

## Methyl Substituted Tin(IV) Derivatives of N-(*o*-Hydroxy Substituted Benzyl) Alanines

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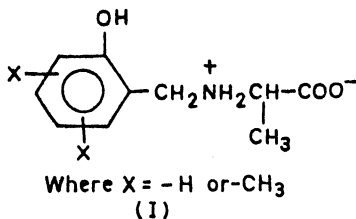
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Several methyl substituted tin(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by the interaction of the corresponding methyl substituted tin isopropoxide with the latter in various stoichiometries which were characterized by azeotrope and elemental analysis, as well as by spectral measurements.

### INTRODUCTION

Preparation and characterization of mono-, di- and tributyl/phenyl substituted tin(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been reported earlier from these laboratories.<sup>1-3</sup> In continuation, the work described here deals with the preparation of mono-, di- and trimethyl substituted tin(IV) derivatives of several N-(*o*-hydroxy substituted benzyl) alanines (I) (Structure I), viz



- (i) N-(2-hydroxy-3-methyl benzyl) alanine (H<sub>2</sub>hmba-3),
- (ii) N-(2-hydroxy-6-methyl benzyl) alanine (H<sub>2</sub>hmba-6), and
- (iii) N-(2-hydroxy-5-methyl benzyl) alanine (H<sub>2</sub>hmba-5)

involving the interaction of mono-, di- or trimethyltin isopropoxide with I in 1 : 1, 1 : 2 or 2 : 1 molar ratios in toluene medium. The various compounds thus prepared were generally obtained as coloured solids which were characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

### EXPERIMENTAL

Owing to highly hygroscopic nature of organotin isopropoxides stringent precautions were taken to exclude moisture throughout the experiments, using

identical assemblies, as before.<sup>4, 5</sup> Benzene (BDH, AR), isopropanol (BDH, Glaxo AR), toluene (E. Merck) and solvent ether (E. Merck) were dried by methods reported earlier.<sup>1-5</sup> Mono-, di- and trimethyltin(IV) isopropoxides were prepared as before,<sup>6</sup> which N-(*o*-hydroxy substituted benzyl) alanines were prepared employing already reported methods.<sup>1</sup>

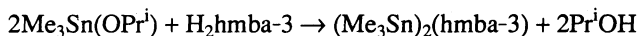
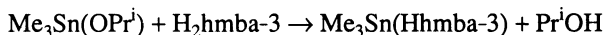
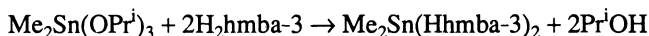
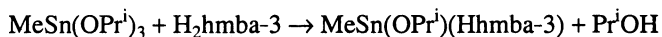
### Reaction between Monomethyltin Triisopropoxide and H<sub>2</sub>hmba-3; 1 : 1 Molar Ratio

A mixture of MeSn(OPr<sup>i</sup>)<sub>3</sub> (1.8596 g; 5.98 m mole) and H<sub>2</sub>hmba-3 (1.2492 g; 5.97 mmole) suspended in dry toluene (60 mL) taken in a R.B. flask was refluxed on a wax bath at 125–130°C, using a fractionating column. After *ca.* 12 h of reflux, isopropanol liberated was fractionated out azeotropically and estimated by an oxidimetric method, as before.<sup>1-5</sup> After completion of the reaction, the excess of solvent from the reaction mixture was removed in *vacuo*, when the product, MeSn(OPr<sup>i</sup>)<sub>2</sub>(Hhmbv-3) isolated as a brown solid which was washed with dry toluene (3–4 times) and then with dry ether (2–3 times) to remove excess of MeSn(OPr<sup>i</sup>)<sub>3</sub> and finally dried under suction. The product was further purified by recrystallization from ethanol. The compound was found to be soluble in dimethyl formamide and dimethyl sulphoxide but insoluble in other common organic solvents.

It may be mentioned here that since MeSn(OPr<sup>i</sup>)<sub>3</sub> is soluble in toluene, while H<sub>2</sub>hmba-3 is insoluble, the latter was taken in slightly less than the required stoichiometric amount (as evident from the weight given before) in order to avoid contamination of impurities likely to occur by the unreacted H<sub>2</sub>hmba-3. The amount of isopropanol liberated was, therefore, calculated according to the amount of H<sub>2</sub>hmba-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 monomethyltin derivatives of H<sub>2</sub>hmba-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 Tables 1–3, respectively.

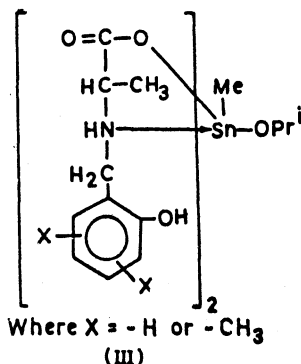
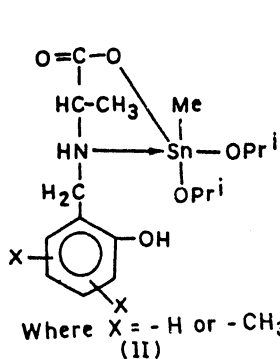
## RESULTS AND DISCUSSION

The various reactions occurring between mono-, di- and trimethyltin isopropoxide and H<sub>3</sub>hmba-3 may be illustrated as:



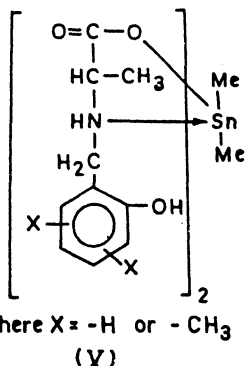
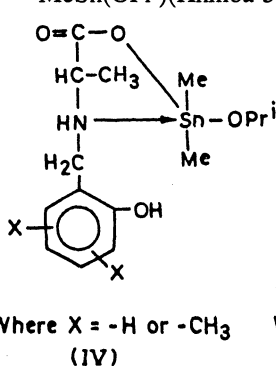
Identical course of reaction followed in case of H<sub>2</sub>hmba-6 and H<sub>2</sub>hmba-5.

Based on azeotrope and elemental analysis, as well as the spectral data<sup>7-12</sup>, the modes of bonding in the various derivatives thus prepared are shown in structures II-VII, and the relevant details are as under:



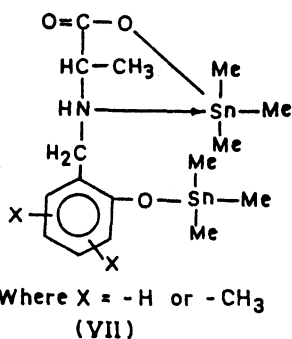
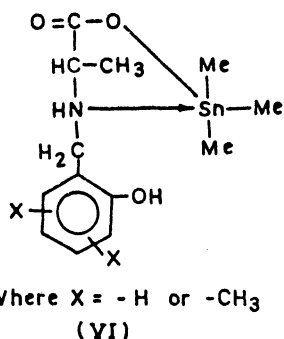
Structure II: MeSn(OPr<sup>i</sup>)<sub>2</sub>(Hhmba-3), MeSn(OPr<sup>i</sup>)<sub>2</sub>(Hhmba-6) and MeSn(OPr<sup>i</sup>)<sub>2</sub>(Hhmba-5)

Structure III: MeSn(OPr<sup>i</sup>)(Hhmba-3), MeSn(OPr<sup>i</sup>)(Hhmba-6) and MeSn(OPr<sup>i</sup>)(Hhmba-5)



Structure IV: Me<sub>2</sub>Sn(OPr<sup>i</sup>)(Hhmba-3), Me<sub>2</sub>Sn(OPr<sup>i</sup>)(Hhmba-6) and Me<sub>2</sub>Sn(OPr<sup>i</sup>)(Hhmba-5)

Structure V: Me<sub>2</sub>Sn(Hhmba-3)<sub>2</sub>, Me<sub>2</sub>Sn(Hhmba-6)<sub>2</sub> and Me<sub>2</sub>Sn(Hhmba-5)<sub>2</sub>



Structure VI: Me<sub>3</sub>Sn(Hhmba-3), Me<sub>3</sub>Sn(Hhmba-6) and Me<sub>3</sub>Sn(Hhmba-5)

Structure VII: Me<sub>3</sub>Sn(hmba-3), Me<sub>3</sub>Sn(Hhmba-6) and (Me<sub>3</sub>Sn)<sub>2</sub>(hmba-5)

TABLE-1  
ANALYTICAL DETAILS OF THE VARIOUS METHYL SUBSTITUTED TIN (IV)  
DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES

Compound (molar ratio) (colour)	m.p. (°C)	Analysis % found (calcd.)			
		C	H	N	Sn
MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-3)(1 : 1) (brown)	215	46.94 (46.99)	6.76 (6.79)	3.00 (3.04)	25.76 (25.79)
MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-3) <sub>2</sub> (1 : 2) (brown)	245	51.20 (51.25)	6.25 (6.29)	4.54 (4.59)	19.44 (19.48)
MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-6)(1 : 1) (brown)	220	46.96 (46.99)	6.76 (6.79)	3.00 (3.04)	25.75 (25.79)
MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-6) <sub>2</sub> (1 : 2) (light brown)	230	51.20 (51.25)	6.25 (6.29)	4.54 (4.59)	19.43 (19.48)
MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-5)(1 : 1) (light brown)	245	46.95 (46.99)	6.76 (6.79)	3.02 (3.04)	25.72 (25.79)
MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-5) <sub>2</sub> (1 : 2) (brown)	215	51.20 (51.25)	6.22 (6.29)	4.55 (4.59)	19.42 (19.48)
Me <sub>2</sub> Sn(OPr <sup>i</sup> )(Hhmba-3)(1 : 1) (brown)	225	46.16 (46.19)	6.50 (6.54)	3.24 (3.37)	28.50 (28.53)
Me <sub>2</sub> Sn(Hhmba-3) <sub>2</sub> (1 : 2) (light brown)	245	50.95 (50.99)	6.20 (6.06)	4.92 (4.96)	20.95 (20.99)
Me <sub>2</sub> Sn(OPr <sup>i</sup> )(Hhmba-6)(1 : 1) (light brown)	260	46.13 (46.19)	6.51 (6.54)	3.32 (3.37)	28.50 (28.53)
Me <sub>2</sub> Sn(Hhmba-6) <sub>2</sub> (1 : 2) (light brown)	270	50.96 (50.99)	6.00 (6.06)	4.91 (4.96)	20.92 (20.99)
Me <sub>2</sub> Sn(OPr <sup>i</sup> )(Hhmba-5)(1 : 1) (brown)	215	46.12 (46.19)	6.50 (6.54)	3.33 (3.37)	28.49 (28.53)
Me <sub>2</sub> Sn(Hhmba-5) <sub>2</sub> (1 : 2) (brown)	210	50.97 (50.99)	6.01 (6.06)	4.91 (4.96)	20.95 (20.99)
Me <sub>3</sub> Sn(Hhmba-3)(1 : 1) (brown)	280	45.14 (45.19)	6.20 (6.23)	3.73 (3.77)	31.85 (31.90)
(Me <sub>3</sub> Sn) <sub>2</sub> (Hhmba-3)(2 : 1) (brown)	280	38.16 (38.18)	5.80 (5.84)	2.60 (2.62)	44.37 (44.39)
Me <sub>3</sub> Sn(Hhmba-6)(1 : 1) (light brown)	>300	45.15 (45.19)	6.19 (6.23)	3.74 (3.77)	31.88 (31.90)
(Me <sub>3</sub> Sn) <sub>2</sub> (hmba-6)(2 : 1) (light brown)	280	38.16 (38.18)	5.80 (5.84)	2.58 (2.62)	44.34 (44.39)
Me <sub>3</sub> Sn(Hhmba-5)(1 : 1) (light yellowish brown)	260	45.13 (45.19)	6.20 (6.23)	3.74 (3.77)	31.86 (31.90)
(Me <sub>3</sub> Sn) <sub>2</sub> (hmba-5)(2 : 1) (light yellowish brown)	280	38.13 (38.18)	5.82 (5.84)	2.59 (2.62)	44.34 (44.39)

Me = —CH<sub>3</sub>, OPr<sup>i</sup> = OC<sub>3</sub>H<sub>7</sub>, H<sub>2</sub>hmba-3 (or -6 or 5) = CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>(OH)CH<sub>2</sub><sup>+</sup>NH<sub>2</sub>CH(CH<sub>3</sub>)COO<sup>-</sup>

TABLE-2  
 CHARACTERISTIC INFRARED FREQUENCIES ( $\text{cm}^{-1}$ ) OF THE VARIOUS METHYL SUBSTITUTED TIN(IV) DERIVATIVES  
 OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES

Compound	$\nu(\text{OH})$	$\nu(\text{N-H})$ and aromatic $\nu(\text{C-H})$	$\nu(\text{C-H})$ of $-\text{CH}_2-$ and $-\text{CH}_3$ groups	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\Delta\nu(\text{COO})$	$\nu(\text{C-N})$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-O})$	$\nu(\text{Sn-N})$
$\text{MeSn}(\text{OPr}^i)_2(\text{Hhmba-3})$	3400-3300 (b)	3160-3000 (mb)	2940 (m), 2900 (w)	1635 (s)	1385 (w)	250	1250 (s)	610 (m), 560 (w)	525 (w)	450 (m)
$\text{MeSn}(\text{OPr}^i)(\text{Hhmba-3})_2$	3500-3300 (vb)	3195-3010 (mb)	2945 (w), 2900 (w), 2885 (w)	1630 (vs)	1385 (w)	245	1260 (s)	600 (mb)	535 (m)	460 (m)
$\text{MeSn}(\text{OPr}^i)_2(\text{Hhmba-6})$	3500-3300 (b)	3200-3000 (mb)	2940 (m), 2900 (w)	1610 (vsb)	1380 (w)	230	1255 (s)	600 (m), 565 (m)	530 (w)	445 (m)
$\text{MeSn}(\text{OPr}^i)(\text{Hhmba-6})_2$	3400-3300 (vb)	3150-3000 (mb)	2960 (m), 2820 (m)	1625 (s)	1380 (w)	245	1260 (s)	600 (m), 570 (m)	460 (w)	435 (m)
$\text{MeSn}(\text{OPr}^i)(\text{Hhmba-5})$	3400-3300 (b)	3200-3040 (mb)	2945 (m), 2850 (m)	1630 (sb)	1370 (m)	260	1255 (s)	600 (mb)	540 (w)	450 (m)
$\text{MeSn}(\text{OPr}^i)(\text{Hhmba-5})_2$	3500-3300 (vb)	3200-3000 (mb)	2980 (w), 2900 (w)	1620 (s)	1380 (w)	240	1250 (s)	600 (mb)	530 (m)	440 (m)
$\text{Me}_2\text{Sn}(\text{OPr}^i)(\text{Hhmba-3})$	3400-3300 (b)	3200-3000 (mb)	2950 (m), 2900 (m), 2870 (w)	1610 (sb)	1380 (w)	230	1260 (s)	610 (m), 530 (w)	480 (w)	430 (m)
$\text{Me}_2\text{Sn}(\text{Hhmba-3})_2$	3500-3300 (vb)	3240-3000 (m)	2940 (w), 2900 (m), 2850 (m)	1630 (sb)	1390 (w)	240	1265 (s)	600 (w), 530 (m)	490 (w)	445 (m)
$\text{Me}_2\text{Sn}(\text{OPr}^i)(\text{Hhmba-6})$	3400-3300 (b)	3200-3000 (mb)	2965 (w), 2900 (w)	1610 (s)	1385 (w)	225	1265 (s)	600 (mb)	560 (w)	440 (m)

$\text{Me}_2\text{Sn}(\text{Hhmba-6})_2$	3500–3300 (vb)	3160–3000 (mb)	2950 (m), 2915 (w), 2850 (w)	1615 (vsb)	1385 (m)	230	1260 (s)	600 (m), 550 (w)	530 (m)	445 (m)
$\text{Me}_2\text{Sn}(\text{OPt}^1)(\text{Hhmba-5})$	3500–3300 (vb)	3200–3000 (mb)	2945 (m), 2870 (w)	1620 (vs)	1365 (m)	255	1245 (s)	610 (m), 565 (m)	475 (m)	435 (m)
$\text{Me}_2\text{Sn}(\text{Hhmba-5})_2$	3400–3300 (b)	3210–3000 (mb)	2980 (m), 2900 (w), 2860 (m)	1625 (s)	1375 (w)	250	1250 (s)	600 (m), 560 (m)	460 (w)	440 (m)
$\text{Me}_3\text{Sn}(\text{Hhmba-3})$	3500–3300 (vb)	3200–3000 (mb)	2940 (m), 2900 (w)	1610 (s)	1380 (w)	230	1250 (s)	600 (m), 520 (w)	450 (w)	425 (m)
$(\text{Me}_3\text{Sn})_2(\text{hmba-3})$	—	3100–3000 (m)	2960 (m), 2900 (w), 2860 (m)	1620 (s)	1385 (m)	235	1260 (s)	610 (mb)	520 (m)	440 (m)
$\text{Me}_3\text{Sn}(\text{Hhmba-6})$	3500–3300 (vb)	3200–3000 (m)	2960 (m), 2900 (w)	1625 (vs)	1375 (m)	250	1265 (s)	610 (m), 540 (m)	465 (m)	440 (m)
$(\text{Me}_3\text{Sn})_2(\text{hmba-6})$	—	3200–3000 (mb)	2960 (m), 2900 (w), 2850 (w)	1630 (sb)	1370 (w)	260	1260 (s)	600 (mb)	530 (m)	435 (m)
$\text{Me}_3\text{Sn}(\text{Hhmba-5})$	3400–3300 (b)	3165–3000 (mb)	2950 (w), 2910 (w), 2860 (w)	1625 (w)	1380 (w)	245	1250 (s)	600 (m), 525 (m)	450 (m)	430 (m)
$(\text{Me}_3\text{Sn})_2(\text{hmba-5})$	—	3120–3000 (b)	2975 (m), 2950 (m), 2850 (w)	1615 (s)	1370 (w)	245	1255 (s)	600 (m), 545 (m)	460 (m)	430 (w)

s = strong, vs = very strong, sb = strong broad, vsb = very strong broad, m = medium, mb = medium broad, vb = very broad, b = broad and w = weak.

TABLE-3  
 PROTON MAGNETIC RESONANCE SPECTRAL DATA ( $\delta$  VALUE) OF THE VARIOUS METHYL SUBSTITUTED TIN(IV) DERIVATIVES OF  
 N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

S. No.	Compound	Aromatic ring	Phenolic (OH)	>CH—	>NH	—CH <sub>3</sub> (attached with benzene ring)	—CH <sub>2</sub> — (attached with benzene ring)	—CH <sub>3</sub> (of the methyl part)	<i>gem</i> dimethyl
1.	MeSn(OPr <sup>i</sup> ) <sub>2</sub> (Hmba-6)	6.65-7.20 (t)	6.55 (s)	3.50-4.00 (m)	3.10 (h)	2.20 (s)	2.10 (d)	0.90 (d)	1.30-1.90 (m)
2.	MeSn(OPr <sup>i</sup> )(Hmba-3) <sub>2</sub>	6.45-7.25 (m)	6.50 (s)	3.55-4.00 (bm)	3.05 (h)	2.20 (s)	2.10 (d)	0.80 (d)	1.00 (d)
3.	Me <sub>2</sub> Sn(OPr <sup>i</sup> )(Hmba-5)	6.40-7.15 (m)	6.65 (s)	3.40-4.00 (bm)	3.15 (h)	2.20 (s)	2.05 (bs)	0.80 (d)	1.15-1.80 (m)
4.	Me <sub>2</sub> Sn(Hmba-6) <sub>2</sub>	6.30-6.80 (t)	6.50 (s)	3.50-4.00 (m)	3.10 (h)	2.15 (s)	2.00 (d)	0.70 (d)	—
5.	Me <sub>3</sub> Sn(Hmba-6)	6.65-7.10 (t)	6.60 (s)	3.80-4.00 (m)	3.05 (h)	2.10 (s)	2.00 (d)	0.85 (d)	—
6.	(Me <sub>3</sub> Sn) <sub>2</sub> (hmba-5)	6.55-7.00 (m)	—	3.30-4.00 (m)	3.15 (h)	2.20 (s)	2.00 (d)	0.75 (d)	—

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

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