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Monobutyl and Monophenyl Substituted Tin Derivatives of N-(*o*-Hydroxy Substituted Benzyl) Alanines

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Several monobutyl and monophenyl substituted tin derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by alcoholysis reactions. The various compounds thus prepared were generally obtained as coloured solids and amongst them those containing isopropoxy group were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

The oganotin compounds have evoked considerable interest owing to their applications as biocidal agents[1–4], polymer stabilizers[5, 6], catalysts for urethane formation and Zeigler catalyst for olefin polymerization[7]. In addition, these compounds are of paramount importance from academic point of view as well as tin may form coordination complexes with suitable organic compounds having enhanced coordination number varying from 5 to 8 in many cases.

The donor sites in N-(*o*-hydroxy substituted benzyl)-α-amino acids provide a favourable geometry for stable metal chelate ring formation. Hence, several derivatives belonging to N-(*o*-hydroxy substituted benzyl) glycine class were prepared and examined for their ligating properties in solution[8, 9]. The preparation of their metallo-organic/organometallic derivatives *via* the reactivity of the corresponding metal alkoxides has also been reported[10–12]. A systematic programme of work on the preparation of metallo-organic/organometallic derivatives of N-(*o*-hydroxy substituted benzyl) alanines on similar lines has recently been undertaken in these laboratories.

The work described here thus deals with the preparation and characterization of monobutyl and monophenyl substituted tin derivatives of some N-(*o*-hydroxy substituted benzyl) alanines (I) *viz.* (*i*) N-(2-hydroxy-3-methyl benzyl) alanine (H_2hmba-3), (*ii*) N-(2-hydroxy-6-methyl benzyl) alanine (H_2hmba-6) and (*iii*) N-(2-hydroxy-5-methyl benzyl) alanine (H_2hmba-5). These derivatives were prepared by alcoholysis reactions involving the interaction of monobutyltin or monophenyltin triisopropoxide with I in appropriate stoichiometric ratios *viz.* 1:1, 1:2 and 1:3 in benzene medium. The various compounds thus prepared were generally obtained as coloured solids and amongst them those containing isopropoxy group were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

EXPERIMENTAL

The details of the glass apparatus are given elsewhere[13]. Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures. Monobutyltin and monophenyltin triisopropoxides were prepared by sodium method[14, 15], using monobutyltin and monophenyltin trichlorides respectively, which in turn were prepared by known methods[16].

Melting points were recorded on a digital m.p. apparatus. Tin was determined by direct ignition of the sample after digestion with nitric and sulphuric acids followed by neutralization and precipitation by ammonia solution[17].

Preparation of N-(*o*-Hydroxy Substituted Benzyl) Alanines

The various N-(*o*-hydroxy substituted benzyl) alanines were prepared adopting procedures almost similar to those employed for the preparation of the corresponding glycine derivatives[18]. To a mixture of equimolar amounts of *o*-cresol (E. Merck), *m*-cresol (Wilson) or *p*-cresol (E. Merck), alanine (Loba) and sodium acetate trihydrate (Sarabhai, GR) in acetic acid (Sarabhai, GR) medium, was added an equimolar amount of formaldehyde solution (Sarabhai, GR), and the contents were heated at 60–80°C till a viscous mass was obtained. This was poured dropwise with brisk stirring in an excess of water, when the free acid precipitated which was washed thoroughly with water and then filtered. The crude product thus obtained was purified by dissolving it in a requisite amount of sodium hydroxide solution followed by its reprecipitation by 50% hydrochloric acid. The precipitate thus obtained was freed from chloride ions by washing it with water and then filtered and air dried. These compounds are soluble in glacial acetic acid, dilute alkali, dimethylformamide and dimethylsulphoxide, sparingly soluble in water, ethanol, dioxan and mineral acids but insoluble in acetone, benzene, toluene and ether. The relevant analytical details of the various derivatives thus prepared are recorded in Table 1.

Reaction Between Monobutyltin Triisopropoxide and H_2hmba-3; 1 : 1 Molar Ratio

A mixture of $BuSn(OPr^i)_3$ (0.9700 g; 2.75 mmole) and H_2hmba-3 (0.5734 g; 2.74 mmole) suspended in dry benzene (60 mL) taken in a R.B. flask was refluxed on a wax bath at 95–100°C, using a fractionating column. After *ca.* 6 h of reflux, isopropanol liberated was fractionated out azeotropically and estimated by an oxidimetric method[19, 20]. After completion of the reaction, the excess of solvent from the reaction mixture was removed in *vacuo*, when the product, $BuSn(OPr^i)$(hmba-3) isolated as a brown solid which was washed with dry benzene (3–4 times) and then with dry ether (2–3 times) to remove excess of $BuSn(OPr^i)_3$ and finally dried under suction. The product was further purified

TABLE 1
ANALYTICAL DETAILS OF THE VARIOUS N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES AND THEIR MONOBUTYL AND MONOPHENYL SUBSTITUTED TIN DERIVATIVES

Compound (molar ratio)/Colour	m.p. (°C)	Azeotrope analysis Pr^{i}OH(g) found (calcd.)	Analysis % Found (calcd.)			
			C	H	N	Sn
H_2hmba-3 (dull white)	110	—	62.85 (63.14)	7.20 (7.23)	6.67 (6.69)	—
H_2hmba-6 (light pink)	105	—	62.87 (63.14)	7.21 (7.23)	6.67 (6.69)	—
H_2hmba-5 (dull white)	95	—	62.87 (63.14)	7.20 (7.23)	6.67 (6.69)	—
BuSn(OPr^i)(hmba-3) (1 : 1) (brown)	210	0.32 (0.33)	48.68 (48.90)	5.59 (5.61)	3.16 (3.17)	26.71 (26.84)
BuSn(OPr^i)(Hhmba-3)$_2$ (1 : 2) (brown)	188	0.16 (0.18)	53.23 (53.48)	6.82 (6.81)	4.29 (4.30)	18.07 (18.22)
BuSn(Hhmba-3)$_3$ (1 : 3) (brown)	226	0.30 (0.32)	55.25 (55.51)	5.40 (5.42)	5.23 (5.25)	14.77 (14.83)
BuSn(OPr^i)(hmba-6) (1 : 1) (light brown)	290	0.29 (0.32)	48.70 (48.90)	5.59 (5.61)	3.16 (3.17)	26.73 (26.84)
BuSn(OPr^i)(Hhmba-6)$_2$ (1 : 2) (light yellowish brown)	240	0.26 (0.28)	53.24 (53.48)	6.78 (6.81)	4.29 (4.30)	18.06 (18.22)
BuSn(Hhmba-6)$_3$ (1 : 3) (light brown)	194	0.41 (0.43)	55.24 (55.51)	5.40 (5.42)	5.23 (5.25)	14.76 (14.83)
BuSn(OPr^i)(hmba-5) (1 : 1) (light brown)	200	0.23) (0.24)	48.69 (48.90)	5.48 (5.61)	3.16 (3.17)	26.72 (26.84)
BuSn(OPr^i)(Hhmba-5)$_2$ (1 : 2) (brown)	190d	0.29 (0.31)	53.23 (53.48)	6.82 (6.81)	4.29 (4.30)	18.14 (18.22)
BuSn(Hhmba-5)$_3$ (1 : 3) (brown)	200d	0.31 (0.33)	55.26 (55.51)	5.40 (5.42)	5.23 (5.25)	14.77 (14.83)
PhSn(OPr^i)(hmba-3) (1 : 1) (light pink)	215	0.47 (0.49)	51.75 (51.98)	5.43 (5.45)	3.02 (3.03)	25.57 (25.68)
PhSn(OPr^i)(Hhmba-3)$_2$ (1 : 2) (light pink)	300	0.24 (0.26)	55.20 (55.46)	5.98 (6.00)	4.16 (4.17)	17.60 (17.68)
PhSn (Hhmba-3)$_3$ (1 : 3) (off white)	268	0.33 (0.35)	56.85 (57.09)	5.75 (5.77)	5.10 (5.12)	14.40 (14.46)
PhSn(OPr^i)(Hhmba-6)$_2$ (1 :1) (light brown)	215	0.22 (0.23)	51.73 (51.98)	5.43 (5.45)	3.02 (3.03)	25.57 (25.68)
PhSn(OPr^i)(Hhmba-6)$_2$ (1 : 2) (light brown)	205	0.19 (0.20)	55.21 (55.46)	5.98 (6.00)	4.16 (4.17)	17.56 (17.68)
PhSn(Hhmba-6)$_3$ (1 : 3) (light pink)	236	0.33 (0.35)	56.88 (57.09)	5.75 (5.77)	5.10 (5.12)	14.35 (14.46)
PhSn(OPr^i)(hmba-5) (1 : 1) (cream coloured)	210	0.34 (0.36)	51.64 (51.98)	5.43 (5.45)	3.03 (3.03)	25.56 (25.68)
PhSn(OPr^i)(Hhmba-5)$_2$ (1 : 2) (cream coloured)	270	0.28 (0.30)	55.20 (55.46)	5.99 (6.00)	4.16 (4.17)	17.59 (17.67)
PhSn(Hhmba-5)$_3$ (1 : 3) (light pink)	235	0.42 (0.44)	56.88 (57.09)	5.75 (5.77)	5.10 (5.12)	14.22 (14.46)

Abbreviations: Bu = C_4H_9, Ph = C_6H_5, OPr^i = OC_3H_7, H_2hmba-3 (or -6 or -5)
= $CH_3C_6H_3(OH)CH_2\overset{+}{N}H_2CH(CH_3)COO^-$

by recrystallization from dry ethanol. The compound was found to be soluble in ethanol, dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like benzene, toluene, ether, chloroform and carbon tetrachloride etc.

It may be mentioned here that since $BuSn(OPr^i)_3$ is soluble in benzene, while H_2hmba-3 is insoluble, the latter was taken in slightly less than the required stoichiometric amount (as evident from the weights given before) in order to avoid contamination of impurities likely to occur by unreacted H_2hmba-3. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_2hmba-3 taken.

Similar procedures of preparation and purification were adopted in case of other derivatives. However, recrystallization from dry ethanol was possible only in case of monobutyltin derivatives of H_2hmba-5.

The relevant analytical details of the various compounds thus prepared, their characteristic IR frequencies and the PMR spectral data are recorded in Tables 1–3, respectively.

RESULTS AND DISCUSSION

The various reactions occurring between monobutyltin or monophenyltin triisopropoxide and H_2hmba-3 may be illustrated as:

$$RSn(OPr^i)_3 + H_2\text{hmba-3} \rightarrow RSn(OPr^i)(\text{hmba-3}) + 2Pr^iOH \qquad (1)$$

$$RSn(OPr^i)_3 + 2H_2\text{hmba-3} \rightarrow RSn(OPr^i)(H\text{hmba-3})_2 + 2Pr^iOH \qquad (2)$$

$$RSn(OPr^i)_3 + 3H_2\text{hmba-3} \rightarrow RSn(H\text{hmba-3})_3 + 3Pr^iOH \qquad (3)$$

where, R = Bu or Ph

Identical course of reactions followed in case of H_2hmba-6 and H_2hmba-5.

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Infrared Spectra: A very broad band observed in the region 3680–3000 cm^{-1} in H_2hmba-3 shows the overlapping of νOH (phenolic) and aromatic νC—H[21, 22]. The medium and weak absorptions, respectively, at 2920 cm^{-1} and 2850 cm^{-1} may be assigned to the overlapping of νC—H of the $—CH_2—$ and $—CH_3$ groups[21], while a weak broad band at 2395 cm^{-1} corresponds to νN—H of the $>\overset{+}{N}H_2$ group[22, 23]. A very sharp broad band at 1625 cm^{-1} with a shoulder indicates possible overlapping of $\nu_{as}COO$ and aromatic νC═C. A weak absorption at 1520 cm^{-1} and the strong one at 1465 cm^{-1} correspond to the overlapping of the aromatic νC═C and C—H bending of the $—CH_2—$ and $—CH_3$ groups. A medium broad band at 1405 cm^{-1} may be attributed to ν_sCOO[23], while another at 1370 cm^{-1} to the O—H bending of the phenolic group. A sharp band at 1270 cm^{-1} shows the interaction of O—H bending and C—O stretching of the phenolic group, while another at 1235 cm^{-1} corresponds to νC—N. A weak band at 1160 cm^{-1} occurs due to the phenolic νC—C—O. The medium to weak bands at 1120 cm^{-1}, 1035 cm^{-1} and 960 cm^{-1} correspond to the aromatic C—H in-plane bending, while those at 815 cm^{-1}, 750 cm^{-1} and 650–600 cm^{-1} indicate the

TABLE 2

CHARACTERISTIC INFRARED FREQUENCIES (in cm^{-1}) OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES AND THEIR MONOBUTYL AND MONOPHENYL SUBSTITUTED TIN DERIVATIVES

Compound	νOH and aromatic νC–H	ν_{NH} and atomic $\nu_{C—H}$	$\nu_{C–H}$ of the —CH_2— and —CH_3 groups	νN–H of the $>\overset{+}{N}H_2$ group	$\nu_{as}COO$	ν_sCOO	ΔνCOO	νC–N	νSn–C	νSn–O	νSn–N
H_2hmba-3	3680–3000 (vb)	—	2920 (m), 2850 (w)	2395 (wb)	1625 (vsb)	1405 (mb)	—	1235 (s)	—	—	—
H_2hmba-6	3660–3000 (b)	—	2920 (m), 2840 (m)	2340 (m)	1630 (vsb)	1405 (wb)	—	1250 (w)	—	—	—
H_2hmba-5	3690–3000 (b)	—	2920 (m), 2850 (w)	2390 (wb)	1630 (vsb)	1390 (s)	—	1220 (m)	—	—	—
$BuSn(OPr^i)$ (hmba-3)	—	3200–3000 (b)	2950 (m), 2900 (w)	—	1635 (vsb)	1390 (w)	245	1255 (s)	600 (w), 570 (w)	530 (m)	465 (m)
$BuSn(OPr^i)$ $(hmba\text{-}3)_2$	3400–3300 (mb)	3200–3020 (b)	2950 (m), 2900 (w)	—	1640 (vsb)	1390 (w)	250	1250 (sb)	600 (m), 580 (w)	530 (m)	460 (w)
$BuSn(hmba\text{-}3)_3$	3500–3300 (vb)	3190–3020 (b)	2950 (m), 2920 (m), 2860 (w)	—	1630 (vsb)	1390 (mb)	240	1250 (s)	600 (m), 540 (w)	530 (m)	440 (wb)
$BuSn(OPr^i)$ (hmba-6)	—	3100–3000 (b)	2960 (m), 2900 (w)	—	1630 (vs)	1375 (sh)	255	1270 (s)	640 (w), 570 (m)	520 (m)	450 (m)
$BuSn(OPr^i)$ $(Hhmba\text{-}6)_2$	3400–3300 (b)	3200–3000 (mb)	2950 (m), 2900 (w)	—	1640 (vsb)	1380 (m)	260	1265 (m)	600 (mb)	530 (mb)	460 (w)

Compound	νOH and aromatic νC–H	ν_{NH} and atomic ν_{C-H}	ν_{C-H} of the —CH$_2$— and —CH$_3$ groups	νN–H of the $>\overset{+}{N}H_2$ group	ν_{as}COO	ν_sCOO	ΔνCOO	νC–N	νSn–C	νSn–O	νSn–N
BuSn(Hhmba-6)$_3$	3400–3300 (b)	3200–3040 (mb)	2900 (m), 2850 (m)	—	1630 (vsb)	1390 (w)	240	1265 (w)	600 (m), 580 (w)	535 (m)	430 (w)
BuSn(OPr^i) (hmba-5)	—	3190–3000 (mb)	2950 (m), 2890 (m)	—	1635 (vsb)	1385 (msh)	250	1260 (s)	620 (m), 585 (m)	530 (m)	440 (m)
BuSn(OPr^i) (Hhmba-5)$_2$	3500–3300 (b)	3200–3000 (mb)	2950 (w), 2910 (w)	—	1640 (vsb)	1380 (msh)	260	1250 (m)	610 (w), 570 (w)	550 (w)	450 (m)
BuSn(Hhmba-5)$_3$	3450–3300 (mb)	3200–3000 (b)	2950 (m), 2850 (w)	—	1620 (vsb)	1380 (w)	240	1270 (m)	600 (mb)	510 (w)	470 (m)
PhSn(OPr^i) (hmba-3)	—	3200–3000 (mb)	2950 (m), 2900 (w) 2850 (w)	—	1615 (vs)	1370 (mb)	245	1250 (s)	1080 (m)	500 (w), 480 (w)	450 (m)
PhSn(OPr^i) (Hhmba-3)$_2$	3500–3300 (vb)	3100–3000 (mb)	2950 (m), 2900 (w), 2840 (w)	—	1640 (vsb)	1390 (w)	250	1250 (s)	1080 (m)	550 (mb)	440 (m)
PhSn(Hhmba-3)$_3$	3600–3300 (vb)	3180—3000 (mb)	2940 (s), 2900 (w), 2850 (w)	—	1640 (vsb)	1370 (m)	270	1250 (vs)	1080 (s)	540 (mb)	440 (m)
PhSn(OPr^i) (hmba-6)	—	3200–3000 (mb)	2940 (w), 2920 (m), 2850 (m)	—	1620 (vsb)	1380 (msh)	240	1255 (s)	1090 (s)	550 (mb)	450 (w)

Compound	νOH and aromatic νC–H	ν_{NH} and atomic $\nu_{C—H}$	ν_{C-H} of the —CH_2— and —CH_3 groups	νN–H of the >$\overset{+}{N}H_2$ group	$\nu_{as}COO$	ν_sCOO	ΔνCOO	νC–N	νSn–C	νSn–O	νSn–N
PhSn(OPr^i)(Hhmba-6)$_2$	3500–3300 (sb)	3150–3000 (mb)	2940 (w), 2920 (m), 2850 (w)	—	1630 (vsb)	1380 (msh)	250	1255 (vs)	1090 (s)	550 (mb)	450 (w)
PhSn(Hhmba-6)$_3$	3500–3300 (sb)	3180–3000 (mb)	2950 (m), 2920 (w), 2850 (w)	—	1630 (vs)	1380 (m)	250	1250 (s)	1090 (s)	550 (mb)	450 (m)
PhSn(OPr^i)(hmba-5)	—	3100–3000 (mb)	2950 (w), 2900 (m), 2860 (m)	—	1620 (vsh)	1370 (msh)	250	1255 (s)	1080 (s)	500 (m)	450 (s)
PhSn(OPr^i)(Hhmba-5)$_2$	3500–3300 (sb)	3150–3000 (mb)	2950 (m) 2910 (w)	—	1615 (vs)	1375 (msh)	240	1250 (vs)	1090 (s)	550 (mb)	450 (w)
PhSn(Hhmba-5)$_3$	3500–3300 (sb)	3150–300 (mb)	2950 (m), 2920 (mb), 2850 (w)	—	1630 (vsb)	1390 (m)	240	1250 (s)	1080 (s)	560 (mb)	470 (m)

Abbreviations: s = sharp, vs = very sharp, vsb = very sharp broad, m = medium, mb = medium broad, sb = strong broad, vb = very broad, b = broad, w = weak, wb = weak broad and sh = shoulder.

TABLE 3

PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUES) OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES AND THEIR MONOBUTYL AND MONOPHENYL SUBSTITUTED TIN DERIVATIVES

Compound	Aromatic ring	Phenolic (OH) group	>CH–	$>\overset{+}{N}H_2$	>NH	$-CH_3$ (attached with the benzene ring)	$-CH_2-$ (attached with the benzene ring)	$-CH_3$ of the alanine part	$-CH_2-$ of the butyl part	$-CH_3$ of the butyl part	*Gem* dimethyl (isopropoxy group)
H_2hmba-3	6.92 (d), 6.85 (d), 6.60–6.70 (m)	6.75 (s)	3.40–4.00 (bm)	3.20–3.40 (h)	—	2.22 (s)	2.05–2.10 (m)	1.35 (d)	—	—	—
H_2hmba-6	7.25 (t), 6.60 (d), 6.50 (d)	6.55 (s)	3.40–4.10 (bm)	3.00–3.30 (h)	—	2.15 (s)	2.00–2.10 (m)	1.20 (d)	—	—	—
H_2hmba-5	6.85 (s), 6.62 (d), 6.55 (d)	6.90 (s)	3.35–4.05 (bm)	3.20 (h)	—	2.15 (s)	2.00–2.10 (m)	1.22 (d)	—	—	—
BuSn(OPr^i) (hmba-3)	6.55–6.85 (t)	—	3.60–4.00 (bm)	—	3.10 (h)	2.20 (s)	2.05 (bs)	1.30(bs)*	—	0.90 (t)	1.10 (d)
BuSn(OPr^i) (Hhmba-5)$_2$	6.60–6.85 (t)	6.90 (s)	3.60–4.00 (m)	—	3.15 (h)	2.10 (s)	2.00 (bs)	1.20–1.50 (m)*	—	0.82 (t)	1.00 (d)
BuSn(Hhmba-3)$_3$	6.40–7.20 (m)	6.60 (s)	3.80–4.00	—	3.10 (h)	2.10 (s)	2.05 (d)	1.15 (d)	1.05 (m)	0.90 (t)	—
PhSn(OPr^i) (hmba-5)	6.40–7.30 (m)	—	3.60–4.00 (m)	—	3.40 (s)	2.15 (s)	2.00 (d)	1.20 (d)	—	—	1.00 (d)
PhSn(OPr^i) (Hhmba-3)$_2$	6.40–7.30 (m)	6.30 (s)	3.60–4.00 (m)	—	3.00 (h)	2.15 (s)	2.00 (d)	1.20 (d)	—	—	1.00 (d)

*Overlapping of $-CH_3$ of the alanine part and $-CH_2-$ of the butyl part.

Abbreviations: s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet, bm = broad multiplet, h = hump characteristic C—H out-of-plane bending of a trisubstituted benzene ring. The absorptions below 600 cm^{-1} occur due to the skeletal vibrations.

The IR spectra of H_2hmba-6 and H_2hmba-5 were interpreted similarly and the characteristic IR frequencies are recorded in Table 2.

Proton Magnetic Resonance Spectra: The PMR spectrum of H_2hmba-3 shows doublets at δ6.92 and δ6.85 and a multiplet in the region δ6.60–6.70 which may be assigned respectively to the protons at positions 4, 6 and 5 of the trisubstituted benzene ring[22]. A singlet at δ6.75 corresponds to the phenolic proton, while the broad multiplet between δ3.40–4.00 may be attributed to the protons associated with the >CH— group of the alanine part of H_2hmba-3[24]. The occurrence of a hump in association with the said multiplet between δ3.20–3.40 may be assigned to the protons of the $>\overset{+}{N}H_2$ gruop[24]. A singlet at δ2.22 and signals between δ2.05–2.10 correspond respectively to the protons of the —CH_3 and —CH_2— groups attached wih the benzene ring[22]. A doublet at δ1.35 appears because of the protons of the —CH_3 group of the alanine part of H_2hmba-3, while the singlet at δ2.50 shows the DMSO impurity. The absence of any signal between δ7.50–13.00 suggests the absence of free carboxylic acid group in the compound.

Upon D_2O exchange, the singlet at δ6.75 and the hump in the region δ3.20–3.40 are observed to disappear which further confirms the presence of the phenolic —OH and $>\overset{+}{N}H_2$ groups. A new signal at δ3.35 possibly arises owing to HOD, as a consequence of D_2O exchange.

The PMR spectra of H_2hmba-6 and H_2hmba-5 were interpreted similarly and the details pertaining to the PMR data are recorded in Table 3.

On the basis of the foregoing considerations it is concluded that all these complexones exist in the zwitter ionic form (I) as Ar—$CH_2\overset{+}{N}H_2CH(CH_3)COO^-$ (where Ar is derived from *o*-, *m*- or *p*- cresol). The solution studies[8, 9] on several derivatives belonging to N-(*o*-hydroxy substituted benzyl) glycines show that the $>\overset{+}{N}H_2$ group is more strongly acidic than the phenolic (—OH) group, suggesting that the dissociation of proton from the $>\overset{+}{N}H_2$ group occurs first which is then followed by the dissociation of the proton from the phenolic group. An identical behaviour is expected to occur in case of the N-(*o*-hydroxy substituted benzyl) alanines. Hence, during the formation of the various organotin derivatives described here, the replacement of hydrogen from the $>\overset{+}{N}H_2$ group would occur first accompanied by bonding of the carboxylate oxygens with tin, along with possible coordination of nitrogen from the >NH group (obtained as a consequence of deprotonation of the $>\overset{+}{N}H_2$ group) to tin as well. In the next step the replacement of hydrogen from the phenolic group would occur resulting in the bonding of the phenolate oxygen with tin.

Monobutyltin and Monophenyltin Derivatives of N-(*o*-Hydroxy Substituted Benzyl) Alanines

Infrared Spectra: The derivative, $BuSn(OPr^i)(hmba\text{-}3)$ displays a broad band in the region 3200–3000 cm^{-1} which may be assigned to the overlapping of νN—H and aromatic νC—H[21, 22]. The appearance of νN—H in the lower region shows possible coordination of nitrogen to tin[25, 26]. The band due to νOH of the phenolic group, as noted in $H_2hmba\text{-}3$, is found to be absent here indicating the participation of the phenolate oxygen in bonding with tin. The medium and weak absorptions respectively at 2950 cm^{-1} and 2900 cm^{-1} occur owing to νC—H of the $—CH_2—$ and $—CH_3$ groups[21]. The weak broad band at 2395 cm^{-1} corresponding to νN—H of the $> \overset{+}{N}H_2$ group, as observed in $H_2hmba\text{-}3$, is found to disappear here. A very strong broad band at 1635 cm^{-1} may be attributed to the overlapping of $\nu_{as}COO$, aromatic νC═C and N—H deformation[27, 28], while the medium bands at 1500 cm^{-1} and 1450 cm^{-1} correspond to the aromatic skeletal vibrations and C—H bending of the $—CH_2—$ and $—CH_3$ groups[21, 22]. Instead of a peak at 1405 cm^{-1}, as noted in $H_2hmba\text{-}3$, here the appearance of a weak band at 1390 cm^{-1} shows ν_sCOO[22, 27]. A shift of 15 cm^{-1} in ν_sCOO, as compared to $H_2hmba\text{-}3$, suggests possible bonding of the carboxylate oxygen with tin. The absence of any characteristic band corresponding to the C═O group in the region 1750–1650 cm^{-1} rules out the possibility of a normal ester type of linkage between the carboxylate oxygen and tin. Further, the separation value,ΔνCOO ($\nu_{as}COO–\nu_sCOO$) of 245 cm^{-1} indicates the absence of a bridged or coordinated carboxylate group[23, 29, 30]. A medium band at 1360 cm^{-1} occurs because of C—H bending of the *gem* dimethyl structure of the isopropoxy group[22, 27]. A sharp peak at 1255 cm^{-1} corresponds to the overlapping of νC—N and νC—O[22]. The medium and weak bands at 1150 cm^{-1}, 1090 cm^{-1} and 1025 cm^{-1} indicate the aromatic C—H in-plane bending[21, 22], while those at 860 cm^{-1}, 800 cm^{-1} and 760 cm^{-1} show the characteristic C—H out-of-plane bending of a trisubstituted benzene ring[22]. The appearance of weak bands at 600 cm^{-1} and 570 cm^{-1} may be assigned to $\nu_{as}Sn—C$ and $\nu_sSn—C$[31, 32], respectively. The medium peak at 530 cm^{-1} may be attributed to νSn—O[33], while a new peak at 465 cm^{-1} corresponds to νSn—N[34, 35].

On the basis of the above observations it appears that the tin atom in $BuSn(OPr^i)(hmba\text{-}3)$ shows penta-coordination[32], as a result of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group and the oxygen from the phenolic group, along with one isopropoxy and one butyl group.

Proton Magnetic Resonance Spectra: The PMR spectrum of $BuSn(OPr^i)(hmba\text{-}3)$ displays a triplet in the region δ6.55–6.85, which may be assigned to the aromatic ring protons[22, 24]. The absence of a hump between δ3.20–3.40 due to the protons of the $>\overset{+}{N}H_2$ group, as observed in H_2hmba-3, together with the appearance of a new hump at δ3.10 suggests possible coordination of nitrogen to tin. The new hump corresponds to the proton of the >NH group obtained as a result of deprotonation of the $>\overset{+}{N}H_2$ group. The signal due to the unbonded phenolic group proton, as noted in H_2hmpa-3, disappears here indicating the deprotonation of the phenolic group as a result of bonding of the phenolate oxygen with tin. The broad multiplet in the region δ3.60–4.00 may be attributed to the >CH— group proton of the alanine part of H_2hmba-3. The singlet at δ2.20 and a broad singlet at δ2.05 correspond respectively to the protons of the $—CH_3$ and $—CH_2—$ groups attached with the benzene ring[22, 24], while another broad singlet at δ1.30 occurs because of the protons of the $—CH_3$ group of the alanine part of H_2hmba-3, as well as the $—CH_2—$ group of the butyl part attached with the tin atom[36, 37]. A new triplet at δ0.90 occurs because of the $—CH_3$ group protons of the butyl part[36, 37], while a doublet at δ1.10 corresponds to the *gem* dimethyl protons of the isopropoxy group[26, 38]. Thus, the inferences drawn here are well in conformity to those derived from the IR measurements earlier.

The IR and PMR (wherever available) spectral data in respect of the other derivatives were interpreted similarly and the main findings relating to their structures are as under:

The derivatives, $BuSn(OPr^i)$(hmba-6), $BuSn(OPr^i)$(hmba-5), $PhSn(OPr^i)$(hmba-3), $PhSn(OPr^i)$(hmba-6) and $PhSn(OPr^i)$(hmba-5) (II), contain a penta-coordinated[32, 39] tin atom in each case displaying similar modes of bonding, as those observed in $BuSn(OPr^i)$(hmba-3).

The tin atom in $BuSn(OPr^i)(Hhmba\text{-}3)_2$, $BuSn(OPr^i)(Hhmba\text{-}6)_2$, $BuSn(OPr^i)(Hhmba\text{-}5)_2$, $PhSn(OPr^i)(Hhmba\text{-}3)_2$, $PhSn(OPr^i)(Hhmba\text{-}6)_2$ and $PhSn(OPr^i)(Hhmba\text{-}5)_2$ (III) displays hexa-coordination[39] in each case as a consequence of bonding with one of the oxygens from each of the two carboxylate groups and the nitrogen from each of the two imino groups available from two moles of I, along with one isopropoxy group and one butyl or phenyl group, as the case may be.

The derivatives $BuSn(Hhmba\text{-}3)_3$, $BuSn(Hhmba\text{-}6)_3$, $BuSn(Hhmba\text{-}5)_3$, $PhSn(Hhmba\text{-}3)_3$, $PhSn(Hhmba\text{-}6)_3$ and $PhSn(Hhmba\text{-}5)_3$ (IV) possess a hepta-coordinated[33, 40] tin atom in each case by way of bonding with one of the oxygens from each of the three carboxylate groups and the nitrogen from each of the three imino groups available from three moles of I, along with one butyl or phenyl group, as the case may be.

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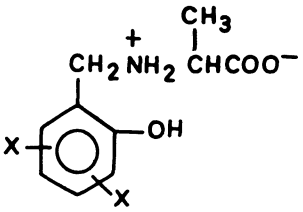
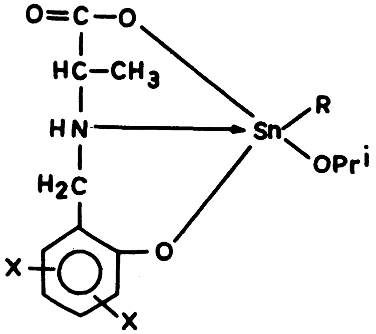


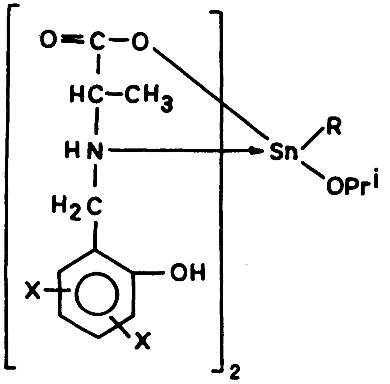
Where $X = -H$ or $-CH_3$

(I)



Where $X = -H$ or $-CH_3$ and
$R = -C_4H_9$ or $-C_6H_5$

(II)



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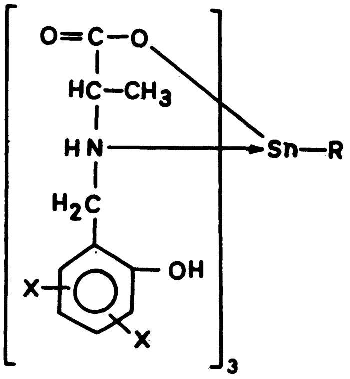

Where $X = -H$ or $-CH_3$ and
$R = -C_4H_9$ or $-C_6H_5$

(IV)

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