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SYNTHESES AND PROPERTIES OF MIXED LIGAND COMPLEXES OF DIORGANOTIN(IV): PART I. β -DIKETONATO DIORGANOTIN DIALKYL (OR ARYL) DITHIOPHOSPHATES AND 1- β -DIKETONATO-3-DIALKYL DITHIOPHOSPHATO TETRABUTYL DISTANNOXANES

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SYNTHESES AND PROPERTIES OF MIXED LIGAND COMPLEXES OF DIORGANOTIN(IV): PART I. β -DIKETONATO DIORGANOTIN DIALKYL (OR ARYL) DITHIOPHOSPHATES AND 1- β -DIKETONATO-3-DIALKYL DITHIOPHOSPHATO TETRABUTYL DISTANNOXANES

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The mixed ligand complexes of the type $R'_2Sn[R''COCHCOR'']$ [$S_2P(OR'')_2$] and $\{(R''O)_2S_2P\}R'_2SnOSnR'_2[R''COCHCOR'']$ have been prepared by the reaction of diorganotin oxide ($R' = Bu, Ph$) or chloride ($R' = Me$) with β -diketones and dialkyl (or aryl) dithiophosphoric acids in 1:1:1 and 2:1:1 molar ratios in refluxing benzene. The products formed are monomeric, non volatile, yellow colored viscous liquids or sticky solids, soluble in common organic solvents and exhibit high sensitivity towards atmospheric moisture. These complexes have been characterized by elemental analyses, molecular weight measurements, IR and NMR (1H , ^{31}P and ^{119}Sn) spectral data. On the basis of ^{119}Sn NMR studies, it was postulated that there might be disproportionation which led to the formation of mixture with fast exchange between $Sn-S$ and $Sn-O$ linkages.

Key words: Diorganotin oxide (or chloride); dialkyl (or aryl) dithiophosphate; β -diketone; β -diketonato diorganotin(IV) dialkyl (or aryl) dithiophosphate; and 1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes.

INTRODUCTION

O,O'-Dialkyl and alkylene dithiophosphoric acids contribute an important series of ligands which show an interesting versatility in their chemical bonding modes (e.g., uni- as well as bidentate chelating/bridging) towards different metals.¹⁻³ Dialkyl dithiophosphates and their metal derivatives are also used as oil additives and as pesticides.^{4,5}

The chemistry of metal β -diketonates has been extensively reported in the literature.^{6,7} An extensive survey of literature reveals that a lot of work has also been carried out on organotin(IV) β -diketonates⁸⁻¹⁰ and organotin(IV) dialkyl (or alkylene) dithiophosphates^{2,3,11,12} during the last ten years.

The mixed derivatives of β -diketonate with tin(IV) alkoxides,⁸ -chlorides,¹⁰ -acetates¹³ and -alkylxanthates¹⁴ have been reported in the literature. The mixed derivatives of the type $R_2Sn[OCOCH_3][S_2P(OR)_2]$ have been recently reported¹⁵ from our laboratory in which mono functional bidentate behaviour of the ligand has been established.

The mixed derivatives of diorganotin(IV) with β -diketonates and dialkyl (or aryl)

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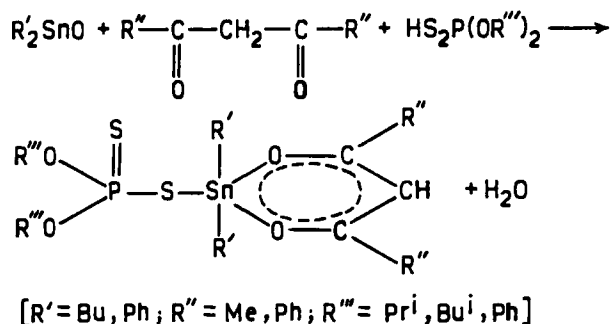
‡This Article is dedicated to Late Dr. G. Srivastava, Assoc. Proff. University of Rajasthan, Jaipur.

dithiophosphates have not been studied so far. In view of the above it was considered of interest to synthesize and study the chemical bonding mode in these new derivatives.

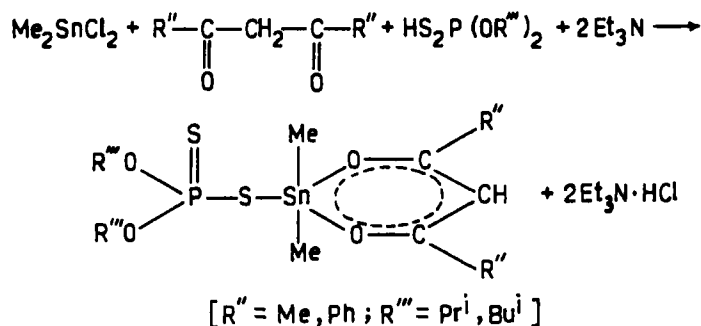
In the present communication, we report the syntheses and physico-chemical studies of the mixed ligand complexes of the type $R'_2Sn[R''COCHCOR''] [S_2P(OR''')_2]$ and $[(OR''')_2S_2P]R'_2SnOSnR'_2[R''COCHCOR'']$.

RESULTS AND DISCUSSION

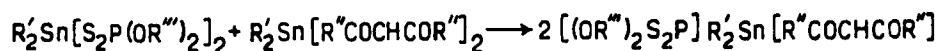
β -Diketonato diorganotin(IV) dialkyl (or aryl) dithiophosphates have been synthesized by mixing and refluxing (6 hours) diorganotin oxide with β -diketonates and dialkyl (or aryl) dithiophosphates in 1:1:1 molar ratio, in dry benzene. The liberated water has been fractionated azeotropically.



The dimethyltin(IV) derivatives have been synthesized by mixing, stirring and then refluxing dimethyltin dichloride with β -diketone and dialkyl dithiophosphate in 1:1:1 molar ratio in the presence of triethylamine. The product formed has been isolated by stripping off the solvent from the filtrate in vacuo.



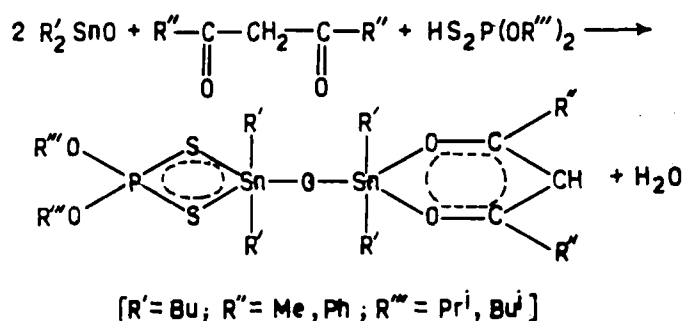
These complexes have also been synthesized by mixing and refluxing the diorganotin(IV)-bis-dialkyl dithiophosphates and diorganotin(IV)-bis- β -diketonates in 1:1 molar ratio.



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

These complexes are yellow colored viscous liquids or sticky solids (methyl and phenyl derivatives) and are found to be non-volatile even under reduced pressure (160°/0.5 mm). Most of them decompose above 160°C. These are soluble in common organic solvents, monomeric in nature and are found to be sensitive towards atmospheric moisture.

1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes have been synthesized by mixing dialkyltin oxide with β -diketonates and dialkyl dithiophosphates in 2:1:1 molar ratio in refluxing benzene. The reaction proceeds to completion within 8 hours and the liberated water has been fractionated azeotropically.



These complexes are yellow colored non-volatile viscous liquids, soluble in common organic solvents and are found to be monomeric in nature.

IR SPECTRA

IR spectra of these complexes have been recorded in the region 4000-200 cm^{-1} . A comparison of the IR spectra of the complexes with those of the starting materials [dialkyl dithiophosphate, β -diketonate, diorganotin oxide (or chloride)] shows the following characteristic changes.

1. The disappearance of a broad and strong absorption band ν S—H which was present at $\sim 2600 \text{ cm}^{-1}$ in dialkyl dithiophosphate.

2. The appearance of a new weak absorption band at $350\text{--}365 \text{ cm}^{-1}$ in β -diketonato diorganotin dialkyl (or aryl) dithiophosphates and medium absorption band at $325\text{--}335 \text{ cm}^{-1}$ in 1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes which may tentatively assigned to ν Sn—S linkage.

3. The appearance of a new sharp absorption band at $435\text{--}455 \text{ cm}^{-1}$, which was assigned to ν Sn—O linkage.

4. A characteristic absorption band in the region $1425\text{--}1455 \text{ cm}^{-1}$ was assigned to the coordinate carbonyl group.

5. The IR spectra of all the complexes show a strong absorption band at $1550\text{--}1580 \text{ cm}^{-1}$ which is characteristic of ν C=C linkage.

In 1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes the ν P=S and ν P—S absorption band is shifted towards lower frequencies ($\sim 50 \text{ cm}^{-1}$) which indicates a strong bidentate chelation^{1,2} of these groups with tin atom.

TABLE I
Syntheses and characterization of β -diketonato dimethyltin dialkyl dithiophosphate

S.N.	Me_2SnCl_2	Reactants, g(mole) $\text{RCOCH}_2\text{COR}'$ $\text{R}' = \text{Me}, \text{Ph}, \text{Et}, \text{Pr}^i, \text{Bu}^i, \text{OBu}^i$	$\text{HS}_2\text{P}(\text{OR})_2$ $\text{R} = \text{Me}, \text{Ph}, \text{Et}, \text{Pr}^i, \text{Bu}^i, \text{OBu}^i$	Et_3N	Product $\text{Me}_2\text{Sn}[\text{RCOCHCOR}][\text{S}_2\text{P}(\text{OR})_2]_2$...g ; ...%	Analyses Sn found % (calcd. %)	S found % (calcd. %)	Molecular weight found... (calcd...)
1.	1.20(5.46)	Me ; Me 0.55(5.5)	Pr^i 1.17(5.46)	1.10(10.89)	$\text{Me}_2\text{Sn}[\text{MeCOCHCOMe}][\text{S}_2\text{P}(\text{OPr}^i)_2]_2$ 2.39	25.82 (25.76)	13.42 (13.89)	--
2.	1.10(5.0)	Me ; Ph 0.81(5.0)	Pr^i 1.07(5.0)	1.02(10.09)	$\text{Me}_2\text{Sn}[\text{MeCOCHCOPh}][\text{S}_2\text{P}(\text{OPr}^i)_2]_2$ 2.53	23.02 (22.70)	11.91 (12.24)	--
3.	0.93(4.23)	Ph ; Ph 0.95(4.24)	Pr^i 0.90(4.20)	0.86(8.51)	$\text{Me}_2\text{Sn}[\text{PhCOCHCOPh}][\text{S}_2\text{P}(\text{OPr}^i)_2]_2$ 2.38	21.12 (20.65)	11.02 (11.13)	542.2 (574.7)
4.	1.49(6.78)	Me ; Me 0.68(6.8)	Bu^i 1.64(6.77)	1.37(13.56)	$\text{Me}_2\text{Sn}[\text{MeCOCHCOMe}][\text{S}_2\text{P}(\text{OBu}^i)_2]_2$ 3.24	24.42 (24.28)	13.21 (13.09)	--
5.	0.99(4.50)	Me ; Ph 0.73(4.50)	Bu^i 1.09(4.50)	0.92(9.10)	$\text{Me}_2\text{Sn}[\text{MeCOCHCOPh}][\text{S}_2\text{P}(\text{OBu}^i)_2]_2$ 2.40	21.73 (21.55)	11.23 (11.62)	538.6 (550.7)
6.	1.07(4.87)	Ph ; Ph 1.09(4.86)	Bu^i 1.18(4.87)	0.99(9.80)	$\text{Me}_2\text{Sn}[\text{PhCOCHCOPh}][\text{S}_2\text{P}(\text{OBu}^i)_2]_2$ 2.79	19.62 (19.37)	10.12 (10.44)	--

TABLE II
Syntheses and characterization of β -diketonato diorganotin dialkyl (or aryl) dithiophosphates

S.N.	Reactants, g(mole)		Product		Analyses		Molecular weight	
R_2SnO $R = \dots$	$RCOCH_2COR'$ $R = \dots$	$HS_2P(OR)_2$ $R = \dots$	$R'_2Sn[R''COCH_2COR'] [S_2P(OR'')]_2$ \dots	\dots	Sn...% found (calcd. %)	S found (calcd. %)	found (calcd. %)	found (calcd. %)
7.	Bu	Me; Me	Pr^I	$Bu_2Sn[MeCOCH_2COMe][S_2P(OPr^I)_2]$ 3.04	21.58 (21.75)	11.62 (11.75)	521.85 (544.7)	
8.	Bu	Me; Ph	Pr^I	$Bu_2Sn[MeCOCH_2COR^I][S_2P(OPr^I)_2]$ 4.24	19.37 (19.56)	10.01 (10.54)	--	
9.	Bu	Ph; Ph	Pr^I	$Bu_2Sn[PhCOCH_2COR^I][S_2P(OPr^I)_2]$ 4.40	18.87 (17.75)	9.32 (9.57)	--	
10.	Bu	Me; Me	Bu^I	$Bu_2Sn[MeCOCH_2COMe][S_2P(OBu^I)_2]$ 4.60	20.43 (20.72)	10.98 (11.17)	--	
11.	Bu	Me; Ph	Bu^I	$Bu_2Sn[MeCOCH_2COR^I][S_2P(OBu^I)_2]$ 5.04	19.30 (18.70)	9.82 (10.08)	619.84 (634.7)	
12.	Bu	Ph; Ph	Bu^I	$Bu_2Sn[PhCOCH_2COR^I][S_2P(OBu^I)_2]$ 3.15	16.82 (17.04)	9.02 (9.18)	--	
13.	Bu	Me; Me	Ph	$Bu_2Sn[MeCOCH_2COMe][S_2P(OPh)_2]$ 3.01	20.17 (19.37)	11.22 (10.44)	--	
14.	Bu	Me; Ph	Ph	$Bu_2Sn[MeCOCH_2COR^I][S_2P(OPh)_2]$ 4.12	18.16 (17.59)	9.06 (9.48)	--	
15.	Bu	Ph; Ph	Ph	$Bu_2Sn[PhCOCH_2COR^I][S_2P(OPh)_2]$ 3.63	16.86 (16.11)	8.12 (8.68)	702.0 (736.7)	
16.	Ph	Me; Me	Pr^I	$Ph_2Sn[MeCOCH_2COMe][S_2P(OPr^I)_2]$ 1.67	20.47 (20.30)	10.62 (10.94)	--	

TABLE III
Syntheses and characterization of 1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes

S.N.	Reactants, g(mole)	Product	Analyses	Molecular weight
R_2SnO $R = \dots$	$RCOCH_2COR'$ $R' = \dots$	$\{(OR)_2S_2P_2Bu_2SnOSnBu_2[RCOCHCOR] \dots \}_n$	Sn found % (calcd. %)	found % (calcd. %)
1.	Bu 3.31(13.30)	$\{(OPr)_2S_2P_2Bu_2SnOSnBu_2[MeCOCHCOMe] \dots \}_n$	30.19 (28.92)	7.52 (8.06)
2.	Bu 2.67(10.73)	$\{(OPr)_2S_2P_2Bu_2SnOSnBu_2[MeCOCHCOPh] \dots \}_n$	27.89 (27.75)	7.19 (7.48)
3.	Bu 2.35(9.45)	$\{(OBu)_2S_2P_2Bu_2SnOSnBu_2[MeCOCHCOMe] \dots \}_n$	28.52 (28.90)	7.22 (7.79)
4.	Bu 2.33(9.37)	$\{(OBu)_2S_2P_2Bu_2SnOSnBu_2[MeCOCHCOPh] \dots \}_n$	27.23 (26.87)	7.04 (7.24)

TABLE IV
Infrared spectral data for β -diketonato diorganotin dialkyl (or aryl) dithiophosphates (in cm^{-1})

Compound No.	$\nu_{\text{C-C}}$	$\nu_{\text{C=O}}$	$\nu_{\text{(P)-O-C}}$	$\nu_{\text{P-O-(C)}}$	$\nu_{\text{P-S}}$	$\nu_{\text{P-S}}$	$\nu_{\text{Sn-C}}$	$\nu_{\text{Sn-O}}$	$\nu_{\text{Sn-S}}$
1.	1580s	1455s	965br	865s	630m	525br	550br	455s	365w
2.	1575s	1440s	970br	875s	625m	520br	535br	455s	360w
3.	1570s	1435s	960br	865s	620m	520br	535br	450m	360w
4.	1575s	1445s	970br	870vs	635s	530br	550br	455s	355w
5.	1570s	1440s	965br	865s	630m	525br	545br	450s	360w
6.	1570s	1435s	960br	865s	630s	520br	540br	445s	355w
7.	1570s	1430s	1000br	870vs	630m	520m	545m	450vs	365w
8.	1565s	1430m	960br	865vs	635m	530m	550w	450vs	360w
9.	1560s	1445s	950br	865s	630m	530br	535br	440vs	360w
10.	1560s	1445m	950br	865s	630m	530br	535br	440vs	360w
11.	1555s	1435m	970br	825s	650s	530br	560br	450s	365w
12.	1560m	1440m	980br	825s	650m	535br	545br	440s	365w
13.	1565m	1430m	965br	830s	635m	525br	535br	450s	360w
14.	1570s	1440s	990br	840vs	635m	540br	555br	435s	350w
15.	1560s	1425s	955br	825vs	640m	575br	545br	450vs	350w
16.	1550s	1430s	965br	835s	630m	525br	545br	445s	355w

vs = very sharp, s = sharp, m = medium, br = broad, w = weak

TABLE V
Infrared spectral data for 1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes (cm^{-1})

Compound No.	$\nu_{\text{C}=\text{C}}$	$\nu_{\text{C}=\text{O}}$	$\nu(\text{P})-\text{O}-\text{C}$	$\nu \text{P}-\text{O}-(\text{C})$	$\nu \text{P}-\text{S}$	$\nu \text{P}-\text{S}$	$\nu \text{Sn}-\text{C}$	$\nu \text{Sn}-\text{O}$	$\nu \text{Sn}-\text{S}$
1.	1575s	1445s	920s	800s	570br	470s	540br	440s	330m
2.	1580s	1440s	915vs	815vs	580br	460s	535br	445s	335m
3.	1580s	1445s	905vs	790s	570br	465br	545br	445s	325w
4.	1580s	1435s	910br	795s	575br	470s	540br	440s	335m

vs = very sharp, s = sharp, m = medium, br = broad, w = weak

NMR SPECTRA [^1H , ^{31}P & ^{119}Sn] ^1H

PMR spectra of these complexes show that there is an overlapping of the multiplet due to methyl and tin-butyl protons (besides in the case of methyl derivatives). The OCH_2 and OCH protons of the dialkyl dithiophosphate moieties however show distinct signals with the usual pattern caused by 3— bond coupling with magnetically active phosphorus atom. The PMR signal due to S—H proton is absent in these complexes. PMR spectra of distannoxanes show a number of resonance signals and are too complicated to give any useful information regarding the structure of the complexes.

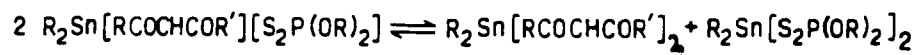
 ^{31}P

^{31}P Chemical shift values for these complexes have been mentioned in Table VI. Only one resonance signal has been observed in the region δ 93 to 99 ppm. The signal appears downfield in comparison to that of the parent acid. This supports the formation of Sn—S—P chemical bond in these (β -diketonato diorganotin dialkyl (or aryl) dithiophosphate) complexes. The value of the chemical shift is in good agreement with the result reported for $\text{R}_2\text{Sn}[\text{OAC}][\text{S}_2\text{P}(\text{OR})_2]$.¹⁵

In case of distannoxanes the ^{31}P chemical shift observed downfield (δ 102 to 107 ppm) in comparison to β -diketonato diorganotin dialkyl (or aryl) dithiophosphates. This indicates a strong bidentate chelation of the thiophosphoryl group with the tin atom.

 ^{119}Sn

In contrast to ^1H and ^{31}P NMR spectra which show the presence of single species, the ^{119}Sn NMR spectra of β -diketonato diorganotin dialkyl (or aryl) dithiophosphates and 1- β -diketonato-3-dialkyl dithiophosphato tetrabutyl distannoxanes (Table VI & VII) show three resonance signals. The spectra of the same compound obtained by two different routes are identical in nature. A comparison of the chemical shift values with those of corresponding $\text{R}_2\text{Sn}(\text{RCOCHCOR}')_2$ and $\text{R}_2\text{Sn}(\text{S}_2\text{P}(\text{OR})_2)_2$ compounds obtained under similar conditions indicates the presence of those species along with the mixed derivative, $\text{R}_2\text{Sn}[\text{RCOCHCOR}'][\text{S}_2\text{P}(\text{OR})_2]$. The above results thus indicate that an equilibrium as a result of disproportionation of the following type exists in these derivatives.



The ^{119}Sn chemical shifts results indicate the pentacoordinated nature of the tin atom in these complexes. The following structure has been tentatively proposed for these unsymmetrical derivatives.

TABLE VI
NMR (^1H , ^{31}P & ^{119}Sn) spectral data (δ ppm) for β -diketonato diorganotin dialkyl (or aryl) dithiophosphates

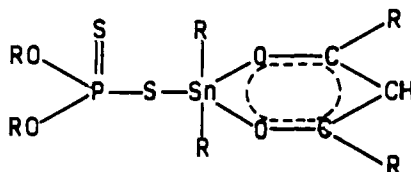
Compound No.	^1H	Chemical shifts	^{31}P	^{119}Sn
1.	—	—	96.65	-171.4 -239.4 -368.6
2.	1.27.d,12H(CH_3); 2.19.s,9H($\text{CH}_3 + \text{Sn} - \text{CH}_3$); 4.84-5.10.m,2H(OCH); 6.10.s,1H(CH); 7.31-7.98.m,5H(C_6H_5)		95.44	-161.81 -232.26 -362.63
3.	1.15.d,12H(CH_3); 2.09.s,6H($\text{CH}_3 + \text{Sn} - \text{CH}_3$); 4.61-4.86.m,2H(OCH); 6.8.s,1H(CH); 7.34-7.95.m,10H(C_6H_5)		94.81	-151.1 -219.2 -358.6
4.	1.12.d,12H(CH_3); 1.90.s,12H($\text{CH}_3 + \text{Sn} - \text{CH}_3$); 2.52-2.80.m,2H(CH); 4.6.q,4H(OCH_2); 5.4.s,1H(CH)		97.02	-174.3 -248.7 -359.6
5.	1.02.d,12H(CH_3); 1.86.s,9H($\text{CH}_3 + \text{Sn} - \text{CH}_3$); 2.21-2.43.m,2H(CH); 4.01.q,4H(OCH_2); 6.12.s,1H(CH); 7.26-7.74.m,5H(C_6H_5)		96.66	—
6.	0.95.d,12H(CH_3); 2.8.s,6H($\text{Sn} - \text{CH}_3$); 1.84-2.06.m,2H(CH); 3.59.q,4H(OCH_2); 6.77.s,1H(CH); 7.31-8.10.m,10H(C_6H_5)		95.49	-163.1 -226.5 -351.5
7.	—	—	93.83	-183.87 -277.70 -398.59
8.	0.82-1.30.m,33H($\text{CH}_3 + \text{Sn} - \text{C}_6\text{H}_5$); 2.09.s,1H(CH); 4.77.m,1H(OCH); 7.47.s,5H(C_6H_5)		94.23	-183.14 -276.26 -389.18

9.	0.85-1.33, m, 30H(CH ₃ + Sn-C ₄ H ₉); 1.87, s, 1H(CH); 4.77, m, 1H(OCH); 7.50, s, 10H(C ₆ H ₅)	93.96	-183.66 -272.75 -384.27
10.	0.89-1.43, m, 26H(CH ₃ + Sn-C ₄ H ₉); 1.93, s, 1H(CH); 3.78, q, 4H(OCH ₂)	98.67	-186.15 -273.72 -399.72
11.	—	98.76	-186.65 -272.46 -392.80
12.	0.85-1.43, m, 30H(CH ₃ + Sn-C ₄ H ₉); 1.90, s, 1H(CH); 3.81, q, 4H(OCH ₂)	99.75	-186.23 -271.00 -386.46
13.	—	91.87	-181.06 -268.56 -398.18
14.	—	91.16	-181.21 -268.13 -391.12
15.	—	92.29	-180.87 -267.82 -383.87
16.	—	90.06	—

TABLE VII
NMR (^{31}P & ^{119}Sn) spectral data (δ ppm) for 1- β -diketonato-3-dialkyl dithiophosphato
tetrabutyl distannoxanes

Compound No.	Chemical shift (δ ppm)	
	^{31}P	^{119}Sn
1.	102.7	-186.02 -279.87 -400.76
2.	104.6	-183.70 -275.09 -388.37
3.	105.3	-189.19 -278.16 -401.52
4.	109.1	-185.29 -276.73 -389.08

It may be noted that ^1H and ^{31}P NMR spectroscopy is unable to give the exact picture and the chemical shifts obtained from these spectra are only average values.



The bidentate nature of the β -diketonate moiety is readily indicated by the position of $\nu \text{C}=\text{O}$ absorption band in the IR spectra. It may also be pointed out that the tendency of the β -diketonate moiety to show bidentate behaviour towards tin is much stronger than that of the dithiophosphate group.

The ^{119}Sn NMR studies for these complexes have also been extended to different concentrations. It appears that the resonance signals are insensitive to concentration changes.

On the basis of above results, it appears that there may be an equilibrium as a result of disproportionation of $\text{R}_2\text{Sn}[\text{RCOCHCOR}'][\text{S}_2\text{P}(\text{OR})_2]$ into $\text{R}_2\text{Sn}[\text{RCOCHCOR}']_2$ and $\text{R}_2\text{Sn}[\text{S}_2\text{P}(\text{OR})_2]_2$ for both $\text{R}=\text{Bu}$ & $\text{R}=\text{Me}$. There may also be fast exchange between $\text{Sn}-\text{O}$ and $\text{Sn}-\text{S}$ linkages.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the experimental manipulations. Sulfur and tin were estimated gravimetrically as barium sulphate (Messenger's method)¹⁶ and tin oxide¹⁶ respectively. Molecular weights were determined by Knauer Vapour Pressure Osmometer in chloroform.

IR spectra were recorded on a Perkin Elmer-577 spectrophotometer in the range of 4000-200 cm^{-1} using CsI cells. ^1H NMR spectra were recorded in deuterated chloroform and ^{31}P & ^{119}Sn were recorded in benzene on JEOL FX 90Q spectrophotometer using TMS (for ^1H), H_3PO_4 (for ^{31}P) and Me_4Sn (for ^{119}Sn) as external references.

Synthesis of $\text{Me}_2\text{Sn}[\text{CH}_3\text{COCHCOCH}_3]/[\text{S}_2\text{P}(\text{OPr})_2]$. A mixture of dimethyltin dichloride (1.20 g, 5.46 mmole) acetylacetone (0.55 g, 5.5 mmole) and diisopropyl dithiophosphate (1.17 g, 5.46 mmole) in benzene (~40 ml) on mixing and stirring followed by refluxing, adding 2 moles of triethylamine (1.10 g), on filtration gave triethylamine hydrochloride (found: 1.55 g; calcd. 1.57 g) and product (after removal excess of benzene *in vacuo*) 2.39 g; 95% as a light yellow colored sticky solid. (Calcd. for $\text{C}_{13}\text{H}_{27}\text{O}_4\text{PS}_2\text{Sn}$: S, 13.89; Sn, 25.76, Found: S, 13.42; Sn, 25.82).

Details of similar derivatives are also summarized in Table I.

Reaction of dibutyltin oxide with acetylacetone and diisopropyl dithiophosphate in 1:1:1 molar ratio. Dibutyltin oxide (1.49 g, 5.99 mmole), acetylacetone (0.60 g, 6.0 mmole) and diisopropyl dithiophosphate (1.28 g; 5.98 mmole) were taken in 30 ml benzene. The reaction mixture was refluxed for about 6 hours, dibutyltin oxide dissolved on refluxing, water formed during the course of reaction, has been removed azeotropically. The solvent was removed under reduced pressure. A yellow colored viscous liquid (3.04 g; 93%) was obtained (Calcd. for $\text{C}_{19}\text{H}_{39}\text{O}_4\text{PS}_2\text{Sn}$: S, 11.75; Sn, 21.79; M, 544.7, Found: S, 11.62; Sn, 21.58; M, 521.85).

Details of the preparation of other derivatives are given in Table II.

Reaction of dibutyltin oxide with acetylacetone and diisopropyl dithiophosphate in 2:1:1 molar ratio. Dibutyltin oxide (3.31 g, 13.30 mmole), acetylacetone (0.67 g, 6.7 mmole) and diisopropyl dithiophosphate (1.42 g, 6.64 mmole) were taken in benzene (~30 ml). After the removal of water azeotropically yields product as a yellow colored viscous liquid, 5.16 g, 98%. (Calcd. for $\text{C}_{27}\text{H}_{57}\text{O}_5\text{PS}_2\text{Sn}_2$: S, 8.06; Sn, 29.92; M, 793.4, Found: S, 7.52; Sn, 30.19, M, 719.6).

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