

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

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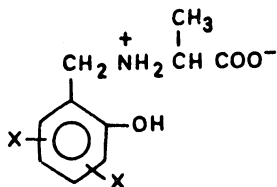
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Several titanium(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by the interaction of titanium tetraisopropoxide with the latter in 1:1, 1:2, 1:3, 1:4 and 2:3 molar ratios in benzene medium. The various compounds 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 analyses, as well by IR and PMR spectral measurements.

### INTRODUCTION

In continuation on preparation of metallo(IV) derivatives<sup>1</sup> of N-(*o*-hydroxy substituted benzyl) alanines (I), the work described here deals with the preparation of several titanium(IV) derivatives of I viz. (i) N-(2-hydroxy-3-methyl benzyl) alanine (H<sub>3</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>3</sub>hmba-5).



Where X = -H or -CH<sub>3</sub>

(I)

### EXPERIMENTAL

Owing to highly hygroscopic nature of titanium tetraisopropoxide, stringent precautions were taken to exclude moisture throughout the experiments as earlier<sup>1</sup>. Benzene (BDH, AR), isopropanol (Glaxo AnalaR), solvent ether (E. Merck) were dried by the method reported before<sup>1</sup>. Titanium tetraisopropoxide (Merck Schuchardt) was used as such, while N-(*o*-hydroxy substituted benzyl) alanines were prepared employing already reported method<sup>1</sup>. Titanium was estimated by digesting the sample with conc. nitric acid followed

by conc. sulphuric acid. From the cooled acidic solutions titanium was precipitated as its cuferron complex, which was ignited and weighed as titanium dioxide<sup>2</sup>. The instrumental details are reported earlier<sup>1</sup>.

### Reaction between titanium tetraisopropoxide and H<sub>3</sub>hmba-3;

#### 1 : 1 molar ratio

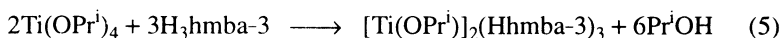
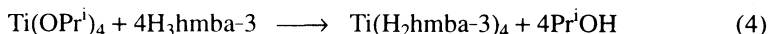
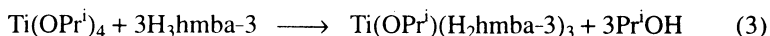
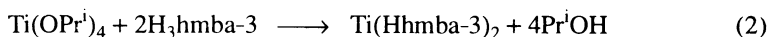
A mixture of Ti(OPr<sup>i</sup>)<sub>4</sub> (1.0200g; 3.5882 mmole) and H<sub>3</sub>hmba-3 (0.7500 g; 3.5880 mmole) suspended in dry benzene (60 mL) taken in a R.B. flask was refluxed on a wax bath (90–95°C), using a fractionating column (30 cm long). After *ca.* 8 h of reflux, isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated to monitor the completion of reaction by an oxidimetric method, as before<sup>1</sup>. On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, Ti(OPr<sup>i</sup>)(hmba-3) isolated as a yellow solid. It was then washed with benzene (3–4 times) followed by dry ether (2–3 times). The compound was found to be soluble in dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like benzene, toluene, ether, chloroform, carbon tetrachloride and ethanol.

It may be mentioned here that since Ti(OPr<sup>i</sup>)<sub>4</sub> is soluble in benzene, while H<sub>3</sub>hmba-3 is insoluble, the latter was taken in slightly less than the required stoichiometric amount (as evident from the weights given above) in order to avoid contamination of impurities likely to occur by unreacted H<sub>3</sub>hmba-3. The amount of isopropanol liberated was, therefore, calculated according to the amount of I taken in each case.

The relevant analytical details, characteristic IR frequencies and PMR spectral data (in several representative cases) are summarized in Tables 1–3, respectively.

## RESULTS AND DISCUSSION

The various reactions between titanium tetraisopropoxide and H<sub>3</sub>hmba-3 may be illustrated as:



Identical reactions occurred in case of H<sub>3</sub>hmba-6 and H<sub>2</sub>hmba-5. (Yield (%) 92–95).

The IR spectrum of Ti(OPr<sup>i</sup>)(hmba-3) shows a very strong broad band in the region 3200–3000 cm<sup>-1</sup> which may be assigned to the aromatic ν(C—H)<sup>3, 4</sup>. The band corresponding to the phenolic (—OH) group, as observed in H<sub>3</sub>hmba-3, is found to be absent here suggesting the bonding of the phenolate oxygen with

titanium. The peaks due to  $\nu(\text{C—H})$  of the  $\text{—CH}_2\text{—}$  and  $\text{—CH}_3$  groups<sup>3</sup> appear at  $2980\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$ . The band due to the  $>\text{NH}_2$  group is observed to disappear here and no peak corresponding to  $>\text{NH}$  is noticed which shows possible bonding of nitrogen to titanium. The absence of any characteristic band corresponding to  $\nu(\text{C=O})$  in the region  $1750\text{—}1650\text{ cm}^{-1}$  rules out the possibility

TABLE-1  
ANALYTICAL DETAILS OF THE VARIOUS TITANIUM(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	Ti
1.	Ti(OPr <sup>i</sup> )(hmba-3) (1 : 1) (Yellow)	200	53.50 (53.59)	6.09 (6.11)	4.44 (4.46)	15.22 (15.26)
2.	Ti(Hhmba-3) <sub>2</sub> (1 : 2) (Dark yellow)	210	57.20 (57.27)	5.55 (5.68)	6.05 (6.07)	10.37 (10.38)
3.	Ti(OPr <sup>i</sup> )(H <sub>2</sub> hmba-3) <sub>3</sub> (1 : 3) (Dark yellow)	225	59.19 (59.21)	6.75 (6.76)	5.74 (5.75)	6.52 (6.55)
4.	Ti(H <sub>2</sub> hmba-3) <sub>4</sub> (1 : 4) (Brownish yellow)	220	59.02 (59.04)	6.28 (6.30)	6.24 (6.25)	5.33 (5.35)
5.	[Ti(OPr <sup>i</sup> ) <sub>2</sub> ](Hhmba-3) <sub>3</sub> (2 : 3) (Yellow)	230	56.13 (56.15)	6.38 (6.40)	5.01 (5.03)	5.72 (5.74)
6.	Ti(OPr <sup>i</sup> )(hmba-6) (1 : 1) (Lemon yellow)	250	53.48 (53.59)	6.09 (6.11)	4.44 (4.46)	15.25 (15.26)
7.	Ti(Hhmba-6) <sub>2</sub> (1 : 2) (Yellow)	260	57.20 (57.27)	5.67 (5.68)	6.06 (6.07)	10.37 (10.38)
8.	Ti(OPr <sup>i</sup> )(H <sub>2</sub> hmba-6) <sub>3</sub> (1 : 3) (Lemon yellow)	252	59.13 (59.21)	6.73 (6.76)	5.74 (5.75)	6.54 (6.55)
9.	Ti(H <sub>2</sub> hmba-6) <sub>4</sub> (1 : 4) (Lemon yellow)	230	58.89 (59.04)	6.29 (6.30)	6.22 (6.25)	5.34 (5.35)
10.	[Ti(OPr <sup>i</sup> ) <sub>2</sub> ](Hhmba-6) <sub>3</sub> (2 : 3) (Yellow)	226	56.08 (56.15)	6.38 (6.40)	5.02 (5.03)	5.73 (5.74)
11.	Ti(OPr <sup>i</sup> )(hmba-5) (1 : 1) (Brown)	>300	53.50 (53.59)	6.10 (6.11)	4.44 (4.46)	15.25 (15.26)
12.	Ti(Hhmba-5) <sub>2</sub> (1 : 2) (Brown)	>300	57.19 (57.27)	5.66 (5.68)	6.05 (6.07)	10.35 (10.38)
13.	Ti(OPr <sup>i</sup> )(H <sub>2</sub> hmba-5) <sub>3</sub> (1 : 3) (Brown)	270	59.15 (59.21)	6.74 (6.76)	5.74 (5.75)	6.54 (6.55)
14.	Ti(H <sub>2</sub> hmba-5) <sub>4</sub> (1 : 4) (Lemon yellow)	265	58.92 (59.04)	6.29 (6.30)	6.23 (6.25)	5.34 (5.35)
15.	[Ti(OPr <sup>i</sup> ) <sub>2</sub> ](Hhmba-5) <sub>3</sub> (2 : 3) (Dark yellow)	280	56.11 (56.15)	6.39 (6.40)	5.01 (5.03)	5.72 (5.74)

Abbreviations: OPr<sup>i</sup> = C<sub>3</sub>H<sub>7</sub>O,



of a normal ester type of linkage between the carboxylate oxygen and titanium<sup>4</sup>. A strong broad band at  $1630\text{ cm}^{-1}$  occurs due to the overlapping of  $\nu_{\text{asym}}\text{COO}$  and aromatic  $\nu(\text{C=C})$ <sup>5,6</sup>. A strong band at  $1450\text{ cm}^{-1}$  and a medium band at

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

S. No.	Compound	$\nu(\text{—OH})$	$\nu\text{N—H}$ and aromatic $\nu\text{C—H}$	$\nu\text{C—H}$ of $\text{—CH}_3$ and $\text{—CH}_2\text{—}$ groups	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\Delta\nu(\text{COO})$	$\nu(\text{C—N})$	$\nu(\text{Ti—O})$	$\nu(\text{Ti—N})$
1.	Ti(OPr <sup>t</sup> )(hmba-3)	—	*3200–3000 (vsb)	2980 (m) 2860 (w)	1630 (sb)	1390 (m)	240	1250 (mb)	575 (m) 520 (w)	460 (w) 410 (w)
2.	Ti(Hhmba-3) <sub>2</sub>	—	3100–3000 (vsb)	2960 (m) 2920 (w)	1620 (sb)	1370 (m)	250	1250 (s)	570 (w) 525 (m)	470 (vw) 410 (w)
3.	Ti(OPr <sup>t</sup> )(H <sub>2</sub> hmba-3) <sub>3</sub>	3500–3200 (vb)	3190–3000 (mb)	2940 (w) 2830 (w)	1610 (s)	1375 (m)	235	1250 (s)	570 (s) 500 (s)	480 (m) 410 (m)
4.	Ti(H <sub>2</sub> hmba-3) <sub>4</sub>	3550–3250 (vb)	3200–3000 (mb)	2940 (m) 2840 (w)	1630 (vs)	1375 (m)	255	1250 (m)	590 (w) 550 (m) 520 (w)	460 (m) 440 (m)
5.	[Ti(OPr <sup>t</sup> ) <sub>2</sub> (Hhmba-3) <sub>3</sub>	—	3300–3000 (vsb)	2940 (m)	1610 (sb)	1390 (sb)	235	1250 (s)	575 (w) 500 (vw)	480 (w) 410 (m)
6.	Ti(OPr <sup>t</sup> )(hmba-6)	—	*3100–3000 (mb)	2980 (m) 2860 (w)	1625 (vs)	1390 (sb)	235	1265 (m)	570 (w) 520 (w)	475 (m) 420 (m)
7.	Ti(Hhmba-6) <sub>2</sub>	—	3150–3000 (vsb)	2920 (m)	1625 (s)	1390 (m)	235	1270 (s)	520 (w)	415 (m)
8.	Ti(OPr <sup>t</sup> )(H <sub>2</sub> hmba-6) <sub>3</sub>	3500–3250 (vsb)	3200–3050 (mb)	2930 (vw)	1630 (mb)	1380 (wb)	250	1270 (m)	520 (wb)	470 (vw) 420 (m)

TABLE-2 (contd.)

S. No.	Compound	$\nu(-OH)$	$\nu N-H$ and aromatic $\nu C-H$	$\nu C-H$ of $-CH_3$ and $-CH_2-$ groups	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$	$\Delta\nu(COO)$	$\nu(C-N)$	$\nu(Ti-O)$	$\nu(Ti-N)$
9.	Ti(H <sub>2</sub> hmba-6) <sub>4</sub>	3500-3200 (vsb)	3100-3000 (mb)	2980 (m)	1630 (sh)	1390 (m)	240	1270 (sh)	525 (m)	460 (m) 420 (w)
10.	[Ti(OPr <sup>i</sup> )(H <sub>2</sub> hmba-6) <sub>3</sub>	—	3250-3000 (mb)	2920 (w) 2860 (w)	1625 (sb)	1385 (sb)	240	1255 (m)	560 (w) 520 (m)	490 (m) 420 (m) 400 (vw)
11.	Ti(OPr <sup>i</sup> )(hmba-5)	—	*3200-3000 (vb)	2920 (m)	1610 (vsb)	1380 (m)	230	1250 (mb)	580 (w) 520 (w)	470 (m) 450 (m)
12.	Ti(Hhmba-5) <sub>2</sub>	—	3250-3000 (b)	2920 (m)	1630 (vsb)	1380 (m)	250	1260 (s)	575 (w) 550 (w)	475 (m) 450 (m)
13.	Ti(OPr <sup>i</sup> )(H <sub>2</sub> hmba-5) <sub>3</sub>	3500-3300 (vsb)	3200-3000 (mb)	2960 (m) 2910 (m)	1610 (sb)	1380 (m)	240	1255 (s)	575 (m) 520 (w)	470 (m) 420 (m)
14.	Ti(H <sub>2</sub> hmba-5) <sub>4</sub>	3500-3300 (vsb)	3100-3000 (mb)	2920 (m)	1620 (sb)	1370 (m)	250	1260 (vs)	560 (s)	470 (w) 440 (vw)
15.	[Ti(OPr <sup>i</sup> ) <sub>2</sub> (Hhmba-5) <sub>3</sub>	—	3200-3000 (vsb)	2920 (m)	1630 (sb)	1360 (m)	250	1255 (vs)	560 (m) 520 (m)	460 (wb) 420 (vw)

Abbreviations: s = strong, m = medium, w = weak, vsb = very strong broad, mb = medium broad, sb = strong broad, vw = very weak, sh = shoulder.  
\*due to aromatic  $\nu(C-H)$  alone.

TABLE-3  
 PROTON MAGNETIC RESONANCE SPECTRAL DATA ( $\delta$  value) OF SEVERAL TITANIUM(IV) DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

Compound	Aromatic ring	Phenolic (—OH)	>CH—	>NH	CH <sub>3</sub> attached with the benzene ring	—CH <sub>2</sub> —	—CH <sub>3</sub> of the alanine part	Gem dimethyl <sup>1</sup>
Ti(OPr <sup>t</sup> ) <sub>2</sub> (Hmba-3)	6.55–7.30 (m)	—	3.45–3.85 (q)	—	2.20 (s)	2.05 (d)	1.35 (d)	0.90 (t)
Ti(Hhmba-6) <sub>2</sub>	6.40–7.35 (m)	—	3.40–4.00 (bm)	3.10 (s)	2.25 (s)	2.05 (d)	1.15 (d)	—
Ti(OPr <sup>t</sup> ) <sub>2</sub> (H <sub>2</sub> hmba-5) <sub>3</sub>	6.60–7.20 (m)	5.40 (s)	3.50–3.80 (m)	3.10 (s)	2.25 (s)	2.05 (d)	1.20 (d)	1.10 (d)
Ti(H <sub>2</sub> hmba-3) <sub>4</sub>	6.50–7.10 (m)	5.65 (s)	3.45–4.00 (bm)	3.10 (s)	2.25 (s)	2.10 (d)	1.30 (d)	—
[Ti(OPr <sup>t</sup> ) <sub>2</sub> (Hhmba-5) <sub>3</sub>	6.50–7.15 (m)	—	3.45–3.85 (m)	3.15 (s)	2.25 (s)	2.05 (d)	1.20 (d)	1.05 (d)

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, bm = broad multiplet, m = multiplet.

1380  $\text{cm}^{-1}$  may be assigned to the C—H bending of the —CH<sub>2</sub>— and —CH<sub>3</sub> groups and aromatic skeletal stretching modes<sup>4,7</sup>. Further, instead of a peak at 1405  $\text{cm}^{-1}$ , as noted in H<sub>3</sub>hmba-3, here the peak at 1390  $\text{cm}^{-1}$  with a shoulder indicates the overlapping of  $\nu_{\text{sym}}\text{COO}$  and C—H bending due to the *gem* dimethyl structure of the isopropoxy group<sup>4,5,7</sup>. A shift of 15  $\text{cm}^{-1}$  in  $\nu_{\text{sym}}\text{COO}$ , as compared to H<sub>3</sub>hmba-3, suggests the bonding of the carboxylate oxygen with titanium. The separation value  $\Delta\nu\text{COO}$  of 240  $\text{cm}^{-1}$ , as observed here, rules out the presence of a bridged or coordinated carboxylate group<sup>8-10</sup>. A medium broad band at 1250  $\text{cm}^{-1}$  may be assigned to the overlapping of  $\nu(\text{C—N})$  and  $\nu(\text{C—O})$ <sup>4</sup>. The peak due to  $\nu(\text{C—N})$  appears at 1270  $\text{cm}^{-1}$  in case of H<sub>3</sub>hmba-3, and thus a shift 20  $\text{cm}^{-1}$  in  $\nu(\text{C—N})$  suggests the bonding of nitrogen with titanium. The weak and medium peaks appearing at 1150  $\text{cm}^{-1}$ , 1070  $\text{cm}^{-1}$  and 1010  $\text{cm}^{-1}$  may be ascribed to the aromatic C—H in-plane bending<sup>11</sup>, while those at 940  $\text{cm}^{-1}$  and 860  $\text{cm}^{-1}$  may be attributed to the characteristic out-of-plane bending of a trisubstituted benzene ring. The medium and weak absorptions at 575  $\text{cm}^{-1}$  and 520  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{Ti—O})$ <sup>12,13</sup>, while the weak peaks at 460  $\text{cm}^{-1}$  and 410  $\text{cm}^{-1}$  correspond to  $\nu(\text{Ti—N})$ <sup>14,16</sup>.

It is thus evident that the titanium atom in Ti(OPr<sup>i</sup>)(hmba-3) [Structure (II)] exhibits tetravalency as a result of bonding with one of the oxygens from the carboxylate group, the oxygen from the phenolate group and the nitrogen obtained by deprotonation of the  $\text{>NH}_2^+$  group, along with an isopropoxy group.

The PMR spectra of Ti(OPr<sup>i</sup>)(hmba-3) shows a multiplet between  $\delta 6.55\text{--}7.30$  which may be attributed to the aromatic ring protons<sup>5,17</sup>. The absence of a singlet at  $\delta 6.75$  due to the phenolic group proton, as noted in H<sub>3</sub>hmba-3, indicates the deprotonation of the phenolic group as a result of bonding of the phenolate oxygen with titanium. A hump in the region  $\delta 3.20\text{--}3.40$  due to the protons of the  $\text{>NH}_2^+$  group, as observed in H<sub>3</sub>hmba-3, is found to disappear here suggesting the bonding of nitrogen with titanium. A quartet corresponding to the  $\text{>CH—}$  group proton of the alanine part of H<sub>3</sub>hmba-3 occurs between  $\delta 3.45\text{--}3.85$ , while the signals due to the protons of the —CH<sub>3</sub> and —CH<sub>2</sub>— groups attached with the benzene ring of H<sub>3</sub>hmba-3 appear in the form of a singlet at  $\delta 2.20$  and a doublet at  $\delta 2.05$ , respectively. A doublet at  $\delta 1.35$  corresponds to the —CH<sub>3</sub> group protons of the alanine part of H<sub>3</sub>hmba-3, while a triplet at  $\delta 0.90$  occurs due to the *gem* dimethyl protons of the isopropoxy group<sup>10,17,18</sup>. Thus, the inferences drawn here are 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 the context of their structures are as under:

The titanium atom in Ti(OPr<sup>i</sup>)(hmba-6) and Ti(OPr<sup>i</sup>)(hmba-5) (structure II) exhibits tetravalency in each case by way of similar modes of bonding as those in case of Ti(OPr<sup>i</sup>)(hmba-3).

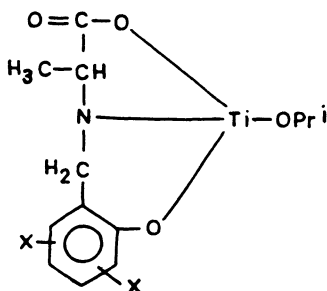
The derivatives, Ti(Hhmba-3)<sub>2</sub>, Ti(Hhmba-6)<sub>2</sub> and Ti(Hhmba-5)<sub>2</sub> (structure III) contain a hexa-coordinated titanium atom in each case by way of bonding

with one of the oxygens from each of the two carboxylate groups, oxygen from each of the two phenolate groups and the nitrogen from each of the two imino groups, available from two moles of I.

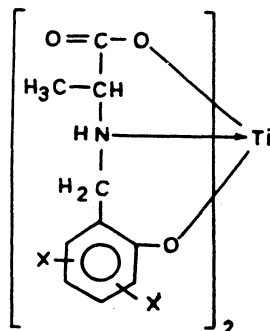
The titanium atom in  $\text{Ti}(\text{OPr}^i)(\text{H}_2\text{hmba-3})_3$ ,  $\text{Ti}(\text{OPr}^i)(\text{H}_2\text{hmba-6})_3$  and  $\text{Ti}(\text{OPr}^i)(\text{H}_2\text{hmba-5})_3$  (structure IV) displays penta-coordination in each case as a consequence of bonding with one of the oxygens from 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.

The derivatives,  $\text{Ti}(\text{H}_2\text{hmba-3})_4$ ,  $\text{Ti}(\text{H}_2\text{hmba-6})_4$  and  $\text{Ti}(\text{H}_2\text{hmba-5})_4$  (structure V) contain an octa-coordinated titanium atom in each case as a result of bonding with one of the oxygens from each of the four carboxylate groups and the nitrogen from each of the four imino available from four moles of I.

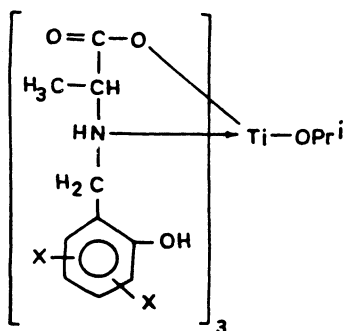
It is rather difficult to assign any definite structure for  $[\text{Ti}(\text{OPr}^i)]_2(\text{Hhmba-3})_3$ ,  $[\text{Ti}(\text{OPr}^i)]_2(\text{Hhmba-6})_3$  and  $[\text{Ti}(\text{OPr}^i)]_2(\text{Hhmba-5})_3$  on the basis of the available data. Adaptation of more sophisticated techniques would be required to arrive at



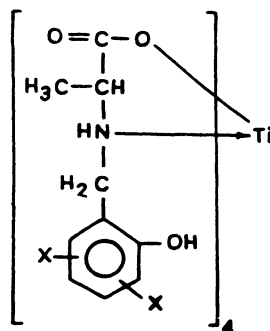
Where  $X = -\text{H}$  or  $-\text{CH}_3$   
(II)



Where  $X = -\text{H}$  or  $-\text{CH}_3$   
(III)



Where  $X = -\text{H}$  or  $-\text{CH}_3$   
(IV)



Where  $X = -\text{H}$  or  $-\text{CH}_3$   
(V)



required to arrive at an unambiguous conclusion, which is not possible under the existing facilities of these laboratories.

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