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SYNTHESIS AND CHARACTERIZATION OF TRI-, DI-, AND CHLORODIORGANOTIN(IV) DERIVATIVES OF 3-BENZOYL-α-METHYLPHENYLACETIC ACID AND 3-(2-THIENYL)ACRYLIC ACID

Muhammad Tariq Masood [a] , Saqib Ali [b] , Muhammad Danish [a] & Muhammad Mazhar [a]
[a] Department of Chemistry , Quaid-i-Azam University , 45320 Islamabad, Pakistan
[b] Department of Chemistry , Quaid-i-Azam University , 45320 Islamabad, Pakistan
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SYNTHESIS AND CHARACTERIZATION OF TRI-, DI-, AND CHLORODIORGANOTIN(IV) DERIVATIVES OF 3-BENZOYL-α-METHYLPHENYLACETIC ACID AND 3-(2-THIENYL)ACRYLIC ACID

Muhammad Tariq Masood, Saqib Ali,* Muhammad Danish, and Muhammad Mazhar

Department of Chemistry, Quaid-i-Azam University,
45320 Islamabad, Pakistan

ABSTRACT

Various organotin derivatives of 3-benzoyl-α-methylphenylacetic acid (HL^1) and 3-(2-thienyl)acrylic acid (HL^2) of the general formulae R_3SnL, R_2SnL_2 and $R_2Sn(Cl)L$ where $R = Me$, Et, *n*-Bu and Ph, $L = L^1$ or L^2, have been synthesized. These compounds were characterized by elemental analyses, infrared, mass, ^1H, ^{13}C and ^{119}Sn NMR spectra and the geometry around the tin atom has been discussed.

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*Corresponding author. E-mail: drsa54@yahoo.com

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INTRODUCTION

Since the last two decades[1–3], organotin carboxylates have been selected as candidates for the study of their diversified applications and interesting structures. Their spectroscopic studies show that there are distinct, phase-dependent geometries around the tin atom in non-coordinating solvents as well as in the solid state[4–7].

In continutaion of our previous research work[8–15], we report here the synthesis, infrared, mass and multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectra of new organotin(IV) carboxylates of 3-benzoyl-α-methylphenylacetic acid (HL^1) and 3-(2-thienyl)acrylic acid (HL^2).

RESULTS AND DISCUSSION

Tri-, di- and monochloroorganotin carboxylates of the ligands HL^1 and HL^2 were prepared by the following general reactions (1)–(3). The elemental analyses and some of their physical data are given in Table I.

$$\begin{gathered} R_3SnCl + AgL^1 \longrightarrow R_3SnL^1 + AgCl \\ R = Me(\mathbf{1}),\ n\text{-Bu}(\mathbf{4})\ \text{and}\ Ph(\mathbf{6}) \end{gathered} \tag{1}$$

$$R_2SnO + 2LH \longrightarrow R_2SnL_2 + H_2O \tag{2}$$

$$L = L^1,\ R = Et(\mathbf{2}),\ n\text{-Bu}(\mathbf{3})\ \text{and}\ Ph(\mathbf{5})$$
$$L = L^2,\ R = Et(\mathbf{7}),\ n\text{-Bu}(\mathbf{9})\ \text{and}\ Ph(\mathbf{11})$$

$$\begin{gathered} R_2SnL_2^2 + R_2SnCl_2 \longrightarrow 2R_2Sn(Cl)L^2 \\ R = Et(\mathbf{8}), n\text{-Bu}(\mathbf{10})\ \text{and}\ Ph(\mathbf{12}) \end{gathered} \tag{3}$$

Infrared Spectroscopy

In the infrared region, the bands of interest are ν(COO), ν(Sn-C), ν(Sn-O) and ν(Sn-Cl) as given in Table II. A marked shifting is observed in the COO frequencies for the complexes as compared to the free acid. This vibration is very important in the prediction of the bonding mode of the ligand. As shown in Table II, the Δν values [$\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$]

Table I. Physical Parameters and ^{119}Sn Chemical Shifts of the Organotin(IV) Derivatives[a]

Compound (Formula Weight)	General Formula	Melting Point, °C	% Yield	%C Calc./ (Found)	%H Calc./ (Found)	^{119}Sn ppm
(**1**) $C_{19}H_{22}O_3Sn$ (431)	Me_3SnL^1	–	67	54.68 (54.20)	5.28 (5.30)	133.0
(**2**) $C_{36}H_{36}O_6Sn$ (683)	$Et_2SnL^1{}_2$	–	70	63.25 (63.40)	5.27 (5.30)	−150.2
(**3**) $C_{40}H_{40}O_6Sn$ (735)	$Bu_2Snl^1{}_2$	–	64	64.95 (64.90)	5.95 (5.85)	144.3
(**4**) $C_{28}H_{40}O_3Sn$ (543)	Bu_3SnL^1	–	70	61.88 (62.00)	7.37 (7.60)	113.2
(**5**) $C_{44}H_{36}O_6Sn$ (779)	$Ph_2SnL^1{}_2$	–	72	67.60 (67.80)	4.61 (4.59)	−202.3
(**6**) $C_{34}H_{28}O_3Sn$ (603)	Ph_3SnL^1	–	82	67.66 (67.00)	4.64 (4.60)	−106.7
(**7**) $C_{18}H_{30}O_4S_2Sn$ (493)	$Et_2SnL^2{}_2$	99–100	84	44.72 (45.00)	4.14 (4.20)	−157.8
(**8**) $C_{11}H_{15}O_2SClSn$ (365.5)	$Et_2Sn(Cl)L^2$	–	60	36.11 (36.20)	4.10 (4.12)	−98.0
(**9**) $C_{22}H_{28}O_4S_2Sn$ (539)	$Bu_2SnL^2{}_2$	67–68	79	48.97 (48.20)	5.23 (5.26)	−150.4
(**10**) $C_{15}H_{13}O_2SClSn$ (411.5)	$Bu_2Sn(Cl)L^2$	–	74	42.70 (41.90)	5.45 (5.50)	−33.0
(**11**) $C_{26}H_{20}O_4S_2Sn$ (579)	$Ph_2SnL^2{}_2$	101–2	83	53.88 (53.72)	3.45 (3.48)	−202.2
(**12**) $C_{19}H_{15}O_2SClSn$ (461.5)	$Ph_2Sn(Cl)^2$	–	69	49.50 (49.30)	3.25 (3.54)	−158.2
HL^1 ($C_{16}H_{14}O_3$) (254)		94	–	–	–	–
HL^2 ($C_7H_6O_2S$) (154)		145–48	–	–	–	–

[a] Compounds **(1)–(4)**, **(8)**, **(10)** and **(12)** were semisolid.

Table II. Assignments of Characteristic Infrared Vibrations (cm^{-1})

	ν(COO)					
Comp.	Asym.	Sym.	Δν	ν(Sn-C)	ν(Sn-O)	ν(Sn-Cl)
HL^1	1677 s	1420 s	257	–	–	–
HL^2	1688 s	1419 s	269	–	–	–
AgL^1	1560 s	1390 s	170	–	–	–
AgL^2	1544 s	1392 s	152	–	–	–
(1)	1550 s	1370 s	180	546 m	417 w	–
(2)	1560 s	1365 s	195	592 m	438 m	–
(3)	1562 s	1370 s	192	548 m	436 m	–
(4)	1573 s	1381 s	192	602 s	417 m	–
(5)	1553 s	1366 s	187	598 s	480 s	–
(6)	1565 s	1382 s	183	602 s	447 w	–
(7)	1555 s	1376 s	179	608 m	488 w	–
(8)	1552 s	1374 s	178	594 m	448 w	357 s
(9)	1563 s	1370 s	193	608 s	488 s	–
(10)	1566 s	1370 s	196	592 m	448 m	348 m
(11)	1572 s	1371 s	201	606 m	482 m	–
(12)	1574 s	1374 s	200	590 s	444 m	353 s

are comparable to the values of the silver salts which clearly indicate the bidentate nature of the ligands[16]. Thus, for triorganotin complexes a bridging nature is most likely and is further supported by the crystal structure of the trimethyl drivative of compound **1**[23]. In case of the chlorodiorganotin derivatives, the presence of a chlorine atom increases the Lewis acidity of tin, thus increasing tin-carbonyl interaction which propose the bridging or chelating nature the of ligand. However, the chelating mode of interaction is more favourable and is suggested for such compounds[17]. For the R_2SnL_2 compounds, a bidentate chelate nature of the corboxylate is suggested which is further suported by the crystal structure[24] of the diethyltin derivative of the ligand HL^2. The bands in the range 600–500 cm^{-1} and 500–400 cm^{-1} indicate Sn-C and Sn-O bonds, respectively. In the chloro derivatives the Sn-Cl band is observed in the region 357–348 cm^{-1}. The band position of the carbonyl group between two benzene rings of the ligand HL^1 is unaffected, showing the non-involvment of this group in bonding to tin.

Multinuclear NMR

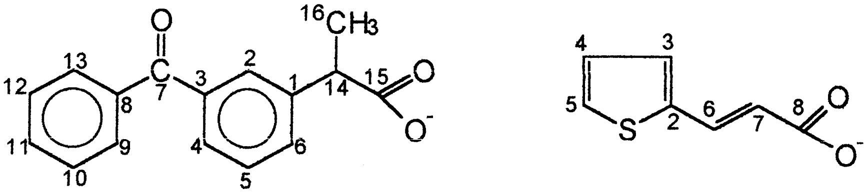
Multinuclear NMR spectra have been carried out in $CDCl_3$. The expected resonances were assigned on the basis of their intensity and multiplicity pattern as well as their coupling constants. The peak integrations of the spectra are in accordance with the number of protons proposed for each fragment of the molecule. The numbering scheme for ligands is given in Fig. 1. The aromatic carbon resonances were assigned by comparing experimental chemical shifts with those calculated by the incremental method[18a] and literature values[18b].

In triorganotin carboxylates $^{1}J[^{119}Sn-^{13}C]$, the indirect tin proton coupling constants $^{2}J[^{119}Sn-^{1}H]$ and ^{119}Sn chemical shifts (Tables I, III–VI) describe a tetrahedral geometry around the tin atom[19,20].

For trimethyltin 3-benzoyl-α-methylphenylacete, $^{1}J[^{119}Sn-^{1}3C]$ and $^{2}J[^{119}Sn-^{1}H]$ are 400 and 58.2 Hz, respectively. Using Lockhart's and Holecek's relations[21,22], the C-Sn-C bond angle calculated for this compound is 111°. However, this angle is a little bit less than the C-Sn-C bond angle obtained from the crystal structure of this compound[23]. This shows that there are two distinct, phase-dependent geometries around the tin atom in such compounds. Therefore, the average C-Sn-C angle (111°) suggests a monomeric tetrahedral environment around the tin atom in non-coordinating solvents. In the solid phase, however, such compounds have a distorted trigonal bipyramidal geometry with a polymeric structure[8,23]. It is, therefore, suggested that all of the triorganotin derivatives are monomeric in non-coordinating solvents with tetrahedral geometry (Fig. 2(a)) and are polymeric in the solid state (Fig. 2(b)).

Unlike triorganotin carboxylates in solution, the geometry of diorganotin carboxylates cannot be defined with certainty because of dynamic processes involving the carboxylate oxygens due to competition in their coordination behaviour with the tin atom[9]. However, in the solid state the tin atom is hexa-coordinated in such systems[24] (Fig. 2(c)).

In chlorodiorganotin carboxylates, $^{1}J[^{119}Sn-^{13}C]$ and $^{2}J[^{119}Sn-^{1}H]$ could only be resolved for $Et_2Sn(Cl)L$ (Tables V and VI) due to very broad



HL^{1} HL^{2}

Figure 1. Structures of the ligands.

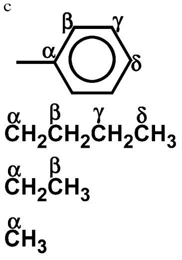
Table III. ^{1}H NMR Data[a,b,c] of Tri- and Diorganotin Carboxylytes of HL [1]

Compound → Proton↓	**(1)** R = Me	**(2)** R = Et	**(3)** R = *n*-Bu	**(4)** R = *n*-Bu	**(5)** R = Ph	**(6)** R = Ph
2	7.76 (s)	7.74 (s)	7.73 (s)	7.76 (s)	7.75 (s)	7.74 (s)
4	7.40 (d, 7.5)	7.66 (d, 7.6)	7.65 (d, 8.0)	7.60 (d, 7.5)	7.67 (d, 7.8)	7.67 (d, 7.5)
5	7.38 (t, 7.6)	7.41 (t, 7.0)	7.40 (t, 7.7)	7.35 (t, 7.6)	7.42 (t, 7.5)	7.40 (t, 7.5)
6	7.40 (d, 7.5)	7.44 (d, 7.5)	7.40 (d, 7.5)	7.40 (d, 8.0)	7.44 (d, 7.8)	7.50 (d, 8.0)
9/13	7.77 (d, 7.3)	7.85 (d, 7.5)	7.76 (d, 7.4)	7.74 (d, 7.4)	7.83 (d, 7.3)	7.78 (d, 7.4)
10/12	7.63 (d, 7.3)	7.55 (d, 7.2)	7.53 (d, 6.9)	7.55 (d, 7.1)	7.53 (d, 7.1)	7.53 (d, 7.1)
11	7.54 (dd, 7.2, 5.8)	7.64 (dd, 7.2, 6.1)	7.63 (dd, 7.2, 6.0)	7.62 (dd, 7.2, 5.7)	7.65 (dd, 7.0, 7.6)	7.67 (dd, 7.3, 5.8)
14	3.76 (q, 7.8)	3.86 (q, 7.8)	3.82 (q, 7.8)	3.75 (q, 7.8)	3.82 (q, 7.8)	3.91 (q, 7.8)
16	1.47 (d, 7.0)	1.14 (d, 7.2)	1.51 (d, 7.0)	1.48 (d, 7.0)	1.50 (d, 7.0)	1.56 (d, 7.0)
α	0.5 ^{2}J[57]	1.54 (m) ^{2}J[68]	1.49–1.62 (m)	1.48–1.58 (m)	–	–
β	–	1.50 ^{3}J[140]	1.19–1.32 (m)	1.42–1.47 (m)	7.76–7.77 (m)	7.74–7.76 (m)
γ	–	–	1.19–1.32 (m)	1.42–1.47 (m)	7.71–7–74 (m)	7.70–7.74 (m)
δ	–	–	1.12 (t)	1.22 (t)	7.75–7.76 (m)	7.54–7.55 (m)

[a] Chemical shifts (δ) in ppm, $^{n}J(^{1}H\text{-}^{1}H)$ and $^{n}J[^{119}Sn\text{-}^{1}H]$ in Hz.

[b] Multiplicity is given by s = singlet, d = doublet, t = triplet, and m = multiplet.

[c]



$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$

$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$

$\overset{\alpha}{C}H_3$

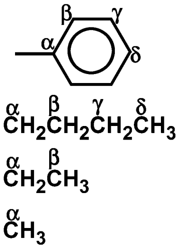
Table IV. ^{13}C NMR Data[a,b,c] of Tri- and Diorganotin Carboxylates of HL^1

Compound → Carbon↓	**(1)** R = Me	**(2)** R = Et	**(3)** R = *n*-Bu	**(4)** R = *n*-Bu	**(5)** R = Ph	**(6)** R = Ph
1	132.4	132.4	132.3	132.3	132.6	135.3
2	130.0	130.0	130.0	130.0	131.7	131.5
3	143.0	141.0	142.4	142.4	140.1	141.5
4	128.6	129.0	128.5	128.5	131.6	128.9
5	128.4	128.5	128.2	128.2	128.6	128.0
6	132.4	132.4	132.3	131.6	132.6	132.2
7	196.6	196.5	196.4	196.6	196.0	196.3
8	138.0	137.8	137.9	137.6	137.4	136.6
9/13	129.2	129.1	129.3	129.3	129.3	129.3
10/12	128.3	128.3	128.2	128.3	128.3	128.3
11	131.6	131.5	131.6	131.8	128.6	129.2
14	29.7	29.7	26.8	26.9	29.7	29.6
15	179.0	184.3	179.1	179.1	180.5	180.2
16	19.4	18.8	19.1	19.3	18.1	19.0
α	−2.3	17.5	29.66	17.52	137.5	138.0
	^{1}J[400]	^{1}J[600]	^{1}J[560]	^{1}J[370]	^{1}J[640]	^{1}J[650]
β	–	8.7	27.75	19.12	136.5	136.0
		^{2}J[43.5]	^{2}J[34]	^{2}J[25]	^{2}J[50]	^{2}J[50]
γ	–	–	19.0	16.5	128.5	128.0
			^{3}J[96]	^{3}J[n.o.]	^{3}J[69]	^{3}J[n.o.]
δ	–	–	13.5	13.6	131.0	130.0
			^{4}J[n.o.]	^{4}J[n.o.]	^{4}J[32]	^{4}J[n.o.]

[a] Chemical shifts (δ) in ppm, $^nJ(^1H\text{-}^1H)$ and $^nJ[^{119}Sn\text{-}^1H]$ in Hz.

[b] n.o. = not observed.

[c]



$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$

$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$

$\overset{\alpha}{C}H_3$

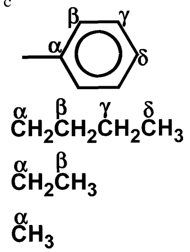
Table V. ^{1}H NMR Data[a,b,c] of Di- and Chlorodiorganotin Carboxylates of HL^{2}

Compound → Proton↓	**(7)** R = Et	**(8)** R = Et	**(9)** R = *n*-Bu	**(10)** R = *n*-Bu	**(11)** R = Ph	**(12)** R = Ph
3	7.6 (d, 7.5)	7.31 (d, 7.6)	7.37 (d, 7.4)	7.33 (d, 7.5)	7.35 (d, 7.5)	7.34 (d, 7.5)
4	7.03 (dd, 4.1)	7.06 (dd, 7.3)	7.05 (dd, 4.2)	7.05 (dd, 7.3)	7.23 (dd, 4.2)	7.04 (dd, 7.3)
5	7.22 (d, 3.8)	7.27 (d, 2.9)	7.23 (d, 2.9)	6.26 (d, 2.9)	7.23 (d, 2.9)	7.28 (d, 2.9)
6	6.25 (d, 15.5)	6.24 (d, 15.7)	6.27 (d, 15.7)	6.23 (d, 15.7)	6.28 (d, 15.7)	6.24 (d, 15.8)
7	7.85 (d, 15.5)	7.86 (d, 15.7)	7.86 (d, 15.7)	7.88 (d, 15.7)	7.86 (d, 15.7)	7.87 (d, 15.8)
α	1.88 (m) ^{2}J[71]	1.80 (m) ^{2}J[64]	1.70 (m)	1.70–1.73 (m)	–	–
β	1.32 (t) ^{3}J[140]	1.28 (t) ^{3}J[125]	1.35–1.40 (m)	1.36–1.40 (m)	7.73–7.75 (m)	7.75–7.77 (m)
γ	–	–	1.35–1.40 (m)	1.36–1.40 (m)	7.76–7.79 (m)	7.60–7.62 (m)
δ	–	–	0.95 (t)	0.92 (t)	7.55–7.57 (m)	7.64–7.66 (m)

[a] Chemical shifts (δ) in ppm, $^{n}J(^{1}H\text{-}^{1}H)$ and $^{n}J[^{119}Sn\text{-}^{1}H]$ in Hz.

[b] Multiplicity is given by s = singlet, d = doublet, t = triplet, and m = multiplet.

[c]



$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$

$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$

$\overset{\alpha}{C}H_3$

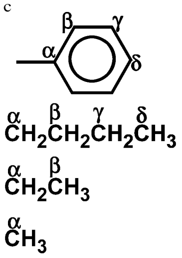
Table VI. ^{13}C NMR Data[a,b,c] of Di- and Chlorodiorganotin Carboxylates of HL^2

Compound → Carbon↓	(**7**) R = Et	(**8**) R = Et	(**9**) R = *n*-Bu	(**10**) R = *n*-Bu	(**11**) R = Ph	(**12**) R = Ph
2	138.6	134.0	138.5	133.0	138.6	133.0
3	129.0	130.0	128.6	129.2	128.9	129.0
4	127.9	128.7	127.9	128.0	128.0	128.0
5	130.8	131.2	130.8	130.4	130.7	130.0
6	139.4	140.0	139.4	139.6	139.4	139.0
7	116.3	115.4	116.4	115.2	116.5	115.0
8	175.8	176.0	175.8	175.6	175.8	176.0
α	17.6	17.9	25.0	26.2	137.6	137.2
	^{1}J[605]	^{1}J[530]	^{1}J[560]	^{1}J[502]	^{1}J[620]	^{1}J[650]
β	8.8	9.1	26.5	26.6	134.0	135.2
	^{2}J[42]	^{2}J[40]	^{2}J[33]	^{2}J[35]	^{2}J[48]	^{2}J[50]
γ	—	—	26.2	26.2	134.8	127.8
			^{3}J[90]	^{3}J[93]	^{3}J[70]	^{3}J[69]
δ	—	—	13.4	13.4	130.0	131.0
			^{4}J[n.o.]	^{4}J[n.o.]	^{4}J[34]	^{4}J[n.o.]

[a] Chemical shifts (δ) in ppm, $^nJ(^1H\text{-}^1H)$ and $^nJ[^{119}Sn\text{-}^1H]$ in Hz.

[b] n.o. = not observed.

[c]



$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$

$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$

$\overset{\alpha}{C}H_3$

signals in the ^{13}C and ^{1}H spectra. The high electronegativity of tin due to the presence of chloride ion increases the magnitude of the $^1J[^{119}Sn\text{-}^{13}C]$ and $^2J[^{119}Sn\text{-}^1H]$ coupling constants[25]. In our compounds, the presence of oxygen and chlorine atoms attached to tin increases its Lewis acidity and facilitates chelation of the carbonyl oxygen resulting in a trigonal bipyramidal geometry. Hence, comparison of these coupling constants and tin chemical shifts with previous data suggests a penta-coordinated state for the tin atom[9,15] (Fig. 2(d)).

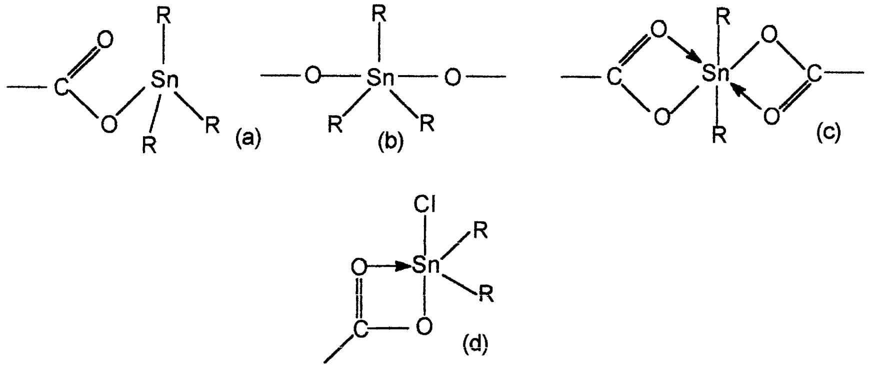


Figure 2. Suggested structures of the complexes.

Mass Spectrometry

The mass fragmentation data of both series are given in Tables VII-IX. The molecular ion peaks, as reported earlier[9,14], are not observed for most of the compounds. Generally, in triorganotin derivatives, the major fragmentation is the loss of an R group followed by the elimination of CO_2. An alternate route of ragmentation is the loss of ligand anion first, followed by the loss of successive R groups until Sn^+ is obtained. For diorganotin dicarboxylates, the main fragmentation is due to the loss of one ligand which follows the loss of CO_2 and then successive losses of two R groups. Chloro derivatives follow the same pattern as the triorganotin carboxylates. The first loss is due to an R group followed by CO_2 and then another R group and some fragments of the ligand.

EXPERIMENTAL

Instrumentation

Melting points were determined in a capillary tube using an electrothermal melting point apparatus Model MP-D, Mitamura Rikero Kogyo (Japan) and are uncorrected. Infrared spectra were recorded in KBr pellets using a Hitachi Model 270-50 infrared spectrophotometer. The NMR spectra were recorded on, Bruker 250ARX spectrometer in $CDCl_3$ using Me_4Si as reference for ^1H and ^{13}C and Me_4Sn as reference for ^{119}Sn.

Table VII. Fragmentation Pattern and Relative Abundance (%) of Triorganotin Carboxylates of HL^1

Fragment ion	(**1**) R = Me	(**4**) R = *n*-Bu	(**6**) R = Ph
$[R_3SnO_2CR']^+$	–	–	4
$[R_2SnO_2CR']^+$	10	56	8
$[R_3SnR']^+$	51	8	38
$[RSnR']^+$	–	21	–
$[R_3Sn]^+$	100	67	96
$[R_2Sn]^+$	–	–	14
$[RSn]^+$	40	38	66
$[HO_2CR']^+$	30	27	12
$[SnO_2CR']^+$	40	6	21
$[C_7H_5O]$	37	84	100

Synthesis

Triorganotin Carboxylates (Compounds (**1**), (**4**), and (**6**))

Compounds with the general formula R_3SnL^1 were prepared by double displacement reaction between AgL^1 and R_3SnCl [eq (1)][13,14]. The silver salt of the ligand, AgL^1 (3.68 g, 0.01 mole) was suspended in 50 mL dry chloroform in a 250 mL two-necked round bottom flask equipped with a water-cooled condenser and a magnetic stirrer. The appropriate triorganotin chloride (0.01 mole) in 50 mL dry chloroform was added dropwise to the suspension with constant stirring. The reaction mixture was then refluxed for 6–8 hours, cooled to room temperature and allowed to stand overnight at room temperature. AgCl formed during the reaction was filtered off using a conventional Schlenk apparatus. The filtrate was treated with activated charcoal at 50 °C, filtered and the solvent was removed under reduced pressure. The solid mass obtained was crystallized from a suitable solvent (dichloromethane or *n*-hexane). Physical parameters of these compounds are given in Table I.

Diorganotin Carboxylates (Compounds (**2**), (**3**), (**5**), (**7**), (**9**), and (**11**))

Diorganotin compounds were prepared by the condensation reaction of the ligand acids, HL and organotin oxide [eq (2)][14]. The ligand acid, HL^1 (5.22 g) or HL^2 (7.22 g, 0.02 mole) and the appropriate organotin oxide (0.01 mole) were refluxed in 100 mL dry toluene for 4–6 hours. Water formed during the reaction was continuously removed using a Dean-Stark apparatus. Toluene was then removed under reduced pressure with a high

Table VIII. Fragmentation Pattern and Relative Abundance (%) of Diorganotin Carboxylates of HL^1 and HL^2

Fragment ion	(**2**) R = Et	(**3**) R = *n*-Bu	(**5**) R = Ph	(**7**) R = Et	(**9**) R = *n*-Bu	(**11**) R = Ph
$[R_2Sn(O_2CR')_2]^+$	–	–	–	–	–	–
$[RSn(O_2CR')_2]^+$	68	42	22	85	84	30
$[RSn(O_2CR')R']^+$	58	16	18	61	27	16
$[RSnR'_2]^+$	10	20	11	49	5	12
$[R_2SnO_2CR']^+$	38	60	8	14	11	31
$[R_2SnR']^+$	16	8	28	12	2	24
$[SnR']^+$	–	6	10	63	65	9
$[HO_2CR']^+$	18	22	6	79	5	74
$[R_2SnO]^+$	70	68	64	–	–	–
$[C_7H_5O]^+$	100	84	82	–	–	–
[SnOH]	–	–	–	100	100	76
$[C_2H_5S]$	–	–	–	82	69	20
$[C_5H_5]$	–	–	–	67	40	76

vacuum pump. The residue was treated with activated charcoal in 150 mL dry chloroform and filtered. The filtrate was concentrated and left overnight at −5 °C. The semisolid/solid mass was crystallized or extracted by using appropriate solvents (dichloromethane, chloroform or *n*-hexane). Physical parameters are given in Table I.

Table IX. Fragmentation Pattern and Relative Abundance (%) of Monochlorodiorganotin Carboxylates of HL^2

Fragmentation ion	(**8**) R = Et	(**10**) R = *n*-Bu	(**12**) R = Ph
$[R_2Sn(O_2CR')(Cl)]^+$	–	–	–
$[RSn(O_2CR')(Cl)]^+$	16	7	100
$[RSn(R')(Cl)]^+$	5	–	–
$[SnR'(Cl)]^+$	4	3	8
$[R_2Sn(O_2CR')]^+$	2	9	76
$[R_2Sn(Cl)]^+$	3	6	8
$[SnR']^+$	26	35	28
$[HO_2CR']^+$	22	78	31
$[C_4H_3SSn]^+$	7	9	6
$[Sn\text{-}OH]^+$	100	100	65
$[C_5H_5]^+$	39	21	–

Chlorodiorganotin Carboxylates (Compounds (**8**), (**10**), and (**12**))

These compounds were prepared according to our previously reported method [eq (3)][15]. Equimolar amounts (100 mmol) of R_2SnL_2 and R_2SnCl_2 were refluxed in 100 mL dry chloroform for 6–8 hours. The reaction mixture was then concentrated under vacuum and kept at −10 °C for 10–15 days. The semisolid or solid mass thus obtained was purified by repeated extraction with an appropriate solvents mixture (dichloromethane/*n*-hexane, 1:1). Physical parameters are given in Table I.

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