with two 200-ml. portions of ether and the organic layers were combined and dried over anhydrous calcium chloride before evaporation and addition of petroleum ether which caused the precipitation of 7.3 g. (73%) of a compound melting at 124–125°. This solid was recrystallized from ethyl alcohol–ethyl acetate and cyclohexane–petroleum ether (b.p. 60–70°) to yield a solid melting at 147–148°.

Anal. Calcd. for $C_{72}H_{62}Si_6$: C, 79.00; H, 5.71; Si, 15.30. Found: C, 79.15, 79.23; H, 6.28, 6.03; Si, 15.50. Hydrogen value: calcd. for seven moles of hydrogen per $C_{72}H_{62}Si_6$, 143.5 [ml. at S.T.P./g. of compound]. Found: 144.5, 147. Molecular Weight (perylene method). Calcd.: 1096. Found: 1105, 1044.

Preparation of 1,1,1,2,2,3,3-heptaphenyltrisilane. A solution of triphenylsilyllithium was prepared from 20 g. of hexaphenyldisilane, excess lithium, and tetrahydrofuran (200 ml.). The solution was assayed to contain 98% of the theoretical amount of triphenylsilyllithium (0.377*N*). To a solution of 8.8 g. (0.020 mole) of *sym*-dichlorotetraphenyldisilane[8] in 50 ml. of tetrahydrofuran was added 55 ml. of the above prepared solution of triphenylsilyllithium (containing 0.020 mole of silyllithium compound). The color of the silyllithium solution disappeared immediately on addition to the dichlorodisilane. A Color Test[14] revealed there was no organosilylmetallic compound present in the solution. To this solution was then added 0.19 g. (0.05 mole) of lithium aluminum hydride and the solution was refluxed for a total of 14 hours. Hydrolysis was accomplished by pouring the solution into 400 ml. of 1.0*N* hydrochloric acid stirred rapidly by a counter-rotating stirrer (1500 r.p.m.). The aqueous layer was extracted with 500 ml. of benzene and the organic extracts combined and dried over anhydrous calcium chloride before concentration and chromatography. There was obtained 1.8 g. (35%) triphenylsilane identified by its infrared spectrum and by mixed melting point with an authentic sample; 2.4 g. (19%) of heptaphenyltrisilane melting at 157–158° after recrystallization from benzene–petroleum ether (b.p. 60–70°), a mixed melting point with an authentic sample[3] was not depressed; 3.4 g. (27%) heptaphenyltrisilanol-1, m.p. 165–166° after recrystallization from benzene–petroleum ether (b.p. 60–70°); 0.5 g. (5%) decaphenyltetrasilane, m.p. 350–352°; and various other minor quantities of pentaphenyldisilane, m.p. 122–123°, *sym*-tetraphenyldisilanediol, and *sym*-tetraphenyldisilane were identified.

Anal. Calcd. for heptaphenyltrisilanol-1 $C_{42}H_{36}Si_3O$: C, 78.70; H, 5.66; Si, 13.22. Found: C, 79.05, 79.12; H, 5.75, 5.60; Si, 13.05, 13.09.

Reaction of dichlorodiphenylsilane with sodium dispersion. A 500-ml. flask was equipped with an efficient stirrer, a condenser topped by a nitrogen inlet, and an addition funnel constructed in such a manner that its content could be stirred by a magnetic stirrer before addition to the flask. The reaction flask was charged with 21.2 g. (0.082 mole) of dichlorodiphenylsilane and 100 ml. of ether. Sodium dispersion (22.6% sodium in alkylate) was added dropwise until a total of 20 ml. (16 g., 0.158 mole) had been added. After 1 min. stirring, a considerable amount of heat was generated and the solution refluxed rapidly while the reaction mixture turned dark brown with a purple precipitate. Sufficient heat was generated during the following 30 min. to maintain reflux. The mixture was stirred for an additional 24 hours while heat was supplied to keep the solvent refluxing. The suspended material was allowed to settle and a Color Test[14] revealed the presence of an organosilylmetallic species. An aliquot was removed for analysis of base content after hydrolysis. The solution was found to be 1.4*N* in base.

To the reaction mixture was added a mixture of 40 ml. of glacial acetic acid, 60 ml. of absolute ethanol, and 100 ml. of petroleum ether (b.p. 60–70°). Heat was evolved and the brown color of the solution changed to light purple. The suspension was then added to 400 ml. of water and the precipitate filtered off and washed thoroughly on the filter with water. The solid was dried in air to give 12.5 g. (70%) of a compound melting at 155–160°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) yielded 1,1,2,2,3,3,-4,4-octaphenyltetrasilane[10] as the major fraction, m.p. 161–162°, mixed m.p. with an authentic sample was not depressed and the infrared spectra were superimposable.

Anal. Calcd. for $C_{48}H_{42}Si_4$: C, 78.84; H, 5.79; Si, 15.37. Found: C, 78.54, 78.54; H, 5.68, 5.73; Si, 15.10, 15.42. Hydrogen value: calcd. for 5 mole of hydrogen per mole of compound: 153 [ml. at S.T.P./g.]. Found: 150, 158.

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AMES, IOWA

[CONTRIBUTION FROM MIDWEST RESEARCH INSTITUTE]

Triorganosilyl Derivatives of Chelated Titanates[1]

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Silyl titanates of titanium (IV), with two normal valences and two coordinating valences forming chelate rings with 8-quinolinol, dibenzoylmethane, and acetylacetone, are prepared by a variety of procedures. The methods involve displacements of functional groups on titanium chelates without disturbing the chelate rings.

Because compounds of titanium(IV) are tetrafunctional and do not form stable bonds with carbon except in the cyclopentadienyl series, they are not considered suitable for the preparation of linear polymers similar to siloxanes derived from difunctional silicon compounds. However, titanium derivatives may be partially substituted with groups capable of forming very stable chelate rings by coordination with the titanium atom. If a titanium compound is substituted with two chelating groups and if the remaining two groups may be preferentially displaced in condensation reactions, the compound is effectively difunctional in polymerization reactions.

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Condensation of titanium derivatives containing two chelating substituents with certain difunctional silicon compounds may be expected to yield chains of alternately ordered silicon and titanium atoms joined by oxygen. Prototypes of silicon- and titanium-containing polymers should be obtained when chelated titanium intermediates are treated with monofunctional silicon compounds.

An investigation of the preparation of prototype compounds containing the Si-O-Ti-O-Si group has been undertaken to determine if those derivatives in which titanium is substituted by two chelating groups may be satisfactorily obtained. Condensation reactions between silicon- and titanium-containing compounds have been discussed recently in a review by Shiihara *et al.*[2] and good yields of compounds containing the Si-O-Ti group were usually obtained. The extension of these procedures to the synthesis of organosilyl derivatives of chelated titanium compounds has not been previously investigated.

Although titanium (IV) coordination complexes were reported as early as 1905 by Dilthey,[3] only in 1957 did Yamamoto and Kambara[4] isolate and identify monomeric acetylacetone and ethyl acetoacetate derivative of titanium alkoxides. In 1958 Pande and Mehrotra[5] demonstrated that the acetylacetone derivative of titanium tetrachloride was monomeric (structure A, Fig. 1) rather than the double salt (structure B, Fig. 1) suggested by Dilthey.[3]

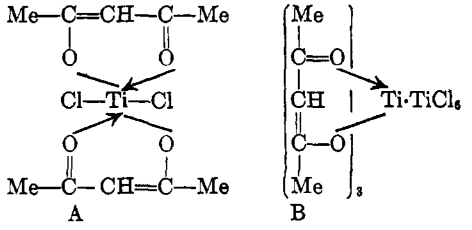

Fig. 1. Structure of chelated titanium compounds

More recently, Frank *et al.* reported the products obtained by treating titanium isopropylate with various chelating compounds,[6] and Takimoto prepared chelated silyl titanates from silyl titanates or mixed silyl alkyl titanates and acetylacetone, dibenzoylmethane, and 8-quinolinol.[7]

DISCUSSION

Silyl titanates of titanium (IV), with two normal valences and two coordinating valences forming a chelate ring with 8-quinolinol, were readily prepared by the reaction sequences shown in Fig. 2. The structure of the titanium chloride intermediate is undoubtedly not truely represented by the simple molecular formula shown in Fig. 2, as the material is insoluble in non-polar solvents and does not melt below 280°

8-Quinolinol Derivatives

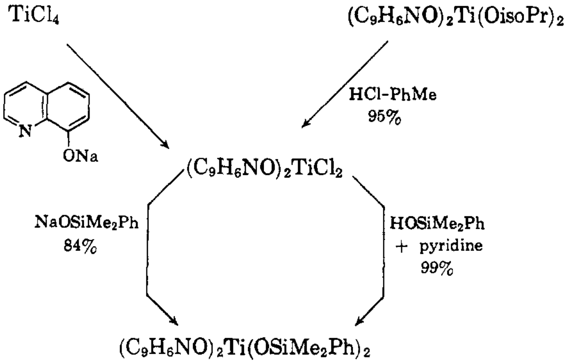

Fig. 2. Synthesis of chelated silyl titanates

Quantitative yields of the products resulting from the displacement of isopropylate groups without disturbing the chelate groups were obtained when the dibenzoylmethane or the 8-quinolinol derivatives of titanium isopropylate were treated with triphenylsilanol. Similarly, the 8-quinolinol derivative of titanium isopropylate and dimethylphenylsilanol gave products in which the chelate group remained intact.

8-QUINOLINOL DERIVATIVES

$$(C_9H_7NO)_2Ti(OisoPr)_2 + Ph_3SiOH \xrightarrow{C_6H_6} (C_9H_7NO)_2Ti(OSiPh_3)_2$$

$$(C_9H_7NO)_2Ti(OisoPr)_2 + Me_2PhSiOH \xrightarrow{C_6H_6} (C_9H_7NO)_2Ti(OSiMe_2Ph)_2$$

DIBENZOYLMETHANE DERIVATIVE

$$(C_{15}H_{11}O_2)_2Ti(OisoPr)_2 + Ph_3SiOH \xrightarrow{C_6H_6} (C_{15}H_{11}O_2)_2Ti(OSiPh_3)_2$$

The compounds are the first reported partially substituted triphenylsiloxy derivatives of titanium.

The preparation of analogous compounds by the displacement of alkoxy groups in acetylacetone chelates with triphenylsilanol was unsuccessful.

Acetylacetone Derivative

$$(C_5H_7O_2)_2Ti(OisoPr)_2 + Ph_3SiOH \xrightarrow{C_6H_{12}} Ti(OSiPh_3)_4$$

Only tetrakis(triphenylsiloxy)titanium was obtained. This result is consistent with Zeitler's observation that only tetrasubstituted derivatives are obtained by treating orthotitanates with triphenylsilanol, regardless of the stoichiometry of the starting materials.[8]

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[2] I. Shiihara, T. Willis, T. Schwartz, Jr., and H. W. Post, *Chem. Revs.*, 61 (1961).

[3] W. Dilthey, *Ann.*, **344**, 305 (1905).

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

[5] K. C. Pande and R. C. Mehrotra, *Chem. & Ind.* (*London*), 1198 (1958).

[6] R. L. Frank, A. Baldoni, and T. R. Patterson, Jr., AFOSR-TR-58-18 (1958); ASTIA Document No. AD 148137.

[7] J. B. Rust, C. L. Segal, and H. H. Takimoto, Technical Report No. 3, Contract Nonr 2540(00) (1959). Abstracts of Papers, 137th Meeting, American Chemical Society, Cleveland, Ohio, p. 88–O

[8] V. A. Zeitler and C. A. Brown, *J. Am. Chem. Soc.*, **79**, 4616 (1957).

Another satisfactory method for preparing chelated silyl titanates makes use of condensed titanium oxide derivatives. The use of condensed titanium compounds as starting materials in the synthesis of titanium derivatives is advantageous as the oxides are insoluble and nonvolatile and may be easily separated from the products.

Condensed titanium oxides, which are presumably dimeric, are obtained when dichelated titanium derivatives are hydrolyzed. The dimeric structure is consistent with the currently accepted models for the structure of titanium alkoxides.[9] Although oxides have been reported as the product of the hydrolysis of a bis-8-quinolinol derivative and a bis-acetylacetone derivative of titanium isopropylate, only the latter oxide has been satisfactorily characterized.[4,6]

Preferential displacement was observed in the 8-quinolinol series when the hydrolyzed titanium chelate was treated with triphenylsilanol and the water formed in the reaction was removed by azeotropic distillation.

8-Quinolinol Derivative

$$[(C_9H_7NO)_2TiO]_2 + Ph_3SiOH \longrightarrow (C_9H_7NO)_2Ti(OSiPh_3)_2 + H_2O$$

The oxide of the dichelated derivative of acetylacetone, treated with ethoxytrimethylsilane, gave a significant quantity of the *disubstituted* silyl titanate.

Acetylacetone Derivative

$$[(C_5H_7O_2)_2TiO]_2 + Me_3SiOEt \xrightarrow{C_6H_{14}} (C_5H_7O_2)_2Ti(OSiMe_3)_2$$

As Nesmeyanov had reported that a monomeric dialkoxytitanium oxide condensed with silicon isopropylate and gave a product with a ketal-like structure,[10] failure to obtain a similar addition with the analogous chelated titanium oxide derivative confirms that the structures of the two oxides are not identical.

Another method of preparation of silyl titanates is a transesterification reaction between the appropriate titanium alkoxides and silicon acetates. Although these reactants in refluxing cyclohexane give high yields of silyl ortho-titanates,[11] no evidence could be found that a reaction had occurred when bis(8-oxyquinoline)bis(isopropoxy)titanium was treated with acetoxydimethylphenylsilane in refluxing cyclohexane or toluene. But after the solvent was removed from the mixture and the residue was heated at 150–160° for several hours, a near quantitative yield of the silyl titanate was obtained.

8-Quinolinol Derivative

$$(C_9H_7NO)_2Ti(OisoPr)_2 + Me_2PhSiOAc \longrightarrow (C_9H_7NO)_2Ti(OSiMe_2Ph)_2 + isoPrOAc$$

Attempts to prepare acetylacetone derivatives by similar procedures gave isopropyl acetate, which would be expected if a transesterification reaction had occurred. It was subsequently shown, however, that the isopropyl acetate was produced as a result of the thermal decomposition of the titanium-containing starting material rather than from transesterification, and no silyl titanates were obtained.

EXPERIMENTAL[12]

Bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium. *Intermediates.* Chlorodimethylphenylsilane, b.p. 191–194°, was obtained in a 57% yield by treating dichlorodimethylsilane with ethereal phenylmagnesium bromide. The chlorosilane was converted into acetoxydimethylphenylsilane, b.p., 128–129° at 40 mm., n_D^{25} 1.4869, in a 74% yield with glacial acetic acid in the presence of pyridine.

Bis(8-oxyquinoline)diisopropoxytitanium was prepared as follows: After 125.2 g. (0.44 mole) titanium tetraisopropylate in 200 ml. of toluene was added slowly (2 hr.) to a stirred solution of 145.1 g. (0.88 mole) 8-quinolinol in 400 ml. toluene, the product was stirred for an additional 1/2 hr. and then about one-half the toluene was removed by distillation. Crystallization occurred when the solution was cooled at 4° overnight. The crystalline mass, separated by decantation and dried *in vacuo*, gave 178.5 g. of a yellow-orange product melting at 174–176°. (Reported m.p. 172–173°,[17] 160–170°.)[7] An additional 5.5 g. (total yield, 92%) was obtained by concentrating and cooling the mother liquor.

Anal.[13] Calcd. for $C_{24}H_{26}N_2O_4Ti$: Ti, 10.54. Found: Ti, 10.50, 10.58.

Sodium dimethylphenylsilanolate, prepared from *sym*-diphenyltetramethyldisiloxane according to the procedure of Hyde,[14] had a neutralization equivalent of 189.7 and 190.9 (calcd., 174.2) and was not sufficiently pure. The crude salt was converted to the silanol by treating its solution in ether with aqueous acetic acid and distilling the product to yield pure dimethylphenylsilanol, b.p. at 16 mm., n_D^{25} 1.5090. The over-all yield from the disiloxane was 61%. When an ether solution of the silanol was treated with sodium ribbon and the resulting ether solution of the product was decanted and evaporated, 98% of sodium dimethylphenylsilanolate, m.p. 84–92°, was obtained as a residue.

Sodium 8-oxyquinoline, prepared by the method described by Süe,[15] had a neutralization equivalent of 170 and 171 (calcd., 167.2) and did not melt below 260°.

Bis(8-oxyquinoline)dichlorotitanium could not be purified when it was prepared by treating either sodium 8-oxy-

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(9) D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.*, 3977 (1955).

(10) A. N. Nesmeyanov and O. V. Nogina, *Doklady Akad. Nauk S.S.S.R.*, **117**, 249 (1957).

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

(12) All reactions involving silicon chloride or acetates or titanium alkoxides or chlorides were protected from atmospheric moisture with calcium chloride. Glassware was oven-dried prior to use, assembled, and flushed with dry nitrogen before the reactants were introduced. Anhydrous solvents were used with moisture sensitive compounds. Titanium tetrachloride, titanium tetraisopropylate, acetylacetone, and ethyl acetoacetate were each fractionally distilled just prior to use.

(13) Analyses for titanium and for total oxides in compounds containing both silicon and titanium were carried out by decomposing samples in hot sulfuric acid or sulfuric-nitric acid mixtures and determining the weight of the material obtained after ignition. All other analyses were performed by Spang Microanalytical Laboratory, Box 1111, Ann Arbor, Mich.

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

(15) P. Süe and G. Wetroff, *Bull. soc. chim.* [5] **2**, 1002 (1935)

quinolinate or 8-quinolinol with titanium tetrachloride. The pure dichloride, however, was prepared by the following procedure.

Dry gaseous hydrogen chloride was bubbled through a stirred solution of 25 g. (0.055 mole) of bis(8-oxyquinoline)-diisopropoxytitanium until the color of the solution, which changed from yellow to red, became black. After 5 hr. additional stirring, the insoluble product was collected by filtration, washed with toluene, and dried *in vacuo*. The yield of bis(8-oxyquinoline)dichlorotitanium was 21.3 g. (95%), and the compound did not appear to melt or decompose below 280°.

Anal. Calcd. for $C_{18}H_{12}Cl_2N_2O_2Ti$: Cl, 17.42; N, 6.88; Ti, 11.77. Found: Cl, 17.38; N, 6.60; Ti, 11.33, 11.49.

From acetoxydimethylphenylsilane and bis(8-oxyquinoline)-diisopropoxytitanium: When 16.3 g. (0.036 mole) bis(8-oxyquinoline)diisopropoxytitanium, 14.0 g. (0.072 mole) acetoxydimethylphenylsilane, and 100 ml. toluene were heated and the solvent was allowed to distill from the mixture, no isopropyl acetate was detected in the distillate by gas phase chromatography. During the distillation, the volume of the mixture was kept constant by the addition of toluene. After 3 hr. heating the solvents were distilled from the mixture, the residue was heated to 150–160° for 1 hr., at 185° for 5 hr., and finally devolatilized at room temperature under reduced pressure. The product, 25.4 g. (quantitative yield), which melted at 137–139°, was relatively pure bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium. The melting point remained unchanged after the compound was recrystallized from cyclohexane or exposed to atmospheric moisture overnight.

Anal. Calcd. for $C_{34}H_{34}N_2O_4Si_2Ti$: C, 63.92; H, 5.37; N, 4.39; total oxides 31.33; M.W., 638. Found: C, 63.37; H, H. 5.59; N, 4.34; total oxides 30.82, 30.68; M.W. (K_f, benzene = 5.12), 527, 568.

The infrared absorption spectrum of the compound showed a strong band at 906 cm.$^{-1}$ (Si—O—Ti) and the appropriate bands associated with the Si-phenyl and the Si-methyl bonds and the 8-oxyquinoline group.

From the crude titanium chloride and the silanol salt. To a 500 ml. flask was added 18.2 g. (0.109 mole) sodium 8-oxyquinolinate and 150 ml. benzene. The mixture was stirred, and a solution of 10.3 g. (0.054 mole) freshly distilled titanium tetrachloride in 75 ml. benzene was added dropwise over a 5 hr. period. At the end of the addition the mixture was stirred and refluxed for 3 hr.

The crude product (containing unseparated sodium chloride) was treated with a solution of 19.0 g. (0.109 mole) sodium dimethylphenylsilanolate in 50 ml. of anhydrous ether over a 90 min. period, and then the product was refluxed for 15 hr. Filtration gave 13.5 g. insoluble salts (calculated for sodium chloride, 12.7 g.), and a filtrate that was evaporated under reduced pressure to yield 31.7 g. (92%) of crude bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium, melting 120–124°.

Recrystallization of a portion of the product from cyclohexane gave a material that melted at 138–140°, for which an infrared spectrum was obtained identical to the spectrum from the product of the reaction of bis(8-oxyquinoline)diisopropoxytitanium and acetoxydimethylphenylsilane. A mixed melting point of the two samples was 137–139°.

From the pure titanium chloride and the silanol salt: Five grams (0.033 mole) dimethylphenylsilanol dissolved in 25 ml. diethyl ether were added to 1.7 g. (0.074 g. atom) sodium wire covered with 50 ml. of diethyl ether. After the mixture was stored overnight, the filtered solution of the sodium salt was transferred to a dropping funnel and added to a stirred mixture of 6.5 g. (0.16 mole) of pure bis(8-oxyquinoline)dichlorotitanium and 100 ml. benzene over a 1 hr. period. The mixture was heated at reflux during the addition and heating was continued for 4 hr. after the addition was complete. The cooled product was filtered to remove the salts, which were thoroughly washed with benzene, and the combined filtrate and washings were evaporated under reduced pressure to yield 8.6 g. (84%) of crude bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium, which melted at 137–138° after recrystallization from cyclohexane.

From the silanol and the titanium chloride in the presence of pyridine. To a stirred mixture of 9.9 g. (0.024 mole) of bis-(8-oxyquinoline)dichlorotitanium, 4.3 g. (0.055 mole) of pyridine, and 75 ml. benzene was added a solution of 7.4 g. (0.049 mole) of dimethylphenylsilanol in 25 ml. benzene over a 45 min. period. The mixture was heated during the addition, and heating was continued for 2 hr. after the addition was complete. When the product was filtered and the benzene was removed from the filtrate under reduced pressure, 15.8 g. (100%) of crude bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium melting 132–136° was obtained. The product, recrystallized from cyclohexane, melted at 139–140° and did not depress the melting point of an authentic sample.

From the titanium alkoxide and the silanol. A 250 ml. flask was charged with 9.95 g. (0.022 mole) of bis(8-oxyquinoline)-diisopropoxytitanium and 100 ml. of benzene. The stirred mixture was heated to reflux and treated with a solution of 6.7 g. (0.044 mole) dimethylphenylsilanol in 15 ml. of benzene over a period of 1 hr. The benzene–isopropyl alcohol azeotrope, which boiled at 73°, was allowed to distill from the mixture while additional benzene was added to maintain constant volume. When the distillation temperature reached 79°, no more isopropyl alcohol could be detected in the distillate by gas phase chromatography and a total of 150 ml. of solvent had been collected. After the product was filtered to remove a small amount of insoluble material (about 0.1 g.), the benzene was removed under reduced pressure. There was obtained as a residue 14.3 g. (quantitative yield) of bis(dimethylphenylsiloxy)bis(8-oxyquinoline)-titanium, which melted at 139–140°. A mixed melting point with an authentic sample was 138–140°.

Bis(8-oxyquinoline)bis(triphenylsiloxy)titanium. *From the titanium alkoxide and the silanol.* With a procedure similar to to the preparation above, 9.95 g. (0.022 mole) bis(8-oxyquinoline)diisopropoxytitanium in 100 ml. of benzene, treated with 12.1 g. (0.044 mole) of triphenylsilanol in 50 ml. of benzene, gave 19.1 g. (99%) of crude bis(8-oxyquinoline)bis(triphenylsiloxy)titanium melting at 184–188°. A portion of the product, recrystallized from benzene-cyclohexane, gave yellow crystals melting at 189–191°.

Anal. Calcd. for $C_{54}H_{42}N_2O_4Si_2Ti$: C, 73.11; H, 4.77; N, 3.15; total oxides, 22.56. Found: C, 71.91; H, 4.28; N, 3.34; total oxides, 22.83, 22.86.

The infrared absorption spectrum of this compound showed a strong band at 915 cm.$^{-1}$ (Si—O—T), Si-phenyl absorption at 1433 cm.$^{-1}$, and various bands associated with the 8-oxyquinoline group.

From the titanium oxide and the silanol. Bis(8-oxyquinoline) titanium oxide was prepared from bis(8-oxyquinoline)diisopropoxytitanium in a quantitative yield according to the procedure of Frank.[6] The compound decomposed at about 360° when it was heated in a sealed tube.

Anal. Calcd. for $C_{18}H_{12}O_3N_2Ti$: N, 7.96; Ti, 13.60. Found: N, 7.69, 7.82; Ti, 13.00, 13.06.

When 3.52 g. (0.01 mole) of bis(8-oxyquinoline)titanium oxide, 5.52 g. (0.02 mole) of triphenylsilanol, and 50 ml. of benzene were refluxed and stirred for 1 hr., the oxide dissolved and about 0.4 ml. of water was collected in a Dean-Stark trap connected to the system. Evaporation of the benzene *in vacuo* gave 8.6 g. (97%) of crude bis(8-oxyquinoline)bis(triphenylsiloxy)titanium melting at 182–186°. The pure material, recrystallized from methylcyclohexane, melted at 190–191°.

Bis(1-oxy-1-propene-1,3-diphenyl-3-one)bis(triphenylsiloxy)titanium. *Bis(1-oxy-1-propene-1,3-diphenyl-3-one)diisopropoxytitanium.* To a stirred solution of 18.8 g. (0.066 mole) titanium isopropylate in 75 ml. of benzene was added over a period of 1 hr. 29.7 g. (0.132 mole) dibenzoylmethane dissolved in 60 ml. benzene. After the reactants were stirred for 3 hr., a yellow precipitate had formed, which was colected on a Büchner funnel, washed with two 25 ml. portions of benzene, and dried *in vacuo*. The product, which weighed 29.1 g. (72%), melted at 185–187°.

Anal. Calcd. for $C_{36}H_{36}O_6Ti$: C, 70.58; H, 5.92; Ti, 7.82. Found: C, 70.69; H, 6.01; Ti, 7.86, 7.91.

Bis(1-oxy-1-propene-1,3-diphenyl-3-one)bis(triphenylsiloxy)titanium. A solution of 4.45 g. (0.007 mole) of bis(1-oxy-1-propene-1,3-diphenyl-3-one)diisopropoxytitanium in 35 ml. of benzene was treated with 4.0 g. (0.014 mole) of triphenylsilanol over 30 min., while the mixture was stirred and refluxed. Heating was continued for 3 hr. and the benzene–isopropyl alcohol azeotrope was allowed to distill from the reaction flask. The solvents were removed *in vacuo* to yield 7.9 g. of the product melting at 210–216°. An analytical sample, which was prepared by recrystallization from benzene, melted at 233–238°.

Anal. Calcd. for $C_{66}H_{52}O_6Si_2Ti$: C, 75.86; H, 5.02; total oxides, 19.15. Found: C, 75.76; H, 5.26; total oxides, 18.84. 18.75.

Bis(2-oxy-2-pentene-4-one(bis(trimethylsiloxy)titanium. *From bis(2-oxy-2-pentene-4-one)titanium oxide and ethoxytrimethylsilane.* Bis(2-oxy-2-pentene-4-one)diisopropoxytitanium was prepared by treating 145.6 g. (0.51 mole) titanium isopropylate with 102.6 g. (1.01 moles) acetylacetone in 100 ml. cyclohexane. The product, boiling 135–137° at 0.08 to 0.1 mm., was obtained in 79.2% yield after fractional distillation (reported b.p. 121–122° at 0.3 mm.).[6]

Anal. Calcd. for $C_{16}H_{28}O_6Ti$: 13.15. Found: Ti, 12.96, 12.91.

The diisopropylate was converted into bis(2-oxy-2-pentene-4-one)-titanium oxide according to the method of Yamamoto[4] in a yield of 79 per cent.

Anal. Calcd. for $C_{10}H_{14}O_5Ti$: Ti, 18.28. Found: Ti, 18.26, 18.41.

A mixture of 7.9 g. (0.03 mole) bis(2-oxy-2-pentene-4-one)-titanium oxide, 3.8 g. (0.03 mole) ethoxytrimethylsilane, and 20 ml. of *n*-hexane was refluxed for 20 hr. The volatiles were removed under reduced pressure and collected in a Dry Ice trap. The nonvolatile portion was mixed with anhydrous ether, filtered, and the filtrate was evaporated and dried under reduced pressure (final pressure at room temperature, 0.04 mm.). An attempt to distill the 3.6 g. of residue through a short path apparatus at 0.06 mm. gave 1.4 g. of a distillate boiling at 110° which solidified on cooling. This product, melting at 49–50°, was unaffected by atmospheric moisture and was identified as bis(2-oxy-2-pentene-4-one)bis(trimethylsiloxy)titanium (reported m.p. 56–57°.[7] The yield was 9%.

Repetition of the procedure using 10.0 g. (0.038 mole) bis(2-oxy-2-pentene-4-one)titanium oxide, 10.0 g. (0.085 mole) ethoxytrimethylsilane, and 40 ml. benzene gave 3.0 g. (19 per cent) of the same product boiling 113–116° at 0.1 mm.

Anal. Calcd. for $C_{16}H_{32}O_6Si_2Ti$: C, 45.27; H, 7.60; M.W., 425. Found: C, 45.57; H, 8.03; M.W. (K_f, benzene = 5.12), 367, 369).

Although the experimental molecular weights are low, they are low by about the same degree of magnitude as those reported by Yamamoto[4] for the corresponding titanium alkoxides. The infrared spectra of this compound and the titanium oxide contained bands at 1378, 1545, and 1600 cm.$^{-1}$, indicating the presence of the acetylacetone group in both compounds.[4] Absorption at 751, 844, and 1248 cm.$^{-1}$ also established the trimethylsiloxy group[16] in the subject compound. In the region where Si–O–Ti absorption may be expected, 919 and 925 cm.$^{-1}$,[17] no sharp bands were found, but rather a broad band extending from about 980–940 cm.$^{-1}$.

Tetrakis(triphenylsilyl)titanate. *From bis(2-oxy-2-pentene-4-one)diisopropoxytitanium and triphenylsilanol.* A solution of the title compounds,7.26 g. (0.02 mole) and 11.0 g. (0.04 mole), respectively, in 50 ml. cyclohexane was heated at 70° for 24 hr. During the reflux period, 2 g. of tetrakistriphenylsiloxy)titanium formed. This product, which was collected by filtration, decomposed at about 505° in a sealed tube. The compound has been reported to melt at 501–505°.[8] From the filtrate 5.6 g. of triphenylsilanol was recovered.

Anal. Calcd. for $C_{72}H_{60}O_4Si_4Ti$: C, 75.23; H, 5.25. Found: C, 75.53; H, 5.49.

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[Contribution from the Department of Chemistry, Duquesne University]

Preparation and Properties of Trialkylfluorosilanes[1]

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The preparation of symmetric and unsymmetric trialkylfluorosilanes, from C_8H_{17}— to $C_{18}H_{37}$—, by various methods is reported. Since the synthesis of unsymmetrical trialkylfluorosilanes involves preparing the alkyloxysilane and alkyltrifluorosilane as intermediates, the synthesis of those compounds is also described. The physical properties of all the newly synthesized compounds are reported.

Jaeger and Dykstra[4] reported the first synthesis of symmetric trialkylfluorosilanes (R_3SiF) as a side product in the reaction of silicon tetrafluoride with ethylmagnesium bromide. Gierut, Sowa, and Nieuwland[5] obtained yields of R_3SiF up to fifty per cent from the reaction of silicon tetrafluoride with propyl, butyl, and amyl Grignard reagents.

The symmetrical trialkylfluorosilanes in this study were prepared by the method of Gierut et al.[5]

As can be observed from Table I, the yield of

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