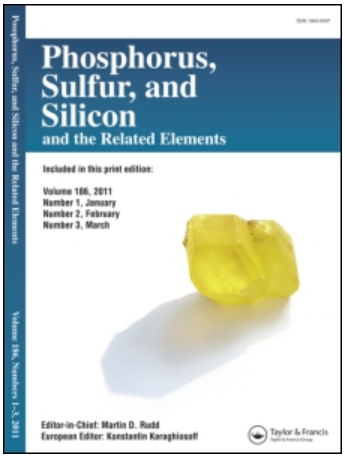

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SYNTHESES AND SPECTROSCOPIC STUDIES OF DIORGANOTIN BIS-O-ALKYL PHOSPHONATES

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SYNTHESES AND SPECTROSCOPIC STUDIES OF DIORGANOTIN BIS-O-ALKYL PHOSPHONATES†

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Diorganotin bis-O-alkyl phosphonates, $R_2Sn[O_2P(H)OR']_2$ (R = Me, Et; R' = Me, Et, Bu, Ph) have been obtained in quantitative yield by reacting sodium salts of O-alkyl phosphonate with diorganotin dichloride. The derivatives are white colored, hydrolytically stable powdery solids, soluble in methanol (when freshly prepared) and are characterized by various physico-chemical as well as spectroscopic IR, NMR (^1H, ^{31}P and ^{119}Sn) studies which are consistent with 6-coordinated tin atom.

Key words: Diorganotin dichloride, O-alkyl phosphonate, NMR spectra, hexacoordinated tin.

INTRODUCTION

There is continued interest in the chemistry of Sn—O—P bonded compounds owing to their use as synthetic intermediates[1,2] (particularly in nucleoside[3] and carbohydrate chemistry[4]) as biocides[5] and as a polymerization catalyst.[6,7] They have interesting structural possibilities because of the presence of both electron donor as well as electron acceptor sites in the molecule. The work in this area of phosphorus chemistry has been mainly considered with triorganotin phosphonate[8,9] and phosphinate.[10] Their structural studies have revealed the bridging bidentate behavior of phosphonate and phosphinate moieties which give rise to oligomeric or polymeric structures due to phosphoryl coordination to tin (P=O → Sn). The present work deals with the syntheses and spectroscopic characterization of diorganotin bis-O-alkyl phosphonates.

RESULTS AND DISCUSSION

Diorganotin bis-O-alkyl phosphonates have been synthesized by reacting sodium salts of O-alkyl phosphonate with diorganotin dichloride in a 2:1 molar ratio. The sodium salt of O-alkyl phosphonate can be prepared by basic hydrolysis of dialkyl phosphonate.

$$H[O]P[OR]_2 + NaOH \rightarrow [RO]P[O]H[ONa] + ROH$$

$$2[RO]P[O]H[ONa] + R'_2SnCl_2 \rightarrow R'_2Sn[O_2P(H)(OR)]_2 + 2NaCl\downarrow$$

[R = Me, Et; R' = Me, Et, Bu, Ph]

†This article is dedicated to the (late) Prof. G. Srivastava, Dept. of Chemistry, University of Rajasthan, Jaipur (India).

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TABLE I

Synthetic and analytical data of diorganotin bis-O-alkyl phosphonate

Compound no.	Reactants: . .g (mmole) [RO]P[O]H[ONa] R = . .	Reactants: . .g (mmole) R'_2SnCl_2 R′ = . .	Product Yield. .g; . . .%	%Sn found (calcd)	Molecular weight found (calcd)
1.	Me	Me	$Me_2Sn[O_2P(H)(OMe)]_2$	35.30	318.
	1.29 (10.93)	1.19 (5.41)	1.55 84	(335.04)	(338.69)
2.	Me	Et	$Et_2Sn[O_2P(H)(OMe)]_2$	32.66	344.
	1.88 (15.93)	1.97 (7.95)	2.42 83	(32.37)	(366.69)
3.	Me	Bu	$Bu_2Sn[O_2P(H)(OMe)]_2$	28.36	—
	2.07 (17.71)	2.76 (9.08)	3.19 85	(28.08)	
4.	Et	Me	$Me_2Sn[O_2P(H)(OEt)]_2$	32.68	—
	1.92 (14.53)	1.60 (7.28)	2.38 89	(32.37)	
5.	Et	Et	$Et_2Sn[O_2P(H)(OEt)]_2$	30.30	377
	1.07 (8.09)	1.00 (4.03)	1.38 86	(30.07)	(394.69)
6.	Et	Bu	$Bu_2Sn[O_2P(H)(OEt)]_2$	26.62	—
	1.27 (9.61)	1.46 (4.80)	1.43 84	(26.33)	
7.	Et	Ph	$Ph_2Sn[O_2P(H)(OEt)]_2$	24.67	—
	1.41 (10.68)	1.83 (5.32)	2.33 89	(24.18)	

TABLE II

IR spectral data of diorganotin bis-O-alkyl phosphonate

Compound	νP—H	νP=O	ν(P)—O—C	νP—O—(C)	νP=O → Sn	νSn—O
$Me_2Sn\ [O_2P(H)(OMe)]_2$	2445s	1170s	1070br	795m	660s	570s
$Et_2Sn\ [O_2P(H)(OMe)]_2$	2470s	1195s	1055br	825m	645s	595s
$Bu_2Sn\ [O_2P(H)(OMe)]_2$	2465s	1145br	1060br	860m	655s	610s
$Me_2Sn\ [O_2P(H)(OEt)]_2$	2420s	1130s	1065br	780m	670s	530s
$Et_2Sn\ [O_2P(H)(OEt)]_2$	2445s	1200s	1060br	845m	630s	545s
$Bu_2Sn\ [O_2P(H)(OEt)]_2$	2460s	1185br	1055br	855m	640s	565s
$Ph_2Sn\ [O_2P(H)(OEt)]_2$	2450s	1160s	1060br	810m	680s	545s

The diorganotin bis-O-alkyl phosphonates are non volatile white colored powdery solids, melt with decomposition (210–235°C), hydrolytically stable and are found to be monomeric in nature. These derivatives are soluble in methanol (when freshly prepared). On storage these tend to be converted into insoluble products (polymeric form), thus showing the tendency of ageing.

IR Spectra

The important IR spectral bands for these derivatives are tabulated in Table II. A strong absorption band in the region 2470–2420 cm^{-1} has been assigned to P—H stretching vibrations. The strong intensity phosphoryl absorption band appear in the range 1200–1130 cm^{-1} which is shifted substantially towards the lower frequencies (65–85 cm^{-1}) from its original position in the dialkyl phosphonate, e.g. $[EtO)_2P(O)H$: 1265 cm^{-1}].[12] This indicates the coordination of phosphoryl oxygen to tin atom. The absorption bands observed in the region 1070–1055 cm^{-1} and 860–780 cm^{-1} are assigned to (P)—O—C and P—O—(C) respectively, and the band observed in the region 610–530 cm^{-1} is due to Sn—C.

TABLE III

NMR (^{1}H, ^{31}P and ^{119}Sn) spectral data of O-alkyl phosphonate derivatives of diorganotin (IV)

Compound	Chemical shift		
	^{1}H	^{31}P	^{119}Sn $^1J(^{119}Sn\text{-}^{13}C)$
$Me_2Sn[O_2P(H)(OMe)]_2$	0.92, s, 6H (CH_3); 3.1, s, 6H (OCH_3); 7.1, s, 1H (P—H); J = 670 Hz.	7.73	−212.6 [542]
$Et_2Sn[O_2P(H)(OMe)]_2$	0.76, t, 3H (CH_3); 1.76, q, 2H (CH_2); 3.2, s, 6H (OCH_3); 7.3, s, 1H (P—H), J = 670 Hz.	5.86	−243.87 [548]
$Bu_2Sn[O_2P(H)(OMe)]_2$	0.78, t, 3H (CH_3); 2.21–2.56, m, 6H (CH_2); 3.0, s, 6H (OCH_3); 7.1, s, 1H (P—H), J = 665 Hz.	6.78	−260.52 [530]
$Me_2Sn[O_2P(H)(OEt)]_2$	0.98, s, 6H (CH); 1.32, t, 6H (CH_3); 3.6, q, 4H (OCH_2); 7.0, s, 1H (P—H), J = 667 Hz.	3.23	−221.3 [556]
$Et_2Sn[O_2P(H)(OEt)]_2$	0.81, t, 3H (CH_3); 1.72, q, 2H (CH_3), 2.6, t, 6H (CH_3); 3.56, q, 4H (OCH_2); 6.8, s, 1H (P—H), J = 630 Hz.	6.62	−235.23 [578]
$Bu_2Sn[O_2P(H)(OEt)]_2$	0.86, t, 3H (CH_3); 2.17–2.55, m, 6H (CH_2); 2.76, t, 6H (CH_3); 3.62, q, 4H (OCH_2); 6.88, s, 1H (P—H), J = 635 Hz.	4.43	−253.58 [544]
$Ph_2Sn[O_2P(H)(OEt)]_2$	2.42, t, 6H (CH_3); 3.62, q, 4H (OCH_2); 6.7, s, 1H (P—H); J = 650 Hz, 7.11–7.83, m, 5H (C_6H_5).	9.26	−261.37 [564]

^{1}H NMR Spectra

The ^{1}H NMR spectra of freshly synthesized derivatives recorded in $CDCl_3$ (Table III) show the usual 3-bond (H—C—O—P) coupling of 12 Hz. The hydrogen atom directly attached to phosphorus atom shows strong coupling with the phosphorus atom (670–630 Hz).[11]

^{31}P NMR Spectra

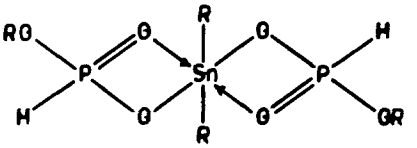
The ^{31}P NMR spectra of the derivatives have been recorded in methanol which show one resonance signal in the range of 3.23–9.26 ppm.

An upfield shift of 4–6 ppm has been observed in the ^{31}P signal compared to its position in corresponding dialkyl phosphonate. This shift may be due to the coordination of the phosphoryl group to the tin atom. A characteristic strong P—H coupling has been observed in the proton coupled ^{31}P NMR spectra of these complexes at 680–630 Hz.

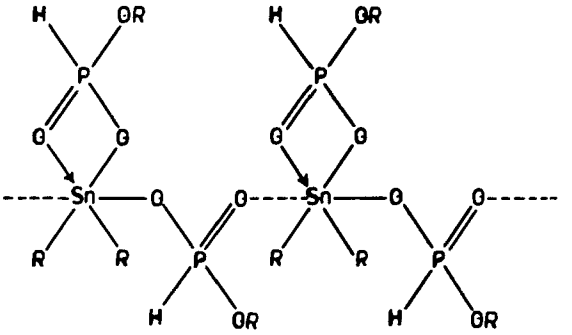
^{119}Sn NMR Spectra

The ^{119}Sn NMR spectra shows only one resonance signal for each derivative in the region −212.6 to −261.37 ppm. A comparison of these chemical shift values with those of the corresponding diorganotin dichloride indicates increased shielding of the tin atom in the phosphonate complexes as expected because of the increase in its coordination number. Observation of $^1J(^{119}Sn\text{-}^{13}C)$ value in the range 530–578 Hz further supports 6-coordination around the central tin atom in these derivatives. The

freshly prepared derivatives are monomeric in nature. On the basis of the above physico-chemical as well as spectroscopic studies an octahedral structure of the following type has been assigned for these complexes.



The P=O → Sn coordination in diorganotin bis-O-alkyl phosphonate appears to be quite strong and the linkage is not cleaved by pyridine. (There is no change in ^{31}P and ^{119}Sn NMR chemical shift value.) The high stability and the insolubility of these phosphonates in organic solvent indicates the polymerization of these derivations on ageing.



Attempts to obtain suitable crystals of the derivatives for an X-ray diffraction study were unsuccessful due to the formation of twin crystals.

EXPERIMENTAL

Benzene (BDH), methanol (BDH) were dried and distilled before use. Diorganotin dichloride and dialkyl phosphonates were purified by distillation under *vacuo*. Tin was estimated gravimetrically as tin oxide.[13] IR spectra were recorded on Perkin Elmer 577 spectrophotometer in the region, 4000–400 cm^{-1} as KBr pellets. ^{1}H NMR spectra were recorded in $CDCl_3$. ^{31}P and ^{119}Sn NMR spectra were recorded in methanol solution on a JEOL FX 90Q spectrometer using TMS (for ^{1}H), 85% H_3PO_4 (for ^{31}P) and Me_4Sn (for ^{119}Sn) as external references.

Reaction of Monosodium Salt of Methyl Phosphonate with Dimethyltin Dichloride in 2:1 Molar Ratio

To a suspension of sodium salt of methyl phosphonate (1.29 g; 10.93 mmole) in benzene (30 ml), dimethyltin dichloride (1.19 g; 5.41 mmole) was added. The reaction mixture was stirred for two hours at room temperature and then refluxed for about five hours. The reaction was complete after complete dissolution of the sodium salt. Excess solvent was removed under reduced pressure. After washing the product 3–4 times with benzene, white colored powdery solid was obtained (1.55 g; 84.7%). Found: Sn, 35.30%; M, 318, Calcd: for $C_4H_{13}O_6P_2Sn$, Sn, 35.0; M, 338.69.

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