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

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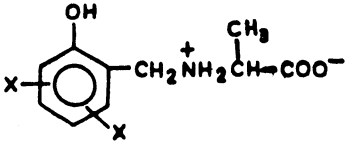
Several tin(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by alcoholysis reactions involving the interaction of tin tetraisopropoxide and the latter in 1:1, 1:2 and 1:3 molar ratios in benzene medium. The compounds thus prepared were generally obtained as coloured solids out of which those containing isopropoxy group(s) were found to be hygroscopic. All these compounds were characterized by elemental and azeotrope analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

Preparation of several organometallic/metallo-organic derivatives of N-(*o*-hydroxy substituted benzyl) alanines (I) *via* the reactivity of the corresponding metal isopropoxide and I, and their charaterization by appropriate physicochemical methods have been reported earlier[1–6]. The work described here relates to the preparation and characterization of some tin(IV) derivatives of 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) on similar lines.



Where X = -H or - CH_3
(I)

EXPERIMENTAL

Owing to highly hygroscopic nature of tin tetraisopropoxide, stringent precautions were taken to exclude moisture throughout the experiments, using identical assemblies, as earlier[7]. Benzene (BDH, AR), isopropanol (BDH Glaxo, AnalaR), solvent ether (E. Merck) and ethanol were dried by already reported procedures[8]. Tin was estimated as tin dioxide, as before[7]. Tin tetraisopropoxide was prepared by sodium method[9], using tin tetrachloride which in turn was prepared by a known method[10]. Method of preparation of N-(*o*-hydroxy substituted benzyl) alanines has been described earlier[1]. The details of the various instruments used have been identical to those reported before[7].

Preparation of tin(IV) derivatives of N-(2-hydroxy substituted benzyl) alanines

General procedure: A mixture of $Sn(OPr^i)_4$ and I taken in appropriate stoichiometry in dry benzene was refluxed on a wax bath (95–100°C). After several hours of reflux, the isopropanol-benzene azeotrope was fractionated out and the amount of isopropanol liberated was estimated oxidimetrically to monitor the completion of reaction, as before[7]. The excess of solvent from the reaction mixture was removed *in vacuo* and the product was washed with dry benzene (2–3 times) followed by dry ether (2–3 times). The product was finally dried under vacuum which was found to be soluble in ethanol, dimethyl formamide and dimethyl sulphoxide but insoluble in other common organic solvents like benzene, toluene and carbon tetrachloride etc. These derivatives were, therefore, further purified by recrystallization from ethanol.

It may be mentioned here that since $Sn(OPr^i)_4$ is soluble in benzene, while I 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 unreacted I. The amount of isopropanol liberated was, therefore, calculated according to the amount of I taken.

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

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

Compound (molar ratio) (Colour)	m.p. (°C)	Azeotrope analysis Pr^iOH (g) Found (Calcd.)	Analysis % Found (Calcd.)			
			C	H	N	Sn
$Sn(OPr^i)_2$(hmba-3) (1:1) (light brown)	210	0.37 (0.38)	45.73 (45.98)	6.12 (6.13)	3.14 (3.15)	26.59 (26.73)
Sn(hmba-3)$_2$ (1:2) (light brown)	200	0.40 (0.41)	49.31 (49.56)	4.90 (4.92)	5.23 (5.25)	22.15 (22.26)
$Sn(OPr^i)_2$(Hhmba-3)$_3$ (1:3) (brown)	220	0.49 (0.49)	53.61 (53.88)	6.14 (6.16)	5.22 (5.24)	14.71 (14.79)
$Sn(OPr^i)_2$(hmba-6) (1:1) (light brown)	240	0.53 (0.54)	45.72 (45.98)	6.11 (6.13)	3.14 (3.15)	26.58 (26.73)
Sn(hmba-6)$_2$ (1:2) (brown)	230	0.68 (0.68)	49.30 (49.56)	4.90 (4.92)	5.24 (5.25)	22.19 (22.26)
$Sn(OPr^i)$(Hhmba-6)$_3$ (1:3) (brown)	200	0.44 (0.45)	53.65 (53.88)	6.13 (6.16)	5.22 (5.24)	14.76 (14.79)
$Sn(OPr^i)_2$(hmba-5) (1:1) (brown)	195	0.40 (0.42)	45.76 (45.98)	6.12 (6.13)	3.13 (3.15)	26.60 (26.73)
Sn(hmba-5)$_2$ (1:2) (brown)	185	0.64 (0.65)	49.31 (49.56)	4.90 (4.92)	5.24 (5.25)	22.17 (22.26)
$Sn(OPr^i)$(Hhmba-5)$_3$ (1:3) (brown)	190	0.40 (0.40)	53.62 (53.88)	6.12 (6.16)	5.21 (5.24)	14.72 (14.79)

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

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

Compound	ν(OH)	ν(N—H) and aromatic ν(C—H)	ν(C—H) —CH_2— and —CH_3— groups		ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Sn—O)	ν(Sn—N)
$Sn(OPr^i)_2$(hmba-3)	—	3200–3000 (m)	2950 (s)	2870 (m)	1635 (sb)	1380 (w)	255	1255 (s)	460 (m)	435 (w)
$Sn(hmba\text{-}3)_2$	—	3160–3040 (mb)	2945 (s)	2850 (m)	1625 (vsb)	1390 (w)	235	1260 (s)	565 (m)	455 (m)
$Sn(OPr^i)(Hhmba\text{-}3)_3$	3500–3300 (sb)	3195–3000 (b)	2960 (s)	2870 (w)	1615 (vsb)	1380 (m)	235	1260 (s)	550 (m) 530 (m)	440 (m)
$Sn(OPr^i)_2$(hmba-6)	—	3200–3000 (b)	2960 (m)	2910 (w)	1620 (vsb)	1385 (w)	235	1260 (s)	565 (m) 535 (m)	440 (m)
$Sn(hmba\text{-}6)_2$	—	3190–3000 (mb)	2980 (m)	2850 (w)	1630 (sb)	1380 (w)	250	1255 (s)	565 (m) 540 (w)	435 (m)
$Sn(OPr^i)(Hhmba\text{-}6)_3$	3460–3300 (sb)	3200–3010 (m)	2950 (m)	2900 (w)	1615 (sb)	1385 (w)	230	1250 (s)	560 (m) 530 (w)	445 (m)
$Sn(OPr^i)$(hmba-5)	—	3160–3000 (mb)	2965 (m)	2900 (w)	1625 (sb)	1360 (w)	265	1260 (s)	535 (mb)	440 (m)
$Sn(hmba\text{-}5)_2$	—	3200–3000 (b)	2935 (w)	2860 (w)	1610 (vs)	1380 (w)	230	1255 (s)	540 (w)	435 (m)
$Sn(OPr^i)(Hhmba\text{-}5)_3$	3500–3300 (sb)	3160–3020 (mb)	2980 (m)	2900 (w)	1620 (mb)	1370 (w)	250	1250 (s)	550 (w)	430 (m)

TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUE) OF THE VARIOUS TIN (IV) DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES (DMSO–d_6)

Compound	Aromatic ring	Phenolic (OH) group	>CH—	>NH	—CH_3 (attached with the benzene ring)	—CH_2 (attached with the benzene ring)	*gem* dimethyl (isopropoxy group)
$Sn(OPr^i)_2$(hmba-6)	6.50–7.25 (t)	—	3.50–4.00 (m)	3.10 (h)	2.20 (s)	2.00 (d)	1.00 (d)
Sn(hmba-5)$_2$	6.65–6.85 (m)	—	3.50–4.00 (bm)	3.15 (h)	2.15 (s)	2.05 (bs)	—
$Sn(OPr^i)$(Hhmba-3)$_3$	6.65–7.10 (m)	6.69 (s)	3.60–4.00 (m)	3.15 (h)	2.10 (s)	2.00 (d)	1.10 (d)

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

RESULTS AND DISCUSSION

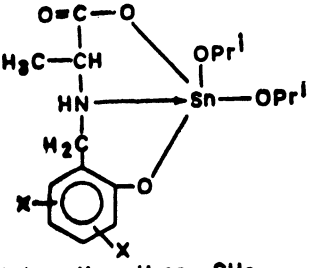
It may be recalled here that N-(*o*-hydroxy substituted benzyl) alanines exist in zwitter ionic form[1] (I). The various reactions between $Sn(OPr^i)_4$ and H_2hmba-3 may be illustrated as

$$Sn(OPr^i)_4 + H_2hmba\text{-}3 \rightarrow Sn(OPr^i)_2(hmba\text{-}3) + 2Pr^iOH$$

$$Sn(OPr^i)_4 + 2H_2hmba\text{-}3 \rightarrow Sn(hmba\text{-}3)_2 + 4Pr^iOH$$

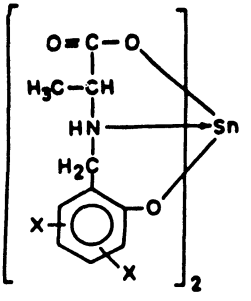
$$Sn(OPr^i)_4 + 3H_2hmba\text{-}3 \rightarrow Sn(OPr^i)(Hhmba\text{-}3)_3 + 3Pr^iOH$$

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



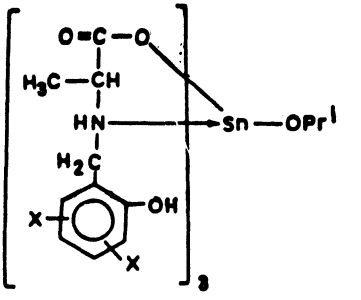
Where X = - H or - CH_3

(II)



Where X = - H or - CH_3

(III)



Where X = - H or - CH_3

(IV)

Based on azeotrope and elemental analysis, as well as the spectral data[1, 11–14] in respect of the various derivatives prepared, the main findings relating to their structure are as under.

The tin atom in $Sn(OPr^i)_2$(hmba-3), $Sn(OPr^i)_2$(hmba-6) and $Sn(OPr^i)_2$(hmba-5) [Structure(II)] displays 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 two isopropoxy groups. The derivatives, $Sn(hmba\text{-}3)_2$, $Sn(hmba\text{-}6)_2$ and $Sn(hmba\text{-}5)_2$ [Structure(III)] 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 and the oxygen from each of the two phenolate groups available from two moles of I. The tin atom in $Sn(OPr^i)(Hhmba\text{-}3)_3$, $Sn(OPr^i)(Hhmba\text{-}6)_3$ and $Sn(OPr^i)(Hhmba\text{-}5)_3$ [Structure (IV)] exhibits hepta-coordination in each case as a consequence 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 an isopropoxy group.

REFERENCES

1. T. Gangwar and M. Chandra, *Asian J. Chem.*, **6**, 932 (1994).
2. T. Gangwar, D. Manral (née Bora) and M. Chandra, *Asian J. Chem.*, **6**, 968 (1994).
3. R. Shah and M. Chandra, *Asian J. Chem.*, **7**, 33 (1995).
4. T. Gangwar, R. Shah and M. Chandra, *Asian J. Chem.*, **7**, 41 (1995).
5. R. Shah, R. Aman and M. Chandra, *Asian J. Chem.*, **7**, 76 (1995).
6. R. Shah, T. Gangwar and M. Chandra, *Asian J. Chem.*, **7**, 109 (1995).
7. D. Manral (née Bora), R. Shah and M. Chandra, *Chim. Acta Turcica*, **21**, 229 (1993).
8. A.I. Vogel, A Text Book of Practical Organic Chemistry, 4th Edn., Longmans , London (1978).
9. D.C. Bradley, D.P. Gaur and R.C. Mehrotra, Metal Alkoxides, Academic Press, London (1978).
10. R.C. Poller, The Chemistry of Organotin Compounds, Logos Press, London (1970).
11. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London (1962).
12. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley, New York (1981).
14. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1978).
15. Asahi Research Centre Co. Ltd., Tokyo (Ed.), Hand Book of Proton NMR Spectra and Data, Vols.1–4, Academic Press, Japan (1985).

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