.8§	—	3420–3450	1085 vs(br), 1010 vs(br), 940 s, 925 s, 905 s, 865 vs, 770 vs, 690 vs, 590 vs(br), 555 vs(br), 430 s, 420 s, 320 s, 305 s.	
$[\text{Et}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OPr}')_2)]$	CDCl_3	97.7	75	3440–3470	990–1020 vs(br), 910 s, 825 m, 790 s, 710 vs, 690 vs, 660 vs, 590 vs, 555 vs, 520 s, 490 s, 430 m(br), 317 (s).	
$[\text{Pr}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OEt})_2)]$	CDCl_3	101.6	60	3385–3400	995 vs, 975 vs(br), 890 s, 805 m, 765 s, 720 s, 670 vs, 615 s(br), 570 s(br), 535 vs, 470 m(br), 405 m(br), 315 m.	
$[\text{Pr}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OPr}')_2)]$	CDCl_3	101.2 96.9§	—	3420–3455	1085 vs(br), 1010 vs(br), 940 s, 925 s, 900 s, 865 vs, 830 vs, 780 vs, 735 s(br), 690 vs(br), 630 vs(br), 580 vs(br), 555 vs, 450 vs, 335 s, 295 s.	
$[\text{Pr}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OPr}')_2)]$	CDCl_3	98.9§ 92.3	63 63	3440–3460	1070 s, 995 vs, 975 vs, 890 s, 805, m, 770, s, 725 m, 670 s, 555 s, 535 s, 470 m, 400 m, 315 m, 305 m.	
$[\text{Bu}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OEt})_2)]$	CDCl_3 C_6D_6	98.6 98.6	164 40	3400–3420	1065 vs, 1035 vs, 975 vs, 900 s, 890 s, 870 s, 805 vs, 740 s, 685 vs, 620 s(br), 575 vs, 545 vs, 415 s, 400 s, 305 m.	
$[\text{Bu}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OPr}')_2)]$	CDCl_3	100.9	139	3390	1070 vs, 1015 vs, 990 vs, 920 m, 910 m, 885 s, 850 s, 775 m, 750 m, 670 s, 620 s(br), 540 vs, 410 s(br), 380 m, 300 m.	
$[\text{Bu}_2\text{Sn}(\text{OH})(\text{SSP}(\text{OPr}')_2)]$	CDCl_3	98.2 92.3	—	3360–3400	1080 s, 990 vs, 965 vs, 880 vs, 760 vs, 720 vs, 660 vs, 600 vs(br), 560 vs(br), 530 vs, 395 s, 280 s.	

† Recorded in nujol mull. vs = very strong, s = strong, m = medium, br = broad.

‡ Broad strong band.

§ Spectra showed an additional ^{31}P peak (8–12% integration) in the region 54–59 ppm.

most of these vibrations did not allow unambiguous assignments of the bands. For **I**, the strong bands observed in the region $655\text{--}700$ and $520\text{--}560\text{ cm}^{-1}$ may be assigned to $\nu\text{P}=\text{S}$ and $\nu\text{P}-\text{S}$ modes, respectively (Table II). The absorption bands in the region $940\text{--}1065$ and $735\text{--}805\text{ cm}^{-1}$ have been attributed to $\nu(\text{P})-\text{O}-\text{C}$ and $\nu\text{P}-\text{O}-(\text{C})$ stretching vibrations.^{13,15-17}

Unlike the ^{31}P NMR spectra of **II** and $[\text{R}_2\text{Sn}(\text{Cl})\{\text{SSP}(\text{OR}')_2\}]$ **III**,^{15,24} the spectra of **I** displayed a broad resonance which was considerably deshielded relative to the resonances observed for the corresponding **II** and **III**. In some

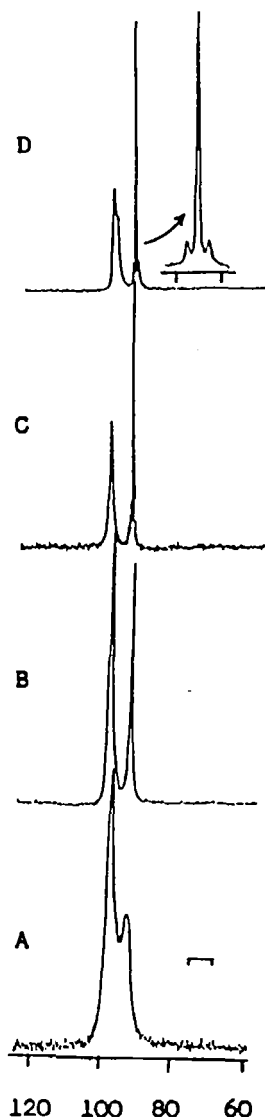
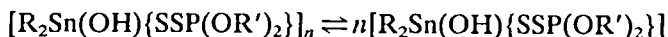


FIGURE 2 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Bu}_2\text{Sn}(\text{OH})\{\text{SSP}(\text{OPr}')_2\}]$ in CDCl_3 . (A) room temperature, bar represents 200 Hz (B) at -15°C (C) at -25°C (D) at -35°C ; inset-scale 100 Hz.

cases two separate or overlapping broad resonances were observed (Table II). Low temperature ^{31}P NMR spectra of two representative complexes, $[\text{Bu}_2\text{Sn}(\text{OH})\{\text{SSP}(\text{OR}')_2\}]$ ($R' = \text{Et}, \text{Pr}^i$), were recorded in CDCl_3 . At -30°C two sharp resonance appeared; the low frequency signal exhibited a $^2J(\text{Sn}-\text{P})$ value of 50 Hz whereas such couplings were not observed with the low field resonance (Figure 2). This indicates that two phosphorus-containing species are in fast exchange at room temperature. Recently a similar hydroxo complex $[\text{Ph}_2\text{Sn}(\text{OH})\{\text{OP}(\text{S})(\text{OPh})_2\}]$ has been reported by Zuckerman *et al.*,¹⁰ for which a dimeric hydroxo-bridged structure has been shown from x-ray diffraction data. Similar hydroxo-bridged structure has been reported for $[\text{Me}_2\text{Sn}(\text{OH})\text{NO}_3]$.⁹ The complexes **I** appear to have similar hydroxo-bridges and in solution dissociate to monomeric species and establishes an equilibrium of the type:



Monomeric **I** are analogous to five coordinate chloro complexes **III**¹⁵ as the magnitude of $^2J(\text{Sn}-\text{P})$ for the two series of complexes is comparable. Thus the resonance at high field is due to five coordinate monomeric species and the low field signal can be assigned to the hydroxo-bridged species.

The ^1H NMR spectra of these complexes were recorded in C_6D_6 . The protons attached to the α -carbon atom of the alkoxy group showed expected multiplets while other protons of the OR' group were merged with the resonances of alkyl tin protons. The $\text{Sn}-\text{R}$ protons displayed multiplets or broad peaks in the region 0.8–2.4 ppm. The SnOH proton resonance is possibly merged with $\text{Sn}-\text{R}$ protons. In triorganotin hydroxides the OH resonance appears at ~ 1.0 ppm.¹⁴

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