1.5156; D, residue 10.5 g. Fraction A corresponded to a 46.1% conversion to 1,3-diphenyltetramethyldisiloxane; fraction C was a 20% yield of crude *p*-phenylenebis(1,1,3,3-tetramethyl-3-phenyldisiloxane).

Phenyltris(dimethylphenylsiloxy)silane. A. From phenyltriacetoxyphenylsilane and dimethylethoxyphenylsilane: A mixture of 30.4 g. (0.169 mole) dimethylethoxyphenylsilane, 15.8 g. (0.056 mole) phenyltriacetoxysilane, and 0.1 g. of ferric chloride was heated for 24 hr. at 145–50°, then an additional 24 hr. at 150–158°. A total of 10.7 g. of distillate, which contained 67% of the expected ethyl acetate along with a small amount of ethyl alcohol and a trace of benzene, was obtained. The residue was dissolved in ether, filtered, neutralized with aqueous sodium bicarbonate, and devolatilized to give 29.4 g. of crude product. Fractional distillation gave 4.3 g. (17.7%) 1,3-diphenyltetramethyldisiloxane boiling 93–100° at 0.03–0.08 mm., n_{D}^{25} 1.5140, d_4^{25} 0.977, and 4.5 g. impure phenyltris(dimethylphenylsiloxy)silane boiling 190–240° at 0.02 mm., n_{D}^{25} 1.529, d_4^{25} 1.076 (reported[23] b.p. 217–225° at 1.0 mm., n_{D}^{25} 1.528, d_4^{25} 1.060). MR$_{\text{D}}$ Calcd.: 165.48. Found: 160.3.

Many small intermediate fractions indicated that the product was a complex mixture of high molecular weight compounds.

B. From acetoxydimethylphenylsilane and phenyltriethoxysilane: After 29.2 g. (0.15 mole) of acetoxydimethylphenylsilane, 12.0 g. (0.05 mole) of phenyltriethoxysilane, and 0.10 g. of ferric chloride were heated at 160° for 48 hr. and the volatiles collected in a Dry Ice trap, the residue was devolatilized at 0.02 mm. for 2 hr. at room temperature. The final weight loss of the mixture was 10.7 g. or 81% of the theoretical amount. The residue was filtered, diluted with ether, washed and dried in the manner described earlier. Fractional distillation through a 2-in. column gave the following fractions: A, 143–144° (6.2 mm.) 10.5 g., n_{D}^{27} 1.5124; B, 80–84° (0.02 mm.) 1.2 g., n_{D}^{27} 1.5131; C, 87–140° (0.02 mm.) 1.0 g.; D, 143–170° (0.03 mm.), 0.8 g. n_{D}^{27} 1.5176; E, residue, 12.6 g. Fraction A represented a 55% yield of 1,3-diphenyltetramethyldisiloxane, but none of the desired tri(siloxy)silane was isolated.

C. From chlorodimethylphenylsilane and phenyltriethoxysilane: When a mixture of 18.5 g. (0.108 mole) of chlorodimethylphenylsilane, 8.7 g. (0.036 mole) of phenyltriethoxysilane, and 0.1 g. of ferric chloride was heated at 100°, ethyl chloride evolution ceased after 4 hr. The crude product, 20.0 g., represented a loss of 104% of the expected weight. Benzene was identified qualitatively by gas chromatography. The neutralized residue was distilled through a 2-in. column at reduced pressure. The following fractions were collected: A, 134–135° (5.0 mm.) 2.5 g., n_{D}^{27} 1.5096; B, 130–160° (0.05 mm.), 1.9 g., n_{D}^{27} 1.5156; C, 170–80° (0.05–0.06 mm.), 1.9 g., n_{D}^{27} 1.5260, d_4^{27} 1.048; D, residue, 9.0 g. Fraction A corresponds to a 46% conversion to 1,3-diphenyltetramethyldisiloxane and Fraction C to a 9% yield of the tri(siloxy)silane MR$_{\text{D}}$ Calcd.: 165.48. Found: 163.7.

Methyltris(dimethylphenylsiloxy)silane. From methyltriacetoxysilane and dimethylethoxyphenylsilane: When 14.1 g. (0.064 mole) of methyltriacetoxysilane, 34.0 g. (0.192 mole) of dimethylethoxyphenylsilane, and 0.1 g. of ferric chloride were heated for 20 hr. at 160°, a total of 15.5 g. of distillate was collected. The volatiles contained 83.4% of the theoretical ethyl acetate and benzene representing cleavage of 8.0% of the available phenyl groups. After the product was filtered and washed, distillation in a Hickman still gave 9.6 g. (35.2%) of 1,3-diphenyltetramethyldisiloxane, 90–95°, 0.002 mm., n_{D}^{25} 1.5118, d_4^{25} 0.978, a second fraction boiling 137–42° at 0.0001 mm. (2.3 g.), and 2.9 g. (7%) impure methyltris(dimethylphenylsiloxy)silane boiling 182–200° at 0.0001 mm., n_{D}^{25} 1.4903, d_4^{25} 1.001.

Anal. Calcd. for $C_{26}H_{36}O_3Si_4$: C, 60.42; H, 7.30; Si, 22.61, MR$_{\text{D}}$ 145.66. Found: C, 58.44; H, 7.45; Si, 25.79; MR$_{\text{D}}$ 143.65.

Thermal decomposition of acetoxydimethylphenylsilane. After 16.6 g. of acetoxydimethylphenylsilane was heated at 160° for 48 hr., the residue was devolatilized for 2 hr. at 0.5 mm. The volatile materials, collected in a Dry Ice trap, weighed 0.1 g. The heating of the residue at 160° was continued for 16 hr. after 0.1 g. of anhydrous ferric chloride was added, and the product was similarly devolatilized. An additional 1.0 g. of distillate was collected and the corresponding weight loss was found in the residue. Analysis indicated that benzene and acetic acid with traces of acetic anhydride and three unidentified components were present. The amount of benzene was equivalent to 7% of the available phenyl groups and the acetic acid to 7% of the available acetoxy groups.

KANSAS CITY 10, MO.

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(23) J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

[CONTRIBUTION FROM HUGHES RESEARCH LABORATORIES, HUGHES AIRCRAFT CO.]

Syntheses and Reactions of Isopropoxy and Trimethylsiloxy Titanium Dichelates[1]

H. H. TAKIMOTO[2] AND J. B. RUST

Received October 10, 1960

Syntheses and reactions of diisopropoxy and bis(trimethylsiloxy) titanium dichelates are described. The chelating groups are those derived from 1,3-diphenyl-1,3-propanedione, 2,4-pentanedione, and 8-quinolinol. These compounds readily replace the isopropoxy and trimethylsiloxy groups attached to a titanium atom. In cases where both groups are present, the isopropoxy groups are preferentially replaced. Hydrolyses of the dichelated titanium derivatives are also described.

Organotitanium compounds have attracted attention in recent years as intermediates for the possible synthesis of semi-inorganic polymers capable of withstanding high temperatures. The excellent thermal stability of the metal chelates is well known, and because of the interest in thermally stable polymers, particularly in organometalloxanes, we have investigated the preparations and reactions of several dichelated titanium titanium derivatives.

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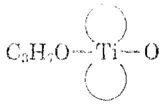
(1) Supported in part by the Office of Naval Research under Contract No. Nonr 2540 (OO).

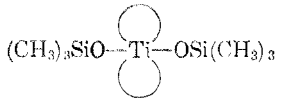
(2) Hughes Research Laboratories, A Division of Hughes Aircraft Co., Malibu, Calif.

Dichelated titanium intermediates having the following structures were prepared:



$C_3H_7O-Ti-OC_3H_7$

I

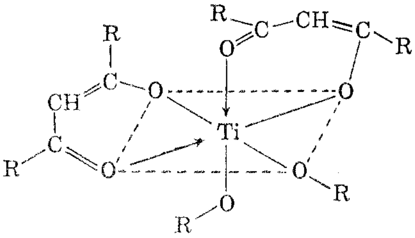


$(CH_3)_3SiO-Ti-OSi(CH_3)_3$

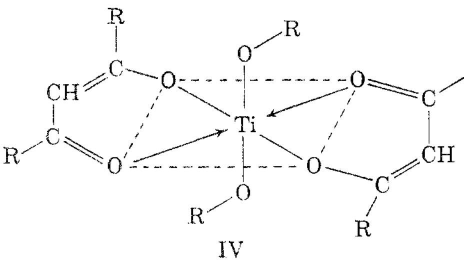
II

where  represents the chelating group derived from 1,3-diphenyl-1,3-propanedione, 2,4-pentanedione, and 8-quinolinol. Compounds having structures I and II were prepared by the reaction of the chelating agent with tetraisopropoxytitanium or with tetrakis (trimethylsiloxy)titanium, respectively. The use of a stoichiometric amount or an excess of the chelating agent resulted in the formation of the dichelated metal derivatives.

Two diasteroisomeric forms of the dichelated titanium derivatives are possible. When a β-diketone is used as the celating agent, diisopropoxy titanium derivatives may be illustrated as follows:



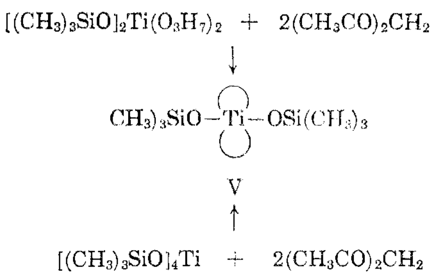
III



IV

The chelating groups are shown in III to have the *cis* configuration, whereas in IV, they have the *trans* configuration.

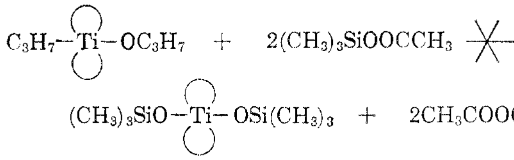
It is interesting to note that the chelating agents such as 1,3-diphenyl-1,3-propanedione, 2,4-pentanedione, and 8-quinolinol readily replaced isopropoxy or trimethylsiloxy groups attached to titanium atom. It is of further interest that these chelating groups preferentially replaced isopropoxy groups rather than trimethylsiloxy groups. Thus, an identical product, as determined from infrared spectra and elemental analyses, was obtained from the reaction of two moles of the chelating agent with one mole of diisopropoxy bis(trimethylsiloxy)titanium, or with one mole of tetrakis (trimethylsiloxy)titanium.



$$[(CH_3)_3SiO]_2Ti(O_3H_7)_2 + 2(CH_3CO)_2CH_2 \rightarrow CH_3)_3SiO-Ti-OSi(CH_3)_3 \leftarrow [(CH_3)_3SiO]_4Ti + 2(CH_3CO)_2CH_2 \quad (1)$$

V

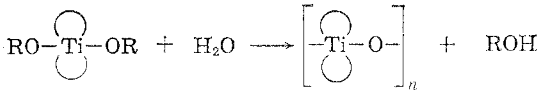
An attempt was made to obtain the siloxy titanium dichelate V by the reaction of diisopropoxy bis(2-ketopent-3-ene-4-oxy)titanium with excess trimethylacetoxysilane.



$$C_3H_7-Ti-OC_3H_7 + 2(CH_3)_3SiOOCCH_3 \not\rightarrow (CH_3)_3SiO-Ti-OSi(CH_3)_3 + 2CH_3COOC_3H_7 \quad (2)$$

The expected ester interchange (alkoxy-acyloxy) reaction, however, did not occur under the conditions used and the desired product, bis(trimethylsiloxy) bis(2-ketopent-3-ene-4-oxy)titanium was not obtained. It may be that the alkoxy-acyloxy condensation reaction is sensitive to the steric environment around the titanium atom. In addition, electrons are not available for association with the trimethylsiloxy group in the transition state; the coordination number of six is already satisfied in the titanium dichelate. These steric and electronic effects are especially evident in view of the fact that tetraisopropoxytitanium readily undergoes the alkoxy-acyloxy reaction with trimethylacetoxysilane to give the trimethylsiloxy titanium derivatives.[3,4]

The hydrolytic stability of the dichelated titanium derivatives was investigated. The compounds containing alkoxy groups were readily hydrolyzed upon contact with moisture and were converted into high-melting solids which were insoluble or only partially soluble in common organic solvents. Thus, bis(quinolin-8-oxy) titanium oxide was obtained by the treatment of diisopropoxy bis(quinolin-8-oxy)titanium with water at room temperature.



$$RO-Ti-OR + H_2O \rightarrow [-Ti-O-]_n + ROH \quad (3)$$

On the other hand, bis(trimethylsiloxy)bis(quinolin-8-oxy)titanium was recovered unchanged under the same conditions as above. It appears, therefore, that the bis(trimethylsiloxy) derivative of the dichelated titanium is less readily attacked by water

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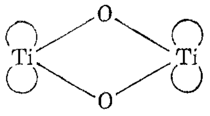
[3] D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 3404 (1959).

[4] J. B. Rust, H. H. Takimoto, and G. C. Denault, "Reaction of Trimethylacetoxysilane with Tetraisopropoxytitanium," *J. Org. Chem.*, 25, 2040 (1960).

than the corresponding diisopropoxy titanium compound. Isolation of the tetrachelated product with the dimeric structure (VI) by the hydrolysis of dialkoxy bis(2-ketopent-3-ene-4-oxy)titanium has been reported.[5]



VI

This dimer could result from only one form (III) of the diasteroisomers, since in the other form (IV) the bond angles of the alkoxy groups (or trimethylsiloxy groups) attached to titanium prohibit the formation of the small ring structure. It is possible, however, that a rearrangement of the diasteroisomers may occur under hydrolytic conditions.

Infrared spectra of the dichelated titanium derivatives were taken in carbon tetrachloride. In addition, spectra of tetraisopropoxytitanium and tetrakis(trimethylsiloxy)titanium as well as those of the chelating agents, *viz.*, 1,3-diphenyl-1,3-propanedione, 2,4-pentanedione, and 8-quinolinol, were obtained for comparison purposes.

The spectra of the chelated titanium compounds of the present study all exhibited a strong, sharp absorption band at about 1375 cm.$^{-1}$ Absorption in the region of 1575 cm.$^{-1}$ and at 1520 cm.$^{-1}$ were also observed. The latter two bands were much more pronounced in the chelates prepared from β-diketone than in the 8-quinolinolates. These results agree with those of Yamamoto and his co-worker,[5] who observed two strong bands at 1376 and 1577 cm.$^{-1}$ for trialkoxy-2-ketopent-3-ene-4-oxytitanium with nearly equal intensity and a strong band at 1523 cm.$^{-1}$ Spectra of various metal chelate compounds of 2,4-pentanedione were reported by Lecomte[6] and Bellamy[7] to exhibit two strong bands of nearly equal intensity near 1560 and 1380 cm.$^{-1}$ These investigators attributed these bands to the carbonyl group weakened by resonance between the C—O—M and C—O . . . M links. The band in the region of 1520 cm.$^{-1}$ was attributed by Lecomte to the vibration of C=C bonds of the enolic form of the β-diketone.

Diisopropoxy chelated titanium compounds showed strong broad absorption bands between 1160 and 1110 cm.$^{-1}$ and also in the region of 1000 cm.$^{-1}$ The former bands were assigned to the isopropyl skeletal vibration[8] and the latter may be a result of C—O—Ti linkage.

Chelated titanium compounds containing the trimethylsiloxy groups showed extremely strong absorption bands at about 845 and 1245 cm.$^{-1}$ These bands have been attributed to stretching and rocking vibrations, respectively, of the trimethylsilyl group.[8] The absorption band produced by C=O—Ti linkage in these compounds was shifted to a lower frequency and appeared in the region of 980 cm.$^{-1}$ instead of 1000 cm.$^{-1}$ as in the diisopropoxy titanium dichelates.

EXPERIMENTAL[9]

Materials. Commercially available tetraisopropoxytitanium and 2,4-pentane-dione were purified by fractional distillation and the fractions with b.p. 89–91°/3–4 mm. and 137–139°, respectively, were used: n_D^{25} for tetraisopropoxytitanium, 1 4608; n_D^{25} for 2,4-pentanedione, 1.4480. Commerically available 8-quinolinol melting at 75–76° and 1,3-diphenyl-1,3-propanedione melting at 76.5–78° were used.

The trimethylsiloxy derivatives of titanium were prepared by the reaction of trimethylacetoxysilane with tetraisopropoxytitanium.[4]

Reaction of tetraisopropoxytitanium with 1,3-diphenyl-1,3-propanedione in cyclohexane. 1,3-Diphenyl-1,3-propanedione (4.48 g., 0.02 mole) in 30 ml of cyclohexane was added to tetrisopropoxytitanium (2.84 g, 0.01 mole) dissolved in 15 ml. of cyclohexane. Addition of the β-diketone caused the mixture to turn bright yellow, and a precipitate of a yellow solid was observed; this solid dissolved upon heating. The refluxing was continued for 45 min. and the contents of the flask were allowed to cool to room temperature. A yellow solid again precipitated and was separated by filtration. The product, diisopropoxy bis(1,3-diphenyl-1-ketoprop-2-ene-3- oxy) titanium, weighed 5 73 g. (93.6 % yield) and melted at 170–175° after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{36}H_{36}O_6Ti$: C, 70.59; H, 5.92. Found: C, 71.10; H, 5.09.

Reaction of diisopropoxy bis(trimethylsiloxy)titanium with 1,3-diphenyl-1,3-propanedione in cyclohexane. 1,3-Diphenyl-1,3-propanedione (4.48 g., 0.02 mole) in 30 ml. of cyclohexane was added rapidly to diisopropoxy bis(trimethylsiloxy)titanium (3.44 g., 0.01 mole) dissolved in 15 ml. of cyclohexane. The mixture turned yellow when the β-diketone was added, and a yellow solid precipitated after several minutes Upon heating, the solid dissolved (slightly cloudy) and the solution was refluxed for 20 min. A yellow solid formed on cooling. The mixture was filtered to yield 5.58 g. (83 %) of solid melting at 150–163°. Recrystallizations from cyclohexane raised the melting point to 159–165°. The infrared spectrum of this solid taken in carbon tetrachloride was identical with that of the product from the reaction of tetrakis(trimethylsiloxy)titanium with 1,3-diphenyl-1,3-propanedione.

Anal. Calcd for $C_{36}H_{40}O_6TiSi_2$: C, 64.27; H, 5 99. Found: C, 64.59; H, 6.28.

Reaction of isopropoxy tris(trimethylsiloxy)titanium with 1,3-diphenyl-1,3-propanedione. 1,3-Diphenyl-1,3-propanedione (4.48 g., 0.02 mole) was added to isopropoxy tris(trimethylsiloxy)titanium (3.74 g., 0.01 mole). The colorless clear organotitanium ester became bright yellow when the β-diketone was added. The mixture was gently heated for 30 min., during which time a volatile product was formed. This volatile product (1.43 g.) was removed by heating under reduced pressure. Recrystallization of the residual material from cyclohexane yielded 3.42 g. (50.9 %) of a solid melting at 160–167°. The infrared spectrum of this product taken in carbon tetrachloride was identical with the spectrum of the

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(5) A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.*, **79**, 4344 (1957).

(6) J. Lecomte, *Disc. Faraday Soc.*, **9**, 125 (1950).

(7) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, 1958, pp. 26 and 274.

(9) All melting points are uncorrected. Microanalyses by Elek Micro Analytical Laboratories, Los Angeles, Calif.

product obtained from the reaction of tetrakiskis(trimethylsiloxy)titanium with 1,3-diphenyl-1,3-propanedione.

Reaction of tetrakis(trimethylsiloxy)titanium with 1,3-diphenyl-1,3-propanedione. 1,3-Diphenyl-1,3-propanedione (4.48 g., 0.02 mole) dissolved in 25 ml. of cyclohexane was added to tetrakis(trimethylsiloxy)titanium (4.04 g., 0.01 mole) dissolved in 10 ml. of cyclohexane. This addition caused the solution to turn yellow and a yellow solid separated out of the reaction mixture. The solid dissolved when heated, and the refluxing was continued for 20 min. Upon cooling to room temperature the entire contents of the flask again became a yellow solid. The mixture was filtered and dried in a desiccator under vacuum to give 6.28 g. (93.5 %) of the product, bis(trimethylsiloxy)bis(1,3-diphenyl-1-ketoprop-2-ene-3-oxy titanium. This material melted at 161–170° after several recrystallizations from cyclohexane.

Anal. Calcd. for $C_{36}H_{40}O_6TiSi_2$: C, 64.27; H, 5.99. Found: C, 64.39; H, 6.06.

Reaction of tetraisopropoxytitanium with 2,4-pentanedione. 2,4-Pentanedione (20.0 g., 0.20 mole) was added to tetraisopropoxytitanium (28.4 g., 0.10 mole). The reaction mixture was heated and stirred for 30 min. to yield a clear, golden solution. The low boiling product was removed under reduced pressure and the residue was fractionated to give 23.67 g. (65 % yield) of diisopropoxy bis(2-ketopent-3-ene-4-oxy)titanium boiling at 138–140°/4–5 mm, n_D^{25} 1.5440. The pale yellow liquid produce turned dark brown on standing.

Reaction of diisopropoxy bis(trimethylsiloxy)titanium with 2,4-pentanedione. 2,4-Pentanedione (2.0 g., 0.02 mole) was added to diisopropoxybis(trimethylsiloxy)titanium (3.44 g., 0.01 mole). The solution turned yellow and heat was evolved. The contents of the flask were heated gently for 1 hr. and the volatile material (1.44 g., n_D^{25} 1.3837) was removed by heating under reduced pressure. Upon cooling, the residual material solidified to a yellow crystalline solid. During the removal of the volatile material, a solid had sublimed on the walls of the flask. This solid melted sharply at 56–57°. The total yield of the crude product, bis(trimethylsiloxy)bis(2-ketopent-3-ene-4-oxy)titanium was 3.75 g. (88.4%). An infrared spectrum of this material was identical with the spectrum of the product obtained from the reaction between tetrakis (trimethylsiloxy)titanium and 2,4-pentanedione.

Anal. Calcd. for $C_{16}H_{32}O_6Si_2Ti$: C, 45.26; H, 7.61. Found: C, 45.20; H, 7.52.

Reaction of tetrakis(trimethylsiloxy)titanium with 2,4-pentanedione. 2,4-Pentanedione (2.0 g., 0.02 mole) reacted with tetrakis(trimethylsiloxy)titanium (4.04 g., 0.01 mole). The mixture became yellow and an evolution of heat was observed. The contents of the flask were heated gently for 30 min. A volatile material refluxed on the walls of the reaction vessel during the heating. At the end of the heating period globules of immiscible liquid were seen at the bottom of the flask. The low-boiling materials (1.79 g.) were removed under vacuum and heat and collected in a Dry Ice trap. Contents of the trap consisted of two phases which were probably water and hexamethyldisiloxane; the by-product of the chelating reaction, trimethylsilanol, would be expected to condense under the reaction conditions to yield these products. The liquid remaining the reaction flask turned into a pale yellow-orange solid upon cooling to room temperature; this solid melted at 54–55° and weighed 3.55 g. (83.7% yield).

Anal. Calcd. for $C_{16}H_{32}O_6Si_2Ti$: C, 45.26: H, 7.61. Found: C, 45.78; H, 7.86.

Reaction of tetraisopropoxytitanium with 8-quinolinol in carbon tetrachloride. A solution of 8-quinolinol (5.80 g., 0.04 mole) in 30 ml. of carbon tetrachloride was added to tetraisopropoxytitanium (5.68 g., 0.02 mole) dissolved in 15 ml. of carbon tetrachloride. The clear, yellow solution was refluxed for 30 min. while stirring, and after standing for 16 hr., a yellow solid had precipitated. The mixture was filtered to yield 5.89 g. (64.9%) of the product, diisopropoxybis(quinolin-8-oxy)titanium. This material, after repeated recrystallizations from either benzene or carbon tetrachloride, melted with decomposition at 170–180°; a volatile product appeared to be evolved at this temperature.

Anal. Calcd. for $C_{24}H_{26}O_4TiN_2$: C, 63.44; H, 5.77. Found: C, 63.70; H, 6.00.

Reaction of diisopropoxybis(trimethylsiloxy)titanium with 8-quinolinol in cyclohexane. A solution of 8-quinolinol (2.90 g., 0.02 mole) dissolved in 30 ml. of cyclohexane was added to diisopropoxybis(trimethylsiloxy)titanium (3.44 g., 0.01 mole) dissolved in 15 ml. of cyclohexane. The mixture turned bright yellow upon the addition of the chelating agent. After refluxing for 20 min., the mixture was allowed to cool to room temperature yielding a bright yellow solid. The mixture was filtered to give a yellow crystalline solid (4.37 g., 85%). This product melted at 144–148° and gave an infrared spectrum identical with the product from the reaction of tetrakis(trimethylsiloxy)titanium with 8-quinolinol.

Anal. Calcd. for $C_{24}H_{30}O_4TiSi_2N_2$: C, 56.02; H, 5.88. Found: C, 54.86; H, 6.11.

Reaction of tetrakis(trimethylsiloxy)titanium with 8-quinolinol in cyclohexane. A solution of 8-quinolinol (2.90 g., 0.02 mole) in 30 ml. of cyclohexane was added to tetrakis(trimethylsiloxy)titanium (4.04 g., 0.01 mole) dissolved in 15 ml. of cyclohexane. The reaction mixture immediately turned bright yellow, and after 10 min. the entire content of the flask was converted into a yellow solid. This solid dissolved on heating, and the solution was then refluxed for 20 min. Upon cooling, the yellow solid again precipitated. The solid was separated and dried under a vacuum in a desiccator to yield 4.69 g. (91 %) of bis(trimethylsiloxy)bis(quinolin-8-oxy)titanium melting at 145–148°.

Hydrolysis of diisopropoxybis(quinolin-8-oxy)titanium. Diisopropoxybis(quinolin-8-oxy)titanium (2.27 g., 0.005 mole) was hydrolyzed by stirring with water (5 ml.) for 30 min. The yellow solid turned orange in color upon contact with water. The mixture was filtered and the solid was washed twice with water and then with benzene, yielding a product which was soluble in chloroform and acetone but insoluble in carbon tetrachloride and benzene. Yellow needles were obtained upon recrystallization of the solid from chloroform, but upon standing for several days, the needles became insoluble in the same solvent. The product did not melt below 300° but turned brown in color at about 280°.

Anal. Calcd. for $C_{18}H_{12}O_3TiN_2$: C, 61.38; H, 3.43. Found: C, 60.26; H, 3.87.

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