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A Study of Trialkyltin β-Aryl-β-triphenylgermyl Propionates

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Twenty new compounds of the form $Ph_3GeCHArCH_2COOSnR_3$ (R = n-Bu, cyclohexyl; Ar = substituted phenyl) have been synthesized. Their structures were characterized by IR and ^{119}Sn and ^1H NMR spectroscopy. The compounds are five-coordinated carboxylate bridged polymers when R = n − Bu; when R = cyclohexyl (Cy) they are four-coordinate. ^{119}Sn NMR measurements of chemical shift for the two series of compounds have shown that there is a good linear relationship for the chemical shift of ^{119}Sn NMR between the tributyltin and tricyclohexyltin propionates), viz. $\delta\,^{119}Sn(Bu_3Sn) = 1.0474$ $\delta\,^{119}Sn(Cy_3Sn) + 95.8076$, n = 5, r = 0.993. The structure of one compound was determined by X-ray diffraction. It exists as a monomeric four-coordinated species in a distorted tetrahedronal geometry.

Keywords: Trialkyltin, triphenylgermanium propionates, synthesis, structure

INTRODUCTION

Japanese workers have synthesized compounds of the form $R^3_3GeCHR^1CHR^2C(O)Z$, (R′, R^2, R^3 = alkyl, aryl; Z = OR, NHR) which can selectively inhibit the decomposition of enzymes; for example, they are effective opiate peptidase inhibitors at 1 mg cm^{-3}. We have synthesized some analogues, viz. $Ar_3GeCHR^1CHR^2COOH$ (Ar = aryl, thiophene; R^1 = aryl, H; $R^2 = CH_3$, H) and characterized

Table 1 The yields and elemental analyses of the compounds

Compound	Yield (%)	State	M.pt (°C)	Elemental analysis: Found (calcd) (%) C	H	Formula for calculation
I_1	76.6	White crystals	128–129	65.92 (65.90)	6.44 (6.88)	$C_{45}H_{56}O_2GeSn$
I_2	82.5	White crystals	155–156	65.86 (66.23)	6.85 (7.01)	$C_{48}H_{58}O_2GeSn$
I_3	60	White crystals	136–138	62.94 (63.24)	6.38 (6.49)	$C_{45}H_{55}O_2ClGeSn$
I_4	70	White crystals	138–140	66.94 (67.14)	6.61 (6.63)	$C_{51}H_{50}O_3GeSn$
I_5	81	White crystals	84–86	65.36 (64.98)	6.71 (6.88)	$C_{46}H_{58}O_3GeSn$
I_6	86.9	White crystals	110–112	64.76 (64.98)	6.57 (6.88)	$C_{46}H_{58}O_3GeSn$
I_7	78.2	White crystals	138–139	63.05 (63.24)	6.11 (6.49)	$C_{45}H_{55}O_2ClGeSn$
I_8	86.6	White crystals	118–119	64.31 (64.48)	6.55 (6.61)	$C_{45}H_{55}O_2FGeSn$
I_9	96.6	White crystals	156–157	66.09 (66.23)	7.01 (7.01)	$C_{45}H_{58}O_2GeSn$
I_{10}	86.9	White crystals	126–127	66.18 (66.23)	7.21 (7.01)	$C_{46}H_{58}O_2GeSn$
II_1	48.1	White crystals	90–92	62.76 (63.12)	6.66 (6.79)	$C_{39}H_{50}O_2GeSn$
II_2	66	White crystals	82–85	63.12 (63.54)	6.72 (6.93)	$C_{40}H_{52}O_2GeSn$
II_3	72	White crystals	73–76	60.38 (60.32)	6.52 (6.36)	$C_{39}H_{49}O_2ClGeSn$
II_4	80	White crystals	102–103	64.67 (64.79)	6.50 (6.52)	$C_{45}H_{54}O_3GeSn$
II_5	72	White crystals	76–78	61.85 (62.22)	6.67 (6.79)	$C_{40}H_{52}O_3GeSn$
II_6	69.2	White crystals	101–103	61.80 (62.22)	6.48 (6.79)	$C_{40}H_{52}O_3GeSn$
II_7	74.3	White crystals	87–90	60.30 (60.32)	6.28 (6.36)	$C_{39}H_{49}O_2ClGeSn$
II_8	78.9	White crystals	96–97	61.19 (61.53)	6.54 (6.50)	$C_{39}H_{49}O_2FGeSn$
II_9	66.2	White crystals	85–86	63.44 (63.54)	6.90 (6.93)	$C_{40}H_{52}O_2GeSn$
II_{10}	75.6	White crystals	90–91	63.21 (63.54)	6.54 (6.93)	$C_{40}H_{52}O_2GeSn$

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Table 2 IR data of carbonyl groups of $Ph_3GeCHArCH_2COOSnR_3$ (cm^{-1})[a]

Compound	ν^{asym}	ν^{sym}	$\Delta\nu$
I_1	1637	1330	307
I_2	1633	1322	311
I_3	1633	1315	318
I_4	1634	1317	317
I_5	1631	1320	311
I_6	1642	1323	319
I_7	1646	1312	334
I_8	1639	1310	329
I_9	1625	1318	307
I_{10}	1629	1310	319
II_1	1548	1380	168
	(1625)	(1331)	(294)
II_2	1545	1386	159
	(1625)	(1320)	(305)
II_3	1549	1372	177
	(1626)	(1317)	(309)
II_4	1550	1374	176
II_5	1548	1378	170
	(1619)	(1315)	(304)
II_6	1545	1369	176
II_7	1553	1386	167
II_8	1557	1376	181
	(1630)	(1315)	(315)
II_9	1548	1386	162
II_{10}	1538	1369	170

[a] Data in solvent $CHCl_3$ are in parentheses.

them by IR and ^1H NMR.[2] It is known that trialkyltin derivatives are generally biologically active. For example, we have reported the preparation and biocidal properties of tributyltin and tricyclohexyltin carboxylates.[3,4] In order to link biological active properties of organotin and organogermanium compounds, we have synthesized two series of compounds containing tin and germanium by the following reaction (Eqn 1).

$$Ph_3GeCHArCH_2COOK + R_3SnCl \rightarrow Ph_3GeCHArCH_2COOSnR_3 + KCl \quad [1]$$

For compounds **I**, R = cyclohexyl (Cy), and Ar is:

C_6H_5 (**I_1**); *p*-$CH_3CH_6H_4$ (**I_2**); *p*-ClC_6H_4 (**I_3**); *m*-$PhOC_6H_4$ (**I_4**); *p*-$CH_3OC_6H_4$ (**I_5**); *o*-$CH_3OC_6H_4$ (**I_6**); *o*-ClC_6H_4 (**I_7**); *p*-FC_6H_4 (**I_8**); *o*-$CH_3C_6H_4$ (**I_9**); *m*-$CH_3C_6H_4$ (**I_{10}**).

For compounds **II**, R = Bu and Ar is:

C_6H_6 (**II_1**); *p*-$CH_3C_6H_4$ (**II_2**); *p*-ClC_8H_4 (**II_3**); *m*-$PhOC_6H_4$ (**II_4**); *p*-$CH_3OC_6H_4$ (**II_5**); *o*-$CH_3OC_6H_4$ (**II_6**); *o*-ClC_6H_4 (**II_7**); *p*-FC_6H_4 (**II_3**); *o*-$CH_3C_6H_4$ (**II_9**); *m*-$CH_3C_6H_4$ (**II_{10}**).

The structures of these compounds were characterized by IR and ^{119}Sn and ^1H NMR spectroscopy and by X-ray determination.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-435 spectrometer in KBr discs. The ^1H and ^{119}Sn NMR spectra were measured on a JEOL-FX-90Q spectrometer or a Bruker Ac-200 spectrometer in $CDCl_3$ solution with TMS as internal and Me_4Sn as external standard.

Elemental analyses were determined on an MT-3 elemental analyzer. Mass spectra were recorded on an HP-5988A at 70 eV; the temperature of ionization was 200 °C.

Table 3 Main NMR (^1H,^{119}Sn) data for compounds $Ph_3GeCHArCH_2COOSnCy_3$ (ppm)

Compound	$\delta^{119}Sn$	δ^1H				
		C_6H_{11}	CH_2	CH	Ar	Ph
I_1	11.8748	0.96–2.04 (33H, m)	2.98 (2H, d)	3.70 (H, t)	6.8–7.2 (5H, m)	7.32 (15H, s)
I_2	11.3188	0.96–2.04 (33H, m)	2.96 (2H, d)	3.68 (H, t)	6.86 (4H, s), 2.24 (3H, s)	7.36 (15H, s)
I_3	14.3938	0.96–2.04 (33H, m)	2.96 (2H, d)	3.67 (H, t)	6.96 (4H, m)	7.36 (15H, s)
I_4	12.8890	0.96–2.04 (33H, m)	2.90 (2H, d)	3.68 (H, t)	6.56–7.2 (9H, m)	7.36 (15H, s)
I_5	11.3842	1.00–2.08 (33H, m)	2.96 (2H, d)	3.74 (H, t)	6.52–7.0 (4H, m), 3.74 (3H, s)	7.38 (15H, s)
I_6	9.5522	1.00–2.04 (33H, m)	2.88–3.08 (2H, dq)	4.20 (H, q)	6.4–7.08, (4H, m), 3.24 (3H, s)	7.36 (15H, s)
I_7	14.3938	0.96–2.04 (33H, m)	2.96 (2H, dq)	4.38 (H, q)	6.92–7.2 (4H, m)	7.36 (15H, s)
I_8	13.0853	0.92–2.04 (33H, m)	2.96 (2H, d)	3.70 (H, t)	6.64–7.0 (4H, m)	7.38 (15H, s)
I_9	10.9262	0.88–2.04 (33H, m)	2.98 (2H, dq)	3.96 (H, q)	6.7–7.1 (4H, m), 1.98 (3H, s)	7.32 (15H, s)
I_{10}	11.1879	0.96–2.04 (33H, m)	2.96 (2H, d)	3.68 (H, t)	6.60–7.04 (4H, m), 2.12 (3H, s)	7.36 (15H, s)

Table 4 Main NMR (^1H,^{119}Sn) data for compounds $Ph_3GeCHArCH_2COOSn(CH_2)_3CH_3$ (ppm)

Compound	$\delta^{119}Sn$	δ^1H					
		CH_3	$(CH_2)_3$	CH_2	CH	Ar	Ph
II$_1$	108.3133	0.82 (9H, t)	0.92–1.6 (18H, m)	2.96 (2H, d)	3.70 (H, t)	6.8–7.18 (5H, m)	7.32 (15H, s)
II$_2$	107.4955	0.84 (9H, t)	0.96–1.6 (18H, m)	2.92 (2H, d)	3.68 (H, t)	6.86 (4H, s), 1.24 (3H, s)	7.34 (15H, s)
II$_3$	110.7341	0.84 (9H, t)	0.96–1.80 (18H, m)	2.92 (2H, d)	3.67 (H, t)	6.96 (4H, m)	7.36 (15H, s)
II$_4$	109.1638	0.84 (9H, t)	1.0–1.8 (18H, m)	2.90 (2H, d)	3.70 (3H, t)	6.60–7.2 (9H, m)	7.38 (15H, s)
II$_5$	107.6425	0.62–1.96 (27H, m)		2.94 (2H, d)	3.76 (H, t)	6.8 (4H, m), 3.76 (3H, s)	7.38 (15H, s)
II$_6$	105.2056	0.84 (9H, t)	1–1.68 (18H, m)	2.96 (2H, dq)	4.12 (H, q)	6.2–7.08 (4H, m), 3.22 (3H, s)	7.30 (15H, s)
II$_7$	110.1452	0.84 (9H, t)	0.96–1.8 (18H, m)	2.92 (2H, dq)	4.34 (H, q)	6.8–7.2 (4H, m)	7.34 (15H, s)
II$_8$	109.7527	0.84 (9H, t)	0.96–1.6 (18H, m)	2.92 (2H, d)	3.68 (H, t)	6.64–7.0 (4H, m)	7.36 (15H, s)
II$_9$	107.2665	0.6–1.8 (27H, m)		2.96 (2H, dq)	3.92 (H, q)	6.64–7.08, (4H, m), 19.6 (3H, s)	7.30 (15H, s)
II$_{10}$	107.4627	0.84 (9H, t)	0.96–1.8 (18H, m)	2.92 (2H, d)	3.64 (H, t)	6.42–7.08 (4H, m), 2.12 (3H, s)	7.34 (15H, s)

Table 5 Fragment ions observed for compounds $\mathbf{I}_1$ and $\mathbf{II}_1$

Compound $\mathbf{I}_1$			Compound $\mathbf{II}_1$		
m/z	Fragment ion	Intensity	*m/z*	Fragment ion	Intensity
736	$Ph_3GeCHC_8H_5CH_2COOSnCy_2^+$	2.5	685	$Ph_3GeCHC_6H_5CH_2COOSnBu_2^+$	5.6
434	$C_6H_5CHCH_2COOSnCy_2^+$	6.8	305	Ph_3Ge^+	78
305	Ph_3Ge^+	71	197	$C_6H_5Sn^+$	28
227	PhGe	31	177	$BuSn^+$	100
203	$CySn^+$	57	151	$PhGe^+$	65
197	$C_6H_5Sn^+$	45	121	SnH^+	79
151	$PhGe^+$	48	41	C_3H_5	31
120	Sn^+	60			
83	$C_6H_{11}^+$	85			
55	$C_4H_7^+$	100			

The β-substituted phenyl-β-triphenylgermylpropionic acids were synthesized via the following reaction (Eqn [2]).

$$GeO_2 + NaH_2PO_2 \cdot H_2O + HCl \rightarrow [HGeCl_3]$$

$$\xrightarrow{ArCH=CHCOOH} Cl_3GeCHArCH_2CO_2H_5$$

$$\xrightarrow[(ii)\ H_2O/HCl]{(i)\ PhMgCl} Ph_3GeCHArCH_2CO_2H \quad [2]$$

Synthesis of products

At the refluxing temperature of acetone, 10 mmol of the β-substituted phenyl-β-triphenylgermylpropionic acid and 5 mmol of K_2CO_3 were allowed to react for 10 min, then 10.5 mmol of the trialkyltin chloride was added. The mixture was stirred under reflux for 10 h. After removing the solvent, the product was obtained after recrystallization from ethanol.

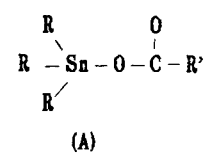
Some data on the products are listed in Table 1.

Table 6 Bond distances and bond angles of compound $\mathbf{I}_{10}$

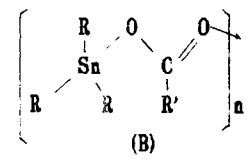
Bond distances (Å)		Bond angles (deg)	
Sn–O(1)	2.803(6)	O(2)–Sn–O(1)	50.8(3)
Sn–O(2)	2.075(6)	O(2)–Sn–C(11)	108.3(3)
Sn–C(11)	1.170(9)	O(2)–Sn–C(21)	111.3(3)
Sn–C(21)	2.150(1)	O(2)–Sn–C(31)	95.4(3)
Sn–C(31)	2.080(2)	O(11)–Sn–C(21)	113.7(3)
Ge–C(1)	1.954(8)	C(11)–Sn–C(31)	115.9(4)
Ge–C(41)	1.965(8)	C(21)–Sn–C(31)	110.8(4)
Ge–C(51)	1.949(9)	C(1)–Ge–C(4)	109.9(3)
Ge–C(6)	1.940(8)	C(1)–Ge–C(51)	108.71(4)
O(1)–C(3)	1.190(1)	C(1)–Ge–C(61)	110.3(3)
O(2)–C(3)	1.285(9)	C(41)–Ge–C(51)	110.6(4)
		C(41)–Ge–C(161)	109.3(3)
		C(51)–Ge–C(61)	108.1(3)

RESULTS AND DISCUSSION

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



(A)



(B)

The vacant 5*d* orbital on tin atoms tend towards high-coordination ligands with strong electronegativity containing lone electron pairs.[3-6] The IR stretching vibration frequencies of carbonyl groups in organotin carboxylates are important for determining their structures: when the structure changes from **A** to **B**, the asymmetric absorption vibration frequencies ($\nu_{CO_2}^{asym}$) of carbonyl groups decrease and the symmetric absorption vibration frequencies ($\nu_{CO_2}^{sym}$) increase. Their difference ($\Delta\nu_{CO_2}$) therefore decreases.[3,5]

We see from Table 2 that the frequency $\nu_{CO_2}^{asym}$ of the $Ph_3GeCHArCH_2COOSnBu_3$ species is about 77–79 cm^{-1} lower than that of the corresponding tricyclohexyltin carboxylates, while $\nu_{CO_2}^{sym}$ is about 46–74 cm^{-1} higher. For tributyltin carboxylates, the difference between $\nu_{CO_2}^{asym}$ and $\nu_{CO_2}^{sym}$ ($\Delta\nu_{CO_2}$) is

Table 7 Fractional coordinates and thermal parameters of non-hydrogen atoms for compound $\mathbf{I}_{10}$

Atom	*x*	*y*	*z*	*Beq./B* (Å^2)
Sn	0.5618(1)	0.44664(8)	0.25955(9)	5.03(3)
Ge	0.4962(2)	−0.0575(1)	0.1983(1)	4.85(4)
O(1)	0.520(1)	0.2989(8)	0.1581(7)	5.7(3)
O(2)	0.589(1)	0.2866(8)	0.2833(7)	6.0(3)
C(1)	0.470(1)	0.094(1)	0.184(1)	4.7(3)
C(2)	0.569(1)	0.129(1)	0.236(1)	.5.3(4)
C(3)	0.556(1)	0.249(1)	0.220(1)	5.0(4)
C(11)	0.369(2)	0.508(1)	0.243(1)	5.5(4)
C(12)	0.338(2)	0.619(2)	0.257(1)	7.5(5)
C(13)	0.196(2)	0.667(2)	0.248(1)	8.5(6)
C(14)	0.122(2)	0.598(2)	0.308(2)	9.6(6)
C(15)	0.154(2)	0.485(2)	0.286(1)	8.4(6)
C(16)	0.291(2)	0.439(2)	0.300(1)	8.1(5)
C(21)	0.678(2)	0.488(1)	0.156(1)	5.7(4)
C(22)	0.784(2)	0.400(1)	0.132(1)	7.0(5)
C(23)	0.867(2)	0.445(2)	0.058(2)	9.1(6)
C(24)	0.796(2)	0.486(2)	−0.015(1)	8.6(6)
C(25)	0.688(2)	0.570(1)	0.006(1)	7.0(5)
C(26)	0.609(2)	0.530(1)	0.079(1)	7.1(5)
C(31)	0.625(2)	0.472(1)	0.372(1)	6.8(5)
C(32)	0.647(2)	0.584(2)	0.373(1)	8.2(5)
C(33)	0.711(2)	0.594(2)	0.451(2)	11.6(8)
C(34)	0.834(2)	0.527(2)	0.453(2)	9.9(7)
C(35)	0.824(2)	0.421(2)	0.455(2)	10.8(7)
C(36)	0.762(2)	0.397(2)	0.385(2)	11.1(7)
C(41)	0.469(1)	−0.103(1)	0.317(1)	4.8(3)
C(42)	0.556(2)	0.097(1)	0.373(1)	7.2(5)
C(43)	0.535(2)	−0.128(2)	0.459(1)	8.6(6)
C(44)	0.433(2)	−0.163(2)	0.487(1)	8.2(5)
C(45)	0.351(2)	0.174(2)	−0.435(1)	8.5(6)
C(46)	0.373(2)	−0.141(1)	0.346(1)	7.2(5)
C(51)	0.384(1)	−0.102(1)	0.131(1)	5.2(4)
C(52)	0.257(2)	−0.068(1)	0.142(1)	5.9(4)
C(53)	0.180(2)	−0.105(1)	0.093(1)	6.4(4)
C(54)	0.228(2)	−0.173(1)	0.035(1)	7.1(5)
C(55)	0.352(2)	−0.207(1)	0.023(1)	6.8(5)
C(56)	0.433(2)	−0.174(1)	0.070(1)	5.6(4)
C(61)	0.662(1)	−0.120(1)	0.160(1)	4.5(3)
C(62)	0.727(2)	−0.214(1)	0.199(1)	6.5(4)
C(63)	0.840(2)	−0.261(2)	0.167(1)	7.5(5)
C(64)	0.896(2)	−0.223(1)	0.098(1)	6.5(4)
C(65)	0.836(2)	−0.128(2)	0.057(1)	8.0(5)
C(66)	0.719(2)	−0.079(1)	0.088(1)	5.8(4)
C(71)	0.343(1)	0.146(1)	0.209(1)	5.0(4)
C(72)	0.304(2)	0.146(1)	0.292(1)	5.9(4)
C(73)	0.174(2)	0.197(2)	0.315(2)	8.7(6)
C(74)	0.099(2)	0.238(2)	0.248(1)	8.3(6)
C(75)	0.139(2)	0.238(2)	0.170(1)	8.4(6)
C(76)	0.268(2)	0.190(2)	0.144(1)	7.9(5)
C(77)	0.132(2)	0.198(2)	0.409(2)	10.6(7)
Cl(1)	0.1658(9)	0.9320(8)	0.6136(7)	15.8(3)
Cl(2)	0.083(1)	1.0350(9)	0.7479(8)	18.5(4)
Cl(3)	−0.039(1)	1.054(1)	0.624(1)	23.4(5)
C	0.046(3)	0.976(2)	0.692(2)	13.2(9)

less than 200 cm^{-1} and it is greater than 300 cm^{-1} for the tricyclohexyltin carboxylates. This suggests that the structures of the tributyltin carboxylates may be five-coordinate (**B**) and those of the tricyclohexyltin carboxylates may be four-coordinate (**A**).

The IR data of some tributyltin carboxylates, in $CHCl_3$, are listed in Table 2. Comparing these with the pure compounds, we find that the asymmetric absorption vibration frequencies of the carbonyl groups are increased and the symmetric absorption vibration frequencies are decreased, so their differences are increased. This suggests that the tributyltin carboxylates have four-coordinate structures in solvent.

The NMR data are listed in Tables 3 and 4. The ^{1}H NMR data of the products show that along with a decrease of the electron density around the hydrogens on C(1) and C(2) of $Ph_3GeCHArCH_2COOSnR_3$, the chemical shift of ^{1}H moved to low field by about 0.10 ppm when the trialkyltin combined with acid to form an ester. C(1) is a chiral centre and C(2) is a prochiral centre, and the three hydrogens on C(1) and C(2) comprise an ABX system. With change of substitute position on Ar, the relationship between the three hydrogens on C(1) and C(2) also changes. With *ortho* substitution the characteristic ABX system is apparent. With *meta* and *para* substitution, the three hydrogens transform to the first-order spectra of an A_2X system.

A subtle structural change around the tin atom can be reflected in the chemical shifts in ^{119}Sn NMR. The substituents on the aromatic group have an influence on δ ^{119}Sn. Electron-withdrawing groups make the chemical shift of ^{119}Sn move to a lower field. We have found that there is a linear relationship between δ ^{119}Sn and the Hammett constants (σ) of the *para* substituent for the **I** and **II** senses of the corresponding compounds (Eqns [3] and [4]).

$$\mathbf{I}: \delta\ ^{119}\mathrm{Sn} = 6.24\sigma + 12.60,\quad n = 5,\ r = 0.930 \quad [3]$$

$$\mathbf{II}: \delta\ ^{119}\mathrm{Sn} = 6.57\sigma + 109.00,\ n = 5,\ r = 0.928 \quad [4]$$

Comparing the relationship of the ^{119}Sn NMR chemical shift between tributyltin and tri[(phenyldimethylsilyl)methylene]tin-substituted benzoates,[4] we also found that there is a good linear relationship for the ^{119}Sn NMR chemical shift between tributyltin and tricyclohexyltin propionates containing germanium (Eqn [5]).

$$\delta\ ^{119}\mathrm{Sn(Bu_3Sn)} = 1.0474\,\delta\ ^{119}\mathrm{Sn(Cy_3Sn)} + 95.8076,\ n = 5,\ r = 0.993 \quad [5]$$

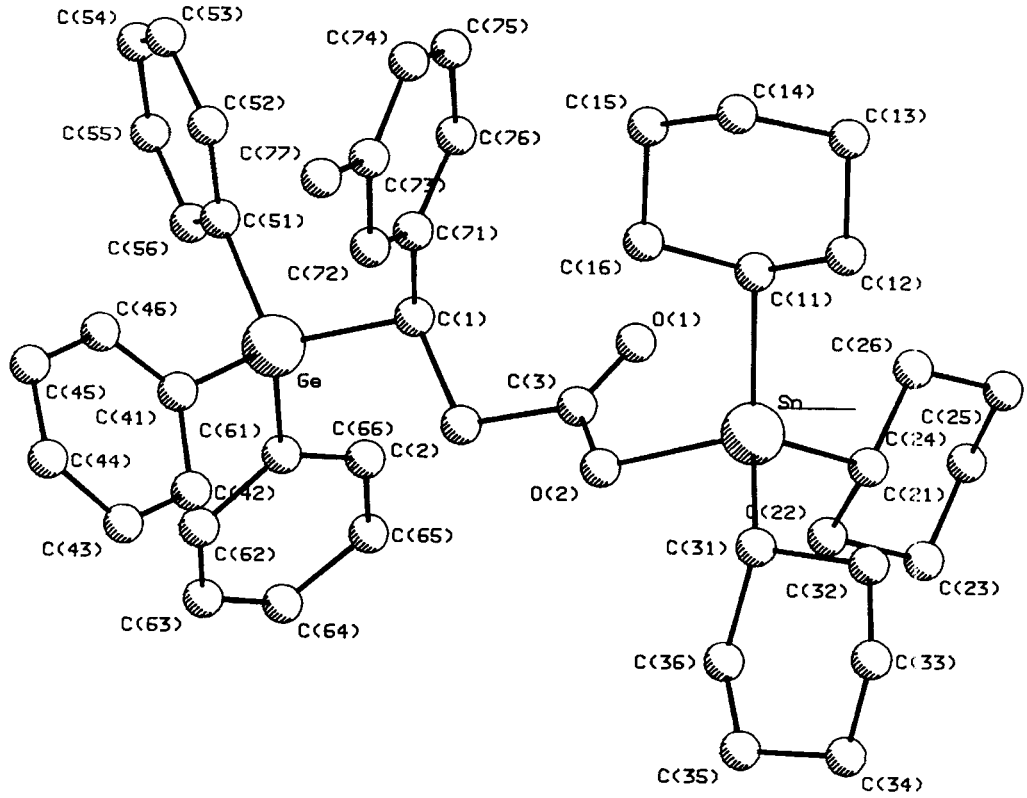


Figure 1 The molecular structure of $Ph_3Ge(CH(C_6H_4CH_3—m)CH_2CO_2SnCy_3$.

This shows that the two series of compounds have the same structure when they are dissolved in the solvent.

The mass spectra (MS) of compounds $\mathbf{I}_1$ and $\mathbf{II}_2$ were recorded and the main data are listed in Table 5. For both there are no molecular ion peaks. Dealkylation from the tin atom was the main breakdown pattern for the two compounds.

A crystal of Compound $\mathbf{I}_{10}$ was obtained from $CHCl_3$ solution and was determined using MoKα radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonious CAD4 four-circle diffractometer. The crystallographic parameters and conditions of data collection are summarized as follows:

$C_{48}H_{58}GeO_2Sn \cdot HCCl_3$

Crystal data: triclinic, space group $P\bar{1}$ with $a = 11.216(3)$, $b = 13.225(7)$, $c = 16.075(3)$ Å, $\alpha = 84.36(3)$, $\beta = 85.27(2)$, $\gamma = 77.45°(4)$, $V = 2312(2)$ Å^3, mol. wt 953.63, $Z = 2$, density = 1.37 g cm^{-3}, $\mu = 13.86$ cm^{-1}, $F(000) = 980$, scan type $\omega - 2\theta$, $2° \leqslant \theta \leqslant 22°$, crystal size 0.2 mm × 0.3 mm × 0.3 mm, number of independent reflection 5783, number of observed reflection 3485 [$I \geqslant 3\sigma(I)$].

The bond distances and angles are listed in Table 6. The fractional coordinates and thermal parameters of non-hydrogen atoms for $\mathbf{I}_{10}$ are listed in Table 7. The crystal structure of compound $\mathbf{I}_{10}$ can be reported as monomeric. The distances of two C–O bonds of the carboxyl group are 1.19 Å and 1.285 Å which are typical bond lengths for C=O and C—O groups, and the distance between tin and the carbonyl oxygen is 2.803 Å, which is longer than the sum of the van der Waals radii between tin and oxygen; therefore there is no coordinated bond. The compound is four-coordinated monomeric in a distorted tetrahedral geometry (Fig. 1), although the bond angle of O(2)–Sn–C(31) (95.4°) deviates obviously from the standard tetrahedronal geometry.

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