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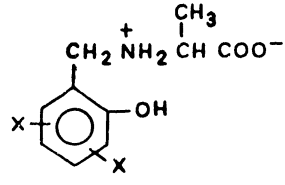
Tributyl and Triphenyl Substituted Tin Derivative of N-(*o*-Hydroxy Substituted Benzyl) Alanines

TRIPTI GANGWAR, RANJANA SHAH and MADHUP CHANDRA*
Department of Chemistry
DSB Campus, Kumaun University
Nainital–263 002, India

Several tributyl and triphenyl substituted tin derivatives of N(*o*-hydroxy substituted benzyl) alanines have been prepared by the interaction of tributyltin or triphenyltin triisopropoxide with the latter employing alcoholysis reactions in 1 : 1 and 2 : 1 stoichiometric ratios in benzene or toluence as the reaction medium. The compounds were obtained as dark viscous liquids in case of tributyltin derivatives and as coloured solids in case of triphenyltin derivatives. All these compounds were characterized by elemental and azeotrope analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

Preparation of several monobutyl-, monophenyl-, dibutyl- and diphenyltin derivatives of N-(*o*-hydroxy substituted benzyl) alanines *via* the reactivity of the corresponding organotin isopropoxide and their characterization by suitable physico-chemical methods have been reported earlier[1, 2]. The work described here deals with the preparation of tributyl and triphenyl substituted tin derivatives of N-(*o*-hydroxy substituted benzyl) alanines (structure 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).



Where X=−H or $-CH_3$

(I)

EXPERIMENTAL

Owing to highly hygroscopic nature of organotin isopropoxides stringent

precautions were taken to exclude moisture throughout the experiments, using identical assemblies as before.[1, 2]

Benzene (BDH, AR), isopropanol (Glaxo, AnalaR), solvent ether (E. Merck) were dried by the methods reported before.[1, 2] Tributyltin[3] and triphenyltin[4] isopropoxides were prepared by sodium method. Tin was estimated by direct ignition of the sample after digestion with nitric and sulphuric acids followed by neutralization and precipitation by liquid ammonia[5]. The details of instruments used are as reported earlier[1, 2].

Reaction between $Bu_3Sn(OPr^i)$ and H_2hmba-6; 1:1 Molar Ratio

A mixture of $Bu_3Sn(OPr^i)$ (1.3556 g; 3.88 mmol) and H_2hmba-6 (0.8106 g; 3.87 mmol) 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.* 7 h of reflux isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated to monitor the completion of reaction by an oxidimetric method, as before[1, 2]. On completion of the reaction the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, Bu_3Sn (Hhmba-6) isolated as a dark brown viscous liquid. It was then purified by repeated washing with carbon tetrachloride and then dried under suction. The product was found to be soluble in benzene, toluene, ethanol, chloroform, ether, DMF and DMSO, but insoluble in carbon tetrachloride. Attempted distillation of the compound resulted in its decomposition, and thus further purification was not possible.

It may be mentioned here that since $Bu_3Sn(OPr^i)$ is soluble in carbon tetrachloride, while H_2hmba-6 is insoluble, the latter was taken in a 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-6. Therefore, it becomes necessary to calculate the amount of isopropanol liberated according to the amount of H_2hmba-6 taken.

Identical procedure was adopted for the preparation of other tributyltin derivatives, all of which isolated as dark viscous liquids. The various triphenyltin derivatives were also prepared similarly but the product in each case isolated as a coloured solid which was washed with dry benzene (3–4 times) and then with dry ether (2–3 times) to remove unreacted $Ph_3Sn(OPr^i)$, if any before drying them *in vacuo*. All the derivatives were found to be soluble in DMF and DMSO but insoluble in other common organic solvents.

Since, $Ph_3Sn(OPr^i)$ is soluble in benzene, while I is insoluble, the latter was taken in slightly less than the required stoichiometric amount as before in order to avoid contamination of impurities likely to occur by unreached I. The amount of isopropanol liberated here too was calculated according to the amount of I taken in each case, as before.

The relevant analytical details, characteristic IR frequencies and PMR data are summarized in Tables 1–3 respectively.

RESULTS AND DISCUSSION

It may be recalled here that N-(*o*-hydroxy substituted benzyl) alanines exist in

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

S. No.	Compound (molar ratio)/(colour)	m.p. (°C)	Elemental analysis %, Found (Calcd.)			
			C	H	N	Sn
1.	*Bu_3Sn(Hhmba-3) (1:1) (red)	—	55.20 (55.44)	8.26 (8.29)	2.80 (2.81)	23.72 (23.82)
2.	*$(Bu_3Sn)_2$(hmba-3) (2:1) (reddish brown)	—	53.25 (53.40)	8.55 (8.58)	1.78 (1.78)	30.04 (30.15)
3.	*Bu_3Sn(Hhmba-6) (1:1) (drak brown)	—	55.19 (55.44)	8.30 (8.29)	2.80 (2.81)	23.70 (23.82)
4.	*$(Bu_3Sn)_2$(hmba-6) (2:1) (reddish brown)	—	53.15 (53.40)	8.53 (8.58)	1.77 (1.78)	30.03 (30.15)
5.	*Bu_3Sn(Hhmba-5) (1:1) (reddish brown)	—	55.19 (55.44)	8.25 (8.29)	2.80 (2.82)	23.72 (23.82)
6.	*$(Bu_3Sn)_2$(hmba-5) (2:1) (brown)	—	53.22 (53.40)	8.55 (8.58)	1.78 (1.78)	30.07 (30.15)
7.	Ph_3Sn(Hhmba-3) (1:1) (cream coloured)	267	62.10 (62.40)	5.22 (5.24)	2.50 (2.51)	21.16 (21.26)
8.	$(Ph_3Sn)_2$(hmba-3) (2:1) (yellowish brown)	232	61.95 (62.22)	4.77 (4.78)	1.54 (1.54)	26.10 (26.16)
9.	Ph_3Sn(Hhmba-6) (1:1) (cream coloured)	280	62.15 (62.40)	5.22 (5.24)	2.51 (2.51)	21.17 (21.26)
10.	$(Ph_3Sn)_2$(hmba-6) (2:1) (lemon yellow)	270	62.00 (62.20)	4.76 (4.78)	1.54 (1.54)	26.05 (26.16)
11.	Ph_3Sn(Hhmba-5) (1:1) (light brown)	248	62.10 (62.40)	5.22 (5.24)	2.51 (2.51)	21.17 (21.26)
12.	$(Ph_3Sn)_2$(hmba-5) (2:1) (lemon yellow)	265	61.96 (62.22)	4.77 (4.78)	1.54 (1.54)	26.05 (26.16)

*Boiling points could not be determined.

Abbreviations: Bu = C_4H_9, Ph = C_6H_5, OPr^i = OC_3H_7,

H_2hmba-3 (or -6 or -5) = $CH_3C_6H_3(OH)\,CH_2\overset{+}{N}H_2CH(CH_3)COO^-$

zwitterionic form [Structure (I)][1, 2]. The various reactions between tributyltin or triphenyltin isopropoxide and H_2hmba-6 may be illustrated as:

$$R_3Sn(OPr^i) + H_2hmba\text{-}6 \longrightarrow R_3Sn(Hhmba\text{-}6) + Pr^iOH \quad (1)$$

$$2R_3Sn(OPr_i) + H_2Hmba\text{-}6 \longrightarrow (R_3Sn)_2(hmba\text{-}6) + 2Pr^iOH \quad (2)$$

(where, R = Bu or Ph).

Identical course of reactions followed in case of H_2hmba-3 and H_2hmba-5.

The derivative, Bu_3Sn (Hhmba-6) displays a broad band in the region 3400–3300 cm^{-1} which may be assigned to vOH of the unbonded phenolic

TABLE-2

CHARACTERISITIC INFRARED FREQUENCIES (cm^{-1}) OF THE VARIOUS TRIBUTYL AND TRIPHENYL SUBSTITUTED TIN DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES

S. No.	Compound	νOH	νN—H and aromatic νC—H	νC—H of the —CH_2— and —CH_3 groups	$\nu_{asym}COO$	$\nu_{sym}COO$	ΔνCOO	ν(C—N)	ν(Sn—C)	ν(Sn—O)	ν(Sn—N)
1.	Bu_3Sn(Hhmba-3)	3400–3300 (mb)	3300–3080 (mb)	2960 (m) 2840 (w)	1635 (vsb)	1390 (mb)	245	1255 (s)	660 (w)	525 (m)	430 (m)
2.	$(Bu_3Sn)_2$(hmba-3)	—	3100–3000 (b)	2970 (m)	1620 (vsb)	1380 (m)	240	1265 (m)	660 (w)	525 (m)	435 (m)
3.	Bu_3Sn(Hhmba-6)	3400–3300 (b)	3200–3000 (mb)	2970 (m) 2940 (m) 2880 (m)	1610 (vsb)	1380 (w)	230	1260 (s)	600 (m) 535 (m)	460 (m)	420 (m)
4.	$(Bu_3Sn)_2$(hmba-6)	—	3100–3000 (wb)	2970 (m) 2940 (w) 2860 (w)	1620 (vs)	1380 (m)	240	1265 (s)	600 (m) 540 (m)	460 (w)	425 (w)
5.	Bu_3Sn(Hhmba-5)	3380–3200 (b)	3100—3000 (mb)	2960 (m) 2840 (m)	1620 (vs)	1380 (mb)	240	1240 (s)	600 (s)	540 (m)	430 (m)
6.	$(Bu_3Sn)_2$(hmba-5)	—	3100–3000 (wb)	2960 (m) 2850 (w)	1630 (vsb)	1380 (m)	250	1265 (s)	600 (m) 570 (w)	540 (m)	430 (m)
7.	Ph_3Sn(Hhmba-3)	3500—3300 (sb)	3190–3000 (mb)	2960 (m) 2900 (w) 2840 (w)	1630 (vsb)	1380 (m)	250	1250 (vs)	1080 (s)	570 (m)	450 (w)

TABLE 2 (contd.)

8. $(Ph_3Sn)_2$(hmba-3)	—	3200–3000 (mb)	2970 (m) 2950 (m) 2890 (w)	1620 (vsb)	1380 (m)	240	1250 (s)	1070 (s)	550 (mb)	480 (w)
9. Ph_3Sn(Hhmba-6)	3500–3300 (mb)	3050 (m) 3000 (m)	2950 (m) 2900 (w)	1620 (vs)	1370 (s)	250	1260 (m)	1070 (s)	535 (w)	440 (m)
10. $(Ph_3Sn)_2$(hmba-6)	—	3050 (s) 3000 (m)	2950 (m) 2910 (m) 2880 (w)	1610 (vs)	1380 (m)	230	1270 (vs)	1070 (s)	540 (m)	440 (s)
11. Ph_3Sn(Hhmba-5)	3500–3300 (sb)	3190–3000 (mb)	2950 (m) 2900 (w) 2850 (w)	1630 (vs)	1380 (m)	250	1250 (vs)	1080 (s)	560 (m)	470 (m)
12. $(Ph_3Sn)_2$(hmba-5)	—	3190–3000 (mb)	2950 (m) 2900 (w) 2840 (m)	1640 (vsb)	1390 (m)	250	1250 (vs)	1080 (s)	550 (m)	450 (m)

Abbreviations: s = sharp, vs = very sharp, vsb = very sharp broad, m = medium, mb = medium broad, s = strong broad, vb = very broad, b = broad w = weak broad, sh ≙ shouldered

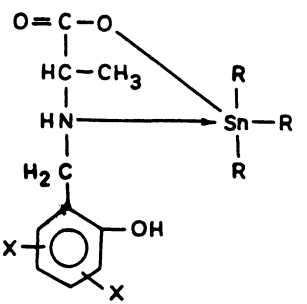
TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ value) OF SEVERAL TRIBUTYL AND TRIPHENYL SUBSTITUTED TIN DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES

S. No.	Compound	Aromatic ring	Phenolic (OH)	>CH—	>NH	—CH_3 (attached with the benzene ring)	—CH_2—(attached with the benzene ring)	—CH_3 (of the alanine part)	—CH_3 (of the butyl part)
1.	Bu_3Sn(Hhmba-6)	6.69–7.00 (t)	6.25 (s)	3.60–4.00 (bm)	3.00 (bs)	2.20 (s)	2.00 (d)	1.25–1.36 (m)*	0.90–0.97 (m)
2.	$(Bu_3Sn)_2$(hmba-6)	6.60–7.20 (t)	—	4.00 (m)	3.15 (s)	2.25 (s)	2.00 (d)	1.20–1.30 (m)*	0.90 (bs)
3.	Ph_3Sn(Hhmba-6)	6.50–7.30 (m)	6.40 (s)	3.80–4.00 (m)	3.05 (h)	2.10 (s)	1.95 (d)	1.10 (d)	
4.	$(Ph_3Sn)_2$(hmba-3)	6.20–7.00 (m)	—	3.40–4.00 (m)	31.0 (h)	2.00 (d)	2.00 (d)	1.05 (s)	

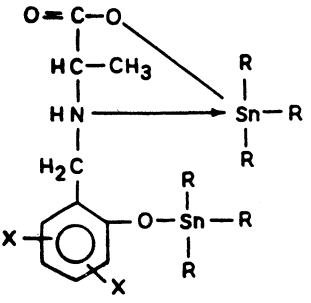
*Overlapping of —CH_3 of the alanine part and —CH_2— of the butyl part.
Abbreviations: s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet, bm = broad multiplet, h = hump.

group[6,7]. A medium broad band between 3200–3000 cm^{-1} occurs due to the overlapping of ν(N—H) and aromatic ν(C—H)[7]. The appearance of ν(N—H) in the lower region suggests possible coordination of nitrogen to tin[8,9]. The band due to ν(N—H) of the $>\overset{+}{N}H_2$ group, as noted in H_2hmba-6, is found to be absent here. The medium bands at 2970cm^{-1}, 2940 cm^{-1} and 2880 cm^{-1} correspond to ν(C—H) of the —CH_2— and —CH_3 groups. A very sharp band at 1610 cm^{-1} may be attributed to the overlapping of $\nu_{asym}COO$, aromatic ν(C=C) and N—H deformation[10,11], while medium bands at 1500 cm^{-1}, 1470 cm^{-1} and 1420 cm^{-1} indicate the overlapping of the aromatic skeletal vibrations and C—H bending of the —CH_2— and —CH_3 groups[6,7]. Instead of a band at 1405 cm^{-1}, as observed in H_2hmba-6, here the appearance of a weak band at 1380 cm^{-1} may be assigned to $\nu_{sym}COO$.[10] A shift of 25 cm^{-1} in $\nu_{sym}COO$, as compared to H_2hmba-6, shows the bonding of carboxylate oxygen with tin. Further, the separation value $\Delta\nu COO(\nu_{asym}COO—\nu_{sym}COO)$ of 230 cm^{-1} suggests the absence of a bridged or coordinated carboxylate group[12–14]. A very weak band at 1340 cm^{-1} corresponds to O—H bending of the phenolic group, while a sharp band at 1260 cm^{-1} due to ν(C—N) instead of at 1250 cm^{-1}, as noted in H_2hmba-6, suggests possible coordination of nitrogen to tin. The other absorptions corresponding to the aromatic C—H bending occur more or less at the similar positions (1200–600 cm^{-1}), as observed in H_2hmba-6. The medium bands at 600 cm^{-1} and 535 cm^{-1} occur due to ν_{asym}(Sn—C) and ν_{sym}(Sn—C), respectively[15], while those at 460 cm^{-1} and 420 cm^{-1} correspond to ν(Sn—O) and ν(Sn—N), respectively[16]. From the foregoing considerations it is inferred that the tin atom in Bu_3Sn(Hhmba-6) shows penta-coordination as a consequence of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group, along with three butyl groups.

The PMR spectrum of Bu_3Sn(Hhmba-6) shows a triplet between δ6.69–7.00 which may be assigned to the aromatic ring protons[7,17]. The singlet at δ6.25 corresponds to the proton of the unbounded phenolic group[7]. The absence of a hump in the region δ3.00–3.30 due to the protons of the $>\overset{+}{N}H_2$ group, as observed in H_2hmba-6, together with the appearance of a new broad singlet at δ3.00 suggests possible coordination of nitrogen to tin. The new signal corresponds to the proton of the >NH group obtained as a result of the deprotonation of the $>\overset{+}{N}H_2$ group. A broad multiplet between δ3.60–4.00 occurs because of the >CH— group proton of the alanine part of H_2hmha-6[7,17]. The signals due to the protons of the —CH_3 and —CH_2— groups attached with the benzene ring[7,17] appear respectively as a singlet at δ2.20 and a doublet at δ2.00. The multiplets in the region δ1.25–1.36 and δ0.90–0.97 may be attributed respectively to the protons of the —CH_2— and —CH_3 groups[15,18] of the butyl part attached with



Where X= −H or −CH_3 and
R= −C_4H_9 or −C_6H_5
(II)



Where X= −H or −CH_3 and
R= −C_4H_9 or −C_6H_5
(III)

the tin atom. Thus, the conclusions drawn here are in conformity to those inferred earlier from the IR measurements.

The IR and PMR spectra of the other derivatives were interpreted similarly and the main findings relating to their structures are as under:

The tin atom in Bu_3Sn(Hhmba-3), Bu_3Sn(Hhmba-5), Ph_3Sn(Hhmba-3), Ph_3Sn (Hhmba-6) and Ph_3Sn(Hhmba-5) (structure II) displays penta-coordination in each case by way of similar modes of bonding as those observed in case of Bu_3Sn(Hhmba-6).

The derivatives $(Bu_3Sn)_2$(hmba-3), $(Bu_3Sn)_2$(hmba-6), $(Bu_3Sn)_2$(hmba-5), $(Ph_3Sn)_2$(hmba-3), $(Ph_3Sn)_2$(hmba-6) and $(Ph_3Sn)_2$(hmba-5) contain two tin atoms in each case, out of which one shows penta-coordination as a consequence of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group, along with three butyl or phenyl groups, as the case may be. The other tin atom, however, displays tetra-coordination as a result of bonding with the oxygen from the phenolic group, along with three butyl or phenyl grups, as the case may be.

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