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Studies on Some Bulky Triorganotin Complexes of Germatranyl-Substituted Carboxylic Acids

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ABSTRACT: *Eleven tris(2-methyl-2-phenylpropyl)tin as well as four methyl bis[(phenyldimethylsilyl)methyl]tin β-germatranylpropionates have been synthesized, and their structures were characterized by elemental analyses, IR, multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR, Mössbauer, and MS spectroscopies. All the spectroscopic studies suggest a tetrahedral geometry for the bulky triorganotin carboxylates. The preliminary bioassays have shown that most of the compounds have good acaricidal activity.*

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INTRODUCTION

Organotin(IV) compounds are among the most actively studied groups of organometallics and possess a wide range of established and potential applications based on their chemical and biological properties [1,2]. It is well known that the biological activities and selectivities of trialkyltin compounds R_3SnX depend mainly on the alkyl groups, and the nature of the X groups have a relatively small influence on the biological activities [3]. However, continuing studies on the structures of various triorganotin compounds have shown that X groups do have some influence on the activity, especially for those that, themselves, have some biological activity [4–8]. In addition, these compounds show an interesting range of structural variations leading to structure–activity relationships [9]. These latter studies have shown that triorganotin carboxylates that have either isolated tetrahedral tin centers or *trans*-R_3SnO_2 tin atom geometry (arising from a bridge carboxylate ligand) possess significantly greater biological activity than the compounds with the monomeric *cis*-C_3SnO_2 structural type; that is, compounds with chelating carboxylate ligand spanning both equatorial and axial sites have greater activity.

Organogermanium compounds, especially germatranes with a cage-like skeleton and those famous germanium sesquioxide (named Ge-132 by Japanese workers), are well known for their biological properties. In our previous papers, we have reported the synthesis and biological evaluation of dialkyltin [10,11] and trialkyltin [12,13] derivatives of β-germatranylpropionic acids [14]. Considering the wide use of the acaricidal activity of bis[tri(2-methyl-2-phenylpropyl)tin] oxide (commercial name *Torque*), as a part of our continuing interest in this area, we have reported studies on tri(2-methyl-2-phenylpropyl)tin derivatives of triphenylgermylpropionic acids. To give a more complete picture for this series, we would like to report herein the syntheses, structure characterizations, and biological studies of related

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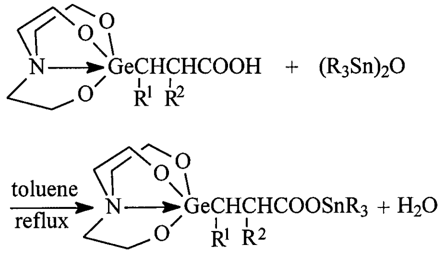


R=$PhC(CH_3)_2CH_2$, 1(R^1=H, R^2=H); 2(R^1=CH_3, R^2=H); 3(R^1=H, R^2=CH_3); 4(R^1=C_6H_5, R^2=H); 5(R^1=p-$C_6H_4OCH_3$, R^2=H); 6(R^1=o-$C_6H_4OCH_3$, R^2=H); 7(R^1=p-$C_6H_4NO_2$, R^2=H); 8(R^1=o-C_6H_4Cl, R^2=H); 9(R^1=p-C_6H_4Cl, R^2=H); 10(R^1=2,4-$C_6H_3Cl_2$, R^2=H); 11(R^1=p-$C_6H_4CH_3$, R^2=H)

R=$[4\text{-}CH_3C_6H_4Si(CH_3)_2CH_2]_2SnCH_3]_2O$, 12($R^1$= C_6H_5, R^2=H); 13(R^1= p-$C_6H_4OCH_3$, R^2=H); 14(R^1= o-C_6H_4Cl, R^2=CH_3), 15(R^1=p-C_6H_4Cl, R^2=H)

SCHEME 1

tris(2-methyl-2-phenylpropyl)tin as well as another bulky methyl bis[(4-methylphenyldimethylsilyl)methyl]tin complexes of β-germatranylpropionates.

EXPERIMENTAL

Material and Instrumentation

Torque [Bis[tri(2-methyl-2-phenylpropyl)tin] oxide] [15] and methyl bis[di(4-methylphenyldimethylsilylmethyl)tin] oxide [16] were prepared using literature methods. The solvents were dried with sodium metal before use. All the substituted germatranylpropionic acids were prepared according to known literature methods [10–13].

The NMR data were recorded with a Bruker AC-P 200 spectrometer with $CDCl_3$ as the solvent, and the references were TMS or Me_4Sn (for ^{119}Sn). The IR spectra (4000–400 cm^{-1}) were recorded with a SHIMADZU IR-435 spectrophotometer using KBr windows. The C, H, and N elemental analyses were determined by the YANACO MT-3 analyzer. The MS data were recorded by the HP-5988A mass spectrometer (EI source at 200°C, 70 eV). The Mössbauer spectra were measured at 80 K on a Ranger Mössbauer spectrometer model MS-900 in the acceleration mode with a moving-source geometry using a liquid nitrogen cryostat. The source was 15 m*Ci* $Ca^{119m}SnO_3$, and the velocity was calibrated at ambient temperatures using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed by a least-squares fit to Lorentzian-shaped lines.

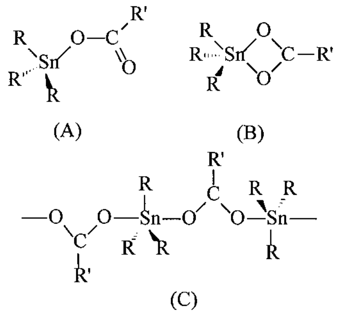
Synthesis of the Products

All the compounds were synthesized using similar procedure as shown in Scheme 1.

Typically, a mixture of bis(triorganotin) oxide (1.0 mmol) and appropriate substituted germatranylpropionic acid (2.0 mmol) was refluxed in dry toluene for 6 h. The water liberated was removed azeotropically by use of a Dean–Stark apparatus. The mixture was cooled and the toluene was removed using a rotary evaporator. The resultant sticky residue was then dried in a vacuum to give a white solid. Recrystallization of the white solid from ethanol or a mixture of chloroform and petroleum ether yielded fine crystals. The analytical and physical data of the products are given in Table 1. Four complexes containing Si, Ge, and Sn elements were also synthesized using the substituted germatranylpropionic acid and bis[methyldi(4-methylphenyldimethylsilylmethyl)tin] oxide as the materials. Their analytical and physical data are also listed in Table 1.

RESULTS AND DISCUSSION

It is well established that triorganotin carboxylates are adopted with three structural types in the solid state [17] (as shown in Scheme 2).



SCHEME 2

TABLE 1 Analytical and Physical Properties of the Titled Compounds

			Elemental Analysis		
Compound	*M.P. (°C)*	*Yield (%)*	*C (%)*	*H (%)*	*N (%)*
1	54–57	74	57.90 (57.89)	6.91 (6.85)	1.70 (1.73)
2	116–118	88	58.20 (58.36)	6.85 (6.98)	1.70 (1.70)
3	95–97	95	58.42 (58.36)	6.82 (6.98)	1.53 (1.70)
4	174–175	80	61.36 (61.06)	6.68 (6.72)	1.41 (1.58)
5	142–144	94	60.19 (60.37)	6.51 (6.72)	1.55 (1.53)
6	150–152	72	60.51 (60.37)	6.62 (6.72)	1.46 (1.53)
7	135–137	94	58.32 (58.10)	6.44 (6.28)	3.02 (3.01)
8	142–144	82	58.77 (58.77)	6.40 (6.36)	1.69 (1.52)
9	137–139	77	58.77 (58.77)	6.16 (6.36)	1.48 (1.52)
10	110–112	73	56.15 (56.65)	5.98 (6.02)	1.23 (1.47)
11	151–153	89	61.50 (61.44)	6.83 (6.84)	1.41 (1.56)
12	47–49	76	52.10 (52.27)	6.34 (6.43)	1.69 (1.69)
13	79–81	61	51.16 (51.84)	6.67 (6.47)	2.09 (1.63)
14	96–98	90	50.10 (50.18)	6.20 (6.08)	1.86 (1.63)
15[a]	60–62	60	48.98 (49.15)	6.00 (6.19)	1.31 (1.59)

[a] One water of hydration was found in the complex.

A monomeric structure (A) can be four-coordinated, whereas a polymeric structure (C) generally contains five-coordinate tin atoms. Five-coordinate compounds, which inevitably adopt structural type (B), occur when the carboxylate groups act as a chelating ligand. The different kinds of structures can be proved by the analysis of the IR, NMR, Mössbauer, and MS spectra of the compounds. All the spectral data of the title compounds revealed that they possess a tetrahedral geometry, as in structure A.

IR Spectra

Important IR data for the titled compounds are reported in Table 2

Two bands at about 925 and 800 cm^{-1} are characteristic for the $\mathrm{Ge}\begin{smallmatrix}\diagup\mathrm{O}\\ -\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$ skeleton. A sharp and strong band at about 700 cm^{-1} indicates the typical intermolecular N → Ge coordination for germatrane derivatives. Absorptions around 580 and 550 cm^{-1} are also observed, which may be assigned to Sn—C asymmetric amd symmetric modes, respectively. Besides this, a weak band at about 460 cm^{-1} is assigned to the Sn—O stretching vibration.

The $\Delta\nu[\Delta\nu = \nu(\mathrm{COO})_{\mathrm{as}} - \nu(\mathrm{COO})_{\mathrm{s}}]$, which is useful in drawing structural influences in the case of metal carboxylates, is used to determine the nature of bonding of the carboxylate group to tin(IV) [18]. The coordination number of tin affects the absorption vibration frequency of the carbonyl group. It is generally believed that the difference [$\Delta\nu$] between

TABLE 2 Important IR Data (cm^{-1}) for the Titled Compounds

Compound	$\nu(COO)_{as}$	$\nu(COO)_s$	$\Delta\nu$	ν(Ge–O)	ν(Sn–C)	ν(Sn–O)	ν(Ge–N)
1	1647 (s)	1380	267	926 (w), 898	464	576 (s), 554	696 (s)
2	1657 (s)	1358	299	925 (w), 896	463	575 (s), 555	684 (s)
3	1654 (s)	1381	273	926 (w), 898	454	579 (s), 554	698 (s)
4	1642 (s)	1358	284	925 (w), 897	467	597 (s), 554	694 (s)
5	1647 (s)	1381	266	928 (w), 899	457	577 (s), 555	697 (s)
6	1642 (s)	1357	285	945 (w), 897	458	584 (s), 555	716 (s)
7	1642 (s)	1361	281	925 (w), 897	473	597 (s), 565	695 (s)
8	1641 (s)	1357	284	926 (w), 897	474	581 (s), 554	697 (s)
9	1647 (s)	1381	266	926 (w), 897	458	579 (s), 552	715 (s)
10	1647 (s)	1381	266	926 (w), 898	467	582 (s), 554	696 (s)
11	1646 (s)	1361	285	926 (w), 898	453	577 (s), 554	715 (s)
12	1659 (s)	1351	308	930 (w), 900	460	576 (s), 531	683 (s)
13	1652 (s)	1361	291	925 (w), 898	464	576 (s), 529	684 (s)
14	1653 (s)	1357	296	926 (w), 898	463	596 (s), 529	589 (s)
15	1639 (s)	1325	314	926 (w), 898	464	596 (s), 553	715 (s)

asymmetric [$\nu(\mathrm{COO})_{\mathrm{as}}$] and symmetric [$\nu(\mathrm{COO})_{\mathrm{s}}$] absorption frequencies is below 200 cm^{-1} for the five-coordinated structure of triorganotin carboxylates, but more than 200 cm^{-1} for the four-coordinated one. From Table 2, we can see that the value of $\Delta\nu$ is between 266 and 314 cm^{-1} in all cases. These data strongly indicate that all the titled compounds are four-coordinated. This contradiction to a bridged structure generally adopted for triorganotin in the solid state can be explained by the introduction of a very bulkyl group in R (2-methyl-2-phenylpropyl)

TABLE 3 Mössbauer Parameters for Selected Complexes and Related Carboxylates

Compounds	*IS (mm s^{-1})*	*QS (mm s^{-1})*	*ρ*	*Γ1 (L)*	*Γ2 (R)*
6	2.34 ± 0.02	1.40 ± 0.03	1.67	0.96	1.10
8	2.43 ± 0.02	1.43 ± 0.03	1.70	0.97	0.89
13	2.56 ± 0.02	1.35 ± 0.03	1.90	1.12	1.22
15	2.57 ± 0.02	1.55 ± 0.03	1.65	1.00	1.08
(neophyl)$_3$SnOAc[a]	2.45	1.35	1.81		
Me$_3$SnOAc[a]	3.47	1.34	2.59		

[a] From Ref. [19].

TABLE 4 ^{1}H NMR Data and $^2J(^1\mathrm{H}, {}^{119}\mathrm{Sn})$ of the Titled Compounds

Compound	*^{1}H NMR (ppm)*	*^2J(Sn–CH$_2$) (Hz)*
1	1.09, 6H [s, 3 × SnCH$_2$]; 1.15, 18H [s, 3 × C(CH$_3$)$_2$]; 1.15–1.30, 2H [m, GeCH$_2$]; 2.40–2.60, 2H [m, CH$_2$CO$_2$]; 2.80, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 3.70, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.90–7.40, 15H [m, 3 × C$_6$H$_5$]	53.1
2	0.70–1.50, 27H [m, GeCH(CH$_3$) + 3× SnCH$_2$C(CH$_3$)$_2$]; 1.60–1.90, 1H [m, GeCH]; 2.60–2.90, 7H [m, CHCO$_2$ + 3× NCH$_2$]; 3.60–3.80, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.90–7.40, 15H [m, 3 × C$_6$H$_5$]	57.3 (25.3)
3	0.70–1.50, 29H [m, GeCH$_2$CH(CH$_3$) + 3 × SnCH$_2$C(CH$_3$)$_2$]; 2.60–2.90, 7H [m, CHCO$_2$ + 3 × NCH$_2$]; 3.60–3.80, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.90–7.40, 15H[m, 3 × C$_6$H$_5$]	45.9 (26.0)
4	0.92, 6H [s, 3 × SnCH$_2$]; 1.05, 18H [s, 3 × C(CH$_3$)$_2$]; 2.75, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.90–3.25, 3H [m, GeCHCH$_2$]; 3.70, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.90–7.40, 20H [m, 4 × C$_6$H$_5$]	50.2
5	0.90, 6H [s, 3 × SnCH$_2$]; 1.03, 18H [s, 3 × C(CH$_3$)$_2$]; 270, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.80–3.10, 3H [m, GeCHCH$_2$]; 3.60–3.80, 9H [m, OCH$_3$ + 3 × OCH$_2$]; 6.60–7.40, 19H [m, 3 × C$_6$H$_5$+ C$_6$H$_4$]	47.4
6	0.78, 6H [s, 3 × SnCH$_2$]; 0.91, 18H [s, 3 × C(CH$_3$)$_2$]; 2.55, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.70–3.00, 3H [m, GeCHCH$_2$]; 3.55, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 3.70, 3H [s, OCH$_3$]; 6.60–7.40, 19H [m, 3 × C$_6$H$_5$ + C$_6$H$_4$]	60.2
7	0.70–1.50, 24H [m, 3 × SnCH$_2$C(CH$_3$)$_2$]; 2.60–2.90, 6H [t, 3 × NCH$_2$]; 2.90–3.25, 3H [m, GeCHCH$_2$]; 3.60–3.80, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.90–7.40, 19H [m, 3 × C$_6$H$_5$ + C$_6$H$_4$]	50.9
8	0.89, 6H [s, 3 × SnCH$_2$]; 1.02, 18H [s, 3 × C(CH$_3$)$_2$]; 2.75, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.90–3.25, 2H [m, GeCHCH$_2$]; 3.70, 7H [m, GeCH +3 × OCH$_2$]; 6.60–7.60, 19H [m, 3 × C$_6$H$_5$ + C$_6$H$_4$]	50.1 (30.0)
9	0.77, 6H [s, 3 × SnCH$_2$]; 0.93, 18H [s, 3 × C(CH$_3$)$_2$]; 2.60, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.70–3.00, 3H [m, GeCHCH$_2$]; 3.60, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.60–7.30, 19H [m, 3 × C$_6$H$_5$ + C$_6$H$_4$]	55.2
10	0.94, 6H [s, 3 × SnCH$_2$]; 1.05, 18H [s, 3 × C(CH$_3$)$_2$]; 2.70, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.80–3.20, 2H [m, GeCHCH$_2$]; 3.50–3.65, 1H [m, GeCH]; 3.73, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.60–7.50, 18H [m, 3 × C$_6$H$_5$ + C$_6$H$_3$]	53.7 (29.0)
11	0.90, 6H [s, 3 × SnCH$_2$]; 1.03, 18H [s, 3 × C(CH$_3$)$_2$]; 2.24, 3H [s, C$_6$H$_4$CH$_3$]; 2.70, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.80–3.20, 3H [m, GeCHCH$_2$]; 3.70, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.60–7.50, 19H [m, 3 × C$_6$H$_5$ + C$_6$H$_4$]	44.1
12	0.02, 4H [s, 2 × SnCH$_2$]; 0.14, 15H [s, SnCH$_3$ + 2 × Si(CH$_3$)$_2$]; 2.31, 6H [s, 2 × C$_6$H$_4$CH$_3$]; 2.73, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 2.90–3.10, 3H [m, GeCHCH$_2$]; 3.69, 6H [t, *J* = 5.4, 3 × OCH$_2$]; 7.00–7.30, 12H [m, 3 × C$_6$H$_4$]	58.0 (26.2)[a], 53.4
13	0.05, 4H [s, 2 × SnCH$_2$]; 0.16, 15H [s, SnCH$_3$ + 2 × Si(CH$_3$)$_2$]; 2.31, 6H [s, 2×C$_6$H$_4$CH$_3$]; 2.73, 6H [t, *J* = 5.4, 3 × NCH$_2$]; 2.80–3.00, 3H [m, GeCHCH$_2$]; 3.70, 3H [s, OCH$_3$]; 3.70, 6H [t, *J* = 5.4, 3 × OCH$_2$]; 6.70–7.30, 12H [m, 3 × C$_6$H$_4$]	60.9 (26.1)[a], 52.9
14	0.05, 4H [s, 2 × SnCH$_2$]; 0.15, 15H [s, SnCH$_3$ + 2 × Si(CH$_3$)$_2$]; 2.31, 6H [s, 2 × C$_6$H$_4$CH$_3$]; 2.73, 6H [t, *J* = 5.6, 3 × NCH$_2$]; 3.00, 2H [d, *J* = 12, CH$_2$CO$_2$]; 3.60, 1H [t, *J* = 12, GeCH]; 3.70, 6H [t, *J* = 5.6, 3 × OCH$_2$]; 6.90–7.40, 12H [m, 3 × C$_6$H$_4$]	60.9 (26.2)[a], 52.2
15	0.03, 4H [s, 2 × SnCH$_2$]; 0.16, 15H [s, SnCH$_3$ + 2 × Si(CH$_3$)$_2$]; 2.31, 6H [s, 2 × C$_6$H$_4$CH$_3$]; 2.74, 6H [t, *J* = 5.5, 3 × NCH$_2$]; 2.85–3.05, 3H [m, GeCHCH$_2$]; 3.69, 6H [t, *J* = 5.5, 3 × OCH$_2$]; 7.00–7.30, 12H [m, 3 × C$_6$H$_4$]	58.6 (26.8)[a], 52.8

[a] ^2J(Sn—CH$_3$).

TABLE 5 ^{119}Sn NMR Data (ppm) for Compounds **1–4** and Related Trineophyltin Derivatives

Compound	δ
1	78.0
2	76.2
3	78.1
4	78.4
$\{[PhC(CH_3)_2CH_2]_3Sn\}_2O^a$	55.5
$[PhC(CH_3)_2CH_2]_3SnCl^b$	118.5
$[PhC(CH_3)_2CH_2]_3SnO_2CCHCl_2{}^b$	79
$[PhC(CH_3)_2CH_2]_3SnO_2CH^b$	89
$[PhC(CH_3)_2CH_2]_3SnO_2CCHMe_2{}^b$	131
$[PhC(CH_3)_2CH_2]_3SnO_2CCCl_3{}^b$	146

[a] ^2J(Sn—O—Sn) = 529.7 Hz.
[b] From Ref. [22].

and the carboxylate branch (germatrane substituted) in the titled compounds, which prevents the coordination of the C=O group to the tin atom. This is in agreement with the results described in our previous publications in this series.

Mössbauer Spectra

Four complexes were selected for Mössbauer study, and their Mössbauer parameters are listed in Table 3.

Mössbauer spectroscopy is very useful for structural studies because indirect evidence for the solid-state structure of organotin compounds can be derived from it [20]. In this context, the most useful parameters are quadruple splitting (QS), for which parameter a given range is associated with a particular coordination number and geometry at tin, and the isomer shift (IS), which is primarily sensitive to changes in *s*-electron density at the tin nucleus. Herber et al. [19] have determined Mössbauer parameters for trimethyltin acetate $(CH_3)_3SnO_2CCH_3$ ($\delta = 1.34$ mm s^{-1}, $\Delta = 3.47$ mm s^{-1}) and tri(2-methyl-2-phenylpropyl)tin acetate $(PhC(CH_3)_2CH_2)_3SnO_2CCH_3$ ($\delta = 1.35$ mm s^{-1}, $\Delta = 2.45$ mm s^{-1}). The large difference in quadruple splittings is due to the fact that the tin atom is in a triorgonal bipyramidal environment in the trimethyltin derivative, while in the tri(2-methyl-2-phenylpropyl)tin derivative, the tin atom is in a tetrahedral geometry because of the bulky 2-methyl-2-phenylpropyl groups. Therefore, the ratio of quadruple splitting to isomer shift (ρ = QS/IS) can be used to distinguish between compounds in which the tin atom is pentacoordinate and those in which it is tetracoordinate. It is suggested [21] that (with δ relative to SnO_2) a value of $\rho > 2.1$ is evidence of pentacoordination about the tin atom, whereas if $\rho < 1.8$ the tin atom is tetracoordinate. All selected four compounds have ρ values in the range 1.67–1.80 (see Table 3), and would therefore satisfy Herber's criterion for tetracoordinate tin.

TABLE 6 ^{13}C NMR Data (ppm) and Coupling Constants $^nJ(^{13}C—Sn)$ (Hz) for Compounds **1–4**

	A	*B*	**1**	**2**^{a}	**3**	**4**^{b}
C1	32.8 (45.7)	33.7 (36.6)	32.5 (44.7)	32.5 (45.8)	32.5 (45.8)	31.6 (39.9)
C2	37.8 (11.0)	38.1 (18.9)	37.6 (19.6)	37.2 (17.4)	37.2 (17.4)	37.2 (19.7)
C3	39.3 (332.7)	38.9 (360.5)	37.0 (349.8)	36.9 (347.2)	36.9 (354.5)	37.2 (350.3)
C4			30.6	36.6	31.9	32.8
C5			14.8	20.2	31.9	33.3
C6			56.6	56.7	56.6	56.6
C7			51.7	51.8	51.8	51.8
C=O			178.9	181.8	177.2	176.9
C*i*	150.4	151.6	150.9	151.0	142.9 152.9	150.8
C*o*	128.3	128.3	128.1	128.1	128.6 127.9	127.9
C*m*	125.2	125.4	125.2	125.1	124.2 125.0	125.3
C*p*	125.8	128.1	125.5	125.5	127.2 125.3	125.8

[a] ^{13}C NMR for CH_3: δ 24.1 ppm.
[b] ^{13}C NMR for *o*-ClC_6H_4: δ 135.0, 126.6, 126.0, 129.3 ppm.

A = $[PhC(CH_3)_2CH_2]_3SnCl$; B = $\{[PhC(CH_3)_2CH_2]_3Sn\}_2O$.

Numbering scheme for the titled compounds:

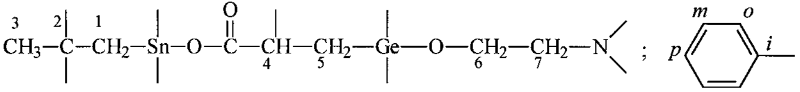


TABLE 7 Relative Intensities of Main Fragment Ions Observed in the Mass Spectra of Compounds **1–4**

	m/e (abund.)			
Ions	**1**	**2**	**3**	**4**
$N(C_2H_4O)_3Ge^+$	220 (11)	220 (12)	220 (28)	220 (18)
$(PhC(CH_3)_2CH_2)_3Sn^+$	519 (2)	519 (2)	519 (3)	519 (2)
$(PhC(CH_3)_2CH_2)_2Sn^{+\cdot}$	386 (1)	386 (1)	386 (1)	386 (1)
$(PhC(CH_3)_2CH_2)Sn^+$	253 (7)	253 (6)	253 (10)	253 (7)
$PhC(CH_3)_2CH_2{}^+$	133 (11)	133 (10)	133 (11)	133 (13)
$PhSn^+$	197 (16)	197 (15)	197 (25)	197 (21)
$PhCH_2{}^+$	91 (100)	91 (100)	91 (100)	91 (100)
$CH_3C(CH_3){=}CH_2{}^{+\cdot}$	56 (3)	56 (6)	56 (10)	56 (7)
$CH_2C(CH_3){=}CH_2{}^+$	55 (19)	55 (19)	55 (20)	55 (20)

Multiple NMR

The ^1H NMR parameters of the titled compounds are given in Table 4. All the resonances with corresponding coupling constances are in good agreement with the expected structures.

To confirm the structures of the titled compounds, ^{119}Sn NMR and ^{13}C NMR were also recorded for the selected four compounds. Their data are given in Tables 5 and 6, respectively. ^{119}Sn NMR studies for four trineophyltin carboxylates in the literature [22] are also listed in Table 5 for comparison.

It is well known in ^{119}Sn NMR studies that raising the coordination number at tin moves the chemical shift upfield of the tetramethyltin standard, while connecting electronegative atoms moves the resonance downfield. It is reported [23] that, in the trialkyltin carboxylate, four-coordinated tin has δ (^{119}Sn) values ranging from about +200 to −60 ppm, five-coordinate tin from −90 to −190 ppm, and six-coordinate tin from −200 to −400 ppm. A single resonance in the range of 76–79 ppm is observed in the ^{119}Sn NMR spectra for all the selected four compounds, which suggests a tetrahedral geometry around the tin atom. Small variations (1–2 ppm) of chemical shifts were observed for the four titled compounds, indicating that changing substituents in the β position of the germatranyl-substituted propionate has little effect on the structure of the triorganotin derivatives.

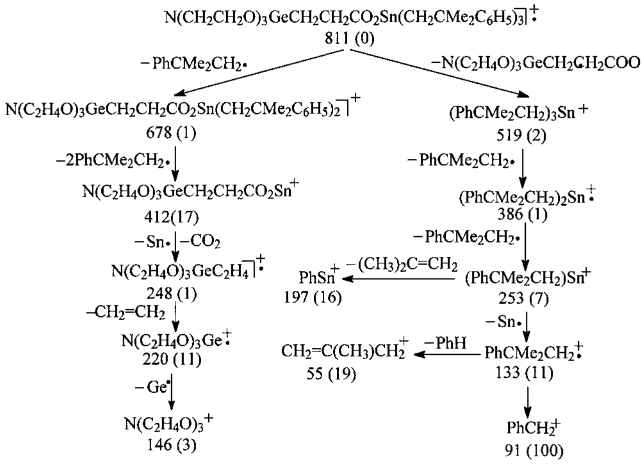
Holecek et al. [24] and a few others [25–27] have reported that the $^1J(^{13}C,\ ^{119}Sn)$ coupling constant can be used as a function of the coordination number of triorganotin compounds, ranging between 327 and 387 Hz for tetracoordinated compounds, and between 442 and 509 Hz for pentacoordinated ones. The triorganotin germylpropionates exhibit ^1J coupling constants in the range of 349.8–354.9 Hz, indicating tetracoordination in chloroform solution, in agreement with our IR spectroscopic study and the ^{119}Sn NMR data. Therefore, the titled complexes adopt the same tetrahedral geometry around tin in the solid state and in solution.

Mass Spectroscopy

The mass spectra of compounds **1–4** are given in Table 7. For all the four compounds, the fragment ion $PhCH_2^+$ is the base peak. $PhSn^+$ is also quite intense. Generally, they have the same fragmentation pattern.

No molecular ion peaks thereafter were found for any of the compounds, which means that there is no intermolecular coordination.

All the fragmentations observed are compatible with the fragmentation rules described in the literature [10,14]. The possible fragmentation pattern of $N(CH_2CH_2O)_3GeCH_2CH_2CO_2Sn(CH_2CMe_2C_6H_5)_3$ is given in Scheme 3.



SCHEME 3

TABLE 8 The Insecticidal and Acaricidal Activity of Compounds **1–11**

	Average Inhibition Percentage after 24 h	
Compound	*Tetraanychus urticae koche*	*Culi cidae*
1	92.9	100
2	0	0
3	94.8	100
4	31.9	0
5	9.0	0
6	89.9	100
7	94.2	100
8	95.5	100
9	97.3	100
10	97.5	100
11	87	0

Biological Tests

The bioassay results of compounds **1–11** against *Tetraanychus urticae koche* and *Culi cidae* are given in Table 8. The results show that most of the tested compounds have very good activities against *T. urticae koche* and *C. cidae* at 200 and 10 ppm, respectively. However, the preliminary screening has shown that all the compounds have poor fungicidal and bactericidal activity.

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