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Tri-*n*-butyltin carboxylate derivatives of *para*-substituted phenyl-ethanoic acids: synthesis, characterization and X-ray structure determination

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Abstract

The tributyltin esters of 4-(ethyl)-phenyl-ethanoic acid and 4-(isopropyl)-phenyl-ethanoic acid have been prepared as model compounds of the repeating unit of the related stannylated polystyrenic derivatives. Both the products were fully characterized by proton and carbon NMR two-dimensional techniques. FT-IR spectra show in the solid state carboxylated moieties bridging R_3Sn groups with the metal atom expanding its coordination number, this structure being destroyed in solution. The supramolecular arrangement of the products in the solid state has been investigated by X-ray diffraction, which confirms the pentacoordination at tin in both the products, and indicates a different spatial arrangement of the alkylated aryl groups, as evidenced also by the slightly different thermal properties.
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Keywords: Tin coordination; Triorganotin carboxylate; X-ray diffraction; NMR spectroscopy; Supramolecular structure

1. Introduction

In the recent years organotin materials have gained relevant interest in several research fields [1]. Apart from academic concern related to fundamental research, tin derivatives are widely used as components for antifouling paints [2–4], as catalysts [5] as well as anti-tumour drugs [6] and ion carriers in electrochemical membrane building [7].

Generally, tin derivatives suffer of some toxicity and applications involving tin leaching should be improved, or even avoided. In order to minimize this drawback, successful results may be obtained by anchoring tin functionalities to a macromolecular chain [8] so as to slower or prevent the release of tin in the environment [9].

Usually, the synthesis of polymeric derivatives is accompanied by the preparation of low molecular weight model compounds resembling the organometallic repeating unit, in order to compare their properties, and hence the influence of the macromolecular chain on the behaviour of the organometal moiety.

In the course of our current investigation [10] on the synthesis and characterization of poly(styrene) derivatives, useful for electrochemical applications, possessing the general structure depicted in Chart 1, we have prepared the 4-(ethyl)-phenyl-ethanoic acid tributyltin ester (**III**) and 4-(isopropyl)-phenyl-ethanoic acid tributyltin ester (**VI**) (Chart 3) as models for the stannylated styrenic repeating unit.

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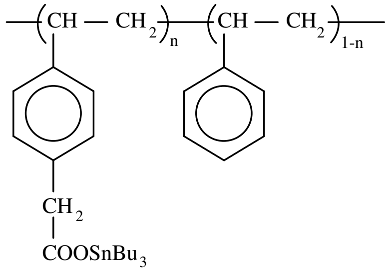


Chart 1.

It is known [11] that organotin carboxylates can exist in at least two different forms (Chart 2). Usually the first one, where the tin atom is tetracoordinated, is adopted in diluted solution, as evidenced by both Sn NMR ($\delta \approx 100$ ppm for tributyltin derivatives) and infrared spectroscopy (band close to 1650 cm^{-1} related to the carbonyl stretching of organotin carboxylate).

Pentacoordinated tin can be observed in concentrated solutions or in the solid state, as shown by the resonance at $\delta \approx -50$ ppm in the Sn NMR spectrum and the IR absorption band at ca. 1570 cm^{-1} attributed to the carbonyl interacting with tin so as to expand its coordination number.

In some cases tin exhibits both tetra- and pentacoordination, in particular in polymeric materials where, in the solid state, the macromolecular chain is unable to assume a conformation involving sufficiently extended pentacoordinated structures. The extent of this behaviour is related to both structural parameters of the polymer itself and to the concentration of stannylated units [8]. Similar results are also obtained when the substituents at tin are particularly hindering and prevent, for sterical reasons, the establishment of a pentacoordinated form.

Aim of the present paper is therefore to investigate the structure of model compounds **III** and **VI** by using the X-ray diffraction technique in order to better understanding the behaviour of the related polymeric derivatives. Particular attention will be focused not only to tin coordination, but also to the superstructure of the aggregates resulting from intermolecular tin coordination.

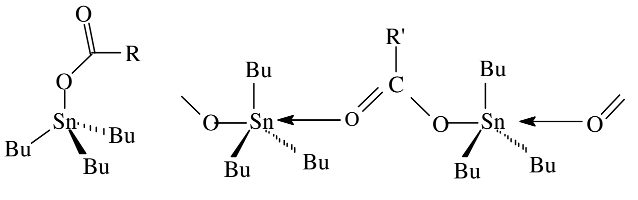


Chart 2.

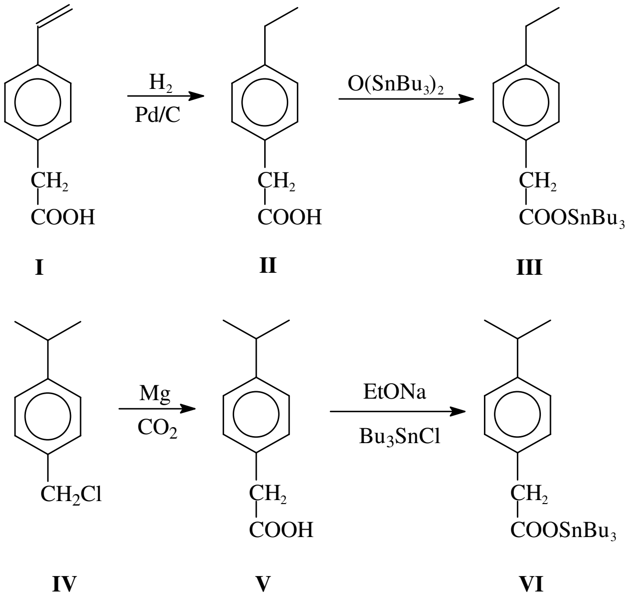
2. Results and discussion

Tri-*n*-butyltin carboxylates can be obtained in several ways [12], the most important being a direct esterification of the carboxylic acid with bis-tributyltin oxide (**BTBTO**). Indeed, using toluene as solvent, the water produced in the reaction can be easily taken off by azeotropic distillation and the product yield is nearly quantitative.

As depicted in Chart 3, we applied this method to the preparation of 4-(ethyl)-phenyl-ethanoic acid tributyltin ester (**III**) starting from the corresponding carboxylic acid (**II**), obtained in turn by catalytic selective hydrogenation of the commercial unsaturated derivative (**I**), an useful monomer for the synthesis of polymeric compounds having **III** as the repeating unit. Although the esterification reaction is readily carried out, some unreacted **BTBTO** can be difficult to be removed because of complexation between tin and carboxylic moieties, thus requiring repeated crystallizations of the reaction product with consequent reduction of yield. For this reason, despite the reaction is very effective and easy to perform, we used a different approach for the synthesis of 4-(isopropyl)-phenyl-ethanoic acid tributyltin ester (**VI**). Since it is known that organotin halides can react with metallic carboxylate [13], we used the sodium salt of 4-(isopropyl)-phenyl-ethanoic acid (**V**) and tri-*n*-butyltin chloride as reactants for the preparation of **VI**. The carboxylic acid **V** can be prepared quenching with carbon dioxide the Grignard reagent obtained form 4-isopropyl-benzylchloride (**IV**) and magnesium.

Model compounds **III** and **VI** were both characterized by proton and carbon NMR spectroscopy.

In the high field section of the ^{13}C NMR spectra recorded in CDCl$_3$, apart from the expected carbon



I **II** **III**

IV **V** **VI**

Chart 3.

resonances, some satellite bands appear, resulting from the coupling between ^{13}C and tin (both ^{117}Sn and ^{119}Sn isotopes) and related to the proximity to tin by the C atoms of *n*-butyl group, while no coupling is observed between tin and the carbonyl or benzylic carbon. In particular for compounds **III** and **VI** it is possible to observe $^{1}J(^{13}C, {}^{117}Sn/^{119}Sn) = 343/357$ and 342/356 Hz (Table 1), respectively, which are values typical of a pseudo-tetrahedral arrangement around tin atom [14].

In order to unambiguously assign the ^{13}C chemical shift values, a combination of two-dimensional NMR techniques has been used: a gCOSY spectrum showing cross peaks correlating the mutually coupled protons and, once this pattern is established, a gHSCQ sequence allowing the attribution of the carbon atoms.

Upon passing from the carboxylic acids to the corresponding tri-*n*-butyl derivatives, the disappearance of the IR carboxyl stretching band centred at 1700 cm^{-1} and new bands at 1572 and 1386 cm^{-1} for **III**, and at 1590 and 1380 cm^{-1} for **VI**, related to organotin carboxylate are observed. Such new bands are visible only in the solid state IR and are typical of pentacoordination at tin due to interaction with carbonyl groups; this is also confirmed by the $\Delta\upsilon$ difference between the frequencies of asymmetrical and symmetrical stretching vibrations of the carboxyl moiety (186 and 210 cm^{-1} for **III** and **VI**, respectively). These values are close to those reported [15] for tin in the ionic form, and support the hypothesis of a structure involving bridged carboxylate groups located between planar SnR_3 groups with pentacoordinated tin, having a trigonal bipyramidal geometry, as formerly depicted in Chart 2.

The IR spectra recorded in dilute chloroform solution show the presence of new bands at nearly 1645 and 1355 cm^{-1}, attributed to the tetracoordinated form of the organotin carboxylate since the bridging by carboxylic groups is broken at the coordination bond upon interaction with the solvent. As expected, the difference between the asymmetrical and symmetrical carbonyl stretching vibrations is now higher, i.e. $\Delta\upsilon = 291$ and 289 cm^{-1}, respectively, and closer to typical values of an organic ester.

Table 1
^{119}Sn NMR data (chemical shifts expressed in ppm) and $^{n}J(^{13}C, {}^{117}Sn/^{119}Sn)$ coupling constants evaluated from ^{13}C NMR spectra (expressed in Hz) for compounds **III** and **VI** in $CDCl_3$ and C_6D_6

	III		VI	
	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
$\delta(^{119}Sn)$	109	97	110	98
$^{1}J(^{13}C, {}^{117}Sn/^{119}Sn)$	343/357	348/364	342/356	344/360
$^{2}J(^{13}C, {}^{117}Sn/^{119}Sn)^{a}$	63	64	62	63
$^{3}J(^{13}C, {}^{117}Sn/^{119}Sn)^{a}$	20	22	20	21

[a] A single approximate value is given when the coupling with ^{119}Sn and ^{117}Sn is unresolved.

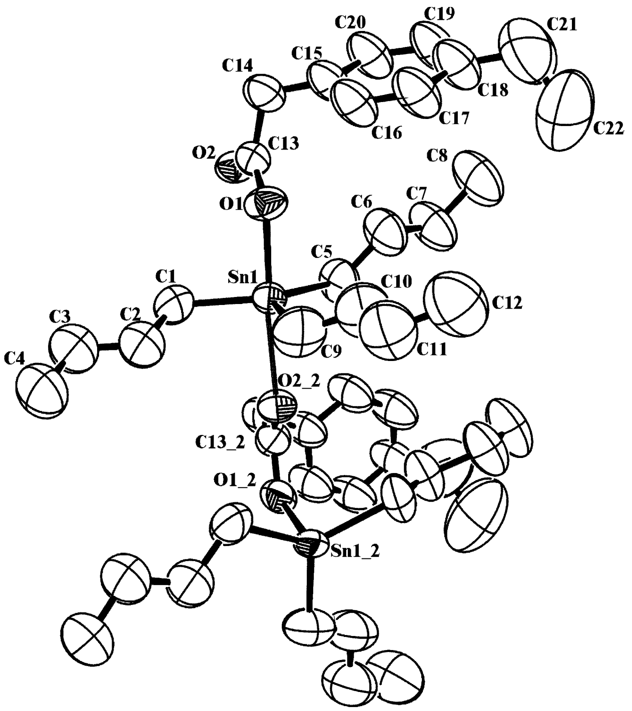


Fig. 1. ORTEP plot of two adjacent molecules of compound **III** belonging to the same chain and interacting through carbonyl oxygen atom.

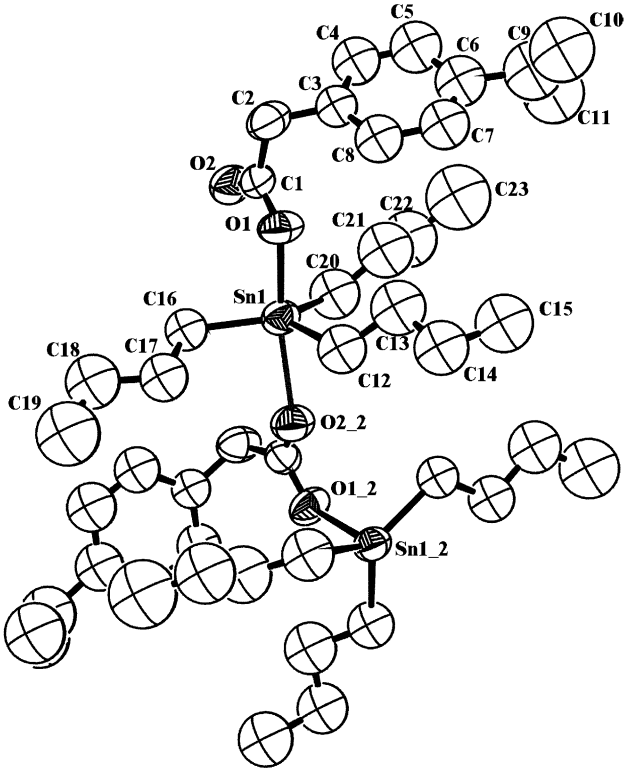


Fig. 2. ORTEP plot of two adjacent molecules of compound **VI** belonging to the same chain and interacting through carbonyl oxygen atom.

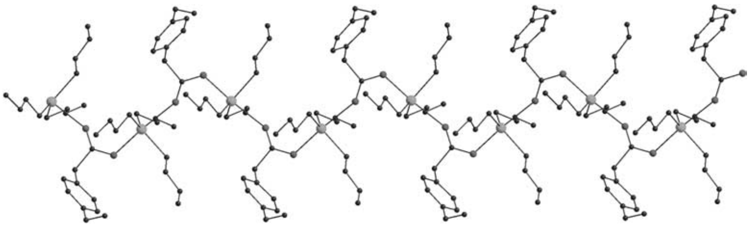


Fig. 3. Single chain structure of organotin carboxylate **III** as determined by X-ray diffraction.

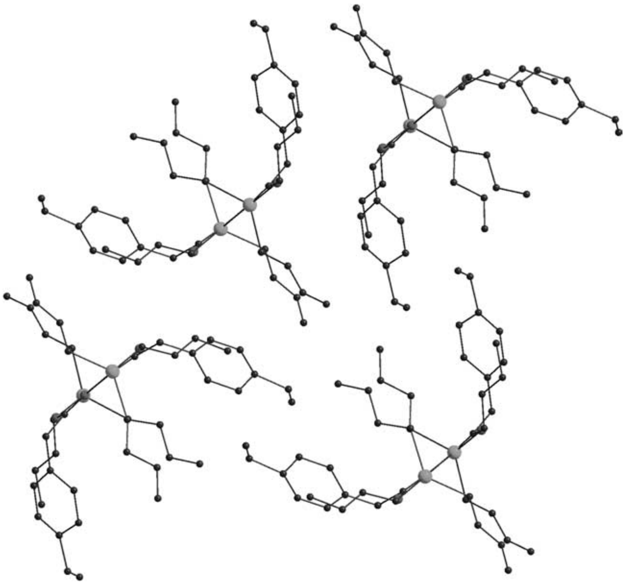


Fig. 4. Supramolecular assembly of tri-*n*-butyltin carboxylate **III** chains as determined by X-ray diffraction, viewed along the chain propagation axis.

The X-ray structures of **III** and **VI** confirm the pentacoordination of tin atoms, as suggested by IR spectra. In **III** (Fig. 1) the tin–oxygen distances are in the range 2.168(9) for the ester oxygen Sn1–O1, to 2.476(11) Å for the carbonyl oxygen atom Sn1–O2_2. Similarly, in compound **VI** (Fig. 2) the range is from 2.165(5) for Sn1–O1 to 2.517(6) Å for Sn1–O2_2.

In the solid state both these compounds are arranged in ordered, quasi-linear, infinite chains and purely steric factors seem to drive their packing (Fig. 3). Steric hindrance appears to originate a different arrangement of the aryl groups along the chains. More precisely, in the case of **III** the aryl groups bearing the ethyl substituent are in *cis* position to one another, with respect to the plane containing oxygen and tin atoms, as evidenced from the view along the polymeric propagation axis (Fig. 4), whereas in **VI** a *trans* arrangement of the isopropyl substituted aryl groups is observed (Fig. 5).

However, the different structure in the crystalline state of **III** and **VI** is not significantly evidenced by their melting temperature (74.5 and 73.1 °C, respectively) nor by their melting enthalpy values (43.3 and 38.1 kJ/mol, respectively), as determined by DSC, thus inducing to consider both **III** and **VI** as substantially equivalent model compounds of the repeating units in the related polymeric derivatives.

On the basis of these observations we can assume that compounds **III** and **VI** are completely pentacoordinated in the solid state and loose this ordered structure when in the presence of a solvating agent. In order to assess the influence of the solvent on the tin coordination number, **III** and **VI** were analyzed by both ^{13}C and ^{119}Sn NMR in C_6D_6 solution, checking the $\delta(^{119}\text{Sn})$ and the $^{1}J(^{13}\text{C}, {}^{117}\text{Sn}/^{119}\text{Sn})$ behaviour (Table 1), since both these parameters are directly related to the central metal atom arrangement [14]. In fact, in the case of a trigonal bipyramidal arrangement, it should be reasonably expected a δ (^{119}Sn) value shifted towards higher field [8]. The $^{4}J(^{119}\text{Sn}, {}^{117}\text{Sn})$ might not be visible anyway, due to the long-range coupling sensitivity to bond length [16], since the coupling pathway passes through a rather long bond distance Sn–O, as evidenced by X-ray structures. None of these changes was however observed

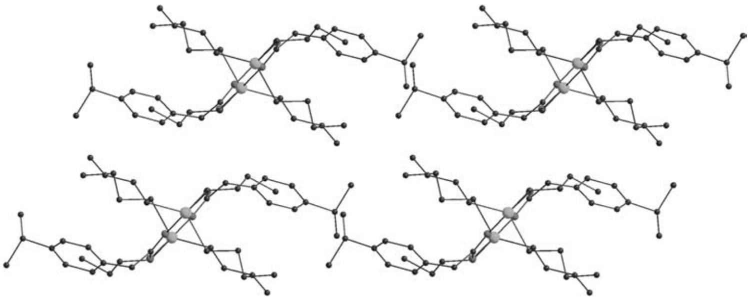


Fig. 5. Supramolecular assembly of tri-*n*-butyltin carboxylate **VI** chains as determined by X-ray diffraction, viewed along the chain propagation axis.

upon passing from $CDCl_3$ to C_6D_6, accounting for a tetrahedral arrangement even in a weakly polar solvent for both the compounds **III** and **VI**. Moreover the ^{13}C NMR spectra display $^1J(^{13}C, ^{117}Sn/^{119}Sn)$ values similar to those observed in $CDCl_3$ (Table 1), thus confirming a pseudo-tetrahedral arrangement of the tin atom.

3. Conclusions

4-(Ethyl)-phenyl-ethanoic acid tributyltin ester and 4-(isopropyl)-phenyl-ethanoic acid tributyltin ester were prepared from the corresponding carboxylic acids by direct esterification with BTBTO and by reaction with Bu_3SnCl of the carboxylic acid sodium salt, respectively.

Both of them exhibit tetracoordinated and pentacoordinated tin atom in solution and in the solid state, respectively, as suggested by IR analysis.

A more detailed structure elucidation carried out by X-ray diffraction techniques confirms the pentacoordination of tin in the solid state and shows a different spatial arrangement for these stannylated derivatives. The difference in supramolecular structure can be attributed to the sterical hindrance of the isopropyl substituent as compared to the ethyl one. Their similar thermal behaviour allows to consider both of these compounds as substantially equivalent models of the related macromolecular derivatives.

4. Experimental

Chemicals are supplied by Sigma–Aldrich and generally used as received. Solvents are purified using normal purification techniques [17].

Elemental analyses were performed by REDOX s.n.c. (Milano).

^1H and ^{13}C NMR spectra are recorded both on a Varian Gemini 300 NMR and Varian Mercury 400 NMR using $CDCl_3$ and C_6D_6 solutions and tetramethylsilane as internal standard. ^{119}Sn NMR spectra are recorded on Varian Mercury 400 using $CDCl_3$ and C_6D_6 solutions and tetramethyltin as external standard. In describing the NMR spectra we will use the following notation: C_i = *ipso* carbon of the functionalized phenyl group, bound to the variable substituent; C_o = *ortho*; C_m = *meta*; C_p = *para*.

Infrared spectra in KBr pellets are recorded by a Perkin–Elmer 1750 FT-IR spectrometer.

Melting points and ΔH_m values of stannylated compounds have been determined by differential scanning calorimetry using a TA Instruments DSC 2920 modulated calorimeter. M.p. values are given as the temperature value at the maximum of the endothermic peak.

A summary of the crystallographic data and structural refinement for compounds **III** and **VI** is reported in Table 2. Both data collections were performed on a

Table 2
Crystal data and structure refinement for **III** and **VI**

Compound	III	VI
Empirical formula	$C_{22}H_{38}O_2Sn$	$C_{23}H_{40}O_2Sn$
Formula weight (g/mol)	453.21	467.24
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
Unit cell dimensions		
a (Å)	14.207(4)	16.182(3)
b (Å)	17.681(6)	10.551(2)
c (Å)	10.292(3)	16.537(3)
β (°)	109.445(8)	114.998(4)
V (Å^3)	2437.9(13)	2559.0(9)
Z	4	4
D_{calc} (Mg/m^3)	1.235	1.213
Absorption coefficient (mm^{-1})	1.059	1.010
Crystal size (mm)	0.80 × 0.10 × 0.10	0.20 × 0.05 × 0.05
θ Range for data collection (°)	1.52–25.00	1.39–25.00
Reflections collected/unique [R_{int}]	21 163/4287 [0.5160]	19 589/4506 [0.0730]
Completeness to $\theta = 25.00$ (%)	100.0	100.0
Absorption correction	Empirical	Empirical
Maximum and minimum transmission	0.9015 and 0.4847	0.9512 and 0.8235
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4287/112/226	4506/154/203
Goodness-of-fit on F^2	0.914	0.956
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1245$, $wR_2 = 0.2015$	$R_1 = 0.0656$, $wR_2 = 0.1721$
R indices (all data)	$R_1 = 0.2709$, $wR_2 = 0.2218$	$R_1 = 0.1156$, $wR_2 = 0.1867$
Largest difference peak and hole (e Å^{-3})	0.726 and −0.742	0.699 and −0.773

Bruker SMART 2000 equipped with a CCD detector. An empirical absorption correction was applied (SADABS) [18]. Crystals of compound **III** were not of a very good quality and this gave high value of R_{int}. The structures were solved by direct methods and refined with full-matrix least-square (SHELX-97) [19]. Non-hydrogen atoms were refined anisotropically with the exception of disordered groups, specifically both alkyl and aryl groups in compund **IV**, which were split in two positions, using distance and anisotropic displacement parameter restraints, and refined isotropically. Hydrogen positions were set geometrically.

*4.1. 4-(Ethyl)-phenyl-ethanoic acid (**II**)*

1.00 g (6.16 mmol) of 2-(4-styryl)-ethanoic acid and 50 mg of Pd 5% on carbon are dissolved in 50 ml of THF. The solution is hydrogenated at 3 atm for 3 h at room temperature in a Parr apparatus. The suspension is filtered on silica and evaporated to give 1.01 g of (4-ethyl)-phenyl-ethanoic acid corresponding to a quantitative yield. M.p. = 91 °C (lit. 91 °C [20])

^{1}H NMR: 10.4 (bs, 1H, COOH); 7.2 (m, 4H, arom.); 3.6 (s, 2H, $\mathbf{CH_2}$CO); 2.6 (q, 2H, $\mathbf{CH_2}$–CH_3); 1.2 (t, 3H, CH_3).

^{13}C NMR: 179.1 (COOH); 144.0 (C_p); 131.1 (C_i); 130.0 (C_o); 128.8 (C_m); 41.4 (Ar-CH_2); 29.1 ($\mathbf{CH_2}CH_3$); 16.2 (CH_3).

FT-IR: 3445 (ν_{OH} acid); 2959–2868 (ν_{CH} aliph.); 1699 (ν_{CO} acid); 824 ($\delta_{\text{1,4-subst.ring}}$ arom.) cm^{-1}.

*4.2. 4-(Ethyl)-phenyl-ethanoic acid tributyltin ester (**III**)*

In a 100 ml flask equipped with a Dean Stark apparatus 0.70 g (4.26 mmol) of (4-ethyl)-phenyl-ethanoic acid is dissolved in toluene (40 ml) and 2.2 ml (4.26 mmol) of bis(tributyltin) oxide is added. The reaction mixture is heated until no more water evolution is observed and toluene is further distilled under reduced pressure. The (4-ethyl)-phenyl-ethanoic acid tributyltin ester gives air stable white prismatic crystals by crystallization with ethanol–water (1:1). Yield: 1.54 g (79%). M.p. = 74.5 °C. ΔH_{m} = 43.3 kJ/mol.

Anal. Calc.: C, 58.30; H, 8.45; O, 7.06; Sn, 26.19. Found: C, 58.49; H, 8.31; O, 6.99%.

^{1}H NMR: 7.1–7.2 (2dd, 4H, arom.), 3.6 (s, 2H, $\mathbf{CH_2}$CO), 2.6 (q, 2H, $\mathbf{CH_2}$–CH_3), 1.6 (m, 6H, $CH_{2\beta Bu}$), 1.2–1.4 (m, 15H, $CH_{2\alpha Bu}$ + $CH_{2\gamma Bu}$ + $\mathbf{CH_3}$–CH_2), 0.9 (t, 9H, CH_{3Bu}).

^{13}C NMR: 177.8 (COO); 143.0 (C_p); 133.7 (C_i); 129.8 (C_o); 128.4 (C_m); 42.3 ($\mathbf{CH_2}$CO); 29.1 ($\mathbf{CH_2}$–CH_3); 28.6 ($CH_{2\beta Bu}$); 27.7 ($CH_{2\gamma Bu}$); 17.1 ($CH_{2\alpha Bu}$); 16.2 ($\mathbf{CH_3}$–CH_2); 14.3 (CH_{3Bu}).

FT-IR: 2956–2854 (ν_{CH} aliph.); 1572 (ν_{COOSn}); 814 ($\delta_{\text{1,4-subst.ring}}$ arom.) cm^{-1}.

*4.3. 4-(Isopropyl)-phenyl-ethanoic acid (**V**)*

In a nitrogen flushed three necked 100 ml round bottomed flask, equipped with magnetic stirrer and dropping funnel, 0.43 g (12.3 mmol) of clean magnesium is added to 30 ml of freshly distilled THF, then a solution of 2.07 g (12.3 mmol) of 4-isopropyl-benzylchloride in 10 ml of THF is slowly dropped in. The mixture is heated at 35 °C and allowed to react until no more magnesium is present. Carbon dioxide is then bubbled in the solution for 3 h. Saturated NH_4Cl aqueous solution is added, the organic phase washed twice with this solution and finally with brine. The organic phase is treated with 10% NaOH solution and extracted with $CHCl_3$, and then the aqueous phase is made acidic by addition of concentrated HCl and further extracted with $CHCl_3$. The organic solvent is distilled off and the product is purified by crystallization with petroleum ether. M.p. = 49 °C (lit. 52 °C [21]). Yield: 0.92 g (42%).

^{1}H NMR: 7.2 (s, 4H, arom.); 3.6 (s, 2H, CH_2); 2.9 (hept, 1H, CH); 1.2 (d, 6H, CH_3).

^{13}C NMR: 178.7 (COOH); 148.7 (C_p); 131.2 (C_i); 129.9 (C_o); 127.4 (C_m); 41.3 (CH_2); 34.4 (CH); 24.6 (CH_3).

FT-IR: 3412 (ν_{OH} acid); 2959 (ν_{CH} aliph.); 1708 (ν_{CO} acid); 815 ($\delta_{\text{1,4-subst.ring}}$ arom.) cm^{-1}.

*4.4. 4-(Isopropyl)-phenyl-ethanoic acid tributyltin ester (**VI**)*

In a nitrogen flushed three necked 100 ml round bottomed flask, equipped with magnetic stirrer and dropping funnel, 0.03 g (3.5 mmol) of sodium is added to 7 ml of absolute ethanol. When the metal is completely reacted, 0.5 g of 4-(isopropyl)-phenyl-ethanoic acid (2.8 mmol) dissolved in 7 ml of absolute ethanol is dropped during 30 min time, then 0.92 g (2.8 mmol) of Bu_3SnCl is slowly added. NaCl formation is observed and after filtration, the solvent is distilled off. The 4-(isopropyl)-phenyl-ethanoic acid tributyltin ester gives air stable white prismatic crystals by crystallization with ethanol–water (1:1). Yield: 0.78 g (65%). M.p. = 73.1 °C. ΔH_{m} = 38.1 kJ/mol.

Anal. Calc.: C, 59.12; H, 8.63; O, 6.85; Sn, 25.4. Found: C, 59.31; H, 8.41; O, 6.98%.

^{1}H NMR: 7.1–7.2 (2dd, 4H, arom.); 3.6 (s, 2H, $\mathbf{CH_2}$CO); 2.9 (hept, 1H, CH); 1.6 (m, 6H, $CH_{2\beta Bu}$); 1.2–1.4 (m, 18H, $CH_{2\alpha Bu}$ + $CH_{2\gamma Bu}$ + $\mathbf{CH_3}$–CH); 0.9 (t, 9H, CH_{3Bu}).

^{13}C NMR: 177.9 (COO); 147.6 (C_p); 133.8 (C_i); 129.8 (C_o); 127.1 (C_m); 42.3 ($\mathbf{CH_2}$CO); 34.4 (CH); 28.5 ($CH_{2\beta Bu}$); 27.7 ($CH_{2\gamma Bu}$); 24.7 ($\mathbf{CH_3}$CH); 17.1 ($CH_{2\alpha Bu}$); 14.3 (CH_{3Bu}).

FT-IR: 2956–2854 (ν_{CH} aliph.); 1572 (ν_{COOSn}); 814 ($\delta_{\text{1,4-subst.ring}}$ arom.) cm^{-1}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 231340 and 231341 for compounds **III** and **VI**, respectively. Copies of this information may be obtained free of charge from: The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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