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

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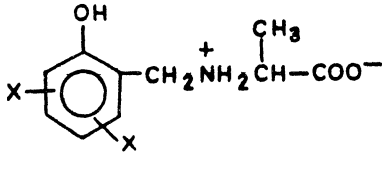
Tellurium(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by the interaction of tellurium(IV) isopropoxide and the latter in appropriate stoichiometry in benzene medium.

INTRODUCTION

Preparation of several metallo(IV) (silicon, titanium, selenium and tin) derivatives of N-(*o*-hydroxy substituted benzyl) alanines (I) *via* the reactivity of the corresponding metallo(IV) tetraisopropoxide and I, and their characterization by suitable physico-chemical methods have recently been reported[1–4]. The work described here deals with the preparation of tellurium(IV) derivatives of I *viz.* (i) N-(2-hydroxy-6-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) in 1 : 1, 1 : 2 and 1 : 3 molar ratios in benzene medium on similar lines. The compounds thus prepared were generally obtained as coloured solids and amongst them those containing isopropoxy group(s) 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

Stringent precautions were taken to exclude moisture throughout the experiments[5]. Benzene (BDH, AR), isopropanol (BDH, Glaxo, AnalaR), sovent ether (E. Merck) and ethanol were dried by standard procedures[6]. Tellurium tetraisopropoxide was prepared by sodium method[7,8], using tellurium tetrachloride (E. Merck), while N-(*o*-hydroxy substituted benzyl) alanines were

prepared by the method described before[9]. Tellurium was estimated as tellurium dioxide[10]. The details of the various glass assemblies and the instruments used have been indentical to those reported earlier[5].

The methods adopted for the preparation and purification of the various tellurium(IV) derivatives of I, using tellurium tetraisopropoxide have been the same as those described for the corresponding tin(IV) derivatives[4]. All the compounds were generally found to tbe soluble in dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like benzene, toluene and carbon tetrachloride etc. However, some of the derivatives which were found to be soluble in ethanol were further purified by recrystallization from the latter (Table-1). The relevant analytical details, characteristic IR frequencies and PMR data (in several representative cases) in respect of the various compounds prepared are summarized in Tables 1–3, respectively.

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

S.N.	Compound (molar ratio)/(colour)	Reflux time (hrs)	m.p. (°C)	Azeotrope analysis Pr^iOH (g) found (calcd)	Analysis % found (calcd)			
					C	H	N	Te
1	$Te(OPr^i)_2$ (hmba-3) (1:1) (light brown)	8	280	0.55 (0.56)	44.90 (45.08)	6.00 (6.01)	3.08 (3.09)	28.06 (28.16)
2	Te(hmba-3)$_2$ (1:2) (light brown)	10	260	0.56 (0.57)	48.50 (48.75)	4.82 (4.84)	5.15 (5.17)	23.41 (23.53)
3	$Te(OPr^i)$ (Hhmba-3)$_3$ (1:3) (light brown)	12	280	0.34 (0.35)	53.05 (53.29)	6.06 (6.09)	5.15 (5.18)	15.63 (15.72)
4	$Te(OPr^i)_2$ (hmba-6) (1:1) (pink)	8	270	0.41 (0.41)	44.91 (45.08)	6.01 (6.01)	3.08 (3.09)	28.05 (28.16)
5	$Te(OPr^i)_2$ (hmba-6) (1:2) (pink)	12	296	0.62 (0.64)	48.49 (48.75)	4.82 (4.84)	5.16 (5.17)	23.40 (23.53)
6	$Te(OPr^i)$ (Hhmba-6)$_3$ (1:3) (light yellowish pink)	10	240	0.40 (0.40)	53.21 (53.29)	6.07 (6.09)	5.14 (5.18)	15.62 (15.72)
7	$Te(OPr^i)_2$ (hmba-5) (1:1) (light yellowish brown)	8	265	0.59 (0.61)	44.88 (45.08)	5.99 (6.01)	3.07 (3.09)	28.03 (28.16)
8	Te(hmba-5)$_2$ (1:2) (light brown)	12	285	0.57 (0.58)	48.48 (48.75)	4.83 (4.84)	5.16 (5.17)	23.42 (23.53)
9	$Te(OPr^i)$ (hmba-5)$_3$ (1:3) (light yellowish brown)	10	260	0.40 (0.40)	53.19 (53.29)	6.08 (6.09)	5.14 (5.18)	15.65 (15.72)

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 (in cm^{-1}) OF THE VARIOUS TELLURIUM(IV) DERIVATIVES OR N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

S.N.	Compound	ν(OH)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 groups	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Te—O)
1	$Te(OPr^i)_2$ (hmba-3)	—	3200–3000 (mb)	2970 (m) 2850 (w)	1610 (s)	1385 (w)	225	1255 (s)	530 (w)
2	$Te(hmba\text{-}3)_2$	—	3160–3000 (m)	2950 (m) 2900 (w)	1625 (s)	1370 (w)	255	1260 (s)	530 (w)
3	$Te(OPr^i)(Hhmba\text{-}3)_3$	3500–3300 (sb)	3190–3000 (b)	2955 (m) 2860 (m)	1615 (s)	1380 (m)	235	1265 (s)	540 (m)
4	$Te(OPr^i)_2$(hmba-6)	—	3210–3000 (mb)	2940 (m) 2900 (w)	1625 (s)	1385 (w)	240	1255 (s)	550 (m)
5	$Te(hmba\text{-}6)_2$	—	3160–3000 (m)	2960 (m) 2900 (w)	1610 (sb)	1370 (w)	240	1245 (s)	555 (m)
6	$Te(OPr^i)(Hhmba\text{-}6)_3$	3500–3300 (b)	3180–3000 (mb)	2980 (m) 2900 (w)	1620 (s)	1380 (m)	240	1255 (s)	560 (m)
7	$Te(OPr^i)_2$ (hmba-5)	—	3100–3000 (mb)	2940 (m) 2850 (m)	1625 (s)	1385 (w)	240	1250 (s)	560 (w)
8	$Te(hmba\text{-}5)_2$	—	3200–3000 (b)	2940 (w) 2870 (w)	1620 (vs)	1370 (m)	250	1250 (s)	520 (w)
9	$Te(OPr^i)(Hhmba\text{-}5)_3$	3500–3300 (b)	3210–3020 (m)	2920 (m) 2870 (w)	1610 (s)	1380 (m)	230	1245 (s)	530 (w)

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

S.N.	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)
1	$Te(OPr^i)_2$ (hmba-6)	6.25–7.30 (t)	—	3.50–4.00 (m)	3.10 (h)	2.10 (s)	2.00 (d)	1.10 (d)
2	$Te(hmba\text{-}5)_2$	6.45–7.25 (m)	—	3.00–3.40 (bm)	3.15 (h)	2.20 (s)	2.05 (bs)	—
3	$Te(OPr^i)(Hhmba\text{-}3)_3$	6.70–7.20 (m)	6.65 (s)	3.50–4.00 (m)	3.20 (h)	2.20 (s)	2.10 (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 has been reported earlier that N-(*o*-hydroxy substituted benzyl) alanines exist in zwitter ionic form[9] (I). The various reactions between $Te(OPr^i)_4$ and H_2hmba-3 are

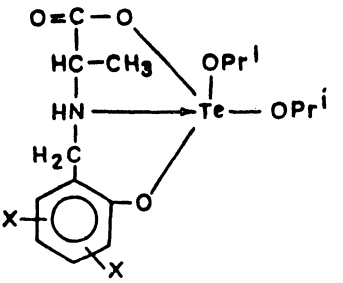
$$Te(OPr^i)_4 + H_2hmba\text{-}3 \rightarrow Te(OPr^i)_2(hmba\text{-}3) + 2Pr^iOH$$

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

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

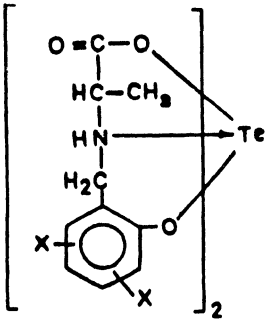
Identical reactions followed in case of H_2hmba-6 and H_2hmba-5. Based on azeotrope and elemental analyses, as well as the spectral data[11–14] in respect of the various derivatives prepared, the main findings relating to their structure are as under:

The derivatives, $Te(OPr^i)_2$(hmba-3), $Te(OPr^i)_2$(hmba-6) and $Te(OPr^i)_2$(hmba-5) (II) contain a penta-coordinated tellurium atom in each case by way of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group and the oxygen from the phenolate group, along with two isopropoxy groups. The tellurium atom in $Te(hmba\text{-}3)_2$, $Te(hmba\text{-}6)_2$ and $Te(hmba\text{-}5)_2$ (III) exhibits hexa-coordination in each case as a result of bonding with one of the oxygens from each of the two carboxylate groups, the nitrogen from each of the two imino groups and



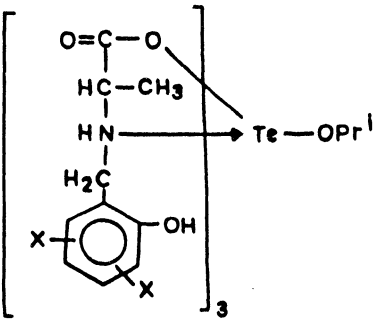
Where X = - H or - CH_3

(II)



Where X = - H or - CH_3

(III)



Where X = - H or - CH_3

(IV)

the oxygen from each of the two phenolate groups available from two moles of I. The derivatives, $Te(OPr^i)(Hhmba\text{-}6)_3$, $Te(Opr^i)(Hhmba\text{-}6)_3$ amd $Te(OPr^i)(Hhmba\text{-}5)_3$ (IV) contain a hepta-coordinated tellurium atom in each case as a result of bonding with one of the oxygens from each of three carboxylate groups and the nitrogen from each of the three imino groups available from three moles of I, along with an isopropoxy group.

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