

Synthesis and Structural Characterization of new Tri (2-methyl-2-phenylpropyl) tin Carboxylates containing Germanium

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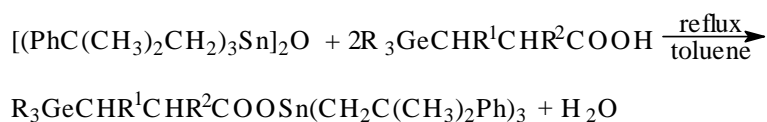
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Abstract: Eight tri(2-methyl-2-phenylpropyl) germylpropionates have been synthesized, and their structures were characterized by elemental analysis, IR, multinuclear NMR (¹H, ¹³C, ¹¹⁹Sn) and MS. The spectroscopic studies revealed that compounds of this type possess a tetrahedral geometry, which have been expected to have good biological activity.

Keywords: Triorganotin carboxylates, IR spectroscopy, multinuclear NMR, ¹J (¹³C, ¹¹⁹Sn).

Organotin compounds are extensively studied for their biological activity¹. Organogermanium is another kind of element that has a wide range of biological activity². To link biological active properties of organotin and organogermanium compounds, we have previously reported the biological activity of trialkyltin germylpropionates³ and anticancer activity of dibutyltin digermylpropionates⁴. It is well known that Torque (bis [tri (2-methyl-2-phenylpropyl) tin] oxide) is widely used in agriculture as an acaricide. In this paper, as the continuation of our previous work^{3,4}, we designed and synthesized eight new triorganotin carboxylates containing germanium using Torque as starting material (IIa-d and IIIa-d). The analytical and physical data of the products were given in **Table 1**. The synthetic procedure is shown in **Scheme 1**.

Scheme 1.



R₃ = Ph₃ (**II**); R¹ = H, R² = H (**IIa**); R¹ = H, R² = CH₃ (**IIb**); R¹ = Ph, R² = H (**IIc**); R¹ = 2-ClC₆H₄, R² = H (**IId**).

R₃ = N(CH₂CH₂O)₃ (**III**); R¹ = H, R² = H (**IIIa**); R¹ = H, R² = CH₃ (**IIIb**); R¹ = Ph, R² = H ; (**IIIc**); R¹ = 2-ClC₆H₄, R² = H (**IIId**).

A mixture of 5 mmol of **I**, 2.5mmol bis [tri (2-methyl-2-phenylpropyl) tin] oxide and 30 ml of dry toluene was heated under reflux with stirring for 6 h. Water formed during the condensation reaction was continuously removed by the use of a Dean and Stark apparatus. The clear solution obtained after filtration was evaporated under vacuum to give a white solid. Pure product was obtained by recrystallization from solvent mixture CHCl_3 /Petroether.

Table 1. The analytical and physical data of the title compounds.

No	Formula	MW	M.P.	Yield	Elemental Analyses		
					C(%)	H(%)	N(%)
Ila	$\text{C}_{51}\text{H}_{58}\text{GeO}_2\text{Sn}$	894.30	90-3	90.6	68.40(68.50)	6.70(6.54)	
Ilb	$\text{C}_{52}\text{H}_{60}\text{GeO}_2\text{Sn}$	908.33	83-5	87.0	68.79(68.76)	6.88(6.66)	
Ilc	$\text{C}_{57}\text{H}_{62}\text{GeO}_2\text{Sn}$	970.40	102-4	84.5	70.60(70.55)	6.64(6.44)	
Ild	$\text{C}_{57}\text{H}_{61}\text{ClGeO}_2\text{Sn}$	1004.84	134-6	86.6	68.21(68.13)	6.41(6.12)	
IIIa	$\text{C}_{39}\text{H}_{55}\text{GeNO}_5\text{Sn}$	809.15	54-7	74.1	57.90(57.89)	6.91(6.85)	1.70(1.73)
IIIb	$\text{C}_{40}\text{H}_{57}\text{GeNO}_5\text{Sn}$	823.18	95-7	94.8	58.42(58.36)	6.82(6.98)	1.53(1.70)
IIIc	$\text{C}_{45}\text{H}_{59}\text{GeNO}_5\text{Sn}$	885.25	174-5	80.2	61.36(61.06)	6.68(6.72)	1.41(1.58)
IIId	$\text{C}_{43}\text{H}_{58}\text{ClGeNO}_5\text{Sn}$	919.69	142-4	81.6	58.77(58.77)	6.40(6.36)	1.69(1.52)

Some important spectroscopic data of the title compounds are given in **Table 2**; for comparison the ^{119}Sn chemical shift and $^1\text{J}(^{13}\text{C}, ^{119}\text{Sn})$ coupling constant of a tetracoordinated tin compound R_3SnCl are also presented in **Table 2**.

In IR spectra, the most important bands arise from $\nu(\text{CO}_2)_{\text{asym}}$ and $\nu(\text{CO}_2)_{\text{sym}}$ occur at 1647-1665 and 1357-1397 cm^{-1} , respectively. The $\Delta\nu$ value [$\nu(\text{CO}_2)_{\text{asym}} - \nu(\text{CO}_2)_{\text{sym}}$] has been used to predict the mode of carboxylate interaction³. In **Table 2**, the $\Delta\nu$ values in the range of 252-284 cm^{-1} strongly indicate the unidentate chelating of the carboxylate groups.

Table 2. Some important spectroscopic data of the title compounds.

No.	$\nu(\text{CO}_2)_{\text{asym}}$	$\nu(\text{CO}_2)_{\text{sym}}$	$\Delta\nu$	^{119}Sn (ppm)	$^1\text{J}(^{13}\text{C}-^{119}\text{Sn})$
Ila	1647(s)	1380(s)	267	78.0	349.8
Ilb	1654(s)	1381(s)	273	76.2	347.2
Ilc	1642(s)	1358(s)	284	78.2	354.5
Ild	1641(s)	1357(s)	284	78.4	350.3
IIIa	1649(s)	1397(m)	252	83.2	349.6
IIIb	1650(s)	1384(m)	266	83.4	353.9
IIIc	1647(s)	1383(m)	264	86.1	352.8
IIId	1665(s)	1383(m)	282	89.0	352.0
*				118.5	332.7

* $(\text{PhC}(\text{CH}_3)_2\text{CH}_2)_3\text{SnCl}$

Holeccek *et al*⁵⁻⁸ noticed the $^1\text{J}(^{13}\text{C}, ^{119}\text{Sn})$ coupling constant to be 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 $^1\text{J}(^{13}\text{C}, ^{119}\text{Sn})$ coupling constants ranging from 347.2 to 354.5 Hz indicating tetracoordination in chloroform solution, in agreement with our IR spectroscopic study demonstrating the synthesized compounds to be a four coordinated monomer in chloroform.

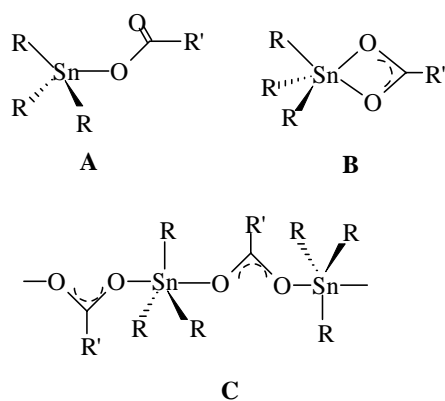
The ^{119}Sn chemical shift data obtained from CDCl_3 solution of the eight compounds are described in **Table 2**. A single resonance in the range of 76.2-89.0 ppm, compatible with the tetrahedral geometry proposed for the solution structure, is observed for each compound. Substitution of a chloride for a carboxylate induces only slight upfield shift of the ^{119}Sn resonance that is unlikely to arise from a significant additional coordination by the oxygen atom of the carbonyl group.

These data combined with 1J (^{13}C , ^{119}Sn) coupling constants and $\Delta \nu$ ($\nu(\text{CO}_2)_{\text{asym}} - \nu(\text{CO}_2)_{\text{sym}}$) values previously discussed tend to confirm that the trineopentyltin carboxylates exhibit a tetracoordinated geometry in solution as well as in solid state.

It is well established that triorganotin compounds (R_3SnL) are significantly more biologically active than other classes with either more or less hydrocarbon groups bonded to tin⁹. Within the R_3SnL unit, the nature of R group determines the species specificity of the biocide. Apparently the function of L is to support the transport of the active organotin moiety to support the site of the action, where it is released by hydrolysis. Hence, anionic ligands L play a secondary role in determining the degree of activity of R_3SnL compounds. In this context, a wide spectrum of biological activity could be achieved by including organogermanium groups in the anionic ligands.

Not all the triorganotin carboxylates are essentially active biocides. Biocidal activity of triorganotin carboxylates is related to their structures by the fact that the species generating a tetrahedral structure in solution are more active⁹. Triorganotin carboxylates adopt three structural type in the solid state¹⁰ (as shown in **Scheme 2**).

Scheme 2



A monomeric structure (**A**), can be 4-coordinate, whereas a polymeric structure (**C**) generally contains 5-coordinate tin atoms. Five coordinate compounds which adopt structural type (**B**) inevitably occur when the carboxylate groups act as a chelating ligand. Both the monomeric 4-coordinate and the polymeric 5-coordinate carboxylates are more active than the 5-coordinate chelated monomer as the former generated tetrahedral

species in solution where the polymeric arrangements are rapidly converted into monomeric forms by intermolecular fragmentation.

Our spectroscopic studies have characterized definitely a four coordinated monomer for this type of triorganotin carboxylates, therefore a good bioassay result is expected.

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