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Mono- and Triphenyltin Derivatives of N-(2-Hydroxy Methyl Substituted Benzyl) Valines

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Mono- and triphenyltin derivatives of N-(2-hydroxy methyl substituted benzyl) valines have been prepared by alcoholysis reaction. The compounds were obtained as coloured solids in each case and amongst them those containing isopropoxy group were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analysis, as well as by spectral measurements.

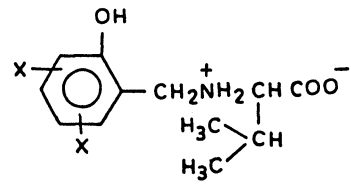
INTRODUCTION

The work described here relates to the preparation of mono- and triphenyltin derivatives of N-(2-hydroxy methyl substituted benzyl) valines (I), *viz.*, (i) N-(2-hydroxy-3-methyl benzyl)valine (H_3hmbv-3), (ii) N-(2-hydroxy-6-methyl benzyl) valine (H_3-hmbv-6), and (iii) N-(2-hydroxy-5-methyl benzyl) valine (H_3hmbv-5) by alcoholysis reaction[1, 2] involving the interaction of mono- and triphenyltin isopropoxides with I in 1 : 1, 1 : 2 and 1 : 3 molar ratios in benzene medium in case of mono-phenyltin derivatives and in toluene medium in case of triphenyltin derivatives. The compounds thus prepared were 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

Owing to extremely hygroscopic nature of organotin isopropoxides stringent precautions were taken to exclude moisture throughout the experiments, using identical assemblies as before[1–3] Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard methods[4]. Mono- and triphenyltin isopropoxides were prepared by sodium method[5]. Tin was determined by direct ignition of the sample after digestion with nitric and sulphuric acids followed by neutralization and precipitation by ammonia solution[6]. The details of the various instruments used have been reported earlier[1, 2].

N-(2-hydroxy methyl substituted benzyl) valines were prepared by methods described before[1–3] which exist in zwitterionic form (Structure I).



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

(I)

Reaction between PhSn $(OPr^i)_3$ and H_3hmbv-6; 1 : 1 Molar Ratio

A mixture of PhSn$(OPr^i)_3$ (1.1060 g; 2.9646 mmole) and H_3hmbv-6 (0.7034 g; 2.9641 mmole) suspended in dry benzene (60 mL) taken in an R.B. flask was refluxed on a wax bath at 95–100°C, using a fractionating column. After *ca.* 9 h of reflux, isopropanol liberated was fractionated out azeotropically and estimated by an oxidimetric method[7,8]. After completion of reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, PhSn(hmbv-6) isolated as a yellowish white solid which was washed with dry benzene (3–4 times) followed by dry ether (2–3 times) to remove the excess of PhSn$(OPr^i)_3$ and finally dried under suction. The compound was found to be soluble in dimethylsulphoxide, sparingly soluble in dimethylformamide but insoluble in other common organic solvents.

It may be mentioned here that since PhSn$(OPr^i)_3$ is soluble in benzene, while H_3hmbv-6 is insoluble, the latter was taken in slightly less than the required stoichiometric amount in order to avoid contamination of impurities likely to occur by the unreacted H_3hmbv-6. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_3hmbv-6 taken.

Similar procedures of preparation and purification were adopted in case of other derivatives. The relevant analytical details of the various compounds prepared, their characteristic IR frequencies and the PMR spectral data are recorded in Table 1–3, respectively.

RESULTS AND DISCUSSION

The various reactions occurring between mono- and triphenyltin isopropoxide and H_3hmbv-6 may be illustrated as:

$$PhSn(OPr^i)_3 + H_3hmbv\text{-}6 \rightarrow PhSn(hmbv\text{-}6) + 3Pr^iOH$$

$$PhSn(OPr^i)_3 + 2H_3hmbv\text{-}6 \rightarrow PhSn(OPr^i)(H_2hmbv\text{-}6)_2 + 2Pr^iOH$$

$$PhSn(OPr^i)_3 + 3H_3hmbv\text{-}6 \rightarrow PhSn(H_2hmbv\text{-}6)_3 + 3Pr^iOH$$

$$Ph_3Sn(OPr^i) + H_3hmbv\text{-}6 \rightarrow Ph_3Sn(H_2hmbv\text{-}6) + Pr^iOH$$

Identical course of reactions followed in case of H_3hmbv-3 and H_3hmbv-5.

TABLE-1
ANALYTICAL DETAILS OF N-(2-HYDROXY METHYL SUBSTITUTED BENZYL VALINES AND THEIR MONOPHENYL AND TRIPHENYL TIN(IV) DERIVATIVES

Compound (molar ratio)/(colour)	Reflux time (h)	m.p. (°C)	Elemental analysis % found (calcd.)			
			C	H	N	Sn
H_3hmbv-3	—	130	65.80 (65.82)	8.12 (8.01)	5.88 (5.90)	—
H_3hmbv-6	—	140	65.79 (65.82)	8.00 (8.01)	5.89 (5.90)	—
H_3hmbv-5	—	120	65.78 (65.82)	8.00 (8.01)	5.87 (5.90)	—
PhSn(hmbv-3) (1 : 1) (off white)	9	225	53.00 (53.06)	4.88 (4.92)	3.20 (3.26)	27.58 (27.60)
$PhSn(OPr^i)(H_2hmbv\text{-}3)_2$ (1 : 2) (off white)	11	310	57.71 (57.79)	6.66 (6.65)	3.80 (3.86)	16.29 (16.32)
$PhSn(H_2hmbv\text{-}3)_3$ (1 : 3) (yellowish white)	14	288	59.68 (59.74)	6.50 (6.57)	4.63 (4.64)	13.08 (13.12)
PhSn(hmbv-6) (1 : 1)	9	215	52.99 (53.06)	4.88 (4.92)	3.26 (3.26)	27.52 (27.60)
$PhSn(OPr^i)(H_2hmbv\text{-}6)_2$ (1 : 2) (yellowish white)	12	300	57.70 (57.79)	6.62 (6.65)	3.82 (3.86)	16.28 (16.32)
$PhSn(H_2hmbv\text{-}6)_3$ (1 : 3) (rose white)	16	235	59.67 (59.74)	6.51 (6.57)	4.62 (4.64)	13.09 (13.12)
PhSn(hmbv-5) (1 : 1) (rose white)	8	235	52.99 (53.06)	4.88 (4.92)	3.21 (3.26)	27.52 (27.60)
$PhSn(OPr^i)(H_2hmbv\text{-}5)_2$ (1 : 2) (rose white)	10	210	57.72 (57.59)	6.64 (6.65)	3.83 (3.86)	16.28 (16.32)
$PhSn(H_2hmbv\text{-}5)_3$ (1 : 3) (rose white)	13	305	59.68 (59.74)	6.50 (6.57)	4.61 (4.64)	13.07 (13.12)
$Ph_3Sn(H_2hmbv\text{-}3)$ (1 : 1) (yellowish white)	20	297	63.48 (63.51)	5.61 (5.67)	2.29 (2.39)	20.20 (20.25)
$Ph_3Sn(H_2hmbv\text{-}6)$ (1 : 1) (off white)	18	268	63.47 (63.51)	5.67 (5.67)	2.29 (2.39)	20.18 (20.25)
$(Ph_3Sn(H_2hmbv\text{-}5)$ (1 : 1) (yellowish white)	23	275	63.43 (63.51)	5.65 (5.67)	2.35 (2.39)	20.22 (20.25)

Abbreviations: Ph = C_6H_5, OPr^i = OC_3H_7,
H_3hmbv-3 (or -6 or -5) = $OHC_6H_3(CH_3)CH_2\overset{+}{N}H_2CHCH(CH_3)_2COO^-$

TABLE-2
CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF N-(2-HYDROXY METHYL SUBSTITUTED BENZYL) VALINES AND THEIR MONOPHENYL AND TRIPHENYL TIN(IV) DERIVATIVES

Compound	ν(OH) and aromatic ν(C—H)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 groups	$\nu(\overset{+}{N}H_2)$	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$	Δν(COO)	ν(C—N)	ν(Sn—C)	ν(Sn—O)	ν(Sn—N)
H_3hmbv-3	3700–3000 (vb)	—	2980 (m) 2860 (w)	2320 (m)	1600 (sb)	1405 (s)	—	1230 (s)	—	—	—
H_3hmbv-6	3670–3000 (vb)	—	2960 (s) 2840 (w)	2340 (m)	1610 (sb)	1410 (m)	—	1240 (s)	—	—	—
H_3hmbv-5	3700–3000 (vb)	—	2940 (s) 2850 (w)	2360 (m)	1610 (vsb)	1410 (s)	—	1230 (m)	—	—	—
PhSn(hmbv-3)	—	3300–3000 (mb)	2965 (s) 2870 (w)	—	1620 (sb)	1380 (msh)	240	1260 (s)	1095 (m)	580 (w)	470 (m)
PhSn(OPr^i)(H_2hmbv-3)$_2$	3680–3300* (vb)	3300–3000 (b)	2980 (s) 2845 (w)	—	1620 (vsb)	1380 (s)	240	1240 (s)	1035 (m)	545 (m)	460 (w)
PhSn(H_2hmbv-3)$_3$	3680–3400* (vb)	3300–3000 (mb)	2965 (s) 2850 (w)	—	1625 (vsb)	1385 (m)	240	1230 (s)	1095 (m)	560 (w)	450 (s)
PhSn(hmbv-6)	3700–3400* (b)	3300–3000 (mb)	2960 (s) 2870 (w)	—	1620 (vsb)	1380 (m)	240	1260 (s)	1095 (m)	580 (w)	470 (m)
PhSn(OPr^i)(H_2hmbv-6)$_2$	—	3300–3000 (b)	2960 (s) 2850 (w)	—	1625 (vsb)	1385 (vsb)	240	1260 (s)	1090 (m)	540 (m)	460 (w)

Compound	ν(OH) and aromatic ν(C—H)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 groups	$\nu(\overset{+}{N}H_2)$	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$	Δν(COO)	ν(C—N)	ν(Sn—C)	ν(Sn—O)	ν(Sn—N)
$PhSn(H_2hmbv\text{-}6)_3$	3680–3400* (b)	3400–3000 (mb)	2965 (s) 2850 (w)	—	1620 (sb)	1390 (s)	230	1240 (s)	1040 (m)	560 (w)	450 (s)
PhSn(hmbv-5)	—	3250–3000 (mb)	2960 (w) 2865 (w)	—	1620 (sb)	1380 (msh)	240	1260 (s)	1090 (m)	560 (m)	470 (w)
$PhSn(OPr^i)(H_2hmbv\text{-}5)_2$	3660–3300* (b)	3300–3000 (mb)	2970 (m) 2850 (w)	—	1620 (msb)	1370 (s)	250	1220 (m)	1035 (m)	545 (m)	460 (msh)
$PhSn(H_2hmbv\text{-}5)_3$	3640–3400* (vb)	3400–3000 (b)	2970 (s) 2845 (w)	—	1610 (sb)	1380 (msh)	230	1250 (s)	1040 (s)	565 (w)	460 (s)
$Ph_3Sn(H_2hmbv\text{-}3)$	3680–3400* (mb)	3210 (m)	2970 (s) 2920 (w) 2850 (w)	—	1620 (vsb)	1390 (s)	230	1260 (s)	1095 (s)	585 (s) 550 (s)	500 (s)
$PH_3Sn(H_2hmbv\text{-}6)$	3700–3400* (vb)	3250–3000 (mb)	2960 (s) 2925 (w) 2870 (w)	—	1615 (vsb)	1380 (s)	235	1260 (m)	1090 (m)	580 (s) 545 (w)	510 (w)
$Ph_3Sn(H_2hmbv\text{-}5)$	3660–3300* (vb)	3240 (m)	2960 (s) 2925 (w) 2870 (w)	—	1615 (vsb)	1380 (s)	235	1260 (m)	1100 (m)	580 (s) 540 (w)	515 (w)

*ν(OH) alone

Abbreviations: s = strong, b = broad, sb = strong broad, vb = very broad, vsb = very strong broad, m = medium, mb = medium broad, msh = medium shouldered, w = weak.

TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUES) OF N-(2-HYDROXY METHYL SUBSTITUTED BENZYL) VALINES AND THEIR MONOPHENYL AND TRIPHENYL TIN(III) DERIVATIVES

Compound	Aromatic ring	Phenolic (—OH)	>CH— group (of valine part)	>NH	$>\overset{+}{N}H_2$	—CH_3 attached with benzene ring	—CH_2— attached with benzene ring	*Gem*-dimethyl
H_3hmbv-3	6.60–6.70 (m) 6.70–6.80 (d) 6.90–7.10 (d)	6.85 (s)	3.46–3.98 (m)	—	3.20–3.40 (h)	2.15 (s)	2.08 (d)	0.86–1.10 (d)
H_3hmbv-6	6.60–6.72 (d) 6.72–6.85 (t) 6.94–7.00 (d)	6.92 (s)	3.42–4.15 (m)	—	3.10–3.42 (h)	2.16 (s)	2.10 (d)	0.92 (d)
H_3hmbv-5	6.60–6.80 (m) 6.80–6.90 (d) 6.94–7.00 (d)	6.92 (s)	3.45–3.96 (m)	—	3.04–3.43 (h)	2.15 (s)	2.10 (d)	0.90–1.05 (d)
PhSn(hmbv-6)	6.50–7.00 (m)	—	3.40–4.05 (bm)	—	—	2.15 (s)	2.10 (d)	1.05 (d)
PhSn(OPr^i)(H_2hmbv-3)$_2$	6.40–7.05 (m)	6.85 (s)	3.45–3.80 (bm)	3.10 (h)	—	2.10 (s)	2.05 (d)	0.90 (d)*
PhSn(H_2hmbv-5)$_3$	6.70–7.00 (m)	6.92 (s)	3.45–4.10 (bm)	3.12 (h)	—	2.15 (s)	2.05 (d)	1.10 (d)
Ph_3Sn(H_2hmbv-3)	6.60–6.80 (m)	6.85 (s)	3.45–4.05 (bm)	3.15 (h)	—	2.10 (s)	2.05 (d)	1.12 (d)

**Gem*-dimethyl of valine part and *gem*-dimethyl of isopropoxy group protons.
Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, bm = broad multiplet

Spectral Studies[9–14]

Infrared spectra: The derivative, PhSn(hmbv-6) displays a medium broad band in the region 3300–3000 cm^{-1} corresponding to aromatic ν(C—H). The band due to ν(OH) (phenolic), as observed in H_3hmbv-6, is found to disappear here indicating bonding of the phenolate oxygen to tin. The absence of band corresponding to ν(N—H) of the $>\overset{+}{N}H_2$ group at 2340 cm^{-1}, as observed in H_3hmbv-6, suggests bonding of nitrogen to tin. The absence of any characteristic band corresponding to ν(C=O) in the region 1750–1650 cm^{-1} rules out the possibility of a normal ester type of linkage between the carboxylate oxygen and tin. A very strong band at 1620 cm^{-1} may be assigned to the overlapping of ν_{asym}(COO) and aromatic ν(C=C). Further, instead of a peak at 1410 cm^{-1}, as observed in H_3hmbv-6, here the appearance of a medium shouldered bond at 1380 cm^{-1} corresponds to ν_{sym}(COO), while the one at 1330 cm^{-1} occurs due to C—H bending of the *gem*-dimethyl structure of valine part. Thus, a shift of 30 cm^{-1} in ν_{sym}(COO), as compared to H_3hmbv-6, suggests possible bonding of the carboxylate oxygen to tin. The separation value, Δν(COO) [ν_{asym}(COO) – ν_{sym}(COO] of 240 cm^{-1} indicates the absence of a bridged or coordinated carboxylate group. A strong band at 1260 cm^{-1} due to ν(C—N) and hence a shift of 20 cm^{-1} as compared to H_3hmbv-6, again supports the bonding of nitrogen to tin, while a medium band at 1095 cm^{-1} appears due to ν(Sn—C). The appearance of two strong bands at 695 cm^{-1} and 670 cm^{-1} indicates C—H out-of-plane bending of the phenyl group attached with the tin atom. A weak band at 580 cm^{-1} and the medium band at 470 cm^{-1} correspond to ν(Sn—O) and ν(Sn—N), respectively.

It is thus evident that the tin atom in PhSn(hmbv-6) shows pentavalency by way 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 a phenyl group (Structure II).

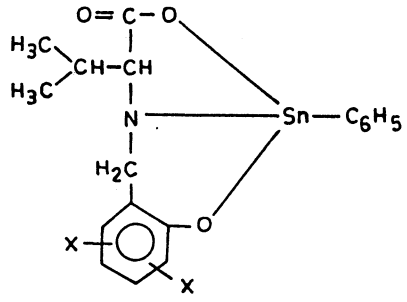
Proton magnetic resonance spectra: A multiplet in the region δ 6.50–7.00 in the PMR spectrum of PhSn(hmbv-6) corresponds to the aromatic ring protons. The singlet at δ 6.92 due to the phenolic group proton, as noted in H_3hmbv-6, is found to disappear here indicating the bonding of the phenolate oxygen to tin. The hump between δ 3.10–3.42 due to the $>\overset{+}{N}H_2$ group protons, as observed in H_3hmbv-6, is found to be absent here suggesting the bonding of nitrogen to tin. A broad multiplet between δ 3.40–4.05 occurs because of the >CH— group protons of the valine part of H_3hmbv-6. The signals corresponding to $-CH_3$ and $—CH_2—$ groups attached with the benzene ring occur as a singlet at δ 2.15 and doublet at δ 2.10, respectively. A doublet at δ 1.05 may be assigned to the **gem**-dimethyl group protons of the valine part.

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

The derivatives, PhSn(hmbv-3) and PhSn(hmbv-5) contain a pentavalent tin

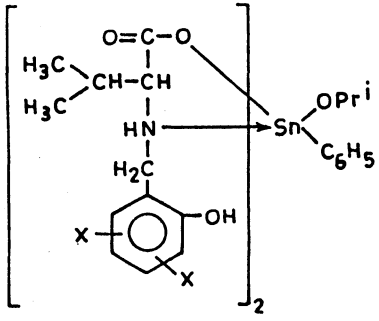
atom in each case displaying similar mode of bonding, as those observed in case of PhSn(hmbv-6) (Structure II).

The tin atom in $PhSn(OPr^i)(H_2hmbv\text{-}3)_2$, $PhSn(OPr^i)(H_2hmbv\text{-}6)_2$ and $PhSn(OPr^i)(H_2hmbv\text{-}5)_2$ shows hexa-coordination in each case as a consequence of bonding with one of the oxygens from each of the two carboxylate groups, the



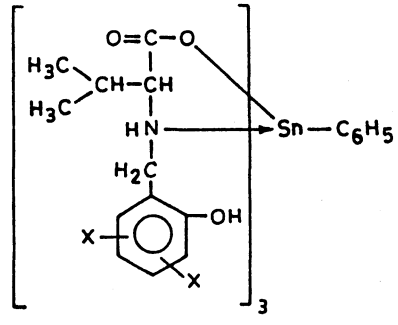
(Where X= -H or $-CH_3$)

(II)



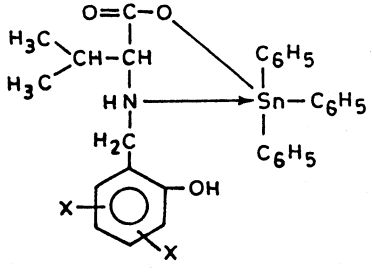
(Where X= -H or $-CH_3$)

(III)



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

(IV)



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

(V)

nitrogen from each of the two imino groups available from two moles of I, along with an isopropoxy and a phenyl group (Structue III).

The derivatives, $PhSn(H_2hmbv\text{-}3)_3$, $PhSn(H_2hmbv\text{-}6)_3$ and $PhSn(H_2hmbv\text{-}5)_3$ contain a hepta-coordinated tin atom in each case by way of bonding with one of the oxygens from each of the three carboxylate groups, the nitrogen from each of the three imino groups available from three moles of I, along with a phenyl group (Structure IV).

The tin atom in $Ph_3Sn(H_2hmbv\text{-}3)$, $Ph_3Sn(H_2hmbv\text{-}6)$ and $Ph_3Sn(H_2hmbv\text{-}5)$ shows penta-coordination in each case as a result of bonding with one of the oxygens from the carboxylate group and the nitrogen from the imino group, along with three phenyl groups (Structure V).

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