PREPARATION, STRUCTURE AND BIOLOGICAL ACTIVITIES OF MIXED METHYLDICYCLOHEXYLTIN CARBOXYLATES

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Abstract: The mixed trialkyltin derivatives, obtained by introducing different alkyls on tin atom, have provoked more interests for their multi-bioactivities. And it has become an important branch of organotin chemistry. A series of novel mixed methyldicyclohexyltin carboxylates were synthesized and characterized through IR, ^{1}H,^{119}Sn,^{13}C NMR and MS. The results showed that the structures of the compounds are dependent on the steric and electronic effects of the carbonyl group. The preliminary pesticidal tests show that all the compounds have excellent acaricidal activity and many of them also exhibit good insecticidal, fungicidal and herbicidal activities. The biological activities are mainly determined by the methyl and cyclohexyl on tin atom and has close relations with the anion group.

Introduction

It is well known that the biological activities and selectivities of trialkyltin derivatives depend mainly on the alkyl groups. For example, tributyltin derivatives possess strong fungicidal activity and tricyclohexyltin derivatives are good acaricide. The mixed trialkyltin compounds, in which the three alkyl groups on tin atom are different, are becoming a new developing field of the organotin chemistry. It is an interesting question that whether a trialkyltin derivative with different alkyl groups on tin atom would be multi-bioactive.

It has been shown that the fungicidal activity of the compounds $Cy_nPh_{3-n}SnOH$ is decreased when n changes from 0 to 3, while the acaricidal activity changes adversly. [1] We have reported that the mixed butyl/cyclohexyl trialkyltin carboxylates have strong antibiotic activities both to plant pathogenenic fungi and two-spotted spider mites [2] and a new pesticide possessed both acaricidal and fungicidal activities was developed.[3] In this paper, we report the synthesis, structure and biological activities of methyldicyclohexyltin carboxylates. The reaction equations are listed in the following:

$$(MeCy_2Sn)_2O + 2\ HO_2CR \longrightarrow 2\ MeCy_2SnO_2CR + H_2O \qquad (1$$

R=								
	CH_3OCH_2	1;	$C_2H_5OCH_2$	2;	$n\text{-}C_3H_7OCH_2$	3;	$i\text{-}C_3H_7OCH_2$	4;
	$n\text{-}C_4H_9OCH_2$	5;	$n\text{-}C_5H_{11}OCH_2$	6;	$n\text{-}C_6H_{13}OCH_2$	7;	$n\text{-}C_8H_{17}OCH_2$	8;
	$\alpha\text{-}C_{10}H_8OCH_2$	9;	$2,4\text{-}Cl_2C_6H_3OCHMe$	10;	$2,4\text{-}Br_2C_6H_3OCHMe$	11;	cyclo-C_6H_{11}	12;
	$C_6H_5CH_2$	13;	$CH_3CONHCH_2$	14;	$CH_3SCH_2CH_2CH(NH_2)$	15;	$CH_3CH(NH_2)$	16;
	$HO_2CCH{=}CH$	17						

$$(MeCy_2Sn)_2O + HO_2CRCO_2H \longrightarrow MeCy_2SnO_2CRCO_2SnCy_2Me + H_2O \qquad (2$$

R= -CH(NH$_2$)- 18 - 19; -CH$_2$- 20; -(CH$_2$)$_2$- 21;
-(CH$_2$)$_6$- 22; -(CH$_2$)$_8$- 23; P-C$_6$H$_4$- 24; O-C$_6$H$_4$- 25;
cis-CH=C- 26; trans-CH=CH- 27

$$[Cy_2MeSn]_2O + X_n\text{-}C_6H_{5\text{-}n}OCH_2CO_2H \longrightarrow X_n\text{-}C_6H_{5\text{-}n}OCH_2CO_2SnMeCy_2 + H_2O \quad (3$$

X= H 28; 4-Me 29; 2-Me 30; 3-Me 31;
3,5-Me$_2$ 32; 2,4-Me$_2$ 33; 3,4-Me$_2$ 34; 2,3-Me$_2$ 35;
2,6-Me$_2$ 36; 4-MeO 37; 2-MeO 38; 2-MeO,4-CH$_2$=CHCH$_2$ 39;
4-Cl 40; 2-Cl 41; 3-Cl 42; 2,4,5-Cl$_3$ 43;
4-Br 44; 2-Br 45; 4-1 46; 3-NO$_2$ 47

Experiments

1. Instrument

Elemental analyses was performed by Yanaco Corder MT-3. Infrared spectra were obtained on a Nicolet 5DX FT spectrometer as liquid films or KBr water in 400-4000cm^{-1}. NMR spectra were acquired on a BRUKER AC-P200 spectrometer in CDCl$_3$ with reference to internal TMS and external Me$_4$Sn(for ^{119}SnNMR). MS were obtained on a Hewlett-Packard-5988A at 70eV with temperature of ionization at 200℃.

2. synthesis of starting materials.

All carboxylic acids and SnCl$_4$ are laboratory reagents. [Cy$_2$MeSn]$_2$O was prepared by the following steps[4]:

$$Me_2SnCl_2 \xrightarrow{CyMgCl} Me_2SnCy_2 \xrightarrow{SnCl_4} \underset{(A)}{MeCy_2SnCl} \xrightarrow{NaOH/H_2O} \underset{(B)}{(MeCy_2Sn)_2O}$$

(A): yield(%): 80.5, m.p. 52-54℃

(B): yield(%): 95.5, viscous oil, elemental analysis(%): C(Calcd.): 51.01(50.69); H(Calcd.): 8.30(8.18).

3. Synthesis of the products

At the refluxing temperature of the solvent, the solution of 2.50 mmol of (Cy$_2$MeSn)$_2$O and 5.18 mmol of the carboxylic acid or 2.59 mmol of dicarboxylic acid in benzene(25ml) were allowed to react for 4-6h. The solvent was removed by rotary evaporation and the raw product was got after cooling. The pure product was recrystallized from alcohol.

The yields and some analytical data of the products were listed in Table 1.

Table 1. Some Important Data of Products

No.	yield(%)	m.p.(℃) or n_d	elemental analysis(%) C(calcd.)	H(calcd.)	ν_{co}(cm^{-1}) asym***	sym	Δν
1	95.4	65-67	49.42(49.83)	7.68(7.79)	1556	1380	176
2	95.7	50-52	50.50(50.61)	7.97(8.00)	1566	1392	174

5	96.6	56-58	52.37(52.91)	8.22(8.43)	1559	1401	158
6	94.9	48-50	53.80(53.94)	8.63(8.62)	1558	1392	166
7	95.2	1.5049	54.61(54.91)	8.96(8.80)	1573	1396	177
8	95.5	1.4980	56.95(56.68)	9.51(9.12)	1580	1369	211
9	91.4	83-85	59.79(59.90)	6.87(6.85)	1583 (1663)	1381	202
10	96.3	66-68	49.28(49.40)	6.06(6.05)	1596 (1645)	1381	215
11	96.6	76-78	42.18(42.41)	5.03(5.19)	1595 (1645)	1379	216
12	91.7	71-74	56.72(56.22)	8.42(8.51)	1558 (1617)	1395	163
13*	92.8	60-62	57.71(57.95)	7.50(7.43)	1558	1380	178
14*	82.5	146-148	49.25(49.06)	7.73(7.52)	1560	1381	179
15	62.8	77-80	48.64(48.22)	7.87(7.89)	1505	1362	143
16	73.4	121-123	49.43(49.50)	7.86(8.07)	1504	1362	142
17	84.6	135-137	49.11(49.18)	6.84(6.81)	1557	1395	162
18	80.2	105-107	48.58(48.56)	7.64(7.46)	1553	1379	174
19	80.4	273	48.71(48.87)	7..38(7.34)	1606 (1623)	1435 (1312)	171 (311)
20	88.1	85-88	49.44(49.60)	7.39(7.48)	1573	1389	184
21	91.8	88-91	50.01(50.31)	7.49(7.61)	1545	1378	167
22	90.0	127-129	52.94(52.87)	8.09(8.11)	1556	1380	176
23	93.3	98-100	54.10(54.02)	8.36(8.33)	1536	1392	144
24	88.4	121-123	53.14(53.43)	7.08(7.14)	1628 (1617)	1303 (1309)	325 (308)
25	92.2	82-84	53.49(53.43)	7.14(7.14)	1562 (1626)	1376 (1320)	186 (304)
26	86.9	83-85	50.55(50.45)	7.53(7.35)	1559 (1601)	1402 (1397)	157 (304)
27	93.6	128-130	49.89(50.45)	7.33(7.35)	1558 (1622)	1363 (1312)	195 (310)
28	94.4	76-78	55.86(55.91)	7.22(7.15)	1579 (1660)	1392	187
29	91.4	69-71	56.84(56.80)	7.35(7.37)	1575	1388	187
30	91.5	72-74	56.97(56.80)	7.38(7.37)	1570 (1658)	1398	172
31	90.8	86-88	56.84(56.80)	7.35(7.37)	1570 (1664)	1394	176

The Continue of Table 1.

No.	yield(%)	m.p.(℃)	elemental	analysis(%)	$\nu_{co}(cm^{-1})$		
		or n_d	C(calcd)	H(calcd.)	asym***	sym	Δν
32	93.5	98-100	57.63(57.65)	7.60(7.57)	1570	1394	176
33	92.4	69-71	57.83(57.65)	7.66(7.57)	1594	1391	203
34	94.1	120-122	57.75(57.65)	7.56(7.57)	1573	1391	182
35	92.7	105-107	57.63(57.65)	7.62(7.57)	1570	1391	179
36	91.6	45-47	57.63(57.65)	7.60(7.57)	1576	1404	172
37	92.3	55-57	54.75(54.91)	7.28(7.12)	1556 (1660)	1386	170
38**	95.5	78-80	52.70(52.93)	7.25(7.27)	1617	1405	212
39**	94.0	63-65	55.49(55.69)	7.49(7.48)	1625	1407	218
40	94.1	90-92	51.84(51.95)	6.43(6.44)	1579 (1668)	1389	190
41	93.2	95-97	51.90(51.95)	6.54(6.44)	1578	1400	178
42	93.7	96-98	51.84(51.95)	6.57(6.44)	1571	1393	178
43	91.0	102-104	45.87(45.49)	5.30(5.27)	1593	1403	190
44	95.0	96-98	47.58(47.58)	5.88(5.89)	1577	1390	187
45	94.3	108-110	47.54(47.58)	5.77(5.89)	1574	1393	181
46	94.2	88-90	43.89(43.71)	5.57(5.41)	1577	1403	174
47*	93.9	116-118	49.97(50.84)	6.38(6.30)	1590	1397	193

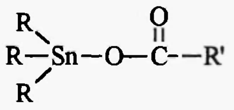
* N% = 13, 2.10(1.95); 14, 3.62(3.37); 47, 2.91(2.77)

** Contain a crystal water in its molecule.

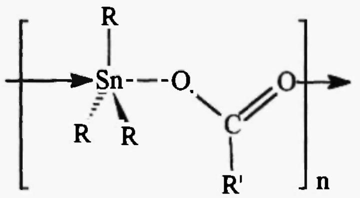
*** Data in the solvent $CHCl_3$ are in the parentheses.

Results and Discussions.

Since the vacant 5d orbital of tin atom is likely to hold the lone-pair electrons of strong electron negative atom to form a high coordinate compound,[5] the trialkyltin carboxylates have the five-coordinated structure for the polymer(B) besides the four-coordinated one for the monomer (A).

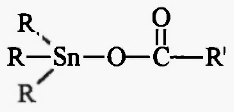


(A)

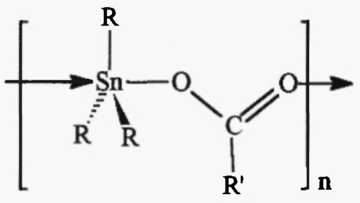


(B)

The different kinds of structures can be infered by the analysis of the IR, NMR, MS spectroscopies of the compounds.



(A)



(B)

The different kinds of structures can be infered by the analysis of the IR, NMR, MS spectroscopies of the compounds.

1 IR spectra

The vibration frequencies of carbonyl groups of trialkyltin carboxylates are important information for determining their structures(see Table 1). When the structure changes from (A) to (B), the asymmetric absorption frequency ($\nu_{CO_2}^{as}$) of carbonyl group is lowered, while the symmetric frequency(ν_{CO}^{s}) is raised . Thus the frequency difference between the two ($\Delta\nu$) in five-coordinated structure becomes smaller[2] We can see from table 1 that the $\nu_{CO_2}^{as}$ and ν_{CO}^{s} of our products are 1505-1628 and 1303-1435 cm^{-1} respectively. For the most of the compounds, the value of $\Delta\nu$ is smaller than 200cm^{-1}and it is much smaller than that of methyldicyclohexyltin benzoates mentioned previously[4]. These data suggest that the compounds may be five-coordinated. But the values of $\Delta\nu$ for the compounds 10, 11, 38 and 39 are 215, 216, 212 and 215 cm^{-1} respectively. In order to make out that whether they have the different structure with the other compounds, the crystal and molecular structure of 11($2,4\text{-}Br_2C_6H_3OCH(CH_3)CO_2SnCy_2Me$) and 39($2\text{-}CH_3O,4\text{-}CH_3CH{=}CHC_6H_3CO_2SnCy_2Me$) were determined by X-ray diffraction.[6] The analysis of the crystal structures shows that the compound 11 is also five coordinated, carboxylate-bridge polymer (B). But the oxygen atom which coordinates to the tin atom in compound 39 is not the one in carbonyl group, but the one comes from the crystal water in its molecula. (The elemental analysis and IR has also proved the presence of the crystal water in the molecules of compounds 38 and 39. ν_{H_2O} : 3457cm^{-1}, 3456cm^{-1}). And the two hydrogen atoms in the crystal water bond to the oxygen atoms in carbonyl group and o-MeO group , respectively. The presence of the hydrogen bond makes the $\Delta\nu$ value much smaller than that of common trialkyltin carboxylates.

In the IR spectra, It can be seen that the absorbtion of the vibration of carbonyl group appears to be a broad peak, and it becomes a sharp narrow one when dissolved in CCl_4. This may be due to the fact that the coordination of the oxygen atom in carbonyl to tin in solid state and the difference of the three alkyl groups make the carbonyl group have different enviroment in the molecule. Therefore, the spectrum of $\nu_{CO_2}^{as}$ are broaded . This is also an evidence of structure (B).

2. NMR

The ^{1}HNMR data are listed in Table 2. (Since there is no proper solvent, the NMR of compounds 15 and 16 has not been determind). The chemical shifts of ^{1}H in $Sn\text{-}CH_3$ are in the range of 0.29-0.45*ppm* with triple peak for coupling of tin atom with hydrogen. The coupling constant $^2J_{Sn\text{-}H}$ are 32.4-45.1*Hz*, which are influenced by the substituents on the carbonyl groups. For an example, the $^2J_{Sn\text{-}H}$ of compound 11 (2,4-Cl_2 substituentd) is smaller than that of the compound 12(2,4-Br_2 substituentd). Obviously, it is caused by the electronic effect. The steric effect makes the $^2J_{Sn\text{-}H}$ of compound 24(para-dibenzoate) bigger than that of the compound 25(ortho-dibenzoate). It deserves to be mentioned that $^2J_{Sn\text{-}H}$ of compound 27 is much smaller than that of compound 26($^2J_{Sn\text{-}H}$ = 32.7 and 42.9*Hz* respectively) because that the trans-structure of 27 have favourable space arrangement. All data of the coupling constants between tin and hydrogen atoms have shown that these compounds are of the same kind of structure in the solution.

The ^{1}H chemical shift of cyclohexyl group is multiple and is in the range of 1.24-2.02*ppm* except compound 27, whose δ (^{1}H)is bigger because of its less shielded space arrangement. The ^{1}H chemical shift of the other groups of the compounds lie in the cooresponding normal ranges. In compound 14, the chemical shift of ^{1}H is different from that of the amides, it is a single broad peak in 6.11*ppm*. This is may be caused by the influence of carbonyl group.

The ^{1}H chemical shift of $-CH_2O-$ is in the range of 3.99-4.73*ppm* and it is obviously bigger for aryloxymethyl than that for alkyloxy methyl. The ^{1}H chemical shifts of benzene ring are influenced by the substituents on the ring. In the graph of the para-substituted compounds, the symmetric AA'BB' peaks of the 1,4-para-substituentd benzene ring can be clearly observed and the coupling constants are in the range of 8.4-10.0*Hz*.

The ^{13}C, ^{119}Sn NMR of some aryloxyacetate are also be determined(see table 3).

The coupling constants of $^{119}Sn-^{13}C$ obtained from ^{13}CNMR are important parameters for the stucture characcterization of organotin compounds. The $^{1}J(^{119}Sn-^{13}C_{\alpha})$ values are between 388.4 and 394.0*Hz* and $^{3}J(^{119}Sn-^{13}C_{\gamma})$, which hardly changed, lie in the range of 64.8-66.6*Hz*. These constants are bigger than those of the corresponding tricyclohexyltin derivaties. This may be caused by the methyl group whose volume are much smaller than that of the cyclohexyl.

A slight structural change of organotin compounds would be reflected on the ^{119}Sn chemical shift. The δ (^{119}Sn) is in the range of 93.23-99.71*ppm*. For the small steric effect of the methyl group on the tin atom, the value of δ (^{119}Sn) is larger than that of tricyclohexyltin derivative, the δ (^{119}Sn) moves to downfields[7]. Compared with the corresponding methyldicyclohexyltin arylcarboxylates[4], the substituent on phenyl group of aryloxyacetate has smaller influence on δ (^{119}Sn), since this influence has been weakened by $-OCH_2-$.

For the methyldicyclohexyltin aryloxyacetates, we found a linear relationship between δ (^{119}Sn) and the Hammett constants (σ) of the substituents of the corresponding compounds by the linear regresion:

$\delta(^{119}Sn)=6.23\sigma+94.67$, r=0.943(for compds: **28**,**37**,**42**,**44**,**46**,**47**)

The linear relationship also prove that these compounds have similar structure.

Table 2. Chemical Shifts of ^{1}HNMR of Some Products(*ppm*)

No	CH_3-Sn ($3H,t$)	$^{2}J_{Sn-H}$ (*Hz*)	cyclo-C_6H_{11}-Sn and $(CH_2)_n$ (*m*)	others
1	0.35	44.54	1.33-1.89(22H)	3.99(2H,s,CH_2O), 3.40(3H,s,CH_3)
2	0.35	43.99	1.32-1.89(22H)	4.03(2H,s,CH_2O), 3.54(2H,q,OCH_2) 1.22(3H,t,CH_3)
3	0.35	44.54	1.33-1.89(24H)	4.03(2H,s,CH_2O), 3.45(2H,t,OCH_2) 0.90(3H,t,CH_3)
4	0.35	44.54	1.33-1.89(22H)	4.02(2H,s,CH_2O), 3.64(1H, m,OCH) 1.16(6H,d,2CH_3,J=6.1*Hz*)
5	0.34	43.99	1.29-1.89(26H)	4.01(2H,s,CH_2O), 3.48(2H,t,OCH_2) 0.88(3H,t,CH_3)
6	0.35	44.54	1.33-1.89(28H)	4.02(2H,s,CH_2O), 3.47(2H,t,OCH_2), 0.86(3H,t, CH_3)
7	0.34	42.88	1.26-1.90(30H)	4.02(2H,s,CH_2O), 3.47(2H,t,OCH_2) 0.85(3H,t,CH_3)
8	0.34	42.88	1.24-1.90(34H)	4.02(2H,s,CH_2O)3.47(2H,t,OCH_2) 0.85(5H,m,CH2CH_3)
9	0.38	44.39	1.32-1.92(22H)	4.73(2H,s,CH2O), 7.05-7.75(7H,m,a-C10H7)
10	0.34	43.99	1.31-1.83(22H)	4.69(1H,q,CHO), 1.66(3H,d,CH_3) 6.72-7.34(3H,m,ArH)
11	0.33	45.09	1.30-1.83(22H)	4.67(1H,q,CHO), 1.62(3H,d,CH_3) 6.67-7.27(3H,m,ArH)
12	0.29	44.68	1.23-1.88(33H)	

13	0.32	44.68	1.33-1.86(22H)	3.61(2H,s,CH_2),7.21(5H,t,ArH)
14	0.31	43.98	1.33-1.88(22H)	1.99(3H,s,CH_3),3.96(2H,d,OCH_2),6.11(1H,br,NH)
17	0.46	43.98	1.37-2.02(22H)	6.36(2H,s,CH=CH),11.83(1H,s,HO_2C)
18	0.31	45.08	1.32-1.84(44H)	2.55-2.84(2H,m,NH_2),3.71(1H,m,CH)
19	0.30	45.09	1.32-1.91(44H)	
20	0.32	43.44	1.34-1.89(44H)	3.34(2H,s,CH_2)
21	0.41	44.54	1.34-1.89(44H)	2.57(4H,s,CH_2CH_2)
22	0.30	43.99	1.27-1.89(52H)	2.27(4H,t,$2CH_2CO$)
23	0.29	43.99	1.27-1.89(56H)	2.26(4H,t,$2CH_2CO$)
24	0.43	45.08	1.38-1.98(44H)	8.05(4H,s,ArH)
25	0.39	43.98	1.37-1.99(44H)	7.37(2H,m,ArH),7.61(2H,m,ArH)
26	0.35	42.88	1.35-1.93(44H)	6.13(2H,s,cis-CH=CH)
27	2.24	32.37	2.95-3.36(44H)	6.90(2H,s,trans-CH=CH)
28	0.38	43.85	1.34-1.92(22H)	4.60(2H,s,CH_2O).6.87-7.29(5H,m,ArH)
29	0.38	45.09	1.34-1.91(22H)	4.58(2H,s, CH_2O),6.79 and 7.05(2H, d,ArH, J=8.4*Hz*),2.20(3H,s,CH_3)
30	0.39	44.54	1.34-1.91(22H)	4.63(2H,s, CH_2O),6.67-7.14(4H,m,ArH),2.28(3H,s,CH_3)
31	0.38	44.39	1.34-1.90(22H)	4.56(2H,s, CH_2O),6.70-7.12(4H,m,ArH),2.28(3H,s,CH_3)
32	0.36	44.39	1.33-1.90(22H)	4.55(2H,s,CH_2O),6.50-6.57(4H,m,ArH),2.24(3H,s,CH_3)
33	0.39	44.39	1.33-1.91(22H)	4.57(2H,s,CH_2O),6.56-6.93(4H,m,ArH),2.19(3H,s,CH_3)
34	0.37	44.39	1.33-1.91(22H)	4.55(2H,s,CH_2O),6.69-6.96(4H,m,ArH),2.19(3H,5,CH_3)
35	0.38	44.89	1.33-1.92(22H)	4.58(2H,s,CH_2O),6.58-6.97(4H,m,ArH),2.22(3H,s,CH_3)
36	0.39	45.09	1.36-1.96(22H)	4.36(2H,s,CH_2O),6.36(3H,m,ArH),2.28(6H,s,$2CH_3$)
37	0.36	44.39	1.33-1.90(22H)	4.52(2H,s,CH_2O),6.76-6.84(4H,q,ArH),3.72(3H,s,OCH_3)
38	0.34	43.98	1.30-1.87(22H)	4.63(2H,s,CH_2O),6.75-6.86(4H,m,ArH),3.83(3H,s,OCH_3)
39	0.35	42.88	1.23-1.88(22H)	4.62(2H,s,CH_2O),6.67(3H,m,ArH),3.83(3H,s,OCH_3),3.29(2H,d,CH_2),5.04(2H,m, CH_2=),5.80(1H,m,=CH)
40	0.37	44.39	1.34-1.90(22H)	4.55(2H,s,CH_2O),6.81and 7.20(2H,d,ArH, J=10.0*Hz*)
41	0.37	44.68	1.38-1.88(22H)	4.67(2H,s,CH_2O),6.67-7.36(4H,m,ArH)
42	0.35	44.68	1.32-1.88(22H)	4.67(2H,s,CH_2O),6.67-7.36(4H,m,ArH)
43	0.39	45.48	1.33-1.90(22H)	4.65(2H,s,CH_2O),6.84,7.44(2H,d,ArH)
44	0.37	44.54	1.33-1.89(22H)	4.54(2H,s,CH_2O),6.76 and 7.33(2H, d,ArH, J=8.8 *Hz*)
45	0.38	45.09	1.32-1.89(22H)	4.66(2H,s,CH_2O) 6.73-7.54(4H,m,ArH)
46	0.37	43.88	1.33-1.89(22H)	4.54(2H,s,CH_2O) 6.66 and 7.52 (2H,d,ArH,J=8.8*Hz*)
47	0.39	45.09	1.33-1.92(22H)	4.67(2H,s,CH_2O),7.24-7.68(4H,m,ArH)

Table 3. The Chemical Shifts of ^{119}Sn and ^{13}C NMR of Some Products*

No	δ (^{119}Sn) (*ppm*)	δ^{13}C(*ppm*)				
		Sn-CH_3	cyclo-C_6H_{11}	C=O, CH_2O	Ar	others
28	95.56	-7.13(266.3)	34.22(394.0),30.44, 28.59(66.6),26.72	173.58,65.51	158.09,129.37,121.28, 114.66,121.28,129.37	
30	94.15	-7.28(266.3)	34.02(388.6),30.37, 28.49(64.7),26.65	173.78,65.86	156.27,130.81,127.10, 126.50,120.97,111.13	16.20
37	93.23	-7.39(266.3)	34.03(393.6),30.30, 28.49(64. 8),26.61	173.81,65.61	154.12,152.29,115.56, 114.48,152.29,115.56	66.35
41	95.72	-7.45(266.3)	33.76(388.4),30.04, 28.21(66.6),26.34	172.59,66.11	153.57,130.03,107.00, 122.70,121.49,113.21	
42	96.83	-7.36(266.3)	34.03(388.4),30.36, 28.49(66.6),26.61	172.84,65.63	156.55,128.94,125.88, 115.75,125.88,128.94	
44	95.52	-7.34(266.3)	33.35(394.0),30.22, 28.34(66.6),26.47	172.88,65.62	157.10,131.91,116.26, 113.17,116.26,131.91	
46	94.75	-7.22(266.3)	34.17(393.0),30.41, 28.53(65.5),26.65	172.53,65.64	158.03,138.11,117.04, 83.35,117.04,138.11	
47	99.71	-7.35(266.3)	34.01(394.0),30.18, 28.30(66.6),26.40	172.25,65.63	158.50,148.84,129.64, 121.61,115.86,108.62	

* Data in parentheses are the coupling constants of ^{13}C-^{119}Sn

3. MS

The main data of mass spectra of some compounds are listed in Table 4. The fragmentions of MS depend on the structure of the compounds and there are some common features: **a)**. Dealkylation is one of the main break-down patterns, the abundance of the ions formed by dealkylation depends on the properties of the carbonyl groups, The values of abundances have clearly shown that the fragment ion $RCO_2SnCy_2^+$ formed by demethylation is not as stable as the fragment ion $RCO_2SnMeCy^+$ formed by decyclohexylation, which even becoms the base peak of some compounds. For an example, the compound 14, the decyclohexylation makes the coordination of the oxygen in acetyl to the tin atom much easier, and forms a stable fragment ion of seven-member ring(see Fig. 1) :

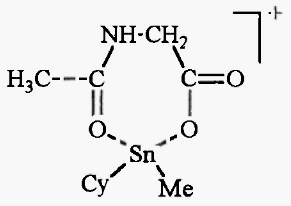


Fig. 1

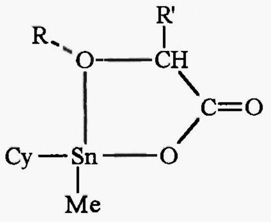


Fig. 2

and M-Cy^+ is base peak. For alkyloxyacetates, a stable five-member ring, whose abundance is relatively big, may be formed after the decyclo-hexylation (see Fig. 2), **b)**. the aboundance of fragment ion $SnMe^+$ is very large in all determined compounds and in the compound 18 $SnMe^+$ Becomes the base peak. This may be explained by the stable of Sn-Me bond. **c)**. The proton transformation can be observed in the dealkylation. **d)**. The ions formed by dealkylation can further be split into smaller fragment ions. The ion CH_3CH-CH-CH_2^+ from Cy^+ is the base peak for most of the compounds.

Table 4. Important MS Data of Some Compounds

No	M	M/Z(abund.)											
		$M\text{-}Me^+$	$M\text{-}Cy^+$	$HM\text{-}2Cy^+$	Cy_2MeSn^+	Cy_2SnH^+	$HSnCyMe^+$	$CySn^+$	$MeSn^+$	SnH^+	Sn^+	Cy^+	$C_4H_7^+$
6	446	431(2.1)	363(98.3)	281(57.0)	301(55.8)	285(23.7)	219(35.5)	203(9.8)	135(99.6)	121(23.4)	120 (16.0)	83 (47.2)	55 (100)
10	534	519(1.0)	451(71.4)	367(15.7)	301(14.8)	285(5.5)	219(20.0)	203(8.1)	135(68.3)	121(15.8)	120 (15.5)	83 (62.2)	55 (100)
14	417	402(0)	334(100)	251(3.3)	301(12.7)	285(5.1)	219(13.7)	203(5.5)	135(40.9)	121(10.9)	120 (7.8)	83 (9.7)	55 (35.1)
18	718	703(0)	635(0)	553(0)	301(25.0)	285(4.0)	219(58.0)	203(13.0)	135(100)	121(14.0)	120 (12.0)	83 (96.0)	55 (87.0)
25	764	751(0)	681(13.0)	599(0)	301(6.0)	285(9.0)	219(44.0)	203(5.0)	135(64.0)	121(6.0)	120 (5.0)	83 (72.0)	55 (100)
28	452	437(0)	369(46.5)	287(24.8)	301(5.5)	285(24.8)	219(7.5)	203(5.1)	135(63.8)	121(13.1)	120 (9.4)	83 (70.6)	55 (100)
39	522	507(0)	439(51.1)	357(6.3)	301(5.1)	285(10.9)	219(12.9)	203(5.5)	135(48.6)	121(11.0)	120 (8.7)	83 (49.3)	55 (100)
42	486	471(1.4)	403(60.0)	321(41.5)	301(11.8)	285(2.1)	219(10.7)	203(7.6)	135(77.8)	121(12.4)	120 (12.0)	83 (79.5)	55 (100)
47	497	482(0)	414(19)	331(5)	301(3)	285(0)	219(10)	203(5.0)	135(36.0)	121(8.0)	120 (6.0)	83 (100)	55 (94.0)

Table 5. Results of Preliminary Bioassay

No.	C.R.S (250ppm)	Fungicidical Activity (Prtri dish test(in vivo))					Herbicidical Activity (2.25Kg/ha)												Plant growth-regulating activity (10ppm)		
							Soil Treatment						Stem Lesf Treatment								
		F1	F2	F3	F4	F5	H1	H2	H3	H4	H5	H6	H1	H2	H3	H4	H5	H6	P1	P2	P3
1	A	C	B	B	C	A	D	D	D	C	D	A	B	A	B	A	A	D	-B	D	-D
2	A	B	B	B	C	C	D	D	D	D	D	B	A	A	B	A	A	A	-A	C	C
3	A	B	A	B	A	A	C	D	D	D	C	A	A	A	B	A	A	A	-B	D	D
4	A	C	C	C	D	D	C	D	D	D	D	A	B	A	A	A	A	A	-B	D	D
5	A	B	A	B	C	A	D	D	D	D	D	B	A	A	A	A	A	A	-B	D	D
6	A	C	C	C	C	C	D	D	D	D	C	A	A	A	A	A	D	A	-B	D	D
7	A	A	A	A	A	A													-B	D	D
8	A	B	B	C	C	B	A	A	D	A	D	A	A	A	D	A	A	A	-B	C	D
9	A	A	A	A	A	A	D	D	D	B	A	A	D	D	D	A	C	A	-B	-A	D
10	A	A	A	A	A	A	B	A	D	A	A	A	A	A	C	A	A	A	-C	-D	D
11	A	A	A	A	A	A	C	D	C	B	A	A	D	D	D	A	C	A	-C	D	-C
12	A	D	D	D	D	D	C	D	D	D	D	C	A	A	D	A	A	A	-B	A	D
13	A	A	A	A	A	A	B	A	D	D	D	A	C	C	D	A	B	A	-B	-B	D
14	A	A	B	A	A	A	A	A	C	B	C	A	A	D	D	A	A	A	-A	D	D
16	A	C	D	D	D	B	D	C	D	D	D	D	D	D	D	D	D	D	-D	-D	-D
17	A	A	A	A	A	A	A	A	A	C	D	A	A	C	D	A	A	A	-A	C	D
18	A	A	B	A	A	A	A	A	D	A	D	A	A	D	D	A	A	A	-B	D	D
19	A	A	A	A	A	A	A	A	B	A	C	A	A	A	D	A	A	A	-A	D	D
20	A	B	A	B	C	A	C	D	D	C	B	C	B	A	A	A	A	A	-B	D	-D
21	A	B	B	B	C	A	B	D	D	B	D	D	A	A	D	A	A	A	-B	C	D
22	A	C	C	C	D	C	D	D	D	D	B	D	B	D	D	A	D	D	-B	D	D
23	A	B	A	B	C	A	D	D	D	D	D	D	A	B	D	A	C	C	-C	D	D
24	A	B	A	B	A	A	C	D	D	D	D	D	A	A	B	A	A	A	-A	C	D

No.	C.R.S (250ppm)	Fungicidical Activity (Prtri dish test(in vivo))					Herbicidical Activity (2.25Kg/ha)												Plant growth-regulating activity (10ppm)		
							Soil Treatment						Stem Leaf Treatment								
		F1	F2	F3	F4	F5	H1	H2	H3	H4	H5	H6	H1	H2	H3	H4	H5	H6	P1	P2	P3
25	A	C	C	C	D	D	C	D	D	B	D	A	C	A	A	A	A	A	-A	C	D
26	A	A	A	A	A	A	A	A	B	A	D	A	A	A	D	A	A	A	-A	D	D
27	A	C	C	C	C	D	B	D	D	B	C	B	A	A	D	A	C		-B	-D	D
28	A	A	A	A	A	A	D	A	A	B	A	A	A	D	C	D	D	A	-B	-C	D
29	A	A	A	A	A	A	C	D	C	C	D	A	D	D	D	A	C	A	-C	D	D
30	A	D	D	D	D	D	A	C	B	A	B	A	C	D	C	A	A	A	-C	A	C
31	A	A	A	A	A	A	B	D	D	B	D	A	A	A	D	A	A	A	-C	-C	D
32	A	A	A	A	A	A	C	D	D	C	D	D	A	A	D	A	A	A	-B	A	D
33	A	A	A	A	A	A	A	B	C	A	B	A	A	A	D	A	A	A	-B	B	C
34	A	D	D	D	D	B	A	C	C	A	C	A	A	A	D	A	A	A	-B	A	D
35	A	A	A	A	A	A	A	D	D	B	D	A	D	D	D	A	C	A	-B	A	C
36	A	C	B	B	A	A	C	D	D	C	D	D	A	A	C	A	A	A	-B	A	D
37	A	A	A	A	A	A	B	D	D	A	A	C	A	B	D	A	A	A	-B	D	D
39	A	B	B	B	B	A	B	D	D	D	D	D	A	D	D	A	B	B	-B	D	D
40	A	A	A	A	A	A	A	A	B	A	A	A	A	D	D	A	B	A	-B	D	D
41	A	A	A	A	A	A	D	A	A	B	A	A	A	D	C	D	D	A	-B	-C	-D
42	A	C	C	D	C	D	C	D	D	B	D	B	A	B	D	A	A	A	-B	-D	-D
43	A	D	D	B	D	D	B	A	C	A	B	A	A	A	D	A	A	A	-C	D	-D
44	A	A	A	A	A	A	A	A	C	B	D	A	D	D	D	A	C	A	-C	D	D
45	A	B	C	B	C	C	C	C	D	D	C	A	B	A	B	A	A	D	-B	B	D
46	A	D	D	D	D	D	D	D	D	D	D	C	A	A	D	A	A	A	-B	A	D
47	A	A	A	A	A	A	A	A	D	D	A	A	C	D	D	A	D	A	-B	C	D

F1: Scab of wheat head (Gibberella); F2: Tomato gray mold, F3: Rhizoctonia rot of cooton; F4: Ring rot of apple; F5: Stem Blight of asparagi
H1: Barnyard grass; H2: Oat; H3: Carb grass; H4: Rape; H5: Alfalfa; H6: Pigweed
P1: Wheat coleoptile straight growth bioassay; P2: Excised cucumber cotyledon root formation bioassay; P3: cucumber cotyledon expansion bioassay
C.R.S. : Cotton red spider

4. Preliminary biossay results are summarized below(see table 5):

a). All determined compounds were 90-100%(A class) in controlling the T. Urticue in 250*ppm*.

b). The antifungal activities of compounds to some plant pathogenic fungi were tested by the agar dilution method at a concentration of 50*ppm*. There was no regularity about the fungicidal activity. Some of them reached A class. Others were C or D class.

c). The results of herbicidal activities have shown that the activity of stem and leaf treatment is higher than that of soil treatment.

d). All treated compounds have good inhibition of wheat coleoptile straigh growth and poor effect on cucumber cotyleden root formation and expansion.

e). Preliminary analysis on the relationship of bioactivity and structure have shown that the activity of aryloxyacetate is better than that of alkoxyacetate; in bis(methyldicyclohexyltin) dicarboxylates(**19-22**), the activity of compound **19** seems to be the best and it has a tendency that along with the increase of *n* in -$(CH_2)_n$-, the activity is decreased. Activities of maleate(**26**) are much higher than that of fumarate(**27**).

References

1. M. H. Gitlitz, ***Organotin Compounds***(Advances in Chem. Series, 157), J. J. Zuckerman ed,. P167(1976)
2. Xie, Q-L., Yang, Z-Q.; Zhang, Z-X.; Zhang, D-K., ***Appl. Organomet. Chem.***, 1992, 6, 193
3. Xie, Q-L.; Yang, Z-Q.; Chen, X-R.; Zhang, Z-X.; Zhu, L-H., ***Chinese Patent ZL 9110933.2***
4. Yang, Z-Q.; Xie, Q-L.; Zhou, X-Z., ***Acta Chimica Sinica***(CHN), 1995, 53, 721
5. J. J. Zuckerman, ***Inorg. Chem.***, 1973, 1552
6. Mao, Z-H.; Zhou, Z-H., Hong, Z.; Shang, S-X.; Jiang, L.; Xie, Q-L., ***Structural Chemistry***(CHN), 1994, 13, 183
7. Zhang, D-K.; Xie, Q-L.; Zheng, J-Y.; Li, J.; Li, S-J., ***Spectroscopy***(CHN), 1990, 7, 101

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