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Synthesis, Spectroscopic, and Biological Studies of Tris[(dimethylethylsilyl) methylene]tin Mono(or di)thiophosphates

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ABSTRACT: *Twenty-one new compounds of the general structure $(EtMe_2SiCH_2)_3SnSP(X)(OR_1)(OR_2)$ ($X=O:R_1=C_2H_5$, R_2-substituted phenyl; $X=S:R_1=R_2=$hydrocarbyl) have been synthesized. Their structures were characterized by IR, ^1H, ^{119}Sn, and ^{31}PNMR spectroscopy and by MS and elemental analyses. ^{119}Sn NMR measurements of chemical shifts have shown that there is a good linear relationship of ^{119}Sn chemical shifts with Hammett para-substituent constants. The results of biological tests show that the compounds possess good acaricidal activity.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:299–305, 1998

INTRODUCTION

Acaricidal activity of Sila-Torque $[(PhMe_2SiCH_2)_3Sn]_2O$ [1] is comparable with that of Torqu $[(PhMe_2CCH_2)_3Sn]_2O$ [2]. In view of this fact [3–5], we have synthesized 21 new tris[(dimethylethylsilyl)methylene]tin mono (or di)thiophosphates in which the tris[(dimethylethylsilyl)methylene] group is the same as in silatorque except that the phenyl group has been replaced by ethyl, as indicated by the following general equation:

$$(EtMe_2SiCH_2)_3SnC + (R_1O)(R_2O)P(X)S^-K^+ \xrightarrow{\text{acetone}} (EtMe_2SiCH_2)_3SnSP(X)(OR_1)(OR_2) + KCl$$

For compounds I (as shown in Tables 1–7), X = O, R_1 = Et, and R_2 is C_6H_5 (I_1); p-$CH_3C_6H_4$ (I_2); p-ClC_6H_4 (I_3); p-BrC_6H_4 (I_4); p-$CH_3OC_6H_4$ (I_5); m-ClC_6H_4 (I_6); m-$CH_3C_6H_4$ (I_7); o-ClC_6H_4 (I_8); o-$CH_3C_6H_4$ (I_9); 2,4-$Cl_2C_6H_3$ (I_{10}); C_2H_5 (I_{11}). For compounds II, X = S, R_1 and R_2 are C_6H_5 (II_1); p-$CH_3C_6H_4$ (II_2); p-ClC_6H_4 (II_3); p-$CH_3OC_6H_4$ (II_4); m-$CH_3C_6H_4$ (II_5); C_2H_5 (II_6); ^iPr (II_7); $(CH_2)_4CH_3$ (II_8); $(CH_2)_6CH_3$ (II_9); $(CH_2)_7CH_3$ (II_{10}).

It has been found that their biological activities depend upon the substitution on silicon in the following order:

$$(Me_3SiCH_2)_3SnY \geq (EtMe_2SiCH_2)_3SnY > (PhMe_2SiCH_2)_3SnY$$

The structures of these compounds were determined by IR and multinuclear (^1H, ^{31}P, ^{119}Sn) NMR spectroscopy.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR -435 spectrometer as liquid films. The ^1H, ^{119}Sn, and ^{31}P NMR spectra were measured on a Bruker Ac-200 spectrometer in $CDCl_3$ solution with TMS as internal and Me_4Sn, 85% H_3PO_4 as external standards.

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TABLE 1. The Yields and Elemental Analyses of the Compounds

Compound	*Yield (%)*	*State*	*Found (calcd) %* *Elemental C*	*Analysis H*	*Formula for Calculation*
I_1	78.5	colorless viscous oil	43.01 (43.19)	7.39 (7.79)	$C_{23}H_{49}O_3SPSi_3Sn$
I_2	76.9	colorless viscous oil	43.94 (44.09)	7.85 (7.86)	$C_{24}H_{51}O_3SPSi_3Sn$
I_3	74.1	colorless viscous oil	41.11 (40.98)	7.28 (7.18)	$C_{23}H_{48}O_3ClSPSi_3Sn$
I_4	79.1	colorless viscous oil	38.53 (38.44)	6.83 (6.73)	$C_{23}H_{48}O_3BrSPSi_3Sn$
I_5	70.2	yellow viscous oil	43.25 (43.04)	7.51 (7.68)	$C_{24}H_{51}O_4SPSi_3Sn$
I_6	77.8	colorless viscous oil	40.89 (40.98)	7.17 (7.18)	$C_{23}H_{48}ClO_3SPSi_3Sn$
I_7	75.4	yellow viscous oil	43.88 (44.10)	7.92 (7.86)	$C_{24}H_{51}O_3SPSi_3Sn$
I_8	74.3	yellow viscous oil	40.91 (40.98)	7.07 (7.18)	$C_{23}H_{48}O_3ClSpSi_3Sn$
I_9	96.9	colorless viscous oil	44.16 (44.10)	8.03 (7.86)	$C_{24}H_{51}O_3SPSi_3Sn$
I_{10}	77.5	colorless viscous oil	38.44 (39.02)	6.69 (6.66)	$C_{23}H_{47}O_3ClPSi_3Sn$
I_{11}	80.5	colorless viscous oil	38.67 (38.57)	8.08 (8.35)	$C_{19}H_{49}PSO_3Si_3Sn$
II_1	75	colorless viscous oil	46.33 (46.07)	6.71 (7.02)	$C_{27}H_{49}PSO_3Si_3Sn$
II_2	72.9	colorless viscous oil	47.26 (47.60)	7.55 (7.30)	$C_{29}H_{53}PS_2O_2Si_3Sn$
II_3	77.4	colorless viscous oil	42.16 (41.97)	5.90 (6.13)	$C_{27}H_{47}PS_2O_4Si_3Sn$
II_4	96.1	colorless viscous oil	45.63 (45.60)	7.24 (6.99)	$C_{29}H_{53}PS_2O_4Si_3Sn$
II_5	77.4	colorless viscous oil	47.35 (47.60)	7.65 (7.30)	$C_{29}H_{53}PS_2O_2Si_3Sn$
II_6	78.5	colorless viscous oil	37.47 (37.55)	7.84 (8.13)	$C_{19}H_{49}PS_2Si_3Sn$
II_7	70.9	colorless viscous oil	39.60 (39.68)	8.25 (8.40)	$C_{21}H_{53}S_2PO_2Si_3Sn$
II_8	71.9	colorless viscous oil	42.92 (43.25)	8.37 (8.79)	$C_{25}H_{64}PS_2O_2Si_3Sn$
II_9	73.3	colorless viscous oil	46.36 (46.57)	9.40 (9.30)	$C_{29}H_{69}S_2PO_2Si_3Sn$
II_{10}	76.9	black viscous oil	47.55 (47.98)	9.42 (9.48)	$C_{31}H_{23}S_2PO_2Si_3Sn$

Elemental analyses were determined on an MT-3 elemental analyzer. Mass spectra were recorded on a ZAB-HS at 70 ev; the temperature of ionization was 200 °C.

The tris[(ethyldimethylsilyl)methylene]tin chloride was synthesized via the following reaction (Scheme 1), whereas mono(or di)thiophosphates were synthesized by the published procedures [6,7].

$$Me_3SiCl \xrightarrow[Cl_2]{hv} Me_2SiClCH_2Cl \xrightarrow{EtMgBr}$$

$$EtMe_2SiCH_2CL \xrightarrow{Mg} EtMe_2SiCH_2MgCl$$

$$\xrightarrow{SnCl_4} (EtMe_2SiCH_2)_3SnCl$$

SCHEME 1

GENERAL SYNTHETIC PROCEDURE

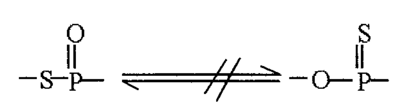
A mixture of 3 mmol tris[(ethyldimethylsilyl)methylene]tin chloride and 3.3 mmol potassium mono(or di)thiophosphates in acetone (20 mL) was placed in a three-necked flask fitted with a reflux condenser and a magnatic stirrer, and the mixture was refluxed for 5 hours. After the reaction time had been completed, acetone was removed under vacuum. The residue thus obtained was purified by extraction with petroleum ether and then with acetonitrile. In each case, removal of the solvent yielded a viscous liquid product.

RESULTS AND DISCUSSION

Analytical data and some of the physical properties of the compounds are given in Table 1. The IR data are listed in Table 2. The absorption frequencies of $\nu_{sym}(PS_2)$ and ν_{asym}(Sn-C) often overlapped. $\nu_{Si\text{-}C}$, $\nu_{P=O\text{-}}$, and $\nu_{P=O}$ vibrations are generally found in the range of 800–825 cm^{-1}, 1130–1190 cm^{-1}, and 1200–1125 cm^{-1}, respectively.

The NMR data are listed in Tables 3 and 4. The proton magnetic resonance spectra of all of the synthesized compounds agree (very) well with the proposed tetrahedral structures [3].

The ^{31}P NMR data of monothiophosphates appear in the usual range of P=O, i.e., δ 54.00 to 55.00, suggesting that there exists no P=S tautomer as indicated below:



A subtle structural change around the tin atom is reflected from ^{119}Sn NMR chemical shifts. The substituents on the aromatic group influence ^{119}Sn NMR shifts. Electron-withdrawing groups on the phenyl ring displace δ^{119} Sn resonances to a lower field. We

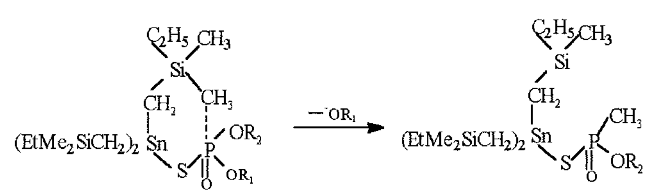
TABLE 2 IR Data of Compounds **I** and **II**

No.	$\nu_{Si\text{-}CH2}$	$\nu_{Si\text{-}C}$	$\nu_{P\text{-}O\text{-}C}$ or $\nu_{P\text{-}O\text{-}\Phi}$		$\nu_{P=O}$	$\nu^{asym}_{(Sn\text{-}C)}$ / $\nu^{sym}_{(Sn\text{-}C)}$	$\nu^{asym}_{(PS_2)}$ / $\nu^{sym}_{(PS_2)}$
I$_1$	1244 (s)	821 (s)	1007 (s)	1155 (m)	1221 (s)	517 (w)	
			774 (s)	949 (s)		465 (w)	
I$_2$	1245 (s)	810 (s)	1014 (s)	1158 (w)	1213 (m)	517 (w)	
			776 (s)	950 (m)		481 (w)	
I$_3$	1244 (s)	825 (s)	1009 (s)	1154 (w)	1223 (s)	518 (w)	
			774 (s)	949 (m)			
I$_4$	1244 (s)	808 (s)	1009 (s)	773 (s)	1206 (s)	517 (m)	
			1155 (w)	949 (m)		492 (w)	
I$_5$	1245 (s)	827 (s)	1005 (s)	1175 (w)	1201 (s)	518 (w)	
			776 (s)	950 (m)			
I$_6$	1244 (s)	805 (s)	1005 (s)	1150 (w)	1209 (s)	517 (w)	
			774 (s)	950 (s)		446 (w)	
I$_7$	1245 (s)	805 (s)	1009 (s)	1143 (m)	1209 (s)	515 (w)	
			776 (s)	948 (s)			
I$_8$	1244 (s)	808 (s)	1005 (s)	1155 (m)	1209 (s)	521 (m)	
			774 (s)	951 (s)		465 (w)	
I$_9$	1246 (s)	808 (s)	1007 (s)	1137 (w)	1209 (s)	522 (w)	
			776 (s)	951 (s)			
I$_{10}$	1249 (m)	808 (s)	1011 (s)	1179 (m)	1225 (m)	519 (w)	
			776 (s)	949 (m)			
I$_{11}$	1245 (s)	809 (s)	1010 (s)		1210 (s)	520 (w)	
			776 (s)				
II$_1$	1244 (s)	809 (s)		1178 (s)		489 (w)	685 (s)
				945 (m)			519 (m)
I$_2$	1249 (m)	812 (s)		1185 (m)		486 (w)	681 (w)
				931 (m)			509 (w)
II$_3$	1244 (m)	826 (s)		1188 (m)		489 (w)	688 (m)
				932 (m)			519 (w)
II$_4$	1244 (s)	824 (s)		1173 (s)		521 (m)	680 (m)
				921 (m)			521 (m)
II$_5$	1249 (s)	826 (s)		1131 (s)		515 (w)	683 (m)
				940 (m)		490 (w)	542 (w)
II$_6$	1244 (m)	808 (s)	1015 (s)			509 (w)	655 (m)
			774 (s)			480 (w)	535 (w)
II$_7$	1245 (s)	809 (s)	1006 (s)			515 (w)	650 (s)
			772 (s)				545 (w)
II$_8$	1249 (m)	809 (s)	1007 (s)			509 (w)	657 (m)
			773 (s)			482 (w)	542 (w)
II$_9$	1244 (m)	809 (s)	1003 (m)			510 (w)	657 (w)
			774 (m)				510 (w)
II$_{10}$	1244 (m)	809 (s)	1007 (m)			510 (w)	657 (w)
			774 (m)				510 (w)

have also found that there exists a linear relationship between δ^{119} Sn and the Hammett constants (σ) of the para substituent for the corresponding compounds:

$$\delta(^{119}\mathrm{Sn}) = 14.4901\sigma + 192.3247 \ (r = 0.9815,\ \mathrm{I}_1\text{–}\mathrm{I}_5)$$

Mass spectra of compounds I_1–I_5 and II_1–II_4 are shown in Tables 5 and 6. No molecular ion peak was found in the mass spectrum of any isolated compound. The general breakdown pattern for all of the compounds involves dealkylation. Methyl groups on silicon may migrate to phosphorus. As a result, phosphorus loses an OR group as shown below (Scheme 2).



SCHEME 2 Methyl group migration and elimination of OR_1 group at phosphorus.

TABLE 3 Main NMR (^{1}H) Data for Compounds **I** and **II** δ

Compound	C_2H_5	CH_3	$SiCH_2Sn$	R_1 *and* R_2
I$_1$	0.54 (6H, q), 0.92 (9H, t, 7.83 Hz)	0.049 (18H, s)	0.40 (6H, s)	1.28 (3H, t, 7.18 Hz), 4.09 ~ 4.13 (2H, m), 7.05, 7.41 (4H, dd, 9.17 Hz).
I$_2$	0.51 (6H, m), 0.92 (9H, t, 7.54 Hz)	0.046 (18H, s)	0.39 (6H, s)	1.29 (3H, t, 7.20 Hz), 2.28 (3H, s), 4.10 ~ 4.13 (2H, q) 7.06 (4H, s)
I$_3$	0.53 (6H, m), 0.92 (9H, t, 7.85 Hz)	0.05 (18H, s)	0.40 (6H, s)	1.28 (3H, t, 7.20 Hz), 4.09 ~ 4.13 (2H, q), 7.13, 7.24 (4H, dd)
I$_4$	0.52 (6H, q), 0.92 (9H, t, 7.86 Hz)	0.05 (18H, s)	0.50 (6H, s)	1.29 (3H, t, 7.05 Hz), 4.14 ~ 4.17 (2H, m), 7.24 (5H, m)
I$_5$	0.54 (6H, q), 0.94 (9H, t, 7.8 Hz)	0.07 (6H, s)	0.41 (6H, s)	1.32 (3H, t, 7.08 Hz), 3.77 (3H, s), 4.09 ~ 4.13 (2H, m), 6.80, 7.11 (4H, dd)
I$_6$	0.54 (6H, q), 0.94 (9H, t, 7.83 Hz)	0.07 (6H, s)	0.42 (6H, s)	1.32 (3H, t, 7.03 Hz), 4.10 ~ 4.14 (2H, m), 7.26 (4H, m)
I$_7$	0.56 (6H, m), 0.94 (9H, t, 7.49 Hz)	0.07 (6H, s)	0.42 (6H, s)	1.32 (3H, t, 7.03), 2.32 (3H, s), 4.09 ~ 4.13 (2H, m), 6.09 ~ 7.23 (4H, m)
I$_8$	0.55 (6H, q), 0.95 (9H, t, 7.86 Hz)	0.08 (6H, s)	0.42 (6H, s)	1.34 (3H, t), 4.10 ~ 4.14 (2H, m), 7.00 ~ 7.57 (4H, m)
I$_9$	0.52 (6H, q), 0.98 (9H, t, 7.80 Hz)	0.05 (18H, s)	0.43 (6H, s)	1.29 (3H, t, 7.08 Hz), 4.09 ~ 4.13 (2H, m), 7.11 ~ 7.47 (3H, m)
I$_{10}$	0.55 (6H, q), 0.94 (9H, t, 7.92 Hz)	0.06 (18H, s)	0.39 (6H, s)	1.28 (3H, t), 2.32 (3H, S), 4.09 ~ 4.13 (2H, m), 7.00 ~ 7.55 (4H, m)
I$_{11}$	0.55 (6H, q), 0.95 (9H, t, 7.65 Hz)	0.07 (18H, s)	0.43 (6H, s)	1.32 (6H, t, 6.95 Hz), 4.00 ~ 4.05 (6H, m)
II$_1$	0.53 (6H, m), 0.92 (9H, q)	0.03, 0.07 (18H, d)	0.26, 0.33 (6H, d)	6.79 ~ 7.24 (10H, m)
II$_2$	0.53 (6H, m), 0.92 (9H, q, 7.89 Hz)	0.06 (18H, s)	0.25 (6H, s)	2.25 (6H, s), 6.69 ~ 7.04 (8H, dd, 8.34 Hz)
II$_3$	0.52 (6H, m), 0.96 (9H, t, 7.44 Hz)	0.03 (18H, s)	0.34 (6H, s)	6.77 ~ 7.31 (8H, dd)
II$_4$	0.50 (6H, q), 0.93 (9H, t, 7.90 Hz)	0.043, 0.10 (18H, d)	0.296, 0.35 (6H, d)	3.60 (6H, s), 6.67, 7.27 (8H, dd, 9.09 Hz)
II$_5$	0.58 (6H, m), 0.92 (9H, t)	0.07, 0.10 (18H, d)	0.29, 0.37 (6H, d)	2.32, 2.36 (6H, d), 6.61 ~ 7.25 (8H, m)
II$_6$	0.543 (6H, q), 0.96 (9H, t)	0.09 (18H, s)	0.46 (6H, s)	1.35 (6H, t, 7.10 Hz), 4.14 (4H, q)
II$_7$	rr0.58 (6H, q), 0.95 (9H, t, 7.78 Hz)	0.08 (18H, s)	0.45, 0.57 (6H, d)	1.32, 1.35 (12H, d, 6.24 Hz), 4.80 (2H, m)
II$_8$	0.28 ~ 0.57 (12H, m), 0.96 (15H, s)	0.08 (18H, s)	0.28 ~ 0.57 (12H, m)	1.64 ~ 1.77 (4H, m), 1.36 (8H, q), 4.07 (4H, s), 0.96 (15H, s)
II$_9$	0.54 (6H, q), 0.88–0.99 (15H, m)	0.08 (18H, s)	0.43 (6H, s)	0.88 ~ 0.99 (15H, m), 1.29 (16H, m), 1.64 ~ 1.77 (4H, m), 4.07 (4H, m)
I$_{10}$	0.55 (6H, q), 0.88–0.95 (15H, m)	0.08 (18H, s)	0.43 (6H, s)	0.88 ~ 0.95 (15H, m), 1.27 (20H, s), 1.64 ~ 1.77 (4H, m), 4.00 (4H, s)

TABLE 5. MS Data for Compounds **I**

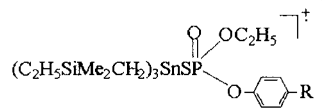
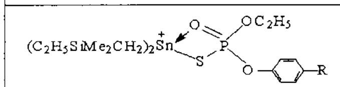
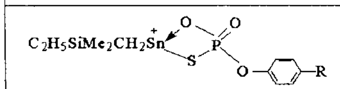
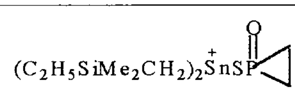
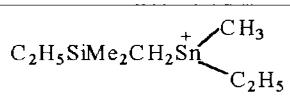
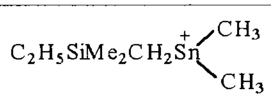
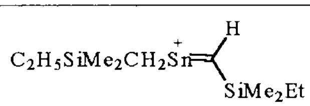
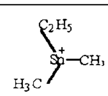
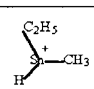
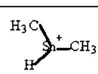
fragments \ m/z(bound) \ No.	I_1	I_2	I_3	I_4	I_5
	640(0)	654(0)	674(0)	718(0)	670(0)
$M-CH_3]^{+}$	625(5)	639(9)	659(6)	703(5)	655(6)
$M-C_2H_5]^{+}$	611(8)	625(11)	645(10)	689(8)	641(9)
	539(100)	553(100)	573(100)	617(100)	569(100)
	409(5)	423(9)	443(13)	409(12)	439(10)
	429(18)	429(10)	429(10)	429(16)	429(4)
$(C_2H_5SiMe_2CH_2)_3Sn^{+}$	423(2)	423(9)	423(5)	423(3)	423(4)
$(C_2H_5SiMe_2CH_2)_2\overset{+}{Sn}CH_3$	337(0)	337(0)	337(2)	337(0)	337(4)
	265(3)	265(2)	265(8)	265(6)	265(6)
	251(4)	251(0)	251(8)	251(5)	251(7)
	321(0)	321(2)	321(4)	321(0)	321(3)
$C_2H_5SiMe_2CH_2Sn^{+}$	221(3)	221(0)	221(6)	221(4)	221(4)
	179(8)	179(2)	179(10)	179(11)	179(7)
	165(6)	165(6)	165(7)	165(8)	165(6)
	151(4)	151(4)	151(5)	151(8)	151(4)
$\overset{+}{Sn}CH_3$	135(5)	135(0)	135(6)	135(7)	135(3)
$\overset{+}{Sn}C_2H_5$	149(10)	149(5)	149(6)	149(6)	149(3)
$H\overset{+}{Sn}$	121(0)	121(2)	121(4)	121(0)	121(3)
$C_2H_5SiMe_2CH_2^{+}$	101	101(7)	101	101	101
$C_2H_5\overset{+}{Si}Me_2$	87	87	87	87	87
$C_2H_5\overset{+}{Si}HMe$	73	73	73	73	73
$C_2H_5\overset{+}{Si}$	57	57	57	57	57

TABLE 6. MS Data for Compounds **II**

fragments \ m/z(bound) \ No.	II_1	II_2	II_3	II_4
$(C_2H_5SiMe_2CH_2)_3SnSP(=S)(O-C_6H_4-R)_2]^{+\cdot}$	704(0)	732(0)	772(0)	764(0)
$M-CH_3]^{+}$	689(3)	717(0)	757(0)	749(2)
$M-C_2H_5]^{+}$	675(3)	703(0)	743(0)	735(2)
$(C_2H_5SiMe_2CH_2)_3\overset{+}{Sn}$	423(5)	423(3)	423(5)	423(8)
$(C_2H_5SiMe_2CH_2)_2\overset{+}{Sn}SP(=S)(O-C_6H_4-R)_2$	603(4)	631(4)	671(4)	663(100)
$(C_2H_5SiMe_2CH_2)_2\overset{+}{Sn}SP(=O)(C_2H_4)$	429(100)	429(75)	429(100)	429(46)
$\overset{+}{Sn}SP(=S)(O-C_6H_4-R)_2$	401(10)	429(75)	469(0)	461(9)
$\overset{+}{Sn}OC_6H_4R\text{-}p$	213(10)	227(12)	247(5)	243(12)
$(C_2H_5SiMe_2CH_2)_2\overset{H}{Sn}S^{+}$	355(18)	355(10)	355(15)	355(13)
$(C_2H_5SiMe_2CH_2)_2\overset{+}{Sn}CH_3$	337(8)	337(2)	337(2)	337(5)
$C_2H_5SiMe_2CH_2\overset{+}{Sn}(CH_3)(C_2H_5)$	265(5)	265(3)	265(5)	265(30)
$C_2H_5SiMe_2CH_2\overset{+}{Sn}(CH_3)(CH_3)$	251(6)	251(4)	251(6)	251(34)
$C_2H_5SiMe_2CH_2\overset{+}{Sn}=C(H)(SiMe_2Et)$	321(5)	321(2)	321(3)	321(6)
$C_2H_5SiMe_2CH_2Sn(H)(S^{+})(C_2H_5)$	283(14)	283(8)	283(12)	283(10)
$(C_2H_5)(H_3C)\overset{+}{Sn}-CH_3$	179(12)	179(18)	179(22)	179(41)
$C_2H_5SiMe_2CH_2\overset{+}{Sn}=CH-Si(C_2H_5)(=)$	305(4)	305(0)	305(3)	305(5)
$C_2H_5SiMe_2CH_2\overset{+}{Sn}=CH-Si(CH_3)(=)$	291(3)	291(0)	291(3)	291(4)
$C_2H_5SiMe_2CH_2\overset{+}{Sn}$	211(8)	211	211	211
$^{+}SP(=S)(O-C_6H_4-R)_2$	281(9)	309(0)	349(0)	341(5)
$^{+}SP(O-C_6H_4-R)_2$	249(13)	277(2)	317(0)	309(3)
$(H_3C)(H_5C_2)\overset{+}{Sn}-SP(=O)(C_2H_4)$	271(46)	271(27)	271(39)	271(34)
$(C_2H_5SiMe_2CH_2)(H_5C_2)\overset{+}{Sn}-SP(=O)(C_2H_4)$	357(24)	357(13)	357(20)	357(17)

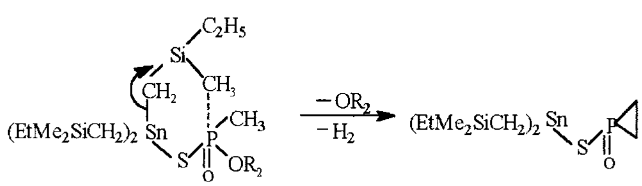
TABLE 4 ^{119}Sn and ^{31}P NMR Data for Some Compounds

No.	^{119}SnNMR(*ppm*)	$J_{Sn\text{-}p}$(*Hz*)	^{31}*P NMR* (*ppm*)
I_1	195.86	95.53	
I_2	190.55		54.6021
I_3	195.69	76.89	
I_4	191.89	69.41	54.2800
I_5	188.91	95.53	

TABLE 7. The Effectiveness of the Compounds in Combating Fungi and Insects

	Concentration	*Effection* (*%*)						
	$\times 10^6$	I_1	I_2	I_3	I_4	I_5	I_{11}	II_1
A	50	48			60		52	
B	50	57.8			57.8		57.8	
C	50	67.8			72.9		67.5	
D	50	64.7			58.8		52.9	
E	50	61.5			46.1		46.1	
F	500	40			20		50	
G	500	30			10		40	
H	500	40			20		32.5	
I	100	30			0		20	
J	200	7			61		5.8	
K	50	20			80		80	
L	200	100	100	100	100	100	97.6	100

In a second step, a methyl group migration from silicon to phosphorus and an apparent elimination of hydrogen at the phosphorus moiety, a phosphorus containing a three-membered ring is produced, as indicated by an *m/z* ratio of 429 (50–100%) in all of monothiophosphates (Scheme 3).



SCHEME 3 Methyl group migration elimination of OR_2 and H_2 group at phosphorous.

The base peak of the $[M\text{-}R]^+$ ion for compounds I_1–I_5 (Tables 5 and 6) suggest that the O→Sn coordination bond is formed after cleavage of a Sn–C bond, which makes the ion stable. The base peak for compounds II_1–II_4 is the phosphorus three-membered ring ion indicating ease of cleavage of the OR group at phosphorus.

BIOACTIVITY

The bioactivities of these compounds has been tested, and the results are shown in Table 7. The antifungal activities of some compounds toward some plant pathogenic fungi are inoculated by the agar dilution method. The chemicals are applied in the culture medium, and the fungus cakes to be tested are placed on the surface of the medium. Growth of the fungi is then observed. The test stairs used were as follows:

A. Wheat Scab (*Gibberella zeae (Schw.)Petch*)
B. Tomato gray mold (*Botrytis cinerea Pers*)
C. Rhizoctonia cotton rot (*Rhizactonia solani Ku ehn*)
D. Apple Ring rot (*Macrophoma kuwatsukai Hara*)
E. Cercospora leare spot of pearnt
F. Leare rust of wheat
G. Gray mold of cucumber
H. Rape seed selerotinia blight
I. TMV tobaco mosaic virus

The results show that these compounds possess antibiotic activities toward plant pathogenic fungi.

Insecticidal and acaricidal activities were tested on the green bean plant at 50 or 200 ppm. The killing rate after 24 hours for two-spotted spider mites (*Tetranychus urticae Koch*) is 100%. The killing rate is assessed by checking the number of dead and live mites, by use of a binocular microscope.

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