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Mono-, Di- and Tributyltin Derivatives of N-(2-Hydroxy Methyl Substituted Benzyl) Valines

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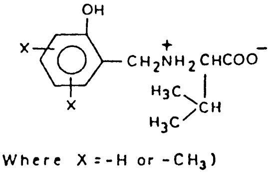
Mono-, di- and tributyltin derivatives of N-(2-hydroxy methyl substituted benzyl) valines have been prepared by alcoholysis reaction. The compounds were obtained as coloured solids in case of mono- and dibutyltin derivatives and as dark viscous liquids in case of tributyltin derivatives. Amongst these derivatives 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

Preparation of elemento(III) derivatives of N-(2-hydroxy methyl substituted benzyl)-valines(I) (Structure-I) and their characterization have been reported earlier from these laboratories[1–3]. The work described here deals with the preparation of mono-, di- and tributyltin derivatives of I, *viz.*, (*i*) N-(2-hydroxy-3-methyl benzyl) valine (H_3hmbv-3), (*ii*) N-(2-hydroxy-6-methyl benzyl)-valine (H_3hmbv-6), and (*iii*) N-(2-hydroxy-5-methyl benzyl) valine (H_3hmbv-5) by alcoholysis reaction[1,2] involving the interaction of mono-, di- or tributyltin isopropoxides with I in 1 : 1, 1 : 2, 1 : 3 and 2 : 1 molar ratios in benzene medium. The compounds prepared were obtained as coloured solids in case of mono- and dibutyltin derivatives and as dark viscous liquids in case of tributyltin derivatives. Amongst these derivatives those containing isopropoxy group were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analysis, as well as by IR and PMR spectral measurements.



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

EXPERIMENTAL

Owing to extremely hygroscopic nature of organotin isopropoxides stringent precautions were taken to exclude moisture throughout the experiments, using identical assemblies, as before[1,2]. Benzene (BDH, AR), isopropanol (BDH, Glaxo

AnalaR) and solvent ether (E. Merck) were dried by standard methods[4]. Mono-, di- and tributyltin 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 zwitter ionic form (Structure-I).

Reaction between $BuSn(OPr^i)_3$ and H_3hmbv-3, 1 : 1 Molar Ratio

A mixture of $BuSn(OPr^i)_3$ (0.7346 g; 2.0805 mmole) and H_3hmbv-3 (0.4936 g; 2.0800 mmole) suspended in dry benzene (60 mL) taken in a round-bottomed flask was refluxed on a wax bath at 95–100°C, using a fractionating column. After *ca.*, 8 h of reflux, isopropanol liberated was fractionated out azeotropically and estimated by an oxidimetric method[7, 8]. After completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, BuSn(hmbv-3) isolated as a brown solid which was washed with dry benzene (3–4 times) followed by dry ether (2–3 times) to remove the excess of BuSn $(OPr^i)_3$ and finally dried under suction. The compound was found to be soluble in dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents.

It may be mentioned here that since $BuSn(OPr^i)_3$ is soluble in benzene, while H_3hmbv-3 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-3. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_3hmbv-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_3hmbv-5. the relevant analytical details of the various compounds thus prepared, their characteristic IR frequencies and the PMR spectral data (in several representative cases) are recorded in Table 1–3, respectively.

RESULTS AND DISCUSSION

The various reactions occurring between mono-, di- and tributyltin isopropoxide and H_3hmbv-3 may be illustrated as:

$$BuSu(OPr^i)_3 + H_3hmbv\text{-}3 \longrightarrow BuSn(hmbv\text{-}3) + 3Pr^iOH$$

$$BuSn(OPr^i)_3 + 2H_3hmbv\text{-}3 \longrightarrow BuSn(OPr^i)(H_2hmbv\text{-}3)_2 + 2Pr^iOH$$

$$BuSn(OPr^i)_3 + 3H_3Hmbv\text{-}3 \longrightarrow BuSn(H_2hmbv\text{-}3)_3 + 3Pr^iOH$$

$$Bu_2Sn(OPr^i)_2 + H_3hmbv\text{-}3 \longrightarrow Bu_2Sn(Hhmbv\text{-}3) + 2Pr^iOH$$

$$Bu_2Sn(OPr^i)_2 + 2H_3hmbv\text{-}3 \longrightarrow Bu_2Sn(H_2hmbv\text{-}3)_2 + 2Pr^iOH$$

$$Bu_3Sn(OPr^i) + H_3hmbv\text{-}3 \longrightarrow Bu_3Sn(H_2hmbv\text{-}3) + Pr^iOH$$

$$2Bu_3Sn(OPr^i) + H_3hmbv\text{-}3 \longrightarrow (Bu_3Sn)_2(Hhmbv\text{-}3) + 2Pr^iOH$$

Identical course of reactions followed in case of H_3hmbv-6 and H_3hmbv-5.

TABLE-1 ANALYTICAL DETAILS OF N-(2-HYDROXY METHYL SUBSTITUTED BENZYL)- VALINES AND THEIR BUTYL SUBSTITUTED 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	8.12	5.88	—
			(65.82)	(8.01)	(5.90)	
H_3hmbv-6	—	140	65.79	8.00	5.89	—
			(65.82)	(8.01)	(5.90)	
H_3hmbv-5	—	120	65.78	8.00	5.87	—
			(65.82)	(8.01)	(5.90)	
BuSn (hmbv-3)	8	230	49.72	6.10	3.38	28.89
(1 : 1) (brown)			(49.78)	(6.14)	(3.42)	(28.94)
BuSn(OPr^i)(H_2hmbv-3)$_2$	10	210	55.97	7.36	3.97	16.71
(1 : 2) (bown)			(56.02)	(7.41)	(3.96)	(16.78)
BuSn(H_2hmbv-3)$_3$	15	260	58.39	7.10	4.72	13.37
(1 : 3) (brown)			(58.38)	(7.12)	(4.75)	(13.42)
BuSn(hmbv-6)	8	220	49.71	6.90	3.43	28.88
(1 : 1) (light brown)			(49.78)	(6.94)	(3.42)	(28.94)
BuSn(OPr^i)(H_2hmbv-6)$_2$	12	190	56.00	7.38	3.91	16.72
(1 : 2) (light yellowish brown)			(56.02)	(7.41)	(3.96)	(16.78)
BuSn(H_2hmbv-6)$_3$	10	250	58.32	7.10	4.70	13.40
(1 : 3) (light brown)			(58.38)	(7.12)	(4.75)	(13.42)
BuSn(hmbv-5)	10	235	49.72	6.13	3.40	28.90
(1 : 1) (rose white brown)			(49.78)	(6.14)	(3.42)	(28.94)
BuSn(OPr^i)(H_2hmbv-5)$_2$	19	215	55.97	7.38	3.92	16.72
(1 : 2) (rose white brown)			(56.02)	(7.41)	(3.96)	(16.78)
BuSn(H_2hmbv-5)$_3$	15	240	58.32	7.10	4.71	13.39
(1 : 3) (dirty white)			(58.38)	(7.12)	(4.75)	(13.42)
Bu_2Sn(Hhmbv-3)	12	265	53.82	7.50	3.01	25.30
(1 : 1) (light brown)			(53.87)	(7.53)	(3.00)	(25.35)
Bu_2Sn(H_2hmbv-3)$_2$	16	280	57.88	7.73	3.93	16.79
(1 : 2) (brown)			(57.92)	(7.72)	(3.97)	(16.83)
Bu_2Sn(Hhmbv-6)	12	210	53.81	7.49	2.98	25.29
(1 : 1) (sand stone)			(53.87)	(7.53)	(3.00)	(25.35)
Bu_2Sn(H_2hmbv-6)$_2$	10	240	57.88	7.70	3.98	16.80
(1 : 2) (sand stone)			(57.92)	(7.72)	(3.97)	(16.83)
Bu_2Sn(Hhmbv-5)	14	260	53.82	7.50	2.98	25.30
(1 : 1) (pale cream)			(53.87)	(7.53)	(3.00)	(25.35)
Bu_2Sn(H_2hmbv-5)$_2$	15	270	57.87	7.69	3.89	16.78
(1 : 2) (pale cream)			(57.92)	(7.72)	(3.97)	(16.83)
*Bu_3Sn(H_2hmbv-3)	6	—	57.00	8.60	2.60	22.53
(1 : 1) (sand white)			(57.05)	(8.62)	(2.62)	(22.56)
*(Bu_3Sn)$_2$(Hhmbv-3)	22	—	54.47	8.71	1.70	29.09
(2 : 1) (olive green)			(54.50)	(8.78)	(1.71)	(29.12)
*Bu_3Sn(H_2hmbv-6)	9	—	57.01	8.58	2.67	22.54
(1 : 1) (golden brown)			(57.05)	(8.62)	(2.66)	(22.56)
*(Bu_3Sn)$_2$Sn(Hhmbv-6)	24	—	54.48	8.71	1.69	29.09
(2 : 1) (golden brown)			(54.50)	(8.78)	(1.72)	(29.12)
*Bu_3Sn(H_2hmbv-5)	8	—	57.00	8.60	2.66	22.49
(1 : 1) (off white)			(57.05)	(8.62)	(2.63)	(22.56)
*(Bu_3Sn)$_2$(Hhmbv-5)	19	—	54.51	8.70	1.68	29.08
(2 : 1) (white brown)			(54.50)	(8.70)	(1.72)	(29.12)

*Boiling points could not be determined.

Abbreviations: Bu = C_4H_9, OPr^i = OC_3H_7.

H_3hmbv-3 (or -6 or -5) = $CH_3C_6H_3(OH)(CH_2)\overset{+}{N}H_2CHCH(CH_3)_2COO^-$.

TABLE-2

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

Compound (molar ratio)	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	$\nu\overset{+}{N}H_2$	ν_{asym}(COO)	ν_{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)	—	—	—
BuSn(hmbv-3) (1 : 1)	—	3400–3000 (b)	2965 (s) 2850 (w)	—	1625 (sb)	1390 (w)	235	1260 (s)	700 (w) 600 (w)	560 (w)	480 (w)
BuSn(OPr^i)(H_2hmbv-3$)_2$ (1 : 2)	*3680–3400 (b)	3300–3000 (b)	2965 (s) 2870 (w)	—	1620 (sb)	1380 (m)	240	1285 (m)	680 (w) 775 (w)	520 (w)	465 (w)
BuSn(H_2hmbv-3$)_3$ (1 : 3)	*3660–3400 (mb)	3250–3000 (b)	2970 (s) 2850 (w)	—	1615 (sb)	1390 (s)	225	1270 (s)	610 (m) 545 (m)	500 (w)	460 (w)
BuSn(hmbv-6) (1 : 1)	—	3400–3000 (b)	2965 (s) 2850 (w)	—	1625 (vsb)	1390 (s)	235	1260 (s)	700 (w) 600 (w)	560 (w)	485 (m)
BuSn(OPr^i)(H_2hmbv-6$)_2$ (1 : 2)	*3700–3400 (mb)	3300–3000 (b)	2965 (s) 2870 (w)	—	1620 (vsb)	1380 (m)	240	1280 (mb)	685 (m) 775 (w)	520 (w)	465 (m)
BuSn(H_2hmbv-6$)_3$ (1 : 3)	*3660–3400 (mb)	3260–3000 (b)	2965 (s) 2850 (w)	—	1615 (sb)	1390 (m)	225	1270 (s)	610 (w) 550 (m)	500 (mb)	460 (m)

Compound (molar ratio)	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	$\nu\overset{+}{N}H_2$	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Sn—C)	ν(Sn—O)	ν(Sn—N)
BuSn(hmbv-5) (1 : 1)	—	3360–3000 (b)	2960 (s) 2850 (w)	—	1625 (sb)	1390 (s)	235	1260 (s)	690 (m) 610 (w)	565 (w)	480 (w)
BuSn(OPr^i)(H_2hmbv-5)$_2$ (1 : 2)	*3680–3400 (b)	3250–3000 (b)	2960 (s) 2870 (w)	—	1620 (vsb)	1380 (m)	240	1275 (m)	680 (m) 770 (w)	525 (w)	460 (w)
BuSn(H_2hmbv-5)$_3$ (1 : 3)	*3680–3400 (mb)	3300–3000 (wb)	2965 (s) 2865 (w)	—	1615 (vsb)	1390 (m)	225	1270 (s)	600 (w) 545 (m)	500 (mb)	465 (w)
Bu_2Sn(Hhmbv-3) (1 : 1)	—	3300–3000 (mb)	2960 (s) 2925 (w) 2855 (w)	—	1640 (vsb)	1380 (s)	260	1260 (s)	680 (m) 590 (w)	545 (w)	475 (mb)
Bu_2Sn(H_2hmbv-3)$_2$ (1 : 2)	*3680–3300 (vb)	3300–3000 (b)	2960 (s) 2920 (w) 2850 (w)	—	1620 (sb)	1390 (m)	230	1260 (m)	600 (m) 540 (w)	460 (s)	455 (w)
Bu_2Sn(Hhmbv-6) (1 : 1)	—	3400–3000 (mb)	2970 (s) 2910 (w) 2870 (w)	—	1640 (vsb)	1390 (m)	250	1240 (m)	680 (m) 580 (w)	545 (w)	470 (mb)
Bu_2Sn(H_2hmbv-6)$_2$ (1 : 2)	*3660–3300 (vb)	3300–3000 (mb)	2960 (s) 2925 (w) 2870 (w)	—	1615 (sb)	1375 (mb)	240	1260 (m)	600 (w) 540 (w)	480 (m)	455 (s)
Bu_2Sn(Hhmbv-5) (1 : 1)	*3680–3300 (vb)	3300–3000 (b)	2965 (s) 2870 (w)	—	1610 (sb)	1380 (s)	230	1260 (w)	605 (s) 535 (s)	460 (m)	450 (w)
Bu_2Sn(H_2hmbv-5)$_2$ (1 : 2)	*3700–3400 (vb)	3300–3000 (b)	2965 (s) 2920 (w) 2870 (w)	—	1625 (sb)	1380 (m)	245	1260 (m)	610 (w) 540 (s)	490 (s)	460 (w)

Compound (molar ratio)	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	$\nu\overset{+}{N}H_2$	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Sn—C)	ν(Sn—O)	ν(Sn—N)
$Bu_3Sn(H_2hmbv\text{-}3)$ (1 : 1)	*3680–3300 (vb)	3300–3000 (b)	2965 (s) 2920 (w) 2850 (w)	—	1620 (sb)	1380 (s)	240	1260 (sb)	605 (s) 545 (w)	465 (s)	425 (s)
$(Bu_3Sn)_2(Hhmbv\text{-}3)$ (2 : 1)	—	3300–3000 (wb)	2965 (s) 2930 (w) 2865 (w)	—	1620 (vsb)	1390 (s)	230	1260 (w)	610 (s) 520 (mb)	460 (s)	410 (w)
$Bu_3Sn(H_2hmbv\text{-}6)$ (1 : 1)	*3660–3300 (vb)	3300–3000 (b)	2960 (s) 2870 (w)	—	1610 (vsb)	1380 (s)	230	1260 (sb)	600 (s) 540 (s)	460 (s)	450 (w)
$(Bu_3Sn)_2(Hhmbv\text{-}6)$ (2 : 1)	—	3300–3000 (wb)	2960 (s) 2920 (w) 2870 (w)	—	1610 (sb)	1380 (s)	230	1260 (m)	605 (m) 520 (m)	450 (w)	405 (m)
$Bu_3Sn(H_2hmbv\text{-}5)$ (1 : 1)	*3680–3300 (vb)	3300–3000 (b)	2960 (m) 2920 (w) 2870 (w)	—	1620 (sb)	1375 (s)	245	1260 (sb)	605 (s) 540 (s)	460 (w)	440 (w)
$(Bu_3Sn)_2(Hhmbv\text{-}5)$ (2 : 1)	—	3300–3000 (wb)	2965 (s) 2940 (w) 2865 (w)	—	1615 (vsb)	1390 (s)	225	1240 (wb)	600 (w) 540 (m)	450 (w)	400 (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 BUTYL SUBSTITUTED TIN(IV) DERIVATIVES

Compound (molar ratio)	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	—CH_2— of butyl part	*Gem* dimethyl	—CH_3 of butyl part
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)	—

Compound (molar ratio)	Aromatic ring	Phenolic (—OH)	>CH— group (of valine part)	>NH	$>\overset{+}{N}NH_2$	—CH_3 attached with benzene ring	—CH_2— attached with benzene ring	—CH_2— of butyl part	*Gem* dimethyl	—CH_3 of butyl part
BuSn(hmbv-3) (1 : 1)	6.40–7.10 (t)	—	3.35–4.00 (bm)	—	—	2.15 (s)	2.10 (d)	1.45 (s)	1.35 (d)	0.90–1.00 (t)
$BuSn(OPr^i)$ $(H_2hmbv\text{-}6)_2$ (1 : 2)	6.40–6.90 (t)	6.92 (s)	3.35–4.00 (bm)	3.15 (h)	—	2.15 (s)	2.10 (d)	1.20–1.50 (m)	1.00 (d)	0.60 (t)
$BuSn(H_2hmbv\text{-}5)_3$ (1 : 3)	6.40–6.75 (m)	6.92 (s)	3.40–3.45 (bm)	3.10 (s)	—	2.10 (s)	2.05 (d)	0.85–1.05 (t)	1.40 (d)	0.50–0.70 (m)
$Bu_2Sn(Hhmbv\text{-}3)$ (1 : 1)	6.90–7.05 (t)	—	3.40–3.45 (bm)	3.10 (h)	—	2.15 (s)	2.10 (d)	1.20–1.00 (m)	1.35 (d)	0.70–0.90 (m)
$Bu_2Sn(H_2hmbv\text{-}6)_2$ (1 : 2)	6.70–7.00 (m)	6.92 (s)	3.45–3.80 (bm)	3.20 (h)	—	2.15 (s)	2.10 (d)	—	1.00 (d)	0.60–0.90 (bm)
$Bu_3Sn(H_2hmbv\text{-}3)$ (1 : 1)	6.60–7.10 (m)	6.85 (s)	3.40–4.10 (bm)	3.15 (h)	—	2.15 (s)	2.10 (d)	—	1.10 (d)	0.60–0.90 (m)
$(Bu_3Sn)_2(Hhmbv\text{-}5)$ (2 : 1)	6.65–7.00 (m)	6.92 (s)	3.45–3.95 (bm)	3.20 (h)	—	2.15 (s)	2.10 (d)	—	1.10 (d)	0.60–0.90 (m)

Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, bm = broad multiplet, h = hump.

Spectral studies[9–14]

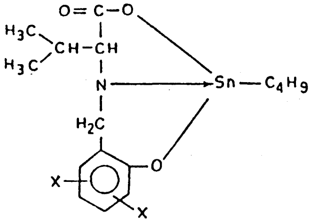
Infrared spectra: The derivative, BuSn(hmbv-3) displays a broad band in the region 3400–3000 cm^{-1} corresponding to aromatic ν(C—H). The band due to the phenolic ν(OH), as observed in H_3hmbv-3, is found to disappear here indicating bonding of the phenolate oxygen to tin. The absence of band corresponding to ν(N—H) of the $>\overset{+}{N}H_2$ group at 2320 cm^{-1}, as observed in H_3hmbv-3, 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 strong band at 1625 cm^{-1} may be assigned to the overlapping of ν_{asym}(COO) and aromatic ν(C=C). Further, instead of a peak at 1405 cm^{-1}, as noted in H_3hmbv-3, here the appearance of weak band around 1390 cm^{-1} corresponds to ν_{sym}(COO) and C—H bending of the *gem* dimethyl structure of valine part. Thus, a shift of 15 cm^{-1} in ν_{sym}(COO), as compared to H_3hmbv-3, suggests possible bonding of the carboxylate oxygen to tin. The separation value, Δν(COO) [ν_{asym}(COO)–ν_{sym}(COO)] of 235 cm^{-1} indicates the absence of a bridged or coordinated carboxylate group. A strong band at 1260 cm^{-1} corresponds to ν(C—N) and hence a shift of 30 cm^{-1} in ν(C—N) as compared to H_3hmbv-3 further supports the bonding of nitrogen to tin. The appearance of weak bands at 700 cm^{-1} and 600 cm^{-1} may be assigned to ν_{asym}(Sn—C) and ν_{sym}(Sn—C) respectively. The weak absorptions at 560 cm^{-1} may be attributed to ν(Sn—O) while the one at 480 cm^{-1} corresponds to ν(Sn—N).

It is thus evident that tin atom in the derivative BuSn(hmbv-3) shows pentavalency by the 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 butyl group (Structure-II).

Proton magnetic resonance spectra: The triplet in the region δ6.40–7.10 in the PMR spectrum of BuSn(hmbv-3) corresponds to the aromatic ring protons. The singlet at δ6.85 due to the phenolic group proton, as noted in H_3hmbv-3, is found to disappear here indicating the bonding of the phenolate oxygen to tin. The hump between δ3.20–3.40 due to the $>\overset{+}{N}H_2$ group protons, as observed in H_3hmbv-3, is found to be absent here suggesting the bonding of nitrogen to tin. A broad multiplet between δ3.35–4.00 corresponds to the proton of the >CH— group of the valine part. The singlet at δ2.15 and a doublet at δ2.10 occur, respectively, due to the protons of —CH_3 and —CH_2— groups attached with the benzene ring, while a singlet at δ1.45 occurs because of the protons of the —CH_2— group of the butyl part attached with the tin atom. The doublet at δ1.35 corresponds to the *gem* dimethyl group protons, while a triplet at δ0.90–1.00 occurs because of the —CH_3 group protons of the butyl part attached with the tin atom.

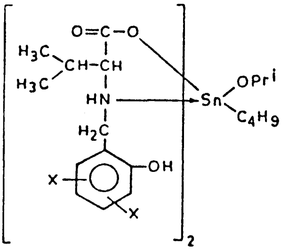
The IR and PMR spectral data in respect of other derivatives were interpreted similarly and the main findings relating to their structures are as under:

The derivatives, BuSn(hmbv-6) and BuSn(hmbv-5) contain a pentavalent tin atom in each case displaying similar mode of bonding, as those observed in case of BuSn(hmbv-3) (Structure-II).



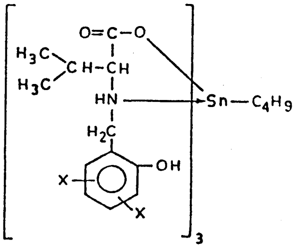
(Where X = - H or -CH_3)

(II)



(Where X = -H or -CH_3)

(III)



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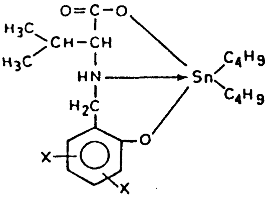
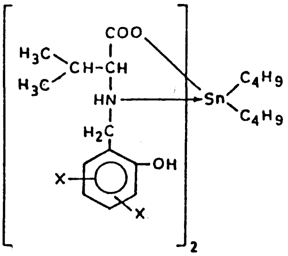
(IV)



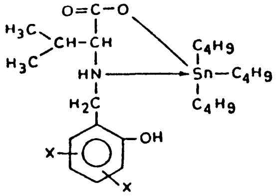
(Where X = -H or -CH_3)

(V)



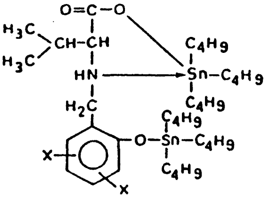
(Where X = -H or -CH_3)

(VI)



(Where X = -H or -CH_3)

(VII)



(Where X = -H or -CH_3)

(VIII)

The tin atom in the derivatives, $BuSn(OPr^i)(H_2hmbv\text{-}3)_2$, $BuSn(OPr^i)(H_2hmbv\text{-}6)_2$ and $BuSn(OPr^i)(H_2hmbv\text{-}5)_2$ shows hexa-coordination in each case as a consequence of bonding with one of the oxygens from each of the two carboxylate groups, the nitrogen from each of the two imino groups available from two moles of I, along with an isopropoxy group (Structure-III). The derivatives, $BuSn(H_2hmbv\text{-}3)_3$, $BuSn(H_2hmbv\text{-}6)_3$ and $BuSn(H_2hmbv\text{-}5)_3$ 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 and the nitrogen from each of the three imino groups, available from three moles of I, along with a butyl group (Structure-IV). The tin atom in the derivatives, $Bu_2Sn(Hhmbv\text{-}3)$, $Bu_2Sn(hhmbv\text{-}6)$ and $Bu_2Sn(Hhmbv\text{-}5)$ shows penta-coordination in each case as a consequence 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 two butyl groups (Structure-V). The derivatives, $Bu_2Sn(H_2hmbv\text{-}3)_2$, $Bu_2Sn(H_2hmbv\text{-}6)_2$ and $Bu_2Sn(H_2hmbv\text{-}5)_2$ contain a hexa-coordinated tin atom in each case by way of bonding with one of the oxygens from each of the two carboxylate groups, the nitrogen from each of the two imino groups available from two moles of I, along with two butyl groups (Structure-VI). The tin atom in the derivatives, $Bu_3Sn(H_2hmbv\text{-}3)$, $Bu_3Sn(H_2hmbv\text{-}6)$ and $Bu_3Sn(H_2hmbv\text{-}5)$ 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 butyl groups (Structur-VII). The derivatives, $(Bu_3Sn)_2(Hhmbv\text{-}3)$, $(Bu_3Sn)_2(Hhmbv\text{-}6)$ and $(Bu_3Sn)_2(Hhmbv\text{-}5)$ contain two tin atoms in each case out of which one shows penta-coordination by way of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group, along with three butyl groups. The other tin atom, however, displays tetra-coordination by way of bonding with the oxygen from the phenolic group, along with three butyl groups (Structure-VIII).

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