APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 660–664

Environment, Biology and Toxicology **AOC**

Studies on mixed trialkyltin derivatives: preparation and biological activity of (2-phenyl-2-methylpropyl)dicyclohexyltin *O,O*-dialkyldithiophosphates

Fei Yuan, Yanqin Huang and Qinglan Xie*

State Key Laboratory of Element-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

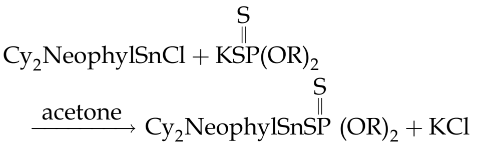
Received 8 February 2002; Revised 12 July 2002; Accepted 17 July 2002

Fifteen compounds based on (2-phenyl-2-methylpropyl)dicyclohexyltin *O,O*-dialkyldithiophosphates have been synthesized by the reaction of (2-phenyl-2-methylpropyl)dicyclohexyltin chloride with potassium *O,O*-dialkyldithiophosphoric acids. Their structure and composition were characterized by ^{1}H NMR, IR spectroscopy, elemental analysis and X-ray diffraction. The structure of $PhMe_2CCH_2Sn(Cy_2)S_2P(OC_6H_4{}^tBu\text{-}4)_2$ has been shown to consist of a four-coordinate tin atom in a slightly distorted tetrahedral geometry. Biological activities were tested for some of the compounds. The results show that these kinds of compound have acaricidal activity. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: mixed trialkyltin; synthesis; crystal structure; structural characterization; acaricidal activity

INTRODUCTION

Cy_3SnOH (plictran) has strong acaricidal activity, but it has been found that this kind of compound does considerable harm to some plants. $[(PhMe_2CCH_2)_3Sn]_2O$ (Torque) is also an efficient acaricide, but its effect is much less and the cost is more than Cy_3SnOH. Therefore, we have introduced cyclohexyl and 2-phenyl-2-methylpropyl ligands into a tin atom and synthesized a mixed trialkyltin chloride. Then, we used this intermediate in reactions with the potassium salts *O,O*-dialkyldithiophosphoric acids to synthesize the target compounds. The route is as shown in Equation (1):



$$\mathrm{Cy_2NeophylSnCl} + \mathrm{KS}\overset{\overset{\displaystyle\mathrm{S}}{\|}}{\mathrm{P}}\mathrm{(OR)_2} \xrightarrow{\text{acetone}} \mathrm{Cy_2NeophylSnS}\overset{\overset{\displaystyle\mathrm{S}}{\|}}{\mathrm{P}}\mathrm{\ (OR)_2} + \mathrm{KCl} \qquad (1)$$

where R = CH_3 (**1**), C_2H_5 (**2**), *n*-C_3H_7 (**3**), *i*-C_3H_7 (**4**), *n*-C_4H_9 (**5**), *n*-C_5H_{11} (**6**), *i*-C_5H_{11} (**7**), *n*-C_6H_{13} (**8**), *n*-C_7H_{15} (**9**), *n*-C_8H_{17} (**10**), C_6H_5 (**11**), 4-Cl-C_6H_4 (**12**), 4-MeC_6H_4 (**13**), 3-MeC_6H_4 (**14**), 4-$^t BuC_6H_4$ (**15**); Cy = cyclohexyl; Neophyl = $PhCMe_2CH_2$.

EXPERIMENTAL

Apparatus and chemicals

Elemental analysis was determined on an MT-3 elemental analyzer (Yanaco, Japan); IR spectra were recorded on a Shimadzu-IR 453 spectrometer as liquid films and on KBr disks (for compounds **15** and **16**; ^{1}H NMR spectra were obtained using an AC-P200 instrument with $CDCl_3$ as solvent and tetramethylsilane as internal standard; an HP-5988 instrument was used for mass spectrometry) (MS) at 70 eV, and the ionization temperature was 200 °C.

O,O-Dialkyldithiophosphatic potassium salts were synthesized according to the literature methods.[1,2] Neophyl-Cy_2SnCl was synthesized according to Scheme 1.

Preparation of products

The physical properties, yields, and element analysis of the compounds prepared are shown in Table 1.

Preparation of NeophylCy$_2$SnS$_2$P(OR)$_2$

See Ref. 3. 2 mmol of $NeophylCy_2SnCl$ was dissolved in 40 ml

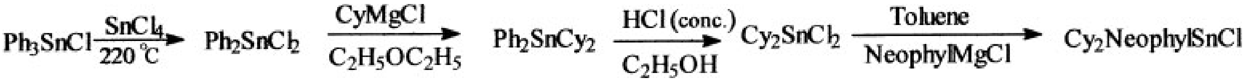
---

*Correspondence to: Q.-L. Xie, State Key Laboratory of Element–Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China.
E-mail: xieql@public.tpt.tj.cn

Table 1. Yields and elemental analysis of the compounds

Compound	Formula	M.W.	State	Yield (%)	Elemental analysis (%) Found (calc.) C	H
1	$C_{24}H_{41}O_2PS_2Sn$	575.37	Yellow viscous liquid	97.15	50.27 (50.09)	7.09 (7.13)
2	$C_{26}H_{45}O_2PS_2Sn$	603.43	Yellow viscous liquid	72.36	51.75 (51.74)	7.47 (7.46)
3	$C_{28}H_{49}O_2PS_2Sn$	631.48	Yellow viscous liquid	82.61	52.71 (53.25)	7.77 (7.77)
4	$C_{28}H_{49}O_2PS_2Sn$	631.48	Yellow viscous liquid	89.38	52.87 (53.25)	7.96 (7.77)
5	$C_{30}H_{53}O_2PS_2Sn$	659.53	Yellow viscous liquid	80.50	54.65 (54.63)	8.20 (8.04)
6	$C_{32}H_{57}O_2PS_2Sn$	687.59	Yellow viscous liquid	77.87	55.79 (55.90)	8.10 (8.30)
7	$C_{32}H_{57}O_2PS_2Sn$	687.59	Yellow viscous liquid	81.15	55.65 (55.90)	8.10 (8.30)
8	$C_{34}H_{61}O_2PS_2Sn$	715.64	Yellow viscous liquid	85.31	56.96 (57.06)	8.41 (8.53)
9	$C_{36}H_{65}O_2PS_2Sn$	743.69	Yellow viscous liquid	87.08	57.97 (58.14)	8.86 (8.75)
10	$C_{38}H_{69}O_2PS_2Sn$	771.75	Yellow viscous liquid	76.46	59.17 (59.14)	9.05 (8.95)
11	$C_{34}H_{45}O_2PS_2Sn$	699.51	Yellow viscous liquid	75.64	58.20 (58.37)	6.40 (6.44)
12	$C_{36}H_{49}O_2PS_2Sn$	727.57	Yellow viscous liquid	83.36	59.07 (59.42)	6.65 (6.74)
13	$C_{36}H_{49}O_2PS_2Sn$	727.57	Yellow viscous liquid	95.75	59.40 (59.42)	6.55 (6.74)
14	$C_{34}H_{43}Cl_2O_2PS_2Sn$	768.40	Yellow viscous liquid	74.50	53.06 (53.12)	5.71 (5.60)
15	$C_{42}H_{61}O_2PS_2Sn$	811.73	Colorless solid, m.p. 114–116 °C	74.37	62.22 (62.15)	7.58 (7.52)

16: $[(PhMe_2CCH_2)Cy_2Sn]_2O$. Colorless solid, m.p. 110–112 °C. ^1H NMR, δ (ppm): 1.17–1.65 (m, 60H, $2Me_2CCH_2$+4Cy), 7.23–7.28 (m, 10H, $2C_6H_5$). IR, v_{max} (cm^{-1}): 1169, 990 (s, P—O—C), 490, 417 (w, Sn—C), 553 (m, Sn—O).



Scheme 1.

acetone, then 2.5 mmol of *O,O*-dialkyldithiophosphatic potassium salt was added. The reaction mixture was refluxed for 6 h with stirring; it was then cooled and filtered, and the solvent was removed. The crude product was purified from petrolium ether. Yellow vicious liquid compounds were obtained except for compound **15**. The larger the molecular weight is, the more viscous the compound is.

Preparation of (NeophylCy$_2$Sn)$_2$O

0.005 mol NeophylCy$_2$SnCl was dissolved in 20 ml methanol, then 0.04 mol NaOH and 5 ml H_2O was added. After 6 h of reflux with stirring, the reaction mixture was cooled and filtered, then treated with petrolium ether. The organic layer was dried over Na_2SO_4 and filtered. Then the crude oil was obtained after removal of solvent. The product was recrystallized from alcohol.

RESULTS AND DISCUSSION

IR data

The important data for the IR spectra are listed in Table 2. The $v^{as}_{PS_2}$ and $v^{s}_{PS_2}$ absorption vibration frequencies are located in the range 654–694 cm^{-1} and 523–553 cm^{-1} respectively. v_{Sn-C} are located in the range 492–505 cm^{-1} for asymmetric absorption, and 416–417 cm^{-1} for symmetric absorptions; these are a group of weak peaks, whose frequencies are lower than for $Cy_3SnS_2P(OR)_2$.[4] The vibration absorptions of

Table 2. Important IR data for compounds **1–15**

Compound	v_{P-O-C}	$v^{as}_{PS_2}$	$v^{s}_{PS_2}$	$v^{as}_{Sn—C}$	$v^{s}_{Sn—C}$
1	1172(m), 1031(s)	662(m)	531(m)	505(m)	417(w)
2	1170(m), 1021(s)	661(m)	543(m)	505(m)	417(w)
3	1170(m), 992(s)	659(m)	549(m)	505(m)	417(w)
4	1174(m), 990(s)	654(m)	549(m)	503(m)	415(w)
5	1170(m), 1020(s)	665(m)	553(m)	500(m)	416(w)
6	1170(m), 991(s)	665(m)	553(m)	501(m)	417(w)
7	1170(m), 991(s)	667(m)	553(m)	502(m)	418(w)
8	1170(m), 992(s)	665(m)	553(m)	503(m)	417(w)
9	1170(m), 994(s)	665(m)	552(m)	501(m)	417(w)
10	1171(m), 992(s)	666(m)	553(m)	503(m)	417(w)
11	1197(m), 1025(s)	667(m)	554(m)	492(m)	418(w)
12	1171(m), 990(s)	667(m)	547(m)	495(m)	418(w)
13	1190(m), 992(s)	657(m)	545(m)	501(m)	418(w)
14	1192(m), 992(s)	694(m)	523(m)	501(m)	418(w)
15	1166(m), 994(s)	690(m)	534(m)	505(m)	416(w)

Table 3. ^{1}H NMR data for the compounds

1	1.43–1.57 (m, 30H, $Me_2CCH_2 + 2Cy$), 3.69–3.76 (d, 6H, $2OCH_3$), 7.24–7.26 (m, 5H, C_6H_5)
2	1.16–1.62 (m, 36H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_3}$), 4.13–4.15 (m, 4H, $2OCH_2$), 7.26–7.41 (m, 5H, C_6H_4)
3	0.95 (t, 6H, $2CH_2\mathit{CH_3}$), 1.43–1.72 (m, 34H,$Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2}$), 3.98–4.02 (m, 4H, $2OCH_2$), 7.23–7.39 (m, 5H, C_6H_5)
4	1.30–1.60 (m, 42H, $Me_2CCH_2 + 2Cy + 2OCH\mathit{CH_3CH_3}$), 4.13 (m, 2H, 2OCH), 7.26–7.41 (m, 5H, C_6H_5)
5	0.92 (t, 6H, $2OCH_2CH_2CH_2\mathit{CH_3}$), 1.43–1.86 (m, 38H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2CH_2}$), 4.01 (m, 4H, $2OCH_2$), 7.23–7.28 (m, 5H, C_6H_5)
6	0.90 (t, 6H, $2OCH_2CH_2CH_2CH_2\mathit{CH_3}$), 1.14–1.65 (m, 42H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2CH_2CH_2}$), 4.00–4.05 (m, 4H, $2OCH_2$), 7.30–7.40 (m, 5H, C_6H_5)
7	0.90 (t, 12H, $2OCH_2CH_2CH\mathit{CH_3CH_3}$), 0.95–1.79 (m, 36H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2CH}$), 4.05–4.09 (m, 4H, $2OCH_2$), 7.30–7.40 (m, 5H, C_6H_5)
8	0.90 (t, 6H, $2OCH_2CH_2CH_2CH_2CH_2\mathit{CH_3}$), 1.33–1.69 (m, 46H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2CH_2CH_2CH_2}$), 4.05–4.09 (m, 4H, $2OCH_2$), 7.26 (m, 5H, C_6H_5)
9	0.89 (t, 6H, $2OCH_2CH_2CH_2CH_2CH_2CH_2\mathit{CH_3}$), 1.26–1.66 (m, 50H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2CH_2CH_2CH_2CH_2}$), 4.05 (m, 4H, $2OCH_2$), 7.26 (m, 5H, C_6H_5)
10	0.87 (t, 6H, $2OCH_2CH_2CH_2CH_2CH_2CH_2CH_2\mathit{CH_3}$), 1.26–1.67 (m, 54H, $Me_2CCH_2 + 2Cy + 2OCH_2\mathit{CH_2CH_2CH_2CH_2CH_2CH_2}$), 4.05 (m, 4H, $2OCH_2$), 7.26–7.41 (m, 5H, C_6H_5)
11	1.17–1.85 (m, 30H, $Me_2CCH_2 + 2Cy$), 7.19–7.37 (m, 15H, $2OC_6H_5$, C_6H_5)
12	1.36–1.96 (m, 30H, $Me_2CCH_2 + 2Cy$), 2.34 (s, 6H, $2\mathit{CH_3}C_6H_4$), 7.14–7.24 (m, 13H, $2OC_6H_4 + C_6H_5$)
13	1.36–1.98 (m, 30H, $Me_2CCH_2 + 2Cy$), 2.31 (s, 6H, $2\mathit{CH_3}C_6H_4$), 7.14–7.25 (m, 13H, $2C_6H_4 + C_6H_5$)
14	1.35–1.91 (m, 30H, $Me_2CCH_2 + 2Cy$), 7.23–7.33 (m, 13H, $2OC_6H_4 + C_6H_5$)
15	1.27–1.90 (m, 48H, $Me_2CCH_2 + 2Cy + 2OC_6H_4C\mathit{CH_3CH_3CH_3}$), 7.22–7.32 (m, 13H, $2OC_6H_4 + C_6H_5$)

v_{P-O-C} are strong or medium peaks, located at 1166–1197 cm^{-1}, or bending frequencies at 990–1020 cm^{-1}. Cyclohexyl carbon frame vibrations appear at 1064–1090 and 993–994 cm^{-1}; the methylene asymmetric absorption vibration frequencies are at 2916–2930 cm^{-1}. The bands between 1587–1612 and 1465–1506 cm^{-1} are attributed to aromatic ring vibrations.

^{1}H NMR data

The ^{1}H NMR data are illustrated in Table 3. The ^{1}H NMR chemical shifts of the methylene group, attached to the tin atom and the two methyl groups of the neophyl and cyclohexyl groups overlapp as multiplets and wide peaks, in the range 1.14–1.98 ppm. The chemical shifts of the H atom in the C_6H_5 of the neophyl group exhibit multiples in the range 7.13–7.41 ppm, and overlap with the ^{1}H NMR aromatic groups. The proton NMR chemical shifts of the alkyl groups in the *O*,*O*-dialkyldithiophosphatic group were observed at 3.69–4.15 ppm.

MS data

Compounds **2** and **15** were selected for MS study (Table 4). The peaks of the molecular ion and higher ion are not observed. This means that there is no intermolecular association. The tin atom has ten isotopes and the ion peaks containing tin fragments are generally cluster peaks. Dealkylation to M^+ resulted in $(M - C_6H_{11}{}^+)$ and $(M - R')^+$. The splitting of the Sn—S bond is another of the main breakdown patterns. The small fragment ions that were produced from splitting of the Sn—C and the Sn—S are relatively stable, and the base peaks of both compounds are $CH_3CH{=}C^+CH_2$.

Crystallography

Colorless crystal of the compound $Cy_2NeophylSnS_2P(OC_6H_4{}^tBu\text{-}4)_2$ were obtained by recrystallization from petroleum solvent. Intensity data for a crystal with approximate dimensions of 0.25 × 0.20 × 0.15 mm^3 were measured at 293(2) K on a Bruker SMART 1000 diffractometer using graphite monochromatic **Mo** *Kα* radiation, $\lambda = 0.71073$ Å. A total of 8687 independent reflections were collected in the

Table 4. The mass spectra data for compounds $PhMe_2CCH_2Sn(Cy_2)S_2P(OR)_2$

Fragment ions	*m/e* (abundance)		Fragment ions	*m/e* (abundance)	
	2	**15**		**2**	**15**
M^+	604(0)	811(0)	R'	133(10)	133(24)
$M - C_6H_{11}{}^+$	521(54)	728(6)	SnH^+	121(2)	121(1)
$M - R'^+$	471(12)	628(6)	Sn^+	119(2)	119(6)
$R'Sn^+ (C_6H_{11})_2$	419(3)	419(2)	$C_6H_5CCH_2CH_3^+$	117(10)	117(10)
$R'Sn^+C_6H_{11}$	335(3)	335(3)	$C_6H_5CH_2^+$	91(63)	91(63)
$Sn^+S_2P(OR)_2$	305(42)	513(15)	$C_6H_{11}{}^+$	83(48)	83(69)
$R'Sn^+$	253(16)	253(13)	$C_6H_5^+$	77(7)	77(8)
$SnC_6H_5^+$	197(23)	197(47)	$CH_3CCH_2CH_2$	55(100)	55(100)
$S_2P(OR)_2$	186(2)	394(0)	$CH_3CCH_2^+$	41(50)	41(48)

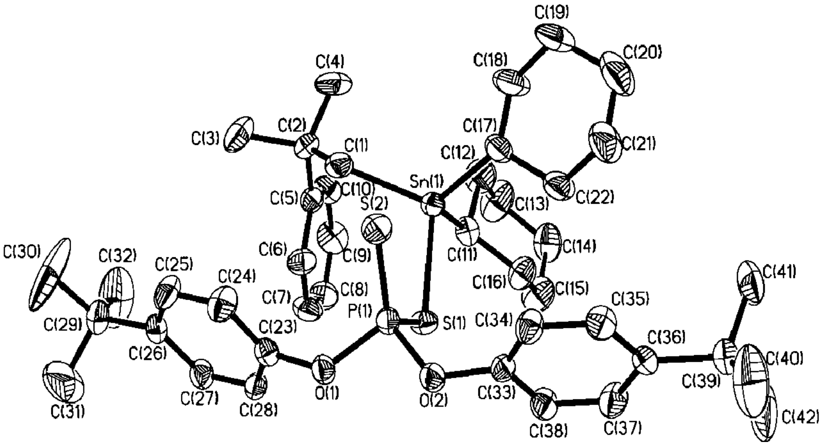


Figure 1. Molecular structure of compound $Cy_2NeophylSnS_2P(OC_6H_4{}^tBu\text{-}4)_2$

range of $1.33 < \theta < 25.03°$ by using the ω–2θ scan technique. The structure was solved from the interpretation of the patterns on synthesis using direct methods, and refined by a full-matrix least-squares procedure on F^2. Nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the calculated positions and were isotropically refined. Absorption correction was made using SADABS.

Table 5. Crystal data and structure refinement for $Cy_2NeophylSnS_2P(OC_6H_4{}^tBu\text{-}4)_2$

Empirical formula	$C_{42}H_{61}O_2PS_2Sn$
Molecular weight	811.69
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal size (mm^3)	0.25 × 0.20 × 0.15
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions	
a (Å)	11.042(6)
b (Å)	12.344(7)
c (Å)	17.095(10)
α (deg)	107.507(10)
β (deg)	107.728(10)
γ (deg)	92.931(11)
Volume (Å^3)	2090(2)
Z	2
Density (calc) (Mg m^{-3})	1.290
Absorption coefficient (mm^{-1})	0.782
F (000)	852
Limiting indices	$-13 \leq h \leq 10$, $-12 \leq k \leq 14$, $-20 \leq l \leq 17$
Reflections collected	8687
Final R indices [$I > 2\ \sigma\ (I)$]	$R = 0.0571$, $wR = 0.1176$
Goodness-of-fit on F^2	1.022
Data/parameters	7334/433
Largest diff. peak, hole (e$^-$ Å^{-3})	0.820, −0.583

The structural details of $Cy_2NeophylSnS_2P(OC_6H_4{}^tBu\text{-}4)_2$ are displayed in Fig. 1 as provided by a single-crystal X-ray diffraction study (Table 5). Selected bond lengths and angles are listed in Table 6. This compound exhibits the tin(IV) center in a distorted tetrahedral geometry defined by the carbon atoms from the methylenes of the neophyl and the two Cy groups, and the sulfur atom, which exists as a bridge between the tin atom and the phosphorus atom. From the data for S1–P1 (2.021 Å) and S2–P1 (1.905 Å), we can infer that there is a stronger bond between S2 and P1. And because of the neophyl arrangement, this makes the two $-OC_6H_4{}^tBu\text{-}4$ groups asymmetric, being slightly different in bond distances and angles. The average of the C–Sn–C

Table 6. Selected bond distances and bond angles

	Bond distances (Å)		
Sn(1)–S(1)	2.477(3)	P(1)–O(2)	1.582(5)
Sn(1)–C(1)	2.133(7)	P(1)–S(1)	2.021(3)
Sn(1)–C(11)	2.152(7)	P(1)–S(2)	1.905(3)
Sn(1)–C(17)	2.143(8)	O(1)–C(23)	1.401(8)
P(1)–O(1)	1.576(5)	O(2)–C(33)	1.398(8)
	Bond angles (deg)		
C(1)–Sn(1)–C(11)	120.7(3)	O(2)–P(1)–S(2)	115.5(2)
C(1)–Sn(1)–C(17)	110.5(3)	O(1)–P(1)–S(1)	106.5(2)
C(11)–Sn(1)–C(17)	115.0(3)	O(2)–P(1)–S(1)	105.7(2)
C(1)–Sn(1)–S(1)	104.4(2)	S(2)–P(1)–S(1)	116.86(13)
C(11)–Sn(1)–S(1)	104.4(2)	P(1)–S(1)–Sn(1)	105.08(9)
C(17)–Sn(1)–S(1)	110.2(2)	C(23)–O(1)–P(1)	123.5(4)
O(1)–P(1)–O(2)	93.4(3)	C(33)–O(2)–P(1)	122.5(4)
O(1)–P(1)–S(2)	115.9(2)	C(2)–C(1)–Sn(1)	119.2(5)

Data is lodged at the Cambridge Crystallographic Data Centre (deposition no. CCDC 18947).

Table 7. Preliminary acaricidal tests of some compounds (200 μg ml^{-1})

Compound	**16**	**1**	**3**	**5**	**6**	**10**	**11**	**13**
Death rate (%)	100	100	100	100	100	100	100	100

angles is 115.4° and that of the C—Sn—S angles is 106.3°, indicating a relatively small distortion from ideal tetrahedral angles because of repulsion existing among the neophyl and the two Cy groups.

Acarcidal activity

At room temperature, we put a quantity of *Tetranychus urticae* on the plant leaves on which had been sprayed solutions of the target compounds; then we observed the number of dead *Tetranychus urticae*. We selected eight compounds for the preliminary acaricidal test using a 200 μg ml^{-1} dose; all the compounds killed *Tetranychus urticae* at 100% (see Table 7).

The results of further of tests of the acaricidal activity of **16** and **2** are shown in Table 8. The miticidal activity is better than the acaricides R-28627[5] and Torque[6] using a 2 μg ml^{-1} dose. From these (2-phenyl-2-methylpropyl) dicyclohexyltin *O,O*-dialkyldithiophosphate compounds we have found a new kind of organo-tin acaricide that is more efficient and has economic benefits.

Table 8. Further tests of acaricidal activity for some compounds

	Death rate (%)				
Concentration (μg ml^{-1})	CK[a]	**16**	**2**	R-28627	Torque
2	2.6	91.1	98.1	95.1	2.6
10	2.6	100	100	100	97.9
20	2.6	100	100	100	100

[a] CK: Control solution, no tin compound added.

REFERENCES

1. Zemlyanskii NI and Drach BS. *Zh. Obshch. Khim.* 1962; **32**: 1962 (*Chem. Abstr.* 1963; **58**: 4450d).
2. Kabachmik MI. *Tetrahedron* 1960; **9**: 10.
3. Imazaki H, Karya H and Fujikawa M. *Jpn Kokai* 1980; **9**: 59; *Chem. Abstr.* 1980; **93**: 39537a.
4. Xie Q-L, Luo N and Li J *et al. Chem. Res. Chin. Univ.* 1992; **8**: 365.
5. Baker DR. *US Patent* 3 919 418, 1976.
6. Horne Jr CA (Modesto, California). *US Patent* 3 657 451, 1972.