APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 6, 193–196 (1992)

Preparation and biocidal properties of mixed butyl/cyclohexyl trialkyltin carboxylates

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Two series of trialkyltin carboxylates containing butyl and cyclohexyl groups on tin, $Bu_nCy_{3-n}SnO_2CR$ ($n = 1, 2$; $R = n-Pr$, Ph, $4-ClC_6H_4$, $4-NO_2C_6H_4$) have been synthesized and their structures characterized by IR, and ^{119}Sn and ^{13}C NMR spectroscopies. The compounds are five-coordinate, carboxylate-bridged polymers when $R = n-Pr$, while the other aromatic carboxylates are four coordinate. The compounds were also tested for their fungicidal, insecticidal and acaricidal activities.

Keywords: Trialkyltin, butyl, cyclohexyl, carboxylates, preparation, biocidal

INTRODUCTION

Trialkyltin derivatives are generally biologically active and they are mainly used as fungicides, pesticides, antifouling coating materials and preservatives for wood.[1] Brestan,[2] $Ph_3SnO_2CCH_3$, introduced by Hoechst, was the only commercial product of triorganotin carboxylates used in crop protection. In order to develop new kinds of organotin agricultural chemicals, we synthesized tricyclohexyltin[3,4] and tributyltin carboxylates[5,6] and tested their acaricidal and fungicidal activities respectively; we found that tricyclohexyltin carboxylates are highly effective acaricides, while tributyltin derivatives are good fungicides.

It is an interesting question whether a compound will have acaricidal and/or fungicidal activities when introducing butyl and cyclohexyl groups into a single molecule. Wishing to find such organotin compounds, we synthesized two series of mixed tri(butyl/cyclohexyl)tin carboxylates by the reactions shown in Eqns [1] and [2].

$$(Bu_2CySn)_2O + 2HO_2CR \rightarrow 2Bu_2CySnO_2CR + H_2O \qquad (1)$$

I-1, $R = n-C_3H_7$; **I-2**, $R = C_6H_5$;

I

I-3, $R = 4-ClC_6H_4$; **I-4**, $R = 4-NO_2C_6H_4$.

$$(BuCy_2Sn)_2O + 2HO_2CR \rightarrow 2BuCy_2SnO_2CR + H_2O \qquad (2)$$

II-1, $R = n-C_3H_7$; **II-2**, $R = C_6H_5$;

II

II-3, $R = 4-ClC_6H_4$; **II-4**, $R = 4-NO_2C_6H_4$.

EXPERIMENTAL

IR spectra were recorded on a Shumaz spectrometer as KBr disks or liquid films. NMR spectra (^1H, ^{13}C, ^{119}Sn) were measured on a JEOL-FX-90Q spectrometer in $CDCl_3$ relative to internal TMS and external $(CH_3)_4Sn$ (for ^{119}Sn). The coupling constants $^nJ(^{119}Sn-^{13}C)$ were obtained from ^{13}C NMR spectra measured with a digital resolution of 0.6 Hz. Elemental analyses were determined on an MT-3 elementary analyzer (Yanaco, Japan). Mass spectra (MS) were recorded on an HP-5988A at 70 eV; the temperature of ionization was 200 °C.

Syntheses

At the refluxing temperature of the solvent, 5 mmol of the mixed trialkyltin oxide and a slight excess of 10 mmol acid were allowed to react for 4–5 h. Then the solvent was removed by rotary evaporation and the product was obtained after purification.

Some data on the products are listed in Table 1.

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0268-2605/92/020193-04 $05.00

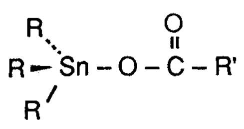
Received 12 July 1991
Accepted 16 December 1991

Table 1 The reaction conditions and elementary analysis of tri(butyl/cyclohexyl)tin carboxylates

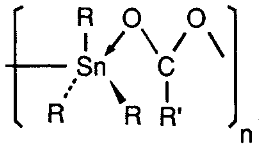
	Conditions				Elementary analysis (%)		
Compd.	Solvent	time(h)	Yield (%)	State (M.p.)	C(Calcd)	H(Calcd)	Formula for calculation
I-1	Toluene	4	91.3	White crystals (59–61 °C)	53.6 (53.6)	9.4 (9.0)	$C_{18}H_{36}O_2Sn$
I-2	Toluene	5	83.2	Colourless viscous oil	58.2 (57.7)	7.6 (7.8)	$C_{21}H_{34}O_2Sn$
I-3	Benzene	5	85.6	Yellow viscous oil	53.4 (53.5	7.2 (7.1)	$C_{21}H_{33}O_2ClSn$
I-4	Benzene	5	87.1	Red viscous oil	52.3 (52.3)	7.2 (6.9)	$C_{21}H_{33}O_4NSn$
II-1	Toluene	4	90.1	White crystals (61–63 °C)	55.9 (55.6)	9.3 (8.9)	$C_{20}H_{38}O_2Sn$
II-2	Toluene	4	81.0	Colourless viscous oil	59.5 (59.6)	7.6 (7.8)	$C_{23}H_{36}O_2Sn$
II-3	Benzene	5	83.3	Yellow viscous oil	55.3 (55.5)	7.3 (7.1)	$C_{23}H_{35}O_2ClSn$
II-4	Benzene	5	84.1	Red viscous oil	54.5 (54.3)	7.3 (6.9)	$C_{23}H_{35}O_4NSn$

RESULTS AND DISCUSSION

There may be two kinds of structures for trialkyltin carboxylates. These are the four-coordinated structures for the monomers (**A**) and the five-coordinated structure for polymers (**B**).

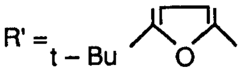


A



B

For example, A^7 includes R = cyclohexyl (Cy) $R' = m-ClC_6H_4$ or $m-BrC_6H_4$. The polymer series $B^{7,8}$ includes $R = Cy$, $R' = n-C_3H_7$; R = Bu or $C_6H_5CH_2$,



The difference between the two kinds of structures can be seen in the IR absorption frequency of the carbonyl group and in the parameters of the ^{119}Sn and ^{13}C NMR.[4,9]

We see from Table 2 that the $\nu^{asym}_{C=O}$ frequency of the $Bu_nCy_{3-n}SnO_2CC_3H_7$ species is about 100 cm^{-1} lower than that of the corresponding benzoates, while the $\nu^{sym}_{C=O}$ is about 45–80 cm^{-1} higher. For butyrates, the difference between $\nu^{asym}_{C=O}$ and $\nu^{sym}_{C=O}$ ($\Delta\nu = \nu^{asym}_{C=O} - \nu^{sym}_{C=O}$) is less than 200 cm^{-1} and it is greater than 300 cm^{-1} for the benzoates. This suggests that the structures of the butyrates may be five-coordinated (**B**) and those of the benzoates may be four-coordinated (**A**).

The NMR data are listed in Table 3. As we have discussed in a previous paper,[9] the chemical shift of ^{119}Sn depends mainly on the electron density around the tin atom, the coordination number and steric factors. So, both the alkyl and the carboxy groups bonded with the tin atom will

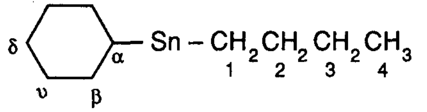
Table 2 IR data of carbonyl group in $Bu_nCy_{3-n}SnO_2CR$ (cm^{-1})

	$n=3$			$n=2$			$n=1$			$n=0$		
	ν^{asym}	ν^{sym}	$\Delta\nu$	ν^{asym}	ν^{sym}	$\Delta\nu$	ν^{asym}	ν^{sym}	$\Delta\nu$	ν^{asym}	ν^{sym}	$\Delta\nu$
$n-C_3H_7$	1548	1411	137	1562	1400	162	1565	1385	180	1536	1404	132
C_6H_5	1650	1334	316	1640	1325	315	1640	1340	300	1647	1340	307
$4-ClC_6H_4$	1650	1338	314	1640	1325	315	1640	1325	315	1650	1349	301
$4-NO_2C_6H_4$	1655	1330	325	1650	1320	330	1650	1320	330	1622	1328	294

Table 3 Main NMR (^{1}H, ^{13}C, ^{119}Sn) data for the compounds **I** and **II**[a, b]

Compd	$\delta(^{119}Sn)$	$^1J(^{119}Sn-^{13}C_\alpha)$	$^1J(^{119}Sn-^{13}C_1)$	$\delta(^{13}C_\alpha)$	$\delta(^{13}C_1)$	$\delta(^{13}C_{C=O})$	$\delta(^1H)$			
I-1	78.17	395.5	332.0	34.07	15.17	177.04	0.92 (9H, m)	1.83–1.14 (25H, m)	2.28 (2H, t, $J=7$ Hz)	
I-2	86.79	376.5	329.6	33.85	15.55	171.4	0.54 (6H, t, $J=7$ Hz)	0.87–1.5 (23H, m)	6.98–7.1 (3H, m)	7.62–7.76 (2H, m)
I-3	90.30	381.4	327.2	33.86	15.55	170.4	0.92 (6H, t, $J=7$ Hz)	1.20–1.88 (23H, m)	7.36 (2H, m)	7.98 (2H, d)
I-4	100.16	383.3	324.7	33.97	15.55	168.7	0.92 (6H, t, $J=7$ Hz)	1.25–1.92 (23H, m)	8.21 (4H, s)	
II-1	45.51	371.1	295.0	33.49	14.30	178.98	0.92 (6H, t, $J=7$ Hz)	1.18–1.83 (30H, m)	2.28 (2H, t, $J=7$ Hz)	
II-2	53.69	368.8	300.0	33.74	14.57	171.2	0.52 (3H, t, $J=7$ Hz)	0.9–1.48 (28H, m)	6.97 (2H, d, $J=6$ Hz)	7.67 (2H, d, $J=6$ Hz)
II-3	58.22	367.4	300.3	33.80	14.63	170.3	0.92 (3H, t, $J=7$ Hz)	1.24–2.02 (28H, m)	7.36 (2H, d, $J=7$ Hz)	7.98 (2H, d, $J=7$ Hz)
II-4	69.55	361.3	307.6	34.02	14.84	168.9	0.92 (3H, t, $J=7$ Hz)	1.20–2.40 (28H, m)	8.22 (4H, s)	
$(Bu_2CySn)_2O$	65.46	307.6	341.8	32.61	15.06	—				

[a] The carbon atoms in the compounds are labelled as follows:



[b] Units: δ is in ppm; J is in Hz.

influence the value of δ ^{119}Sn. For example, with $Bu_nCy_{3-n}SnO_2CC_6H_5$, when n changes from 0 to 3, the δ ^{119}Sn value is 16.5($n=0$),[9] 53.69 ($n=1$), 86.79 ($n=2$) and 110.50 ($n=3$).[5] That may be due to the shielding and steric effect of the cyclohexyl group which can weaken the interaction of the tin atom with the oxygen atom in the carboxy group. Thus, the chemical shift of ^{119}Sn moves to high field along with an increase of the number of cyclohexyl groups. Besides the three alkyl groups, the electronic effect of the carboxylate group will have an influence on the value of δ ^{119}Sn. The value of δ ^{119}Sn for trialkyltin butyrates is about 10 ppm less than that of the corresponding benzoates.

Also, the substituents on the aromatic group have an influence on δ ^{119}Sn. The electron-withdrawing group, NO_2, made the chemical shift of ^{119}Sn move to low field.

The ^{13}C chemical shift can also reflect the structure changes of these compounds, but not so clearly as the ^{119}Sn chemical shift.

The ^{119}Sn–^{13}C coupling constant, $^1J(^{119}Sn-^{13}C)$, however, which is obtained from ^{13}C spectra, can reflect the structure differences as well δ ^{119}Sn. $^1J(^{119}Sn-^{13}C)$ also changed with a change of the substituent on the tin atom. For $Bu_nCy_{3-n}SnO_2CC_6H_5$, for example, the value of $^1J(^{119}Sn-^{13}C_\alpha)$ was 339.3 ($n=0$),[9] 360.8 ($n=1$), 368.6 ($n=2$) and ($n=3$) Hz respectively, while $^1J(^{119}Sn-^{13}C_1)$ was ($n=0$), 300.0 ($n=1$), 322.3 ($n=2$) and 385.9 ($n=3$) Hz.[5] Meanwhile, $^1J(^{119}Sn-^{13}C)$ will change considerably with variation of the electronegativity of the anion bonded to the tin atom in addition to the three alkyl groups.

The mass spectra (MS) of compounds **I-2** and **II-3** were recorded and the main data are listed in

Table 4 Tin-containing fragment-ions observed for compounds **I-2** and **II-3**

Compound I-2			Compound II-3		
m/z	Fragment-ion	Intensity	*m/z*	Fragment-ion	Intensity
381	PhCOOSnBuCy$^+$	44	441	ClPhCOOSnCy$_2^+$	12
355	PhCOOSnBu$_2^+$	81	415	ClPhCOOSnBuCy$^+$	78
297	PhCOOSnC$_4$H$_7^+$	10	357	ClPhCOOSnC$_6$H$_9^+$	1
269	PhCOOSnC$_2$H$_4^+$	24	275	ClPhCOOSn$^+$	100
241	PhCOOSn$^+$	100	177	BuSn$^+$	13
197	PhSn$^+$	34	121	HSn$^+$	19
177	BuSn$^+$	42			
121	HSn$^+$	29			

Table 5 The effectiveness of the compounds in combating fungi and insects[a]

	Fungus[b]								
No.	A	B	C	D	E	F	G	H	I
I-1	88.2	85.7	100	100	88.3	14.3	100	100	100
I-2	88.2	100	100	100	86.7	0	100	100	100
II-1	78.8	85.7	100	100	80.3	0	100	100	100
II-2	76.5	87.5	84.4	84	78.3	0	100	100	100

[a] The concentration was 50 ppm for tests A–E and 500 ppm for F, G, I. For test H, it was 10 μg/fly. The solvent was . . .

[b] The pathogenic fungi A–E are listed in the text (q.v.).

F Oriental pea aphid (*Aphis craccivora* Koch)
G Army worm (*Leucania separata* Walker)
H Housefly
I Two-spotted spider mite (*Tetranychus urticae* Koch

Table 4. For both of them, there are no molecular ion peaks. Dealkylation from the tin atom was the main breakdown pattern for the two compounds. The ions formed by dealkylation were precursor ions and they further split into other fragment ions. The base peaks of the two compounds are at m/z 241 and 275 respectively. This represents the ion $ArCOOSn^+$. This shows that the tin–oxygen bond is relatively stable.

Bioactivity

The bioactivities of these compounds were tested and the results are shown in Table 5. The antifungal activities of asymmetric tri(butyl/cyclohexyl)tin carboxylates to some plant pathogenic fungi were tested by the agar dilution method at a concentration of 50 ppm. The chemicals were applied in the culture medium and the fungus cakes to be tested were placed on the surface of the medium. Growth of the fungi was then observed.

The test strains used were as follows:

A *Rhizoctonia* cotton rot (*Rhizoctonia solani* Kuehn)
B Wheat Scab (*Gibberella zeae* (Schw.) Petch)
C Apple Ring rot (*Macrophoma kuwatsukai* Hara)
D Tomato grey mold (*Botrytis cinerea* Pers)
E *Cercospora* beet leaf spot (*Cercospera beticola* Sacc.)

The results showed that these asymmetric tri(butylcyclohexyl)tin carboxylates have strong antibiotic activities to plant pathogenic fungi, especially to C and D.

Insecticidal and acaricidal activities were tested on the green bean plant at 500 ppm. The killing rate after 24 h for two-spotted spider mites (*Tetranychus urticae* Koch), houseflies and army worms (*Leucania separata* Walker) is 100%, but they produced little effect against the oriental pea aphid (*Aphis craccivora* Koch). The killing rate was assessed by checking the numbers of dead and live mites, by means of a binocular microscope.

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