

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE LABORATORY OF POLYMER CHEMISTRY, TOKYO INSTITUTE OF TECHNOLOGY]

## Chelate Compounds of Titanium with 2-Methylpentane-2,4-diol

BY AKIO YAMAMOTO AND SHU KAMBARA

RECEIVED JUNE 9, 1958

The reactions of a series of tetraalkoxytitaniums with 2-methylpentane-2,4-diol in a variety of molar ratios were studied and new organic titanium compounds (I, II and III) having one, two and three chelate rings were obtained. It was ascertained that tris-(2-methylpentane-2,4-diol)-titanium (III) dissociates to bis-(2-methylpentane-2,4-diol)-titanium (II) and 2-methylpentane-2,4-diol. The infrared absorption spectra and the molecular weights of these compounds were measured and the structures are discussed.

## Introduction

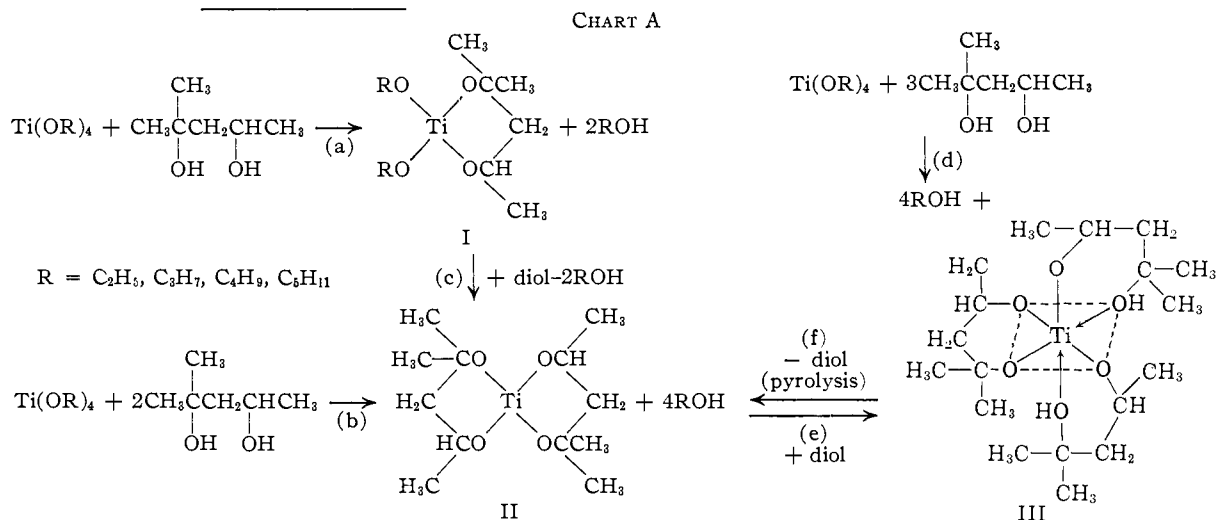
The reactions of tetraalkoxytitaniums (tetraalkyl titanates) with bidentate chelating agents of enolizable 2,4-diketone type were reported previously.<sup>1</sup> In connection with the previous paper, the reactions of tetraalkoxytitaniums with chelating agents of the 2,4-diol type were studied.

Reeves and Mazzeno<sup>2</sup> have studied the composition of the reaction products of tetra-*t*-butoxytitanium (tetra-*t*-butyl titanate) with 2-ethylhexane-1,3-diol, butane-2,3-diol and ethylene glycol using polarimetric and cryoscopic methods. They have obtained evidence that a compound having a titanium:diol ratio of 2:3 was formed and also suggested the formation of other compounds having

and 2,3-diols and little is known of the reaction of tetraalkoxytitanium with 2,4-diols. In the present study, the reactions of a series of tetraalkoxytitaniums with various molar ratios of 2-methylpentane-2,4-diol were carried out and the reaction products were isolated in pure state and analyzed. It was found that the reaction of tetraalkoxytitaniums with 2-methylpentane-2,4-diol differs from those described in the literature referred to above. The structures of the chelated titanium compounds isolated were studied by infrared analysis and cryoscopic molecular weight determination.

## Results

The results obtained can be represented schematically as:



the compositions 2:2, 2:4 and 3:6. They have not isolated the reaction products in pure state nor analyzed them except the reaction product of tetra-*t*-butoxytitanium with butane-2,3-diol. Similar reaction of tetraalkoxytitanium with 2,3-diorgano-1,3-diols have been described in a patent<sup>3</sup> and compounds having the compositions of 1:1, 1:2, 1:3 and 1:4 have been claimed to be obtained. In this case, however, the reactions were not carried out under rigorous exclusion of moisture and the analytical data obtained do not agree with the proposed structures.

The studies referred to above concern 1,2-, 1,3-

The reaction of one mole of 2-methylpentane-2,4-diol with one mole of tetraalkoxytitaniums (tetraethoxy-, tetrapropoxy-, tetrabutoxy- and tetrapentoxytitanium) yielded two moles of alcohols (ethyl, propyl, butyl and pentyl alcohol) and liquid titanium compounds. The physical constants and analytical data of the titanium compounds are summarized in Table I (nos. 1 to 4).

The results of the chemical analyses lead to structure I, which is considered to be formed by an exchange reaction of two alkoxy groups of each tetraalkoxytitanium with 2-methylpentane-2,4-diol according to equation a in Chart A.

In case of the reaction of a series of tetraalkoxytitaniums with 2-methylpentane-2,4-diol in a molar ratio of 1:2, crystalline titanium compounds and

(1) A. Yamamoto and S. Kambara, *THIS JOURNAL*, **79**, 4344 (1957).  
 (2) R. E. Reeves and L. W. Mazzeno, Jr., *ibid.*, **76**, 2533 (1954).  
 (3) C. O. Bostwick, U. S. Patent 2,643,262 (1953).

TABLE I  
 PHYSICAL CONSTANTS AND ANALYTICAL DATA OF THE REACTION PRODUCTS IN 1:1 MOLAR RATIO

No.	Formula	B.p.		$d^{25}_4$	$n^{25}_D$	Analyses, %					
		°C.	Mm.			Calcd.			Found		
						Ti	C	H	Ti	C	H
1	(H <sub>5</sub> C <sub>2</sub> O) <sub>2</sub> Ti(O <sub>2</sub> C <sub>6</sub> H <sub>12</sub> )	137-138	0.025	1.115 <sup>a</sup>	1.517 <sup>a</sup>	18.85	47.25	8.73	18.9	47.6	10.6
2	(H <sub>7</sub> C <sub>3</sub> O) <sub>2</sub> Ti(O <sub>2</sub> C <sub>6</sub> H <sub>12</sub> )	140-142	.025	1.067	1.512	16.97	51.06	9.29	17.0	50.9	8.9
3	(H <sub>9</sub> C <sub>4</sub> O) <sub>2</sub> Ti(O <sub>2</sub> C <sub>6</sub> H <sub>12</sub> )	150-152	.035	1.055	1.506	15.44	54.19	9.75	15.6	54.2	10.2
4	(H <sub>11</sub> C <sub>5</sub> O) <sub>2</sub> Ti(O <sub>2</sub> C <sub>6</sub> H <sub>12</sub> )	174-175	.030	...	1.505	14.16	56.80	10.13	14.2	56.8	10.2

<sup>a</sup> On account of the extremely hygroscopic and viscous nature of the compounds, the measurements were very difficult.

four moles of alcohol were formed. Regardless of the sort of alkoxytitaniums used, the same yields of the titanium compounds were obtained and these compounds were shown to be identical by chemical analyses and the melting point. From these results, the reaction is considered to proceed according to equation b in Chart A, forming bis-(2-methylpentane-2,4-diol)-titanium (II).

The bis-compound II could be derived also by the reaction of I with an equimolecular quantity of 2-methylpentane-2,4-diol with the formation of two moles of alcohols according to equation c in Chart A.

When three moles of 2-methylpentane-2,4-diol were used per mole of tetraalkoxytitaniums, four moles of alcohol and crystalline titanium complexes were obtained. Any tetraalkoxytitanium gave the same yield of crystalline complex having the same melting point and the same chemical composition which conforms to structure III. The reaction is considered to proceed according to equation d in Chart A, forming a hexacoordinated titanium compound. When an excess of 2-methylpentane-2,4-diol was used, the same compound III and four moles of alcohol were obtained and the excess of the diol was recovered.

The tris-compound III was derived also from the bis-compound II by the reaction of II with an equimolecular quantity of 2-methylpentane-2,4-diol according to equation e in Chart A.

When the tris-compound III was heated, its crystalline form was changed and one mole of III was converted to an equimolar quantity of the bis-compound II with the production of one mole of 2-methylpentane-2,4-diol according to equation f in Chart A.

In Table II are listed the X-ray diffraction data for the compounds II and III. The X-ray data of the pyrolysis product of III were completely identical

with those of the bis-compound II prepared from one mole of tetraalkoxytitaniums and two moles of 2-methylpentane-2,4-diol by reaction b.

### Discussions

**Infrared Spectra.**—If the tris-compound III has the hexacoordinated structure with three chelate rings, two of the six oxygen atoms should link with the central titanium atom by coordinate links Ti ← O—C, and two OH groups should present in the H molecule, while no OH group is expected in I and II. The infrared spectra of I, II and III were measured and compared with those of 2-methylpentane-2,4-diol and of tetrabutoxytitanium. The absorption maxima are listed in Table III with

 TABLE III  
 INFRARED ABSORPTION BANDS OF (2-METHYLPENTANE-2,4-DIOL)-DI-*n*-BUTOXYTITANIUM I, II, III, TETRA-*n*-BUTOXYTITANIUM AND 2-METHYLPENTANE-2,4-DIOL<sup>a</sup>

III	Wave numbers in cm. <sup>-1</sup>			2,4-Diol
	II	I	Ti(OBu) <sub>4</sub>	
		747m	745m	
767m	770m			766m
793m	796m	797m	800m	
834s		827w		836m
847m	851s	858s	862s	
860m				
877w	885w			878m
905s		900m	901m	903s
925s				
936s	935s	943vs	966s	945m
974s	987s	971vs	988s	969m
		991vs		994w
1040s	1038s	1040vs	1034vs	1042m
1078m	1076m	1081vs	1091vs	1076m
1130m	1135m	1124vs	1123vs	1120w
1158s	1153vs	1150vs		1159s
1183m	1185m	1185m		1199w
1218m	1218m	1219m	1223m	1223m
1260m	1262m	1264m		1257m
		1292w	1291w	1293m
		1327m		1329m
		1364s	1363s	1367s
		1370s	1371s	1378s
				1420s
			1457s	1456s
			2703w	
			2714w	
	2859vs	2869vs	2871vs	2876vs
	2927vs	2927vs	2937vs	2934vs
	3100m			2971vs
				3330vs,b

<sup>a</sup> Relative intensity: weak(w); medium(m); strong(s); very strong(vs); broad(b). The spectra of I, Ti(OBu)<sub>4</sub> and 2,4-diol were measured in thin films; II and III in Nujol mull using a NaCl prism.

 TABLE II  
 X-RAY DIFFRACTION DATA FOR COMPOUNDS II AND III,  
 RELATIVE INTENSITY AND INTERPLANAR SPACINGS IN Å.<sup>a</sup>

Compound II	Compound III
3.96m	3.74m
4.31w	3.92m
4.61w	4.40w
4.89w	4.52w
5.16w	5.14w
5.64m	5.39w
6.58m	5.72m
7.45m	7.46m
7.97s	7.78s
8.52ss	8.54s
9.09m	9.35ss
	10.39s

<sup>a</sup> Relative intensity: weak(w), medium(m), strong(s) and the strongest(ss).

the relative intensities. The spectra of the tris- and bis-compound and 2-methylpentane-2,4-diol

are similar except in the high frequency region. In the 3-micron region a broad strong band is observed near  $3330\text{ cm.}^{-1}$  for 2-methylpentane-2,4-diol, a band of medium intensity near  $3100\text{ cm.}^{-1}$  for III and no bands are observed in this region for I and II.

In order to study the spectra in the  $3\text{-}\mu$  region more accurately, the spectra of III were observed in Nujol mull and in  $\text{CCl}_4$  solutions of various concentrations using a LiF prism (Figs. 1a and 1b). The absorption band which is observed in the Nujol mull of III near  $3100\text{ cm.}^{-1}$  (Fig. 1a, band A) is observed in dilute solution at nearly same frequency but with much diminished intensity, and three bands appear near  $3350\text{ cm.}^{-1}$  (band B), at  $3527\text{ cm.}^{-1}$  (band C) and  $3617\text{ cm.}^{-1}$  (band D). These three bands exist in the spectrum of  $\text{CCl}_4$  solution of 2-methylpentane-2,4-diol at the same frequencies (Fig. 1b, curve 4). In view of the fact that III dissociates to II and 2-methylpentane-2,4-diol when heated, it is reasonable to suppose that the same dissociation occurs in  $\text{CCl}_4$  solution even at room temperature and these three bands can be ascribed to 2-methylpentane-2,4-diol which was formed by the dissociation of III. In Table IV are listed the molar extinction coefficients of III and 2-methylpentane-2,4-diol in  $\text{CCl}_4$  solutions at 3100, 3350, 3527 and  $3617\text{ cm.}^{-1}$ .

TABLE IV

MOLAR EXTINCTION COEFFICIENT OF III AND 2-METHYLPENTANE-2,4-DIOL IN  $\text{CCl}_4$  SOLUTIONS

Concn. mole/l.	Molar extinction coefficients.— l. mole. <sup>-1</sup> cm. <sup>-1</sup>			
	3100 cm. <sup>-1</sup>	3350 cm. <sup>-1</sup>	3527 cm. <sup>-1</sup>	3617 cm. <sup>-1</sup>
III, 0.0048	39	18	95	51
III, 0.037	37	58	54	32
III, 0.052	57	79	53	23
Diol, 0.0085		28	93	60

From these data and the shape of the absorption bands, the following assignments were made in agreement with Kuhn,<sup>4</sup> and Matsumoto and Imai.<sup>5</sup> The very broad band (band B) near  $3350\text{ cm.}^{-1}$  is due to intermolecular bonded OH, the band at  $3527\text{ cm.}^{-1}$  (band C) to intramolecular bonded OH and the band at  $3617\text{ cm.}^{-1}$  (band D) to free OH. The band near  $3100\text{ cm.}^{-1}$  (band A) is considered to be due to the OH groups of the undissociated tris-compound III. In the saturated solution of III (curve 2 in Fig. 1a), band A remains with considerable intensity. When 2-methylpentane-2,4-diol was added to the saturated solution, a white precipitate separated out and the intensity of band A of the remaining solution decreased, while the intensity of the other bands increased (curve 3, in Fig. 1a). The decrease in intensity of band A is considered to be caused by the formation of the precipitate of III from the solution and hence the decrease of the concentration of III in the remaining solution. In consideration of the fact that the band A remains at the same very low frequency in dilute  $\text{CCl}_4$  solution as in solid state, it is reasonable

(4) L. P. Kuhn, *THIS JOURNAL*, **74**, 2492 (1952).

(5) M. Matsumoto and K. Imai, *Chem. High Polymers (Japan)*, **15**, No. 155, 160 (1958).

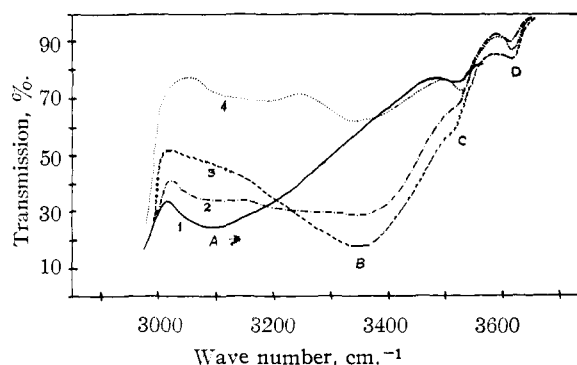


Fig. 1a.—Infrared spectra of the tris-compound in the LiF region: 1, —, Nujol mull; 2, ---,  $\text{CCl}_4$  saturated solution; 3, ····,  $\text{CCl}_4$  saturated solution + diol; 4, — · — ·, 0.052 molar  $\text{CCl}_4$  solution, cell thickness 3.0 mm.

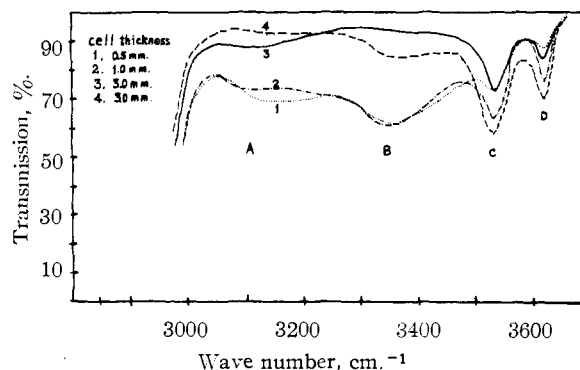


Fig. 1b.—Infrared spectra of the dilute solutions of the tris-compound and the diol: 1, ····, 0.052 molar  $\text{CCl}_4$  solution of III; 2, ---, 0.037 molar  $\text{CCl}_4$  solution of III; 3, —, 0.0048 molar  $\text{CCl}_4$  solution of III; 4, — · — ·, 0.0085 molar  $\text{CCl}_4$  solution of the diol.

to suppose that the band is due to the intramolecularly bonded OH group.

The absorption bands in the region between  $1000$  and  $1200\text{ cm.}^{-1}$  are considered to be characteristic of the alkoxy group.<sup>1,6</sup> The absorption bands of the tris-compound III and the bis-compound II correspond well with those of 2-methylpentane-2,4-diol in this region. The spectrum of (2-methylpentane-2,4-diol)-di-*n*-butoxytitanium (I) shows some difference in the region compared with the spectrum of the tris-compound. The bands of I in this region are explained as due to the overlapping of strong *n*-butoxy group bands.

**Molecular Weight Determinations.**—Many tetraalkoxytitaniums show a tendency of association in non-polar solvent to satisfy the maximum coordination number six of titanium.<sup>7</sup> In this sense the compound I and II are expected to show association, while no association is expected for III where the coordination number six of titanium

(6) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *Anal. Chem.*, **25**, 1720 (1953); H. H. Zeiss and M. Tsutsui, *THIS JOURNAL*, **75**, 897 (1953); T. Takatani, T. Yoshimoto and Y. Mashiko, *J. Chem. Soc. Japan, Ind. Chem. Section*, **60**, 1382 (1957).

(7) C. N. Caughlan, H. S. Smith, W. Katz, W. Hodgson and R. W. Crowe, *THIS JOURNAL*, **73**, 5652 (1951); N. M. Cullinane, S. J. Chard, G. F. Price, B. B. Millward and G. Langlois, *J. Appl. Chem.*, **1**, 400 (1951); D. C. Bradley, R. C. Mehrotra, J. D. Swanwick and W. Wardlaw, *J. Chem. Soc.*, 2025 (1953).

is satisfied. The results of the molecular weight determinations in benzene solution by cryoscopic method are indicated in Figs. 2, 3 and 4 in which

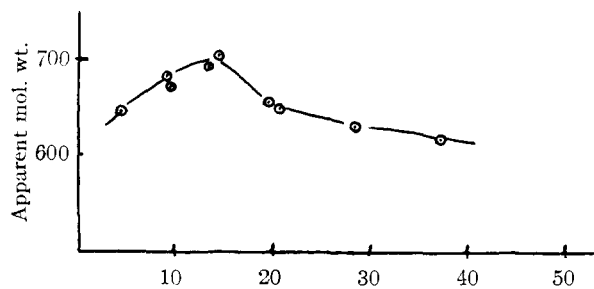


Fig. 2.—Molecular weight of bis-(2-methylpentane-2,4-diol)-titanium (II).

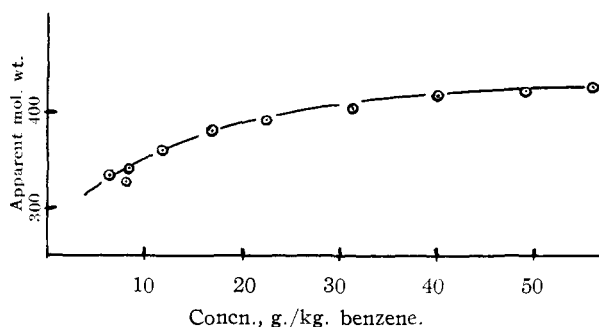


Fig. 3.—Molecular weight of tris-(2-methylpentane-2,4-diol)-titanium (III).

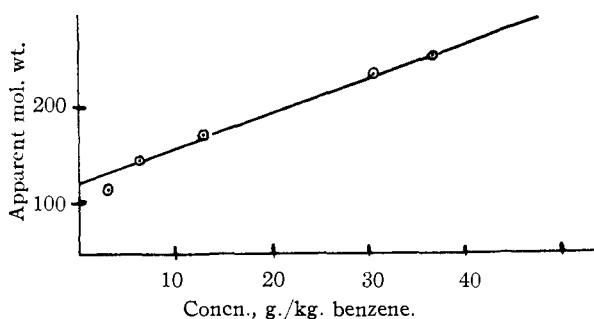
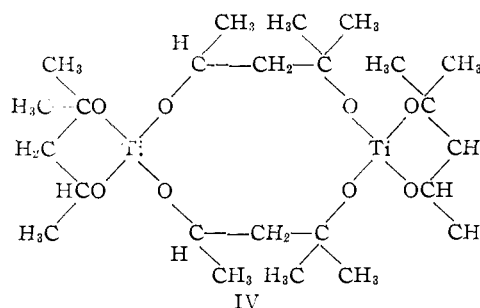


Fig. 4.—Molecular weight of 2-methylpentane-2,4-diol.

the apparent molecular weights are plotted against the concentration of the solute. The observed values of the molecular weight of the bis-compound II (Fig. 2) increase with increasing concentration to the maximum value 700 and then decrease gradually. The increase apparently is due to association. The cause of the gradual decrease of the apparent molecular weight in the high concentration is not clear. Extrapolation of the curve to zero concentration gives the value of 600, the theoretical value for II being 280. This suggests a double nuclei structure IV for the bis-compound as Reeves and Mazzeno<sup>2</sup> pointed out, although the possibility that II is very tightly associated to dimer even in very dilute solution must be considered.

The molecular weight determination of I was very difficult because of the very hygroscopic and unstable nature of the compound. The molecular weight found for the (2-methylpentane-2,4-diol)-di-*n*-butoxytitanium was in the range between

600 and 700, the calculated value being 310. In this case also, two possibilities are considered: (a) double nuclei structure and (b) association in benzene solution.



It is noted that the observed values of the molecular weight of III (Fig. 3) show abnormally low values at low concentration compared with the theoretical value 398 and tend to increase with increasing concentration reaching the constant value 420. It is reasonable to suppose that the discrepancy from the theoretical value is connected with the dissociation of the tris-compound III to the bis-compound and 2-methylpentane-2,4-diol and this causes the increase of the number of molecular species and hence the decrease of the number average molecular weight in the dilute solutions. The diol and the bis-compound which are formed by the dissociation of III associate also as shown in Figs. 4 and 2. Hence as a whole, the number average molecular weight may exceed the theoretical value for III in the concentrated solutions.

### Experimental

**Materials.**—Tetraethoxy-, tetra-*n*-propoxy-, tetra-*n*-butoxy- and tetra-*n*-pentoxytitanium were prepared and purified following the method described in the literature.<sup>3</sup> Tetrapentoxytitanium also was prepared by a transesterification reaction between tetrapropoxytitanium and *n*-pentyl alcohol. In each case satisfactory purity was indicated by chemical analysis of the compound.

2-Methylpentane-2,4-diol, which was supplied by the Shell Chemical Corp. of Tokyo, was dehydrated with sodium sulfate and then with calcium hydride and fractionated under reduced pressure; b.p. 107.5–108.5° (25 mm.),  $n_D^{25}$  1.4265.

**General Synthetic Procedures.** (a) **Reaction of Tetraalkoxytitaniums with 2-Methylpentane-2,4-diol in a Molar Ratio 1:1.**—To 0.010 mole of tetraalkoxytitanium (tetraethoxy-, tetrapropoxy-, tetrabutoxy- and tetrapentoxytitanium) was added 0.010 mole of 2-methylpentane-2,4-diol. Reaction took place with slight evolution of heat. The reaction mixture was fractionated under reduced pressure. The volatile distillates were shown to be alcohols used for the preparation of each tetraalkoxytitanium by measurements of the refractive indices and boiling points. The quantity of alcohol was about 0.020 mole in each case. The viscous residue was distilled under high vacuum. The distillate was a clear, extremely viscous liquid, soluble in most organic solvents and very readily hydrolyzed by moisture in air. The ease of the hydrolysis decreased apparently with the increase of the alkyl chain length.

(b) **Reaction of Tetraalkoxytitanium with 2-Methylpentane-2,4-diol in a Molar Ratio 1:2.**—To 0.010 mole of each tetraalkoxytitanium was added 0.020 mole of 2-methylpentane-2,4-diol. Reaction took place with evolution of heat. From the reaction mixtures about 0.04 mole of alcohol was removed under reduced pressure. About 2.8 g. of glass-like material remained as the residue in each case. Each residue was crystallized from chloroform solution three times to give colorless plates which melted at 148–

(8) J. Nelles, German Patent 720,080.

153°. The crystals were readily soluble in most organic solvents and very hygroscopic and readily hydrolyzed in air. The crystals were introduced into a capillary in a dry-box and the melting points were measured after sealing the capillary tube. The products from various tetraalkoxytitaniums showed the same melting point and showed no depression of the melting point when mixed melting points were observed.

*Anal.* Calcd. for  $TiC_{12}H_{24}O_4$ : Ti, 17.09; C, 51.43; H, 8.64. Found: Ti, 17.0, 17.1; C, 50.5; H, 8.51.

(c) **Reaction of I with an Equimolecular Proportion of 2-Methylpentane-2,4-diol.**—To 3.1 g. (0.012 mole) of (2-methylpentane-2,4-diol)-diethoxytitanium was added 1.4 g. (0.012 mole) of 2-methylpentane-2,4-diol. From the reaction mixture 0.8 g. of volatile matter was removed under reduced pressure. The volatile matter was shown to be ethyl alcohol by measurement of the refractive index. The solidified residue was crystallized from chloroform solution to yield 2.5 g. of colorless plates, m.p. 143–151°.

*Anal.* Calcd. for  $TiC_{12}H_{24}O_4$ : Ti, 17.1. Found: Ti, 17.1.

(d) **Reaction of Tetraalkoxytitaniums with 2-Methylpentane-2,4-diol in a Molar Ratio 1:3 and 1:4.**—(i) To 0.010 mole of each tetraalkoxytitanium was added 0.030 mole of 2-methylpentane-2,4-diol. Reaction took place with evolution of heat, and after several hours white needles appeared from the reaction mixture. Regardless of the sort of tetraalkoxytitanium used, 0.040 mole of alcohol was removed from the reaction mixture under reduced pressure. The theoretical amount of the compound III remained as the residue and the residue was crystallized from chloroform solution. The recrystallized needles melted at 104–106°. Mixed melting point of the samples prepared from various tetraalkoxytitaniums showed no depression of the melting points. The crystals are soluble in most organic solvents.

*Anal.* Calcd. for  $TiC_{12}H_{24}O_6$ : Ti, 12.02. Found: Ti, 12.0.

(ii) To 0.010 mole of each tetraalkoxytitanium was added 0.040 mole of 2-methylpentane-2,4-diol. Reaction took place with evolution of heat. From the reaction mixtures, 0.040 mole of alcohol was removed under reduced pressure. White crystals remained with excess of 2-methylpentane-2,4-diol as the residue. The crystals were filtered and washed with absolute diethyl ether and recrystallized from chloroform solution to give 3.5 g. of the product, m.p. 105–106°.

*Anal.* Calcd. for  $TiC_{12}H_{24}O_6$ : Ti, 12.02; C, 54.26; H, 9.62. Found: Ti, 12.1; C, 54.4; H, 10.1.

The filtrate and the washings were combined, and after evaporating the ether at room temperature the residue was distilled under reduced pressure and 0.010 mole of 2-methylpentane-2,4-diol,  $n_D^{25}$  1.4268, was recovered. About 0.4 g. of white powder remained as the residue, which gave melting point 103–105° after several recrystallization from chloroform. The total yield of the crystals (III) amounted to 3.9 g. in each case. Each product from the various tetraalkoxytitaniums was proved to be identical by mixed melting point determinations.

(e) **Reaction of II with an Equimolecular Quantity of 2-Methylpentane-2,4-diol.**—To 1.8 g. (0.006 mole) of bis-(2-methylpentane-2,4-diol)-titanium (II) dissolved in 3.9 g. of chloroform was added 0.8 g. (0.006 mole) of 2-methylpentane-2,4-diol. Reaction took place with evolution of heat and after standing several hours white needles appeared. The crystals were filtered and washed with di-

ethyl ether in the dry-box and dried *in vacuo*, m.p. 103–106°. Mixed melting point determination with the reaction product in a molar ratio 1:3 showed no depression of melting point.

*Anal.* Calcd. for  $TiC_{18}H_{36}O_6$ : Ti, 12.0. Found: Ti, 12.1.

(f) **Heat Dissociation of III to II and 2-Methylpentane-2,4-diol.**—The tris-(2-methylpentane-2,4-diol)-titanium (III), 4.0 g. (0.010 mole), was heated to 100° for 30 minutes and then to 120° for six hours at  $10^{-4}$  mm., and all the volatile matter was collected in a trap cooled with a Dry Ice-methyl alcohol mixture. The amount of liquid collected in the trap was 1.3 g. (0.011 mole) and was proved to be 2-methylpentane-2,4-diol,  $n_D^{25}$  1.4268. The white porous residue melted at 150.5–152.5°.

*Anal.* Calcd. for  $TiC_{12}H_{24}O_4$ : Ti, 17.1. Found: Ti, 17.1.

(g) **Attempted Preparation of the Pyridinium Salt of III.**—In order to test the acidic nature of the OH groups of III, the following experiment was carried out. To 1.5 g. of the tris-(2-methylpentane-2,4-diol)-titanium (III) dissolved in 2.0 g. of chloroform was added 2.0 g. of pyridine. Evolution of heat was not observed. Chloroform was evaporated from the mixture under reduced pressure and then pyridine was distilled heating the mixture at 80° under reduced pressure. The starting material was recovered as the residue, m.p. 105–108°. The tris-compound III was proved to show no tendency to form the salt with pyridine under the condition employed.

(h) **Attempted Preparation of I from II.**—The bis-(2-methylpentane-2,4-diol)-titanium (II), 0.8 g., was dissolved in 1.6 g. of ethyl alcohol. The solution was heated at 140° and 1.6 g. of ethyl alcohol, b.p. 78°,  $n_D^{25}$  1.3622, was recovered unreacted.

**Molecular Weight Determinations.**—Molecular weights were measured cryoscopically in completely dried benzene as described in the previous paper.<sup>1</sup> The determination of the molecular weight of compound I was very difficult because of the extreme sensitiveness of the compound to moisture. Freezing points of benzene solution of the compound I showed a tendency to decrease with time.

**The infrared absorption measurements** were carried out with a Perkin-Elmer recording spectrophotometer model 112 (single beam type). The spectra of all samples were first measured using a NaCl prism. Liquid samples were measured in thin films and the solid samples were measured using Nujol. The spectra of III and 2-methylpentane-2,4-diol in the 3- $\mu$  region were studied using a LiF prism in Nujol mull and in  $CCl_4$  solutions of various concentrations.

**X-Ray Diffraction Data.**—Samples were ground rapidly to a fine powder using an agate mortar in the dry-box. The powder was loaded on a glass holder shielded with a film of Mylar. The measurements were carried out using a Phillips diffractometer with copper target and nickel filter; voltage, 40 k.v.p.; current, 20 ma.; scale factor, 16; count full scale, 800 c.p.s.; time constant, 2 sec.; scanning speed, 2°/min.; divergence slit,  $1/2^\circ$ ; receiving slit,  $1/2^\circ$ ; exposure time, 30 min.

**Acknowledgment.**—The authors wish to express their sincere thanks to Professor K. Kozima and Dr. W. Suetaka for the infrared spectra and to Professor K. Kubo for X-ray analysis, and to Mr. Kōda for his assistance. The authors are indebted to the Ministry of Education for financial support.

MĒGURO, TOKYO, JAPAN