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

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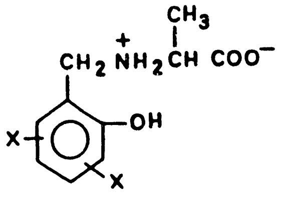
Several silicon (IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by the interaction of silicon tetraisopropoxide with the latter in appropriate stoichiometric ratios *viz.* 1:1, 1:2, 1:3, 1:4 and 2:3 in benzene medium. The compounds thus prepared were generally obtained as coloured solids out of which some were hygroscopic. All these compounds were characterized by elemental and azeotrope analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

A systematic programme of work on preparation of organometallic/metallo-organic derivatives of N-(*o*-hydroxy substituted benzyl)alanines (I) *via* the reactivity of the corresponding metal alkoxide has recently been undertaken in these laboratories. As a consequence, preparation and characterization of several monobutyl-and monophenyltin derivatives of I have recently been reported[1]. The work described here relates to the preparation of silicon (IV) derivatives of (I) *viz.* (*i*) N-(2-hydroxy-3-methyl benzyl) alanine (H_3hmba-3) (*ii*) -N-(2-hydroxy-6-methyl benzyl) alanine (H_3hmba-6) and (*iii*) N-(2-hydroxy-5-methyl benzyl) alanine (H_3hmba-5).



Where X = −H or $-CH_3$

(I)

EXPERIMENTAL

Stringent precautions, were taken to exclude moisture throughout the experiments as earlier[1]. Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures[2]. Silicon tetraisopropoxide was prepared by sodium method[3], using silicon tetrachloride (Fluka), while N-(*o*-hydroxy substituted benzyl)alanines were prepared employing already reported method.[1] Silicon was estimated by digesting the analytical sample with conc. sulphuric acid followed by conc. nitric acid and then ignited and weighed as silicon dioxide[4]. The details of instruments used are as reported earlier.[1]

Reaction between $Si(OPr^i)_4$ and H_3hmba-3, 1:1 Molar Ratio

A mixture of $Si(OPr^i)_4$ (0.7578g; 2.8669 mmol) and H_3hmba-3 (0.60 g; 2.8602 mmol) suspended in dry benzene (60 mL) taken in a R.B. flask was refluxed on a wax bath (90–95°C), using a fractionating column (30 cm long). After *ca.* 14 h of reflux, isopropanol benzene azeotrope liberated during the course of reaction was fractionated out and estimated by an oxidimetric method.[5–7] On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, $Si(OPr^i)_3$ (H_3hmba-3) isolated as a lemon yellow solid. The compound was purified by washing with benzene (3–4 times) followed by dry ether (2–3 times). The compound was found to be soluble in ethanol, dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like benzene, toluene, ether, chloroform and carbon tetrachloride. The compound was further purified by recrystallization from dry ethanol.

It may be mentioned here that since $Si(OPr^i)_4$ is soluble in benzene, while H_3hmba-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 unreacted H_3hmba-3. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_3hmba-3 taken.

Similar procedure of preparation and purification was adopted in case of other derivatives, which were further purified by recrystallization from dry ethanol, wherever possible. The relevant analytical details, characteristic IR frequencies and PMR data (in several representative cases) are summarized in Tables 1–3, respectively.

RESULTS AND DISCUSSION

It may be recalled here that N-(*o*-hydroxy substituted benzyl)alanines exist[1] in zwitter ionic from (I). The various reactions between silicon tetraisopropoxide and H_3hmba-3 may be illustrated as:

$$Si(OPr^i)_4 + H_3\text{hmba-3} \longrightarrow Si(OPr^i)_3(H_2\text{hmba-3}) + Pr^iOH \qquad (1)$$

$$Si(OPr^i)_4 + 2H_3\text{hmba-3} \longrightarrow Si(OPr^i)_2(H_2\text{hmba-3})_2 + 2Pr^iOH \qquad (2)$$

$$Si(OPr^i)_4 + 3H_3\text{hmba-3} \longrightarrow Si(OPr^i)(H_2\text{hmba-3})_3 + 3Pr^iOH \qquad (3)$$

$$Si(OPr^i)_4 + 4H_3\text{hmba-3} \longrightarrow Si(H_2\text{hmba-3})_4 + 4Pr^iOH \qquad (4)$$

$$2Si(OPr^i)_4 + 3H_3\text{hmba-3} \longrightarrow [Si(OPr^i)]_2(H\text{hmba-3})_3 + 6Pr^iOH \qquad (5)$$

Identical reactions occurred in case of H_3hmba-6 and H_3hmba-5. (yield % 93–97)

The derivative, $Si(OPr^i)_3$ (H_2hmba-3) displays a medium broad band in the region 3500–3300 cm^{-1} due to νOH of the unbonded phenolic group[8], while a

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

S. No.	Compound (molar ratio)/(colour)	m.p. (°C)	Elemental analysis % Found (calcd.)			
			C	H	N	Si
1.	$Si(OPr^i)_3$ (H_2hmba-3)	165	55.09	8.52	3.38	6.78
	(1 : 1) (lemon yellow)		(58.19)	(8.54)	(3.39)	(6.80)
2.	$Si(OPr^i)_2$ (H_2hmba-3)$_2$	170	59.75	7.51	4.96	5.49
	(1 : 2) (light brown)		(59.88)	(7.53)	(4.98)	(5.50)
3.	$Si(OPr^i)$ (H_2hmba-3)$_3$	175	60.78	6.92	5.89	3.94
	(1 : 3) (brown)		(60.87)	(6.91)	(5.91)	(3.95)
4.	Si(H_2hmba-3)$_4$	160	61.20	6.53	6.47	3.24
	(1 : 4) (brown)		(61.24)	(6.54)	(6.49)	(3.25)
5.	$[Si(OPr^i)]_2$ (Hhmba-3)$_3$	190	58.90	6.71	5.28	3.52
	(2 : 3) (brown)		(58.98)	(6.72)	(5.29)	(3.53)
6.	$Si(OPr^i)_3$ (H_2hmba-6)	185	57.98	8.51	3.38	6.78
	(1 : 1) (cream)		(57.19)	(8.54)	(3.39)	(6.80)
7.	$Si(OPr^i)_2$ (H_2hmba-6)$_2$	180	59.80	7.52	4.96	4.98
	(1 : 2) (light brown)		(59.88)	(7.53)	(4.98)	(5.50)
8.	$Si(OPr^i)$ (H_2hmba-6)$_3$	178	60.72	6.93	5.89	3.94
	(1 : 3) (cream)		(60.87)	(6.95)	(5.91)	(3.95)
9.	Si(H_2hmba-6)$_4$	175	61.17	6.52	6.45	3.24
	(1 : 4) (light brown)		(61.24)	(6.54)	(6.49)	(3.25)
10.	$[Si(OPr^i)]_2$ (H_2hmba-6)$_3$	170	58.85	6.70	5.27	3.52
	(2 : 3) (cream)		(58.98)	(6.72)	(5.29)	(3.53)
11.	$Si(OPr^i)_3$ (H_2hmba-5)	155	58.10	8.52	3.38	6.78
	(1 : 1) (brown)		(58.19)	(8.54)	(3.39)	(6.80)
12.	$Si(OPr^i)_2$ (H_2hmba-5)$_2$	150	59.80	7.51	4.97	4.49
	(1 : 2)		(59.88)	(7.53)	(4.98)	(5.00)
13.	$Si(OPr^i)$ (H_2hmba-5)$_3$	160	60.81	6.92	5.90	3.24
	(1 : 3) (cream)		(60.87)	(6.95)	(5.91)	(3.95)
14.	Si(H_2hmba-5)$_4$	165	61.15	6.52	6.47	3.24
	(1 : 4) (cream)		(61.24)	(6.54)	(6.49)	(2.25)
15.	$[Si(OPr^i)]_2$ (H_2hmba-5)$_3$	145	58.90	6.70	5.27	3.52
	(2 : 3) (brownish pink)		(58.98)	(6.72)	(5.29)	(3.53)

Abbreviations: $OPr^i = OC_3H_7$, H_3hmba-3 (or -6 or -5)= $CH_3C_6H_3(OH)CH_2\overset{+}{N}H_2CHCH_3COO^-$

broad band between 3250–3000 cm^{-1} shows the overlapping of νN—H and aromatic ν(C—H)[8, 9]. The appearance of ν(N—H) in the lower region suggests possible coordination of nitrogen to silicon[10, 11]. The weak absorptions at 2960 cm^{-1} and 2920 cm^{-1} correspond to ν(C—H) of the —CH$_2$— and —CH$_3$ groups, respectively.[8] The absence of any characteristic band corresponding to ν(C═O) group in the region 1750–1650 cm^{-1} rules out the possibility of a normal ester type of linkage between the carboxylate oxygen and silicon[9]. A strong broad band at 1600 cm^{-1} may be assigned to the overlapping of ν_{assym}COO, aromatic ν(C═C) and N—H deformation[12, 13], while the medium and weak bands at

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

Compound	νOH	νN—H and aromatic νC—H	νC—H of —CH_3 and —CH_2— groups	$\nu_{asym}COO$	$\nu_{sym}COO$	ΔνCOO	ν(C—N)	ν(Si—O)	ν(Si—N)
$Si(OPr^i)_3(H_2hmba\text{-}3)$	3500–3000 (mb)	3250–3000 (b)	2960 (w) 2920 (w)	1600 (sb)	1390 (sh)	210	1260 (vs)	800 (m) 770 (m) 740 (s)	680 (m)
$Si(OPr^i)_2(H_2hmba\text{-}3)_2$	3500–3300 (vsb)	3150–3000 (b)	2930 (w)	1600 (sb)	1390 (m)	220	1260 (s)	820 (s) 800 (s) 770 (m)	675 (m)
$Si(OPr^i)(H_2hmba\text{-}3)_3$	3500–3300 (vb)	3250–3000 (b)	2945 (m)	1600 (sb)	1390 (sh)	210	1255 (vs)	800 (m) 780 (m) 765 (vw)	680 (m)
$Si(H_2hmba\text{-}3)_4$	3600–3000 (vsb)	3200–3000 (mb)	2960 (w) 2840 (m)	1610 (sb)	1395 (mb)	215	1260 (b)	770 (s) 740 (m)	685 (m)
$[Si(OPr^i)]_2(Hhmba\text{-}3)_3$	—	3250–3000 (vsb)	2940 (m) 2910 (w)	1600 (sb)	1375 (m)	225	1260 (m)	770 (m) 740 (m)	680 (w)
$Si(OPr^i)_3(H_2hmba\text{-}6)$	3450–3000 (vb)	3200–3000 (b)	2900 (w)	1630 (m)	1360 (sh)	250	1265 (s)	800 (s) 770 (m) 740 (m)	690 (m)
$Si(OPr^i)_2(H_2hmba\text{-}6)_2$	3450–3300 (b)	3200–3000 (mb)	2940 (m)	1620 (vs)	1395 (sh)	225	1260 (s)	795 (m) 720 (vs)	670 (m)
$Si(OPr^i)(H_2hmba\text{-}6)_3$	3400–3250 (vb)	3150–3000 (mb)	2940 (w) 2860 (m)	1630 (sh)	1400 (sh)	230	1265 (m)	800 (mb) 770 (m) 745 (w)	670 (m)
$Si(H_2hmba\text{-}6)_4$	3500–3300 (vb)	3200–3000 (b)	2960 (m) 2910 (w)	1630 (sb)	1395 (m)	235	1270 (sh)	800 (m) 730 (w)	680 (s)

TABLE 2 (Contd.)

$[Si(OPr^i)]_2(Hhmba\text{-}3)_3$	—	3200–3000 (mb)	2960 (w) 2940 (m)	1630 (sb)	1390 (m)	240	1270 (m)	805 (sb) 730 (w)	680 (m)
$Si(OPr^i)_3(H_2hmba\text{-}5)$	3400–3200 (vb)	3200–3000 (mb)	2940 (w) 2850 (m)	1600 (sb)	1380 (m)	220	1270 (w)	800 (sb) 770 (vw)	680 (s)
$Si(OPr^i)_2(H_2hmba\text{-}5)_2$	3500–3300 (vsb)	3200–3000 (mb)	2900 (w) 2840 (m)	1600 (sb)	1370 (m)	230	1250 (s)	805 (s) 770 (m)	685 (m)
$Si(OPr^i)(H_2hmba\text{-}5)_3$	3500–3250 (vb)	3200–3000 (mb)	2940 (m) 2900 (m)	1600 (sb)	1380 (sh)	220	1250 (s)	790 (vs) 750 (m)	670 (s)
$Si(H_2hmba\text{-}5)_4$	3450–3300 (mb)	3200–3000 (mb)	2960 (m) 2900 (m)	1610 (sh)	1385 (m)	215	1270 (s)	810 (s) 760 (vw)	665 (vs)
$[Si(OPr^i)]_2(Hhmba\text{-}5)_3$	—	3200–3000 (sb)	2960 (m) 2900 (vw)	1600 (sb)	1380 (sb)	220	1260 (b)	800 (s) 770 (w)	685 (vw)

w = weak, m = medium, sb = strong broad, mb = medium broad, vb = very broad, vsb = very strong broad, vs = very strong, s = strong, sh = shoulder

TABLE-3. PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ value) OF SEVERAL SILICON (IV) DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES

S. No.	Compound	Aromatic ring	Phenolic (—OH)	>CH—	>NH—	CH_3 attached with the benzene ring	$—CH_2—$	$—CH_3$ of the alanine part	Iso propoxy (*gem* dimethyl)
1.	$Si(OPr^i)_3(H_2hmba\text{-}3)$	6.30–7.00 (m)	5.70 (s)	3.40–3.65 (bm)	3.10 (s)	2.25 (s)	2.05 (d)	1.30 (d)	1.10 (d)
2.	$Si(OPr^i)_2(H_2hmba\text{-}6)_2$	6.40–7.25 (m)	5.50 (s)	3.40–3.80 (m)	3.30 (s)	2.15 (s)	2.05 (d)	1.15 (d)	1.00 (d)
3.	$Si(OPr^i)(H_2hmba\text{-}3)_3$	6.50–7.00 (m)	5.75 (s)	3.40–3.60 (m)	3.05 (s)	2.25 (s)	2.05 (d)	1.20 (d)	1.10 (d)
4.	$Si(H_2hmba\text{-}5)_4$	6.50–7.10 (m)	5.55 (s)	3.40–3.70 (m)	3.10 (s)	2.20 (s)	2.05 (d)	1.15 (d)	—
5.	$[Si(OPr^i)]_2(Hhmba\text{-}5)_3$	6.40–7.20 (m)	—	3.30–3.90 (m)	3.10 (s)	2.25 (s)	2.10 (d)	1.15 (d)	1.00 (d)

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

1500 cm^{-1} and 1460 cm^{-1} occur because of the overlapping of C—H bending of the —CH_2— and —CH_3 groups and aromatic skeletal vibrations[9, 14]. Instead of a peak at 1405 cm^{-1}, as observed in H_3hmba-3, here the appearance of a medium broad band with a shoulder around 1390 cm^{-1} shows the overlapping of ν_{sym}COO and C—H bending of the gem dimethyl structure of the isopropoxy group[9, 12, 14]. A shift of 15 cm^{-1} in ν_{sym}COO, as compared to H_3hmba-3, suggests the bonding of the carboxylate oxygen with silicon. The separation value, $\Delta\nu$COO(ν_{asym}COO—ν_{sym}COO) of 210 cm^{-1} indicates the absence of a bridged or coordinated carboxylate group[15–17]. The weak absorption at 1290 cm^{-1} may be assigned to O—H bending of the phenolic group. A very strong band due to ν(C—N) at 1260 cm^{-1} instead of at 1265 cm^{-1}, as noted in case of H_3hmba-3, shows possible coordination of nitrogen to silicon, while a medium peak at 1220 cm^{-1} may be assigned to ν(C—O)[9]. The medium and weak peaks at 1160 cm^{-1}, 1110 cm^{-1}, 1080 cm^{-1} and 1020 cm^{-1} show the aromatic C—H in-plane bending modes[9, 18]. The weak absorptions at 950 cm^{-1}, 880 cm^{-1} and 820 cm^{-1} correspond to the characteristic C—H out-of-plane bending of a trisubstituted benzene ring. The medium and strong bands due to ν(Si–O) occur at 800 cm^{-1}, 770 cm^{-1} and 740 cm^{-1}[18–20], while the band at 680 cm^{-1} may be assigned to ν(Si—N)[21].

It is thus evident that the silicon atom in $Si(OPr^i)_3$ (H_2hmba-3) exihibits penta-coordination as a result of bonding with one of the oxygens from the carboxylate group and the nitrogen from the imino group, along with three isopropoxy groups (Structure II).

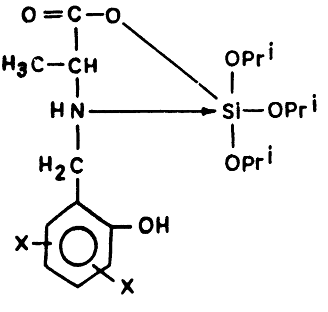
The PMR spectrum of $Si(OPr^i)_3$ (H_2hmba-3) displays a multiplet between δ 6.30–7.00 which may be attributed to the aromatic ring protons[12, 22], while a singlet at δ5.70 corresponds to the unbonded phenolic group proton[12, 14]. A hump in the region δ3.20–3.40 due to the protons of the $>\overset{+}{N}H_2$ group, as observed in H_3hmba-3, is found to disappear here together with the appearance of a new signal at δ3.10 suggesting possible coordination of nitrogen to silicon. 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 corresponding to >CH— group proton of the alanine part of H_3hmba-3 occurs between δ3.40–3.65, while the singnals due to the protons of the —CH_3 and —CH_2— groups attached with the benzene ring of H_3hmba-3 appear in form of a singlet at δ2.25 and a doublet at δ2.05, respectively. The doublets at δ1.30 and δ1.10 may be assigned respectively to the protons of the —CH_3 group associated with the alanine part of H_3hmba-3 and the *gem* dimethyl part of the isopropoxy group attached with the silicon atom[17, 22, 23]. Thus, the inferences drawn here are well in conformity to those derived from the IR measurements earlier. The IR and PMR (wherever available) spectral data were similarly interpreted for the other derivatives and the main findings in context of their structures are as under:

The derivatives $Si(OPr^i)_3$ (H_2hmba-6) and $Si(OPr^i)_3$ (H_2hmba-5) contain a penta-coordinated silicon atom in each case displaying similar modes of bonding as those observed in $Si(OPr^i)_3$ (H_2hmba-3) (Structure II).

The silicon atom in $Si(OPr^i)_2$ (H_2hmba-3)$_2$, $Si(OPr^i)_2$ (H_2hmba-6)$_2$ and $Si(OPr^i)_2$ (H_2hmba-5)$_2$ (Structure III) displays hexa-coordination in each case as a consequence of bonding with one of the oxygens from each of the two carboxylate groups and the nitrogen from each of the two imino groups available from two moles of compound I, along with two isopropoxy groups.

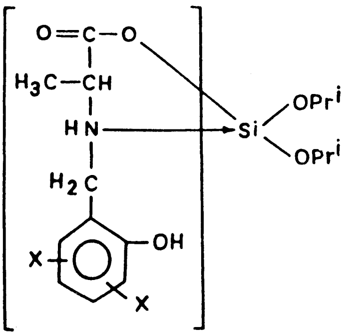
The derivatives, $Si(OPr^i)$ (H_2hmba-3)$_3$, $Si(OPr^i)$(H_2hmba-6)$_3$ and $Si(OPr^i)$ (H_2hmba-5)$_3$ (Structure IV) possess a hepta-coordinated silicon atom in each case by way of bonding with one of the oxygens from each of the three carboxylate groups and the nitrogen from each of the three imino groups available from three moles of compound I, along with one isopropoxy group.

The silicon atom in Si(H_2hmba-3)$_4$, Si(H_2hmba-6)$_4$ and Si(H_2hmba-5)$_4$ (Structure V) displays octa-coordination in each case as a result of bonding with one



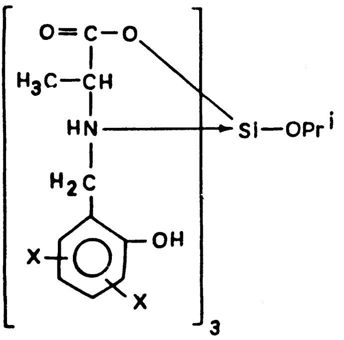
Where X=-H or -CH$_3$

(II)



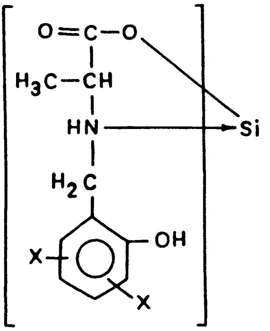
Where X=-H or -CH$_3$

(III)



Where X=-H or -CH$_3$

(IV)



Where X=-H or-CH$_3$

(V)

of the oxygens from each of the four carboxylate groups and the nitrogen from each of the four imino groups available from four moles of compound I.

It is rather difficult to assign any definite structure for $[Si(OPr^i)]_2$ $(Hhmba\text{-}3)_3$, $[Si(OPr^i)]_2$ $(Hhmba\text{-}6)_3$ and $[Si(OPr^i)]_2$ $(Hhmba\text{-}5)_3$ on the basis of the available data. Adaptation of more sophisticated techniques would be required to arrive at an unambiguous conclusion, which is not possible under the existing facilities of these laboratories.

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