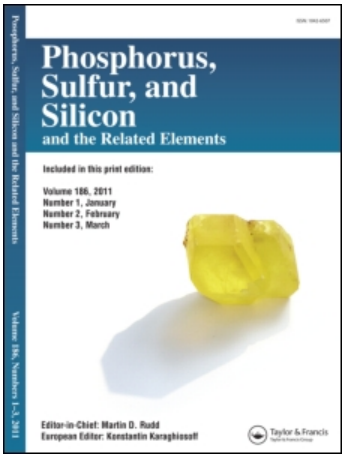

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STUDIES OF TRIS-[(DIMETHYLBENZYLSILYL)METHYLENE]TIN MONO(DI)THIOPHOSPHATES

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STUDIES OF TRIS-[(DIMETHYLBENZYLSILYL)METHYLENE]TIN MONO(DI)THIOPHOSPHATES

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Twenty-five new compounds of the form $(PhCH_2Me_2SiCH_2)_3SnSP(X)(OR_1)(OR_2)$($X=O$:$R_1=C_2H_5$, R_2 = Substituted phenyl; $X=S$:$R_1=R_2$ = hydrocarbyl) have been synthesized. Their structures were characterized by IR, ^1H, ^{119}Sn, ^{31}P NMR, MS and elemental analyses. ^{119}Sn NMR measurement of chemical shift have shown that there is a good linear relationship of ^{119}Sn chemical shift with para-substituent Hammett constants.

Keywords: Organotin containing silicon; mono(di)thiophosphates; synthesis; structure; biological activity

INTRODUCTION

Sila-Torque$[(PhMe_2SiCH_2)_3Sn]_2O$[1] has the similare good acaricidal activity as agricultural acaricide Torque $[(PhMe_2CCH_2)_3Sn]_2O$.[2] We have synthesized many sila-Torque similarities and tested their biological activities.[3] It has been found that the acaricidal activities are connected with the substituent on the silicon atom. The order is below:

$$(Me_3SiCH_2)_3SnY > (PhMe_2SiCH_2)_3SnY > (Ph_2MeSiCH_2)_3SnY$$

*Corresponding author.

In this paper we have synthesized a new class of tris-[(dimethylbenzylsilyl)methylene]tin mono(di)-thiophosphates by the following reaction. $(PhCH_2Me_2SiCH_2)_3SnCl + (R_1O)(R_2O)P(X)S^-K^+ \xrightarrow{acetone} (PhCH_2Me_2SiCH_2)_3SnSP(X)(OR_1)(OR_2) + KCl$ X = O, R_1 = Et: $R_2 = C_6H_5$ (I_1); p-$CH_3C_6H_4$ (I_2); p-BrC_6H_4 (I_3); p-ClC_6H_4(I_4); p-$CH_3OC_6H_4$ (I_5); p-$^tBuC_6H_4$ (I_6); m-$CH_3C_6H_4$ (I_7); m-ClC_6H_4 (I_8); o-$CH_3C_6H_4$ (I_9); o-ClC_6H_4 (I_{10}); 2,4-$Cl_2C_6H_3$ (I_{11}). X = S: $R_1 = R_2 = C_6H_5$ (II_1); p-$CH_3C_6H_4$ (II_2); p-ClC_6H_4 (II_3); p-$^tBuC_6H_4$ (II_4); m-$CH_3C_6H_4$ (II_5); o-$CH_3C_6H_4$ (II_6); 2,4-$Cl_2C_6H_3$ (II_7); CH_3 (II_8); C_2H_5(II_9); ^iPr(II_{10}); $(CH_2)_4CH_3$(II_{11}); $(CH_2)_5CH_3$(II_{12}); $(CH_2)_6CH_3$(II_{13}); $(CH_2)_7CH_3$(II_{14}).

The structures of these compounds were characterized by IR, ^{119}Sn, ^1H, ^{31}P NMR and MS.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-435 spectrometer in liquid film. 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 as external. Elemental analyses were determined on an MT-3 elemental analyzer. Mass spectra were recorded on an ZAB-HS at 70ev, the temperature of ionization was 200°C.

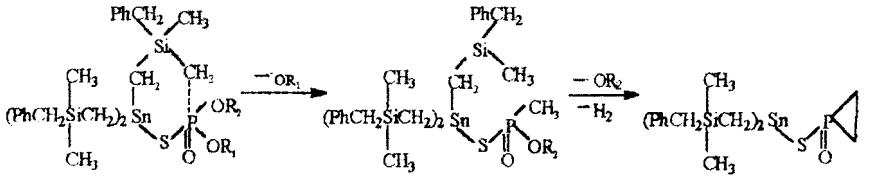
The tris[(benzyldimethylsilyl)methylene]tin chloride was synthesized via the following reaction (Scheme 1).

$$Me_3SiCl \xrightarrow[Cl_2]{h\nu} Me_2SiClCH_2Cl \xrightarrow{PhCH_2MgCl} PhCH_2Me_2SiCH_2Cl \xrightarrow{Mg} PhCH_2Me_2SiCH_2MgCl \xrightarrow{SnCl_4} (PhCH_2Me_2SiCH_2)_3SnCl \quad \textbf{(Scheme1)}$$

The potassium mono(di)thiophosphates was synthesized according to the literature.[4–6]

GENERAL SYNTHESIS PROCEDURE

A mixture of 3 mmol tris[(benzyldimethylsilyl)methylene]tin chloride and 3.3 mmol potassium mono(di)thiophosphates in 20ml of acetone was refluxed with stirring for 5h. After removing the acetone, The residue product was solved in the petroleum ether and the KCl was filtered. The solvent was extracted again



with acetonitrile. The solvent was removed and the viscous liquid product was obtained.

RESULTS AND DISCUSSION

The yield and elemental analysis of the products are given in Table I.

The IR data are listed in Table II. The absorption vibration frequency ν_{PS2}^{sym} was found at 650–607 cm^{-1} as a weak peak, and the absorbtion vibration frequency of P=O was at 1202–1207 cm^{-1} as a strong peak and there exist no P=S tautomer.[7] The frequency of $\nu_{Sn\text{-}C}^{asym}$ was often overlapped with ν_{PS}^{sym}.

The NMR data are listed in Table III and IV. The proton magnetic resonance spectra of compounds I agree very well with the proposed structures.

We found from the ^1H spectra of compounds $(PhCH_2SiMe_2CH_2)_3$-$SnSP(S)(OAr)_2$ that the hydrogen on the Si-CH_3, Si-CH_2, $PhCH_2$, and methyl on the phenyl ring are split to two peaks and the ratio of intensity is connected with the substituent of the aromatic ring: when R is CH_3, the intensity of the two peaks are almost equal. When R is Cl or H, the differences between the two peaks are bigger and when R is ^{t}Bu, are single. The reason need further study.

A subtle structural change around the tin atom can be reflected on the chemical shifts in ^{119}Sn NMR.[8] The electron-withdrawing groups on the aromatic group made the chemical shift of ^{119}Sn moving to lower fields. We have found that there is a linear relationship between $\delta^{119}Sn$ and the Hammett constants (σ) of the para substituent for the I sense of the corresponding compounds.

TABLE IV ^{119}Sn data for some compounds

No.	*^{119}SnNMR(ppm)*	*$J_{Sn\text{-}p}$(Hz)*	*No.*	*^{119}SnNMR(ppm)*	
I_1	182.21		II_1	130.7	172.3
I_2	180.71	88.06	II_2	128.4	172.6
I_3	186.53		II_3	137.4	172.9
I_4	185.22		II_4	120.8	
I_5	180.64				
I_6	180.38	87.85			

TABLE I The yields and elemental analyses of the compounds.

Compound	*Yield(%)*	*State*	*Elemental analysis:*		*Found(calcd)% Formula for calculation*
			C	*H*	
I_1	72.8	yellow viscous oil	54.86(55.27)	7.00(6.71)	$C_{38}H_{55}O_3SPSi_3Sn$
I_2	76.2	yellow viscous oil	55.42(55.77)	6.86(6.84)	$C_{39}H_{57}O_3SPSi_3Sn$
I_3	72.4	yellow viscous oil	50.33(50.45)	6.38(6.02)	$C_{38}H_{54}O_3BrSPSi_3Sn$
I_4	74	yellow viscous oil	53.18(53.05)	6.32(6.33)	$C_{38}H_{54}O_3ClSPSi_3Sn$
I_5	78.7	yellow viscous oil	54.34(54.73)	6.62(6.71)	$C_{39}H_{57}O_4SPSi_3Sn$
I_6	77.3	yellow viscous oil	56.63(57.20)	7.67(7.20)	$C_{42}H_{63}O_3SPSi_3Sn$
I_7	77.4	yellow viscous oil	55.59(55.77)	6.92(6.84)	$C_{39}H_{57}O_3SPSi_3Sn$
I_8	75.6	yellow viscous oil	52.82(53.05)	6.21(6.33)	$C_{38}H_{54}O_3ClSPSi_3Sn$
I_9	74.4	yellow viscous oil	55.89(55.77)	6.71(6.84)	$C_{39}H_{57}O_3SPSi_3Sn$
I_{10}	72.7	yellow viscous oil	52.91(53.05)	6.48(6.33)	$C_{38}H_{54}O_3ClSPSi_3Sn$
I_{11}	72.6	yellow viscous oil	51.00(51.01)	6.02(5.97)	$C_{38}H_{53}Cl_2PSO_3Si_3Sn$
II_1	75.3	yellow viscous oil	56.56(56.68)	5.86(6.23)	$C_{42}H_{55}PS_2O_2Si_3Sn$
II_2	83.3	yellow viscous oil	57.39(57.57)	5.86(6.23)	$C_{44}H_{59}PS_2O_2Si_3Sn$
II_3	78.2	yellow viscous oil	52.62(52.61)	5.78(5.57)	$C_{42}H_{53}Cl_2PS_2O_4Si_3Sn$
II_4	64.9	yellow viscous oil	59.70(59.92)	7.03(7.14)	$C_{50}H_{71}PS_2O_4Si_3Sn$
II_5	73.4	yellow viscous oil	57.75(57.57)	5.94(6.48)	$C_{44}H_{59}PS_2O_2Si_3Sn$
II_6	78.9	yellow viscous oil	57.35(57.57)	6.57(6.48)	$C_{44}H_{59}PS_2O_2Si_3Sn$
II_7	72.8	yellow viscous oil	49.00(49.08)	4.76(5.00)	$C_{42}H_{53}Cl_4S_2PO_2Si_3Sn$
II_8	78.4	yellow viscous oil	49.89(50.19)	6.94(6.71)	$C_{32}H_{51}PS_2O_2Si_3Sn$
II_9	77.5	yellow viscous oil	51.38(51.44)	7.05(6.98)	$C_{34}H_{55}S_2PO_2Si_3Sn$
II_{10}	76.2	yellow viscous oil	52.66(52.61)	7.05(7.24)	$C_{36}H_{59}S_2PO_2Si_3Sn$
II_{11}	90.9	yellow viscous oil	54.44(54.72)	7.42(7.69)	$C_{40}H_{67}S_2PO_2Si_3Sn$
II_{12}	86.1	yellow viscous oil	55.40(55.67)	7.63(7.90)	$C_{42}H_{71}PS_2O_2Si_3Sn$
II_{13}	90.9	yellow viscous oil	56.42(56.57)	8.07(8.09)	$C_{44}H_{75}S_2PO_2Si_3Sn$
II_{14}	93.8	yellow viscous oil	57.48(57.42)	8.27(8.28)	$C_{46}H_{79}S_2PO_2Si_3Sn$

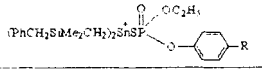
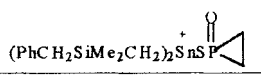
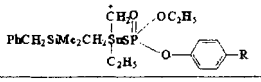
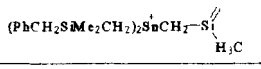
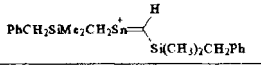
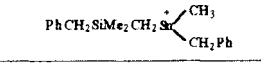
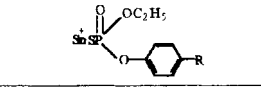
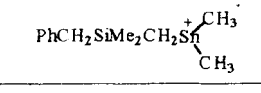
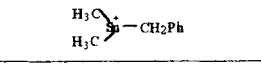
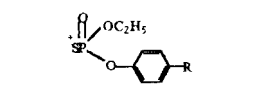
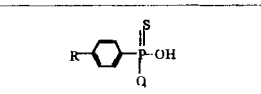
TABLE II IR data of compounds I and II

NO.	$\nu_{Si\text{-}CH2}$	$\nu_{Si\text{-}C}$	$\nu_{P\text{-}O\text{-}C}$ or $\nu_{P\text{-}O\text{-}\Phi}$		$\nu_{P=O}$	$\nu^{asym}_{Sn\text{-}\epsilon}$ $\nu^{sym}_{Sn\text{-}\epsilon}$	$\nu^{asym}_{PS_i}$ $\nu^{sym}_{PS_i}$
I_1	1250(s)	827(s)	1008(s)	1159(s)	1207(s)	524(m)	
			763(s)	960(s)		472(m)	
I_2	1250(s)	827(s)	1015(s)	1155(m)	1207(s)	524(w)	
			763(s)	960(m)		474(m)	
I_3	1250(s)	829(s)	1012(s)	1157(m)	1207(s)	524(w)	
			763(s)	960(m)		472(w)	
I_4	1250(s)	829(s)	1014(s)	1157(m)	1207(s)	524(w)	
			763(s)	960(m)		472(w)	
I_5	1250(s)	831(s)	1037(s)	1157(m)	1205(s)	524(w)	
			763(s)	960(m)		472(w)	
I_6	1250(s)	831(s)	1015(s)	1157(w)	1207(m)	524(w)	
			763(s)	960(m)		472(w)	
I_7	1245(s)	820(s)	1005(s)	1143(s)	1202(m)	521(m)	
			760(s)	946(s)		470(m)	
I_8	1244(m)	820(s)	1027(s)	1148(m)	1202(m)	517(w)	
			759(m)	928(s)		465(w)	
I_9	1245(s)	822(s)	1035(s)	1177(m)	1202(m)	520(w)	
			759(s)	952(m)		488(w)	
I_{10}	1245(s)	822(s)	1028(m)	1149(w)	1202(m)	520(w)	
			760(m)	953(w)		468(w)	
I_{11}	1246(s)	821(s)	1037(s)	1148(m)	1202(m)	520(w)	
			760(s)	955(m)		469(w)	
II_1	1245(m)	821(s)		1180(m)		519(w)	668(m)
				939(m)		469(w)	519(w)
II_2	1245(s)	818(s)		1155(s)		509(m)	651(m)
				932(m)		471(w)	509(m)
II_3	1245(s)	823(s)		1154(s)		519(m)	637(w)
			932(m)			471(w)	519(m)
II_4	1242(m)	821(s)		1156(m)		506(w)	652(m)
				939(m)		469(w)	543(w)
II_5	1244(s)	822(s)		1130(m)		516(w)	667(m)
				940(s)		471(w)	542(w)
II_6	1250(s)	827(s)		1167(s)		530(m)	665(s)
				937(s)		474(m)	530(m)
II_7	1245(s)	819(s)		1147(m)		520(w)	668(m)
						470(w)	520(w)
II_8	1245(m)	821(s)	1018(m)			510(w)	657(m)
			759(m)			470(w)	510(w)
II_9	1245(s)	825(s)	1020(s)			516(w)	655(m)
			763(s)			474(w)	542(w)
II_{10}	1245(m)	820(s)	1010(m)			514(w)	650(m)
			760(s)			468(w)	544(w)
II_{11}	1248(s)	825(s)	1018(s)			519(w)	659(m)
			761(s)			474(w)	519(w)
II_{12}	1248(s)	825(s)	1012(s)			520(w)	659(s)
			761(s)			474(w)	520(w)
II_{13}	1245(m)	820(s)	1050(m)			512(w)	657(m)
			759(s)			470(w)	512(w)
II_{14}	1245(m)	820(s)	1006(s)			512(w)	657(m)
			759(m)			468(w)	512(w)

TABLE III Main NMR (^{1}H) data for compounds I and II (ppm)

Compound	*CH_2*	*CH_3*	*$SiCH_2Sn$*	*R_1, R_2 and Ph*
I_1	2.12(6H,s)	0.07(18H,s)	0.31(6H,s)	1.32(3H,t,7.05Hz), 4.07 ~ 4.22(2H,m), 6.95 ~ 7.36(20H,m,)
I_2	2.13(6H,s)	0.06(18H,s)	0.32(6H,s)	1.32(3H,t,7.10Hz), 2.31(3H,s), 4.07 ~ 4.13(2H,m)7.00 ~ 7.22(19H,m)
I_3	2.11(6H,s)	0.04(18H,s)	0.29(6H,s)	1.27(3H,t,7.08Hz), 4.05 ~ 4.12(2H,m), 6.95 ~ 7.26(19H,m)
I_4	2.11(6H,s)	0.04(18H,s)	0.29(6H,s)	1.25(3H,t,7.05Hz), 4.00 ~ 4.17(2H,m), 6.98 ~ 7.26(19H,m)
I_5	2.11(6H,s)	0.04(18H,s)	0.29(6H,s)	1.27(3H,t,7.02Hz), 3.75(3H,s), 4.00 ~ 4.16(2H,m)6.99 ~ 7.26(19H,m)
I_6	2.12(6H,s)	0.05(18H,s)	0.29(6H,s)	1.30(12H,s), 4.09 ~ 4.23(2H,m), 7.00 ~ 7.21(19H,m)
I_7	2.12(6H,s)	0.05(18H,s)	0.31(6H,s)	1.31(3H,t,7.07Hz),2.32(3H,s), 4.07 ~ 4.22(2H,m), 6.96 ~ 7.21(19H,m)
I_8	2.12(6H,s)	0.06(18H,s)	0.31(6H,s)	1.32(3H,t,7.08Hz), 4.05 ~ 4.18(2H,m), 6.96 ~ 7.22(19H,m)
I_9	2.11(6H,s)	0.04(18H,s)	0.34(6H,s)	1.27(3H,t,7.12Hz), 2.32(3H,s), 4.00 ~ 4.16(2H,m) 7.00 ~ 7.21(19H,m)
I_{10}	2.12(6H,s)	0.06(18H,s)	0.32(6H,s)	1.29(3H,t,7.03Hz), 4.09 ~ 4.23(2H,m), 7.00 ~ 7.22(19H,m)
I_{11}	2.12(6H,s)	0.06(18H,s)	0.32(6H,s)	1.32(3H,t,7.09Hz), 4.08 ~ 4.23(2H,m), 6.96 ~ 7.22(19H,m)
II_1	2.08,2.17(6H,d)	0.006,0.10(18H,d)	0.26,0.31(6H,d)	6.95 ~ 7.35 (25H,m)
II_2	2.08,2.17(6H,d)	0.007,0.09(18H,d)	0.21,0.31(6H,d)	2.30,2.34(6H,d), 6.75 ~ 7.22(23H,m)
II_3	2.09,2.14(6H,d)	0.01,0.10(18H,d)	0.22,0.29(6H,d)	6.75 ~ 7.22(23H,m)
II_4	2.15(6H,s)	0.07(18H,s)	0.19(6H,s)	1.32(18H,s), 6.75 ~ 7.27 (23H,m)
II_5	2.08,2.16(6H,d)	−0.0014,0.09(18H,d)	0.21,0.31(6H,d)	2.33,2.35(6H,d), 6.61 ~ 7.32 (23H,m)
II_6	2.07,2.16(6H,d)	−0.008,0.09(18H,d)	0.21,0.35(6H,d)	2.27,2.33(6H,d), 6.77 ~ 7.31 (23H,m)
II_7	2.07,2.15(6H,d)	−0.01,0.09(18H,d)	0.20,0.37(6H,d)	6.96 ~ 7.27 (21H,m)
II_8	2.14(6H,s)	0.07(18H,s)	0.40(6H,s)	3.67,3.75(6H,d), 7.02 ~ 7.23 (15H,m)
II_9	2.14(6H,s)	0.06(18H,s)	0.41(6H,s)	1.33(6H,t,7.08Hz), 4.00 ~ 4.20(4H,m), 6.96 ~ 7.23 (15H,m)
II_{10}	2.13(6H,s)	0.04(18H,s)	0.40(6H,s)	1.33(12H,d,6.95Hz), 4.68 ~ 4.86(2H,m), 6.95 ~ 7.23 (15H,m)
II_{11}	2.13(6H,s)	0.05(18H,s)	0.40(6H,s)	0.91(6H,t), 1.37(8H,m), 1.64(4H,m)4.05(4H,q), 7.01 ~ 7.27 (15H,m)
II_{12}	2.13(6H,s)	0.05(18H,s)	0.40(6H,s)	0.90(6H,t), 1.33(12H,m), 1.68(4H,m)4.05(4H,q), 6.97 ~ 7.27 (15H,m)
II_{13}	2.13(6H,s)	0.05(18H,s)	0.41(6H,s)	0.90(6H,t), 1.30(16H,m), 1.66(4H,m)4.04(4H,q), 6.97 ~ 7.22 (15H,m)
II_{14}	2.13(6H,s)	0.05(18H,s)	0.40(6H,s)	0.90(6H,t), 1.29(20H,m), 1.68(4H,m)4.05(4H,q), 6.97 ~ 7.25(15H,m)

Table 5. The MS of compounds I

No. / m/z(bound) / fragment	I_1	I_2	I_3	I_4	I_5	I_6
M^+	826(0)	840(0)	904(0)	860(0)	856(0)	882(0)
$M-CH_3]^+$	811(4)	825(4)	889(0)	845(2)	840(3)	867(3)
$M-CH_2Ph]^+$	735(100)	749(100)	813(5)	769(44)	764(100) 765(48)	790(100) 791(66)
	663(35)	677(43)	741(1.5)	697(12)	692(42) 693(18)	718(58) 719(25)
$(PhCH_2Me_2CH_2)_3Sn^+$	609(10)	609(15)	609(4)	609(11)	609(104)	609(16)
	553(6)	553(11)	553(82)	553(100)	553(29)	553(25)
	543(10)	557(10)	621(0)	577(7)	573(3)	599(4)
	517(6)	517(6)	517(2)	517(8)	517(6)	517(7)
$(PhCH_2SiMe_2CH_2)_2Sn^+$	446(6)	446(7)	446(3)	446(9)	446(7)	446(8)
	445(19)	445(19)	445(6)	445(22)	445(23)	445(23)
	389(4)	389(6)	389(4)	389(10)	389(6)	389(11)
	337(9)	351(8)	415(0)	371(8)	369(4)	393(11)
	313(8)	313(9)	313(9)	313(19)	313(14)	313(13)
$PhCH_2SiMe_2CH_2Sn^+$	283(24)	283(26)	283(42)	283(63)	283(36)	283(38)
	241(22)	241(23)	241(25)	241(47)	241(38)	241(36)
	217(0)	231(0)	295(3)	251(4)	247(0)	273(0)
	189(3)	203(5)	267(5)	223(19)	219(5)	245(7)
$PhCH_2Sn^+$	211(17)	211(19)	211(44)	211(66)	211(26)	211(26)

continuons table

No. / m/z(bound) / fragment	II_1	II_2	II_3	II_4
$PhCH_2SiMe_2CH_2$ $Sn=CHMe_2SiCH_2Ph$ H_2C	459(3)	459(5)	459(7)	459(5)
$PhCH_2SiMe_2CH_2Sn=CH-Si(CH_2Ph)(CH_2)$	429(3)	429(9)	429(2)	429(0)
$PhCH_2SiMe_2CH_2Sn(H)(CH_2Ph)S$	407(4)	407(8)	407(4)	407(3)
$SnS(O-C_6H_4-R)_2$	401(3)	429(9)	469(8)	513(0)
$PhCH_2SiMe_2CH_2Sn(H)=C(H)Si(CH_3)_2CH_2Ph$	445(3)	445(6)	445(7)	445(7)
$PhCH_2SiMe_2CH_2Sn(CH_3)CH_2Ph$	389(5)	389(10)	389(9)	389(6)
$PhCH_2SiMe_2CH_2Sn=CH-Si(CH_3)(CH_2)$	353(10)	353(14)	353(5)	353(5)
$PhCH_2Sn(H)(CH_2Ph)(H_3C)CH_3$	333(31)	333(71)	333(20)	333(12)
$PhCH_2Sn(H_3C)=CH_2Ph$	317(8)	317(17)	317(15)	317(6)
$PhCH_2SiMe_2CH_2Sn(CH_3)CH_3$	313(13)	313(27)	313(17)	313(12)
$PhCH_2SiMe_2CH_2Sn$	283(45)	283(77)	283(26)	283(27)
$SnS(O-C_6H_4-R)_2$	281(35)	309(11)	349(0)	393(2)
$SnS(O-C_6H_4-R)_2$	249(5)	227(27)	317(15)	361(0)

$$\delta(^{119}Sn) = 11.5760\sigma + 182.9623 \ (r = 0.9657, I_1 - I_6)$$

The mass spectra of compounds I_1–I_6 and II_1–II_4 were given in Table V and VI. For all there are no molecular ion peaks. Dealkylation from the tin atom

continuous table

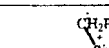
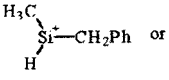
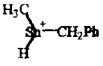
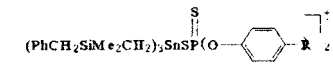
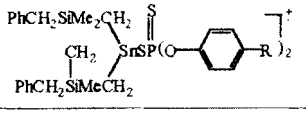
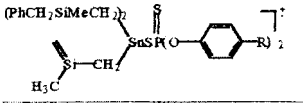
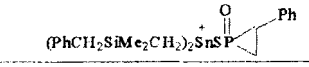
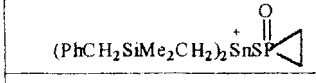
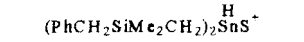
No. / m/z(bound) / fragment	I_1	I_2	I_3	I_4	I_5	I_6
$PhCH_2SiMe_2CH_2^+$	163(5)	163(6)	163(9)	163(19)	163(8)	163(8)
		108(24)	172(100)	127 128(100)	123 124(99)	
	149(15)	149(18)	149(62)	149(94)	149(31)	149(29)
$PhCH_2Si^+$	119(3)	119(5)	119(15)	119(20)	119(6)	119(9)
$PhCH_2CH_2^+$	105(6)	105(5)	105(20)	105(33)	105(8)	105(11)
	135(9)	135(14)	135(13)	135(46)	135(24)	135(79)
SnH^+	121(12)	121(12)	121(54)	121(86)	121(24)	121(21)
	227(0)	227(9)	227(15)	227(26)	227(5)	227(4)

Table 6 . The MS of compounds II

No. / m/z(bound) / fragment	II_1	II_2	II_3	II_4
	890(0)	918(0)	958(0)	1002(0)
	798(1)	826(2)	866(6)	910(0)
	726(3)	754(7)	794(11)	838(1)
	629(3)	629(15)	629(3)	629(8)
$(PhCH_2Me_2CH_2)_3Sn^+$	609(8)	609(24)	609(36)	609(18)
	553(100)	553(100)	553(58)	553(31)
	479(3)	479(7)	479(2)	479(10)

was a main breakdown pattern for these compounds. The methyl group of silicon can migrate to phosphorus and an OR group from the phosphorus was lose. During the second migration of methyl group, a H_2 molecular was losed and a triheterocycle containing phosphorus is formed.

We see that M-CH_2Ph is the base peak for compounds I which para-substituent of phenyl is H, CH_3, OCH_3, ^{t}Bu and when it is Cl and Br, ArO^+ is the base peak. The electrophilioity of Cl and Br make this ion more stable, because the leaving of $\cdot OAr$ and $\cdot SAr$ is more easy, the base peak of some compounds II is the triheterocycle ion containing phosphorus.

BIOACTIVITY

The biological activities have been studied and the result shows that these compounds have no miticidal activity.

References

[1] R. Tacker, *Z. Naturtersch*, **41b**, 1923 (1986).
[2] C. Horne, U.S. Patent **3**, 657,451 (1972).
[3] Qing-lan Xie and Zhi-qiang Yang, Silicon Material & Applications (in China) No. 5, 1 (1994).
[4] N. I. Zemlyanskii and B. S. Drach, *Zh. Obshch. Khim.*, **32** 1962, (1962).
[5] M. I. Kabachnik, *Tetrahedron*, **9** 10, (1960).
[6] Chuchi Tang, Guiping Wu and Youxin Chai, *Chem. J. in Chinese Univ.* (in China) **2**, 70, (1981).
[7] Hua Liu, M. Mazhar, Qinglan Xie and JiTao Wang, *Heteroatom Chemistry* (in press.)
[8] H. C. Clark and V. K. Jain, *J. Organometal. Chem.*, **279**, 385 (1985).