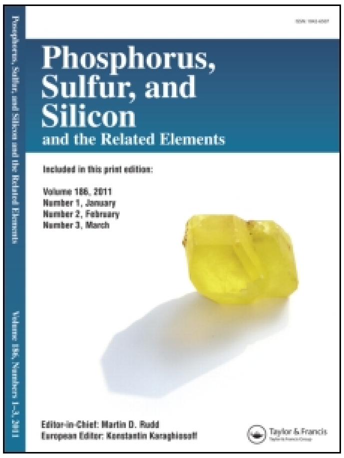

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Synthesis and Properties of Mixed Ligand Complexes of Diorganotin (IV): Part (V): Synthesis and Characterisation of Antifungal Acetylacetonato Diorganotin (IV)-*O*-Alkyl Trithiophosphates

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Some antifungal mixed ligand complexes of the type $R_2Sn[SSH(S)POR']$ $[MeCOCHCOMe]$ have been synthesised by the reactions of diorganotin dichloride, R_2SnCl_2 (R = Me, Bu, Ph) with acetyl acetone and O-alkyl trithiophosphates, $R'OPS_3K_2$ (R' = Me, Et, Pr^i, Bu^i, Ph) in 1:1:1 molar ratio in refluxing benzene. The products formed are monomeric, light yellow colored crystalline solids, soluble in common organic solvents and exhibit high sensitivity towards atmospheric moisture. The complexes have been characterised by elemental analysis (S,Sn), molecular weight measurements, IR and NMR (^1H, ^{31}P, ^{119}Sn) spectral studies. On the basis of spectral studies, it is postulated that acetyl acetonate and O-alkyl trithiophosphate moieties are bidentate and tin is hexacoordinated in nature. On the basis of ^{119}Sn NMR spectral studies, it is postulated that an equilibrium, with the results of disproportion is established. It is observed that when these compounds are applied in the form of dilute solution to various concentrations, they show their effectiveness against powdery mildew disease at a fixed interval of days.

Keywords Acetyl acetone; dialkyltin dichloride; O-alkyl trithiophosphates

INTRODUCTION

In continuation to our earlier investigations on mixed ligand complexes of diorganotin (IV),[1–4] the work has been extended to investigate the effect of O-alkyl trithiophosphates on the bonding modes of the β-diketonate moiety with the central metal atom. Metal complexes of O-alkyl trithiophosphates have been reported in the literature,[5–8] O-alkyl trithiophosphates contribute an important series

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of ligands and which show an interesting versatility in their chemical bonding modes (e.g. bidentate, chelating/bridging) towards different metals.

The chemistry of metal β-diketonate has been extensively reported in the literature.[9,10] An extensive survey of literature reveals that a lot of work has also been carried out on organotin(IV)-β-diketonate[11–13] and organotin (IV) dialkyl or alkylene dithiophosphate[14–16] during the previous years. The mixed derivatives of β-diketonate with alkoxides,[11] chlorides,[13] acetates[17] and alkylxanthates[18] have been reported in the literature.

Mixed ligand derivatives of the type $R_2Sn[OCOCH_3][S_2P(OR)_2]$ have been reported from our laboratory[4] in which monofunctional bidentate behaviour of the ligand has been established. The mixed derivatives of diorganotin (IV) with β-diketonates and alkyl trithiophosphates have not been studied so far. In view of the above, it was considered of interest to synthesis and study the chemical bonding modes in these new derivatives. Commercially available fungicidal carbendzum was tested against powdery mildew. The effectiveness of carbendzum against powdery mildew was found poor as compared to the newly synthesized tin (IV) complexes.

In the present communication, we report the synthesis and spectroscopic properties of some antifungal mixed ligand complexes of the type $R_2Sn[SSH(S)POR'][CH_3COCH\ COCH_3]$

RESULT AND DISCUSSION

Acetylacetonato diorganotin-O-alkyl trithiophosphates have been synthesized (Table 1) by the mixing and refluxing (~10 hours) of diorganotin (IV) dichloride with acetyl acetone and dipotassium salt of O-alkyl trithiophosphates in 1:1:1 molar ratio in dry benzene. The KCl formed has been removed by filtration in alkoxy funnel in anhydrous condition.

$$R_2SnCl_2 + CH_3COCH_2COCH_3 + R_2OP(S)S_2K_2 \xrightarrow[\text{10hours}]{\text{dry benzene}}$$
$$R_2Sn[SSH(S)POR'][CH_3COCHCOCH_3] + 2KCl$$

$[R = Me, Bu, Ph;\ R' = Me, Et, Pr^i, Bu^i, Ph]$

The complexes formed are light yellow colored crystalline solids which are non volatile, soluble in common organic solvents, monomeric in nature and extremely sensitive towards atmospheric moisture. For the sake of brevity, the synthetic and analytical results of the other complexes are summarized in Table I.

TABLE I Syntheses and Characterization of Acetylacetonato Diorganotin -O- Alkyl Trithiophosphates

									Analysis				
	g. m.mole						Product		found–		(Calcd.–)		Molecular weight found–(Calcd.–)
S. No.	R$_2$ SnCl$_2$		R′OPS$_3$K$_2$		CH$_3$COCH$_2$COCH$_3$		R$_2$Sn[SSH(S)POR′][MeCOCHCOMe] g.	% yield	H %	C %	S %	Sn %	
1	R = Me		R′ = Me		0.46	4.60	Me$_2$Sn[SSH(S)POMe][MeCOCHCOMe]		4.07	23.10	22.93	30.12	405
	1.01	4.59	1.08	4.58			1.75	94.09	(4.21)	(23.59)	(23.59)	(29.24)	(407)
2	R = Me		R′ = Et		0.46	4.60	Me$_2$Sn[SSH(S)POEt][MeCOCHCOMe]		4.20	25.22	22.48	27.94	—
	1.02	4.64	1.16	4.64			1.84	94.30	(4.55)	(25.65)	(22.80)	(28.27)	
3	R = Me		R′ = Pr^I		0.46	4.60	Me$_2$Sn[SSH(S)POPr^i][MeCOCHCOMe]		4.62	27.08	22.02	26.82	428
	1.01	4.59	1.21	4.58			1.90	95.48	(4.87)	(27.59)	(22.07)	(27.36)	(435)
4	R = Me		R′ = Bu^I		0.46	4.60	Me$_2$Sn[SSH(S)POBu^i][MeCOCHCOMe]		4.87	29.25	21.28	26.12	—
	1.01	4.59	1.65	4.59			1.98	96.12	(5.16)	(29.40)	(21.38)	(26.50)	
5	R = Me		R′ = Ph		0.49	4.90	Me$_2$Sn[SSH(S)POPh][MeCOCHCOMe]		3.72	33.10	20.38	25.23	—
	1.07	4.86	1.45	4.86			2.19	96.05	(4.08)	(33.26)	(20.47)	(25.37)	
6	R = Bu		R′ = Me		0.35	3.50	Bu$_2$Sn[SSH(S)POMe][MeCOCHCOMe]		5.72	34.01	19.45	23.62	472
	1.06	3.49	0.82	3.47			1.59	92.98	(5.95)	(34.21)	(19.55)	(24.24)	(491)
7	R = Bu		R′ = Et		0.36	3.60	Bu$_2$Sn[SSH(S)POEt][MeCOCHCOMe]		5.83	35.17	18.84	23.12	—
	1.11	3.65	0.91	3.65			1.76	95.65	(6.19)	(35.64)	(19.01)	(23.56)	
8	R = Bu		R′ = Pr^I		0.40	4.00	Bu$_2$Sn[SSH(S)POPr^i][MeCOCHCOMe]		6.15	36.41	18.02	22.34	502
	1.22	4.01	1.06	4.01			1.96	94.23	(6.41)	(36.99)	(18.50)	(22.93)	(519)
9	R = Bu		R′ = Bu^I		0.36	3.60	Bu$_2$Sn[SSH(S)POBu^i][MeCOCHCOMe]		6.41	38.12	17.95	22.04	515
	1.07	3.52	0.98	3.52			1.78	94.68	(6.62)	(38.27)	(18.01)	(22.33)	(533)
10	R = Bu		R′ = Ph		0.38	3.80	Bu$_2$Sn[SSH(S)POPh][MeCOCHCOMe]		5.15	44.09	17.32	21.12	—
	1.15	3.78	1.13	3.79			2.01	96.17	(5.29)	(44.23)	(17.36)	(21.52)	
11	R = Ph		R′ = Me		0.31	3.10	Ph$_2$Sn[SSH(S)POMe][MeCOCHCOMe]		3.84	40.45	18.01	22.03	—
	1.04	3.02	0.72	3.05			1.54	96.25	(3.99)	(40.68)	(18.08)	(22.41)	
12	R = Ph		R′ = Et		0.33	3.30	Ph$_2$Sn[SSH(S)POEt][MeCOCHCOMe]		4.18	41.54	17.45	21.72	520
	1.13	3.28	0.83	3.32			1.70	95.50	(4.25)	(41.83)	(17.61)	(21.83)	(545)
13	R = Ph		R′ = Pr^i		0.31	3.10	Ph$_2$Sn[SSH(S)POPr^i][MeCOCHCOMe]		4.42	42.62	17.02	21.12	—
	1.07	3.11	0.83	3.14			1.68	97.11	(4.51)	(42.93)	(17.17)	(21.29)	
14	R = Ph		R′ = Bu^i		0.34	3.40	Ph$_2$Sn[SSH(S)POBu^i][MeCOCHCOMe]		4.67	43.65	16.53	20.34	—
	1.15	3.34	0.93	3.34			1.82	95.28	(4.75)	(43.98)	(16.75)	(20.77)	
15	R = Ph		R′ = Ph		0.30	3.00	Ph$_2$Sn[SSH(S)POPh][MeCOCHCOMe]		3.81	46.44	16.10	19.40	565
	1.03	2.99	0.90	3.02			1.72	96.17	(3.91)	(46.54)	(16.19)	(20.07)	(593)

TABLE II I.R. Spectral Data of Acelyl Acetonatodiorganotin (IV)- O-Alkyl Trithiophosphate

Compound Me$_2$Sn [SSH (S)POR′] [MeCOCHCOMe)	νS—H	νC=C	νC=O	ν(P)—O—C	νP—O—(C)	νP=S	νP—S	νSn—C	νSn—O	νSn—S
R′ = Me	2485.6 s	1570.25 s	1445.2 s	990.4 m	870.4 m	750.2 s	535.1 s	635.2 vs	440.2 s	385.1 w
R′ = Et	2455.1 s	1555.4 vs	1430.5 s	996.2 br	873.2br	755.4 s	532.4 s	642.5 vs	442.4 s	388.3 w
R′ = Pr^i	2480.0 s	1580.2 s	1435.3 vs	1012.4br	875.4 m	760.2v s	534.3 vs	654.2 s	447.3 vs	395.4 w
R′ = Bu^i	2470.8 s	1568.3 s	1452.8 vs	1023.5m	860.6 br	772.5 vs	529.1 vs	662.4 s	452.6 vs	373.8 w
R′ = Ph	3520.3 s	1593.8 s	1443.8 s	1008.3 m	865.5 m	765.7 s	537.3 s	628.8 vs	455.5 s	386.4 w
Compound Bu$_2$Sn [SSH (S)POR′] [MeCOCHCOMe)										
R′ = Me	2485.0 s	1598.4 s	1455.6 s	1010.3 m	870.3 m	778.2 s	529.8 s	665.8 s	450 .0 s	370.2 w
R′ = Et	2480.4 s	1595.8 s	1463.2 vs	1015.2 m	873.6 m	772.4 s	528.6 vs	655.2 s	452.1 s	374.6 w
R′ = Pr^i	2490.7 s	1594 vs	1459.5 s	1024.6 m	876.4 br	774.1 vs	530.4 vs	677.3 s	455.0 vs	395.6 w
R′ = Bu^i	2420.8 s	1592.5 s	1456.2 s	1018.4 br	872.3 m	776.4 vs	525.7 s	645.6 s	454.2 s	392.4 w
R′ = Ph	2530.0 s	1594.6 vs	1461.2 vs	1021.8 m	876.3 m	770.0 s	530.4 s	630.0 s	453.0 s	380.0 w
Compound Ph$_2$Sn [SSH (S)POR′] [MeCOCHCOMe)										
R′ = Me	2472.3 s	1575.2 s	1431.2 vs	995.5 m	860.2 m	770.1 s	530.8 s	635.2 s	451.3 s	370.8 w
R′ = Et	2502.6 s	1580.4 s	1438.5 s	998.8 m	870.4 br	782.8 vs	525.5 vs	644.4 vs	455.5 vs	371.5 w
R′ = Pr^i	2530.3 s	1591.9 vs	1442.5 vs	1015.5 br	865.2 m	775.5 vs	521.3 s	655.4 vs	454.4 vs	380.4 w
R′ = Bu^i	2540.5 s	1573.2 vs	1453.1 s	1020.1 m	876.4 br	762.6 s	523.8 s	648.8 s	455.8 vs	394.5 w
R′ = Ph	2508.3 s	1585.8 s	1439.3 s	1005.4 br	882.8 m	768.8 s	524.4 s	662.8 s	452.1 s	382.4 w

IR SPECTRA

IR spectra of these complexes have been recorded in the region 4000–200 cm^{-1} (Table II). A comparison of the IR spectra of these complexes with those of the starting material [O-alkyl trithiophosphate, acetyl acetone, diorganotin dichloride] shows the following characteristic changes:

(1) A new week absorption band at 370.2–395.4 cm^{-1} is observed, which is assigned to νSn-S linkage.
(2) The appearance of a new sharp band at 440.2–455.8 cm^{-1}, which is assigned to νSn-O linkage.
(3) A characteristic absorption band at 1430.5–1463.2 cm^{-1} is assigned to the coordinated carbonyl group.
(4) The IR spectra of all these complexes show a strong absorption band at 1555.4–1595.8 cm^{-1} which is characteristic to $\nu C = C$ linkage.
(5) The appearance of a new absorption band in the region 2450-2550 cm^{-1} suggests the formation of νS-H bond in the product.

In these newly synthesized compounds, νP=S absorption band shifted towards lower frequency (~40 cm^{-1}) which indicates strong chelation of this group towards central tin atom.

No absorption band appears at 1100–1200 cm^{-1} which suggests the absence of $\nu P = O$ linkage in the newly synthesized complexes and also indicates that O-alkyl trithiophosphate is moiety present in thiono form in the derivatives.

NMR SPECTRA [^{1}H, ^{31}p and ^{119}Sn]

^1H

The PMR spectra of acetylacetonato diorganotin-O-alkyl trithiophosphates (solution in $CDCl_3$) show the characteristic resonance for alkyl and aryl protons present on tin atom and alkyl protons present on phosphorus atom (Table III). In the derivatives of O-methyl trithiophosphates, a singlet at δ2.5 ppm is observed which is due to O-methoxy protons. The resonance signals of CH proton of acetyl acetonate moiety is appeared as a singlet at $\sim \delta$5.5 ppm. Methyl tin protons appear at δ1.65–1.85 ppm while phenyl tin protons appear at δ7.4–7.8 ppm. SH proton shows singlet at 3.0–3.5 ppm.

^{31}P

^{31}P chemical shift values for these complexes shows only one resonance signal which has been observed in the region δ93.12 to 98.67 ppm (Table IV). There is a downfield shift (δ22-26 ppm) in comparison to the parent compound ($^{31}P = \delta$ 71.21–72.55 ppm). This unexpected downfield shift is very surprising and it may be due to the isomerisation

TABLE III PMR Spectral Data of Acelylacetonato Diorganotin (IV) -O-Alkyl Trithiophosphates

S. N.	Compound	Chemical Shift (δ ppm)
(1)	$Me_2Sn[SSH(S)POMe]$ [MeCOCHCOMe]	1.73,s, 6H(Sn-CH_3)., 2.10,s,6H(CH_3-acac) 2.5,s,3H(OCH_3)., 5.40,s,1H (CH).3.1,s,1H (SH)
(2)	$Me_2Sn[SSH(S)POEt]$ [MeCOCHCOMe]	1.82,s, 6H(Sn-CH_3), 2.05,s,6H(CH_3-acac)2.28-2.40, t,3H(CH_3),2.69–.85,q,2H(OCH_2),5.35,s,1H(CH), 3.0,s,1H(SH)
(3)	$Me_2Sn[SSH(S)POPr^i]$ [MeCOCHCOMe]	1.65,s,6H(Sn-CH_3),1.95,s,6H(CH_3-acac),2.12-2.20,d, 6H(CH_3-Pr^i), 2.55-2.75,m,1H (OCH),5.8,s,1H(CH) 3.2,s,1H (SH)
(4)	$Me_2Sn[SSH(S)POBu^i]$ [MeCOCHCOMe]	1.85,s,6H(Sn-CH_3),2.10,s,6H(CH_3-acac),2.45-2.51,d, 6H(CH_3-Bu^i),4.42–4.5,d, 1H (CH),5.26–5.4, m,2H (OCH_2),5.8,s,1H(CH) 3.1,s1H (SH)
(5)	$Me_2Sn[SSH(S)POPh]$ [MeCOCHCOMe]	1.4,s,6H(Sn-CH_3), 2.35,s,6H(CH_3),5.54,s,1H(CH), 7.31-7.44,m,5H(C_6H_5),3.2,s,1H (SH)
(6)	$Bu_2Sn[SSH(S)POMe]$ [MeCOCHCOMe]	0.85-0.95,t,6H(CH_3),1.60-1.72,m,12H[$(CH_2)_3$], 2.28,s,6H(CH_3),2.5,s,3H(OCH_3), 5.65,s,1H(CH), 3.3, s, 1H(SH)
(7)	$Bu_2Sn[SSH(S)POEt]$ [MeCOCHCOMe]	0.72-0.84,t,6H(CH_3), 1.27–1.52,m,12H(Sn-$(CH_2)_3$), 2.15,s,6H(CH_3-acac), 2.32–2.46,t,3H(CH_3) 2.85-3.05,q,2H(OCH_2), 5.49,s,1H(CH),3.2,s1H(SH)
(8)	$Bu_2Sn[SSH(S)POPr^i]$ [MeCOCHCOMe]	0.80-0.88,t,6H(CH_3),1.63–1.72,m,12H(Sn-$(CH_2)_3$), 2.10,s,6H(CH_3-acac), 2.15-2.20,d,6H(CH_3-Pr^i) 3.65–3.80,m,1H(CH-Pr^i), 5.5,s,1H(CH-acac), 3.3,s1H(SH)
(9)	$Bu_2Sn[SSH(S)POBu^i]$ [MeCOCHCOMe]	0.84-0.97,t,6H(Sn-CH_3),1.38–1.50,m,12H[Sn-$(CH_2)_3$] 2.22,s,6H(CH_3-acac),2.35–2.42,d,6H(CH_3-Bu^i),3.88-3.95,d,2H(OCH_2),4.60-4.85,m,1H(CH-Bu^i), 5.4,s,1H(CH)3.2,s,1H (SH)
(10)	$Bu_2Sn[SSH(S)POPh]$ [MeCOCHCOMe]	0.89–0.97,t,6H(Sn-CH_3),1.26-1.40,m,12H[Sn-$(CH_2)_3$ 1.75,s,6H(CH_3),5.5,s,1H(CH),7.31-7.40,m,5H(C_6H_5) 3.3,s,1H(SH)

(11)	$Ph_2Sn[SSH(S)POMe]$ [MeCOCHCOMe]	2.35,s,6H(CH_3), 3.15,s,3H(OCH_3),4.72,s,1H(CH), 7.68–7.80,m,10H(C_6H_5),3.2,s1H(SH)
(12)	$Ph_2Sn[SSH(S)POEt]$ [MeCOCHCOMe]	2.27,s,6H(CH_3), 2.43–2.52,t,3H(CH_3),2.70–2.83,q,2H (OCH_2), 5.43,s,1H(CH),7.632–7.75,m,10H(C_6H_5) 3.5,s1H (SH)
(13)	$Ph_2Sn[SSH(S)POPr^i]$ [MeCOCHCOMe]	2.15,s,6H(CH_3),2.25-2.30,d,6H(CH_3-Pr^i),2.95–3.07, m,1H(OCH),5.12,s,1H(CH), 7.59–7.68,m,10H(C_6H_5) 3.4,s 1H (SH)
(14)	$Ph_2Sn[SSH(S)POBu^i]$ [MeCOCHCOMe]	1.53,s,6H(CH_3), 2.30–2.35,d,6H(CH_3-Bu^i),4.30–4.43, m,1H(CH-Bu^i),5.45-5.50,d,2H(OCH_2),5.9,s,1H(CH), 7.65–7.72,m,10H(C_6H_5), 3.5s,1H(SH)
(15)	$Ph_2Sn[SSH(S)POPh]$ [MeCOCHCOMe]	2.25,s,6H(CH_3), 5.80,s,1H(CH),7.68-7.74,m,10H (C_6H_5),8.18-8.25,m,5H(OC_6H_5), 3.4,s,1H (SH)

TABLE IV ^{31}P and ^{119}Sn NMR Spectral Data of Acetylacetonato Diorganotin (IV)-O- Alkyl Trithiophosphate

S. n.	Compound	^{31}P NMR	^{119}Sn NMR I	^{119}Sn NMR II	^{119}Sn NMR III
1.	Me$_2$Sn[SSH(S)POMe][MeCOCHCOMe]	93.25	−171.3	−246.5	−372.8
2.	Me$_2$Sn[SSH(S)POEt][MeCOCHCOMe]	94.72	−166.5	−236.2	−366.3
3.	Me$_2$Sn [SSH(S)POPr^i][MeCOCHCOMe]	94.57	−155.8	−226.2	−360.5
4.	Me$_2$Sn[SSH(S)POBu^i][MeCOCHCOMe]	95.85	−172.3	−248.5	−368.8
5.	Me$_2$Sn[SSH(S)POPh][MeCOCHCOMe]	98.67	−180.4	−277.6	−398.4
6.	Bu$_2$Sn [SSH(S)POMe][MeCOCHCOMe]	93.39	−174.8	−249.1	−376.4
7.	Bu$_2$Sn[SSH(S)POEt][MeCOCHCOMe]	95.52	−169.3	−241.3	−369.2
8.	Bu$_2$Sn[SSH(S)POPr^i][MeCOCHCOMe]	96.88	−158.8	−235.8	−363.5
9.	Bu$_2$Sn[SSH(S)POBu^i][MeCOCHCOMe]	98.27	−175.2	−245.6	−371.4
10.	Bu$_2$Sn[SSH(S)POPh][MeCOCHCOMe]	98.39	−183.5	−254.3	−379.7
11.	Ph$_2$Sn[SSH(S)POMe][MeCOCHCOMe]	94.49	−177.3	−252.4	−378.3
12.	Ph$_2$Sn[SSH(S)POEt][MeCOCHCOMe]	93.12	−174.9	−247.3	−374.4
13.	Ph$_2$Sn[SSH(S)POPr^i][MeCOCHCOMe]	97.73	−169.5	−241.5	−368.8
14.	Ph$_2$Sn[SSH(S)POBu^i][MeCOCHCOMe]	97.52	−178.3	−256.7	−379.2
15.	Ph$_2$Sn[SSH(S)POPh][MeCOCHCOMe]	98.45	−185.8	−262.2	−387.4

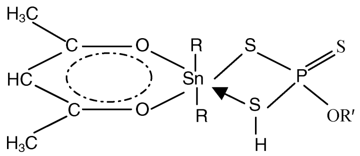
*The I and III resonance peaks correspond to R$_2$Sn[SSH(S)POR′]$_2$ and R$_2$Sn[MeCOCHCOMe]$_2$, respectively.

of S-alkyl trithiophosphate to O-alkyl trithiophosphate in the newly synthesized derivatives. Such type of isomerisation has also been studied in sodium salt of trithiophosphates. This supports that the Sn-S-P bond is formed in these newly synthesized complexes.

^{119}Sn

In contrast to ^{1}H and ^{31}P NMR spectra which show the presence of single species, the ^{119}Sn NMR spectra of acetylacetonato diorganotin-O-alkyl trithiophosphates show three resonance signals (Table IV). A comparison of the chemical shift values with those of corresponding R$_2$Sn(CH$_3$COCHCOCH$_3$)$_2$ and R$_2$Sn[SSH(S)POR′] compounds obtained under similar conditions, indicates the presence of those species with mixed derivative R$_2$Sn[CH$_3$COCHCOCH$_3$][SSH(S)POR′]. The above results indicates that an equilibrium as a result of disproportionation of the following type, exists in these derivatives.

$$
{}_2\mathrm{R_2Sn[CH_3COCHCOCH_3][SSH(S)POR']} \rightleftharpoons \mathrm{R_2Sn[CH_3COCHCOCH_3]_2} + \mathrm{R_2Sn[SSH(S)POR']_2}
$$



It may be noted that ^{1}H and ^{31}P NMR spectroscopy is unable to give the exact picture. The chemical shifts obtained from these spectra gives only average values. The bidentate nature of acetylacetonato moiety is represented by the position of νC=O absorption band in the IR spectra.

Due to chelating tendency of β-diketonate and O-alkyl trithiophosphate moieties, the complexes could expected to have tin atom in the 6- coordinated state. On the basis of above facts, it appears that an equilibrium is established as a result of disproportionation of $R_2Sn[CH_3COCHCOCH_3][SSH(S)POR']$ in $R_2Sn[CH_3COCHCOCH_3]_2$ and $R_2Sn[SSH(S)POR']_2$.

BIOLOGICAL STUDIES

Antifungal activity of newly synthesized complexes has been carried out with the powdery mildew of roses. Percent disease intensity (PDI) was recorded by modifying the Coyier rating scale[19] and it (PDI) was calculated using the following formula[20] :

$$\mathrm{PDI} = \frac{\text{Sum of all ratings} \times\ 100}{\text{Total number of observations} \times\ \text{Maximum class rating}}$$

All these compounds indicates their potency against *Sphaerotheca pannosa var. rosae* at different concentrations (Table V). The rose plants were severely infected by powdery mildew disease when the first foiler spray was carried out. It was observed that intensity of powdery mildew disease decreases after 7 days of the first spray, showed remarkable results. Second spray was done on the 7th day which showed lower PDI values. After 15 days of first spray, the observations were again made. The 21st day resulted in a very small change in PDI values in comparison to previous spray. It may be concluded that the effect of the compounds remained only for 7 days and no appreciable activity of compounds was observed after 7 days of spray.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the experiment. All the solvents used during the present investigation were of reagent grade and were made anhydrous by standard methods. Dipotassium salt of O-alkyl trithiophosphates were prepared as described in the literature. Acetyl acetone was distilled before use. Carbon and hydrogen were estimated by Coleman C,H,N analyzer. Sulphur and tin were estimated gravimetrically as barium sulphate (Messenger's method)[21] and tin oxide, respectively. Molecular weights were determined by Knauer vapour pressure osmometer in chloroform.

TABLE V Effect of Newly Synthesized Complexes on Powdery Mildew Disease of Roses Caused by *Sphaerotheca Pannosa* Pathogens on Different Concentrations

	Percent Disease Intensity (PDI)				
Conc. (%)	During (I) spray	After 7 days During (II) Spray	After 15 days	After 21 days During (III) Spray	After 28 days
0.5000	100	76	62	52	28
0.2500	100	81	62	52	24
0.1250	100	67	57	43	19
0.0625	100	62	57	48	19
0.0312	100	57	43	38	19
0.0156	100	52	43	38	14
0.0078	100	43	38	38	14
0.0039	100	33	29	24	10

FTIR spectra were recorded on a Shimadzu 8201 PC spectrophotometer in the range of 4000–200 cm^{-1} using CsI cells. ^{1}H NMR spectra were recorded in deuterated chloroform and ^{31}P and ^{119}Sn NMR were recorded in benzene on Bruker DRX-300 spectrophotometer using TMS (for ^{1}H), H_3PO_4 (for ^{31}P) and Me_4Sn (for ^{119}Sn) as external references.

Synthesis of $Me_2Sn[SSH(S)POPh][CH_3COCHCOCH_3]$

A mixture of dimethyltin dichloride (1.07g, 4.86 mmole), acetyl acetone (0.49 g, 4.90 mmole) and O-phenyl trithiophosphate (1.45 g, 4.86 mmole) were taken in dry benzene (~35 ml). On mixing, stirring and then refluxing for 10 hours, ppt. of KCl was formed. On filtration of KCl and removal of excess of benzene in vacuo. 2.19 g, 96.05%, light yellow colored crystalline solid product was formed. The product was purified by washing it 3-4 times with n-hexane and recrystallized from benzene/petroleum ether mixture(1:4). (Calcd. For $Me_2Sn[SSH(S)POPh][CH_3COCHCOCH_3]$, S = 20.47%, Sn = 25.37%, C= 33.26%, H = 4.08%; Found: S = 20.38%, Sn = 25.23%, C = 33.10%, H = 3.72%).

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