TABLE I

SOME PROPERTIES OF ANALOGOUS SILICON AND TITANIUM DERIVATIVES

	$[(CH_3)_3SiO]_4Si$	$[(CH_3)_3SiO]_4Ti$	$[(C_6H_5)_3SiO]_4Si$	$[(C_6H_5)_3SiO]_4Ti$
M.p., °C.	−60	.....	235	501–5
B.p., °C.	91 (9 mm.)	106 (7 mm.)	249 (1 mm.)	Subl.
	220 (733 mm.)			370 (1 mm.)
Density	0.8677 (20°)	0.9078 (20°)	.....	1.215 (29°)
Ref. index	1.3895 (20°)	1.4278 (20°)	.....	1.6488 (114°)
Sol. in benzene	Very sol.	Very sol.	Very sol.	Very slightly sol.

In each case, the desired product was obtained but method (a) proved to be the best method and is the only one described below. It should be noted that a transesterification reaction was not successful.

Preparation of $[(C_6H_5)_3SiO]_4Si$.—Triphenylsilanol, 0.257 mole, dissolved in 750 ml. of dry toluene, was placed in a two-liter, three-neck flask. The flask was equipped with a Trubore stirrer, reflux condenser and a dropping funnel. Freshly cut sodium, 0.25 mole, was added in small pieces. The evolution of hydrogen was slow until the temperature was raised to the melting point of sodium. The triphenylsiloxysodium precipitated as a fine white powder[12] upon cooling. Then $SiCl_4$, 0.075 mole, in 50 ml. of dry toluene, was placed in the dropping funnel and added slowly over a period of two hours to the vigorously stirred mixture. The resulting mixture was refluxed 30 hours. On cooling, a heavy deposit of crystals formed on the stirrer and on the walls above the fine deposit of NaCl. The cold solution was filtered and the residue washed with two 250-ml. portions of dry toluene. The washings and filtrate were combined and distilled to recover the bulk of the tetrakistriphenylsiloxysilane which is more soluble in toluene and benzene than hexaphenyldisiloxane. The residue was dried and purified by fractional crystallization. Some hexaphenyldisiloxane was observed in the residue.

Analysis and Molecular Weight.—Samples were heated with concentrated sulfuric acid and ammonium sulfate. The resulting mixture was cooled, diluted with water and filtered. The residue was ignited and weighed as SiO_2.

Anal. Calcd. for $[(C_6H_5)_3SiO]_4Si$: Si, 12.42. Found: Si, 12.26, 12.30.

The molecular weight was determined in the ebulliometer in benzene with hexaphenyldisiloxane as the reference; mol. wt. found, 1128, 1115; calcd., 1129.5.

Properties.—The compound is a colorless, crystalline solid, m.p. 235–235.5°. It is very soluble in benzene and toluene and has limited solubility in carbon disulfide. In open tubes, different samples appeared to have boiling points between 310 and 330°. In evacuated, sealed tubes, the boiling point was about 249°. At 490–510° the liquid appeared to undergo a change, becoming more viscous, but no color developed until 539°. At 605°, the liquid was very viscous and a pale yellow in color. In comparison, a sample of hexaphenyldisiloxane in an open tube was colorless at 532°.

(12) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

Discussion

At first it might be expected that the thermal stabilities of Si–O–Si and Ti–O–Si compounds should be somewhat similar in that the Ti–O and Si–O bonds are of almost the same strength. Comparison of the thermal decompositions of the tetrakistriphenylsiloxy derivatives of titanium and silicon clearly indicated a greater degree of stability for the silicon compound. The titanium compound turned brown around 460–470° whereas the silicon compound showed little change even at 605°. In addition, the titanium compound gave a dark color indicating carbonization. Apparently the introduction of Ti–O bonds for some Si–O bonds has a wakening effect on neighboring Si–C bonds.

A comparison of a few properties of these substituted silicon and titanium compounds (Table I) reveals the unusually high melting point of tetrakistriphenylsiloxytitanium. The effect does not seem to be due to just the presence of titanium or to the phenyl groups.

It has been observed that this compound has low solubility in benzene and toluene; whereas the corresponding phenylsiloxy derivative of silicon has relatively high solubility in the same solvents. These differences suggest that tetrakistriphenylsiloxytitanium may not be monomeric in the solid state. The ebulliometer measurements gave molecular weights slightly above the values calculated for the monomer. It was not determined whether this difference is a real effect or is due to experimental error. Since titanium exhibits a coördination number of six whereas silicon usually observes a coördination number of four, it is possible that a molecule of the titanium compound might coördinate through the siloxy oxygen to a neighboring molecule.

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CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

The Reactions of Triphenylsilanol and Diphenylsilanediol with Some Titanium Esters[1]

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The reaction of triphenylsilanol with condensed esters of titanium leads to rupture of the Ti–O–Ti bonds with the formation of tetrakistriphenylsiloxytitanium. In addition, triphenylsilanol reacts with chloroesters of titanium in a similar fashion to yield the same product. Diphenylsilanediol and *n*-butyl titanate give an unusual spiro compound of the composition $Ti[O_3Si_4(C_6H_5)_8]_2$. Evidence for the composition and structure of this substance is presented.

In the preceding paper,[3] it was reported that triphenylsilanol and tetrabutoxytitanium react quantitatively to give tetrakistriphenylsiloxytitanium. This product has an unusually high melting point and chemical inertness. In an attempt to prepare stable materials of even higher molecular weight, reactions were carried out to prepare materials containing Ti–O–Ti bonds. Due to the stability of the triphenylsiloxy group, blocking of the remaining primary valences of titanium by these groups should lead to either simple molec-

(1) Taken from the Ph.D. thesis of V. A. Zeitler, February, 1956.

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(3) V. A. Zeitler and C. A. Brown, THIS JOURNAL, **79**, 4616 (1957).

ular compounds or polymeric substances, depending on the number of blocking groups per titanium.

Since the reaction of triphenylsilanol and tetrabutoxytitanium does not yield partially substituted products, it was not possible to prepare higher molecular weight substances by the hydrolysis of partially substituted titanium esters. Controlled, partial hydrolysis of tetrabutoxytitanium has been reported[4,5] to yield hexabutoxydititoxane, $(C_4H_9O)_3TiOTi(OC_4H_9)_3$. Attempts to prepare this substance by the reported methods failed. Instead, higher molecular weight substances were obtained. The reaction of triphenylsilanol with these condensed esters of titanium was found to rupture the Ti–O–Ti bonds with the formation of tetrakistriphenylsiloxytitanium. Similarly, the reaction of triphenylsilanol with chloro-esters of titanium resulted only in the formation of tetrakistriphenylsiloxytitanium.

The reaction of diphenylsilanediol with tetrabutoxytitanium yielded a new and unusual compound of the composition $Ti[O_5Si_4(C_6H_5)_8]_2$. The identification of this substance points to a spiro-type compound with two similar tetrasiloxy rings attached to titanium. Although the patent literature[6] refers to preparations from silanediols and titanium esters, no previous description has been found for substances isolated from the reaction mixture.

Experimental

The reagents used and their purification were essentially as previously described.[3] Special care was taken to avoid contamination and hydrolysis of the water-sensitive substances.

Reactions of Triphenylsilanol with Condensed Titanium Esters

The Ishino Method for Preparation of Hexabutoxydititoxane.—Tetrabutoxytitanium (0.147 mole) in 150 ml. of dry toluene was placed in a three-neck, one-liter flask. The flask was equipped with a reflux condenser, a Trubore stirrer and a dropping funnel. In order to add sufficient water to give a 0.5 mole ratio of water to titanium, a solution of 1.32 g. of water in 106 ml. of butyl alcohol was added slowly over a period of four hours. Then, the mixture was placed in a 500-ml. thermometer-well flask and attached to a 20-cm. distillation column. The toluene–butyl alcohol azeotrope and the toluene were removed at reduced pressure. During this time, the still-pot temperature did not exceed 84°. A pale yellow, slightly viscous liquid remained in the still-pot. Analyses of this liquid gave 17.64 and 17.75% titanium. The theoretical composition of hexabutoxydititoxane is 17.41% titanium. Freshly distilled tetrabutoxytitanium analyzed 14.21%, as compared to 14.10% titanium calculated.

Careful titrations of the yellow liquid product by means of Karl Fischer reagent were made in an attempt to detect "apparent water." This "apparent water"[7] would be due to the presence of the titoxane (Ti–O–Ti) bond. Only negative results were obtained and it was concluded that the K-F reagent is unable to detect the presence of Ti–O–Ti bonds.

Reaction with Triphenylsilanol.—Triphenylsilanol, 100 g., dissolved in one liter of dry toluene, was added to a three-neck, two-liter flask, equipped with a reflux condenser, a Trubore stirrer and a dropping funnel. A solution of 30.9 g. of the product from the condensation reaction and 100 ml. of dry toluene was prepared. This solution was added slowly to the flask over a period of two hours, with vigorous stirring. A fine, white precipitate appeared during the addition. The resulting mixture was refluxed four hours and, after cooling, was filtered. The white precipitate was washed with two 250-ml. portions of dry toluene. Butyl alcohol and toluene were removed from the filtrate leaving a viscous, orange-colored residue. Only two grams of triphenylsilanol were obtained from this residue by extraction with benzene. Apparently, the orange-colored residue consisted mainly of highly condensed butoxytitanium compounds.

The white precipitate was dried, purified by vacuum sublimation, and analyzed for titanium and silicon. *Anal.* Calcd. for tetrakistriphenylsiloxytitanium: Ti, 4.17; Si, 9.76. Found: Ti, 4.26; Si, 9.83.

As a further check, ten grams of the white precipitate was extracted with 250 ml. of dry toluene for 72 hours in a Soxhlet extractor. Eight grams of crystals was recovered from the cold toluene solution. Titanium and silicon analyses of these crystals gave 4.38 and 9.81%, respectively. From this evidence, the products of the reaction were established as tetrakistriphenylsiloxytitanium and some highly condensed butoxytitanium compound

The Boyd Method for the Preparation of Hexabutoxydititoxane.—Freshly distilled tetrabutoxytitanium, 102 g., and 150 ml. of dry toluene were placed in a three-neck, one-liter flask. A Trubore stirrer, a reflux condenser and a dropping funnel were attached to the flask. A solution of 2.70 g. of water in 100 ml. of butyl alcohol was prepared and analyzed by K-F titration. The amounts of the reagents were chosen so that the mole ratio of water to titanium was 0.5. The wet butyl alcohol was added slowly, and the mixture stirred for four hours. The mixture was transferred to a thermometer-well flask, and most of the toluene and butyl alcohol were removed at reduced pressure. Then the still-pot temperature was allowed to rise slowly to 193–195°. Unreacted ester distilled at a still-head temperature of 148° (1 mm.). Boyd reported that no unreacted ester was recovered from a reaction run under similar conditions. About 25 ml. of a dark orange, viscous liquid remained in the still-pot after the simple ester had been removed. This liquid was known to contain a small amount of tetrabutoxytitanium due to the hold-up of the column. From all indications, the reaction did not follow the course described by Boyd, and hexabutoxydititoxane was not formed.

In order to remove the last traces of tetrabutoxytitanium, the orange liquid from the above preparation was placed in a small bulb with an inverted U-neck. The bulb was attached to a vacuum chain through a U-trap. The entire bulb and neck were wrapped with nichrome resistance wire. All remaining tetrabutoxytitanium was removed by heating 48 hours at 160°. During this time, the trap was cooled with liquid nitrogen. A dark orange wax remained in the bulb.

Analyses of the wax indicated 28.34 and 28.28% titanium. This composition approximates a polymeric mixture with an empirical formula of $TiO_{1.33}(OC_4H_9)_{1.33}$. Ebullioscopic measurements in benzene, using hexaphenyldisiloxane as the reference material, gave number average molecular weights of 2317, 2307 and 2325. The degree of polymerization is calculated to be about 13.9.

Reaction of Condensed Butoxytitanium with Triphenylsilanol.—A sample of the wax, 4.26 g., was dissolved in 90 ml. of dry toluene and added to a flask containing 12 g. of triphenylsilanol dissolved in toluene. The flask was attached to a reflux condenser and refluxed for four hours. The cold mixture was filtered, and 4.4 g. of a white powder collected. Analysis indicated this solid was tetrakistriphenylsiloxytitanium. Additional triphenylsilanol, 16 g., in 400 ml. of toluene was added to the filtrate from the above filtration. This solution was refluxed eight hours. Separation of the reaction mixture yielded some additional tetrakistriphenylsiloxytitanium. Subsequent repetitions of the same procedure continued to produce small amounts of the same compound.

The condensed ester contained no tetrabutoxytitanium. The reaction with triphenylsilanol yielded only tetrakistriphenylsiloxytitanium. Either the Ti–O–Ti bonds were broken by the chemical reaction with the silanol, or the reaction followed a course similar to that suggested by Bradley[7] for the thermal disproportionation of condensed ethoxytitanium. The condensed ethoxytitanium compounds disproportionate to give tetraethoxytitanium and more highly

(4) T. Boyd, *J. Polymer Sci.*, **7**, 591 (1951).

(5) T. Ishino and S. Minami, *Technol. Repts. Osaka Univ.*, **3**, 357 (1953).

(6) H. C. Gulledge, U. S. Patent 2,512,058; *C. A.*, **44**, 8698*d* (1950).

(7) D. C. Bradley, R. Gaze and W. Wardlow, *J. Chem. Soc.*, 721 (1955).

condensed ethoxytitanium materials. However, the color of the residue in the still-pot did not indicate the formation of a more highly condensed product, since the color gradually became lighter as the tetrakis-material was removed. The depth of the orange color is known to increase with increased polymerization; tetrabutoxytitanium is pale yellow in color.

Some Reactions of Chlorobutoxytitanium

Ishino and Minami[5] reported that the hydrolysis of tributoxychlorotitanium gave a product of approximately the composition of $TiO_{1.5}Cl_{0.5}(OC_4H_9)_{0.5}$. Since the preceding methods did not yield hexakistriphenylsiloxydititoxane, two methods were tried for the synthesis of substituted triphenylsiloxy derivatives. These methods were (1) the reaction of triphenylbutoxysilane with $TiCl_x(OC_4H_9)_{4-x}$, and (2) the reaction of triphenylsilanol with $TiCl_x(OC_4H_9)_{4-x}$.

Preparation of a Chlorobutoxytitanium Compound.—The chlorination of tetrabutoxytitanium with titanium tetrachloride has been reported to produce chlorotributoxytitanium and dichlorodibutoxytitanium[8] in satisfactory yields. Tetrabutoxytitanium (0.123 mole) in 100 ml. of dry toluene was placed in a three-neck, one-liter flask. Titanium tetrachloride (0.043 mole) in 100 ml. of dry toluene was placed in a dropping funnel and was added over a period of two hours to the titanium ester solution. During the addition, the solution was stirred vigorously, and the reaction flask was cooled with an ice-bath. Following three hours of reflux, the cool solution was transferred to a thermometer-well flask and attached to a 20-cm. distillation column. After removal of the toluene at reduced pressure, two fractions were collected. Fraction 1, 31.5 g., a yellow liquid, was collected at 123–126° (3 mm.). This liquid solidified at room temperature. Fraction 2 was a dark brown liquid. Ten milliliters was collected in the range 155–158° at 3 mm. pressure. The analyses of these fractions were: fraction 1: Ti, 19.96, 20.25; Cl, 35.48, 36.64; fraction 2: Ti, 17.18; Cl, 23.73. The average composition of fraction 1 was $TiCl_{2.45}(OC_4H_9)_{1.55}$ and that of fraction 2 was $TiCl_{1.9}(OC_4H_9)_{2.1}$.

Reaction of Fraction 1 with Triphenylbutoxysilane.—A small flask containing 1.53 g. of fraction 1 was connected to a vacuum chain through a U-trap cooled with liquid nitrogen. Triphenylbutoxysilane (3.41 g.) was placed in a small pistol attached to the flask. The pistol could be rotated in order to add the silane to the chlorobutoxytitanium. The system was evacuated and the silane added. No evidence of a reaction was observed. The flask was heated to 170° and the mixture turned to a homogeneous, brown liquid. Nothing was collected in the U-trap. Toluene was introduced by bulb-to-bulb distillation, and again the flask was heated. The toluene and other volatile components of the reaction were removed by distillation, and the distillate was analyzed for chlorine. Only 4% of the chlorine in the original chlorosilane was found in the distillate. No evidence of dibutyl ether or butyl chloride was observed.

Reaction of Fraction 1 with Triphenylsilanol.—A flask was equipped with a Trubore stirrer, a dropping funnel and a reflux condenser containing a coaxial ammonia delivery tube. Triphenylsilanol (0.366 mole), dissolved in 540 ml. of diethyl ether, was placed in the three-neck, one-liter flask. Fraction 1, 29.2 g., dissolved in 200 ml. of ether, was placed in the dropping funnel and was added over a period of two hours to the vigorously stirred solution of triphenylsilanol. Ammonia was bubbled through the solution to avoid the formation of hexaphenyldisiloxane. During the reaction, the flask was cooled with an ice-bath. The contents of the flask were filtered in an atmosphere of dry nitrogen to remove the heavy white precipitate which formed during the addition of the chlorobutoxytitanium. The precipitate was washed with two 250-ml. portions of ether and placed in a vacuum desiccator. The washings and filtrate were combined, and the solvent was removed by distillation. Only triphenylsilanol remained in the still-pot.

Ten grams of the white precipitate were heated repeatedly in boiling water until the wash water failed to give a positive test for the chloride ion. The residue was dried, placed in a Soxhlet apparatus, and extracted with 300 ml. of toluene for 20 hours. A large quantity of crystals precipitated from the cold toluene solution. Analyses of the crystals and the residue in the Soxhlet thimble were: crystals: Ti, 4.35; Si, 9.84. Calcd. for tetrakistriphenylsiloxytitanium: Ti, 4.17; Si, 9.76. Residue: Ti, 5.21; Si, 9.62. Calcd. for hexakistriphenylsiloxydititoxane: Ti, 5.43; Si, 9.56.

A second extraction of the residue in the thimble, this time with nitrobenzene, produced crystals on cooling. Analysis revealed them to contain 4.43% titanium and 9.83% silicon. It was indicated, therefore, that the product of this reaction was again tetrakistriphenylsiloxytitanium. A small amount of titanium dioxide remained in the thimble. The presence of this material accounted for the high titanium analysis for the residue.

Reaction of Tetrabutoxytitanium and Diphenylsilanediol

Preliminary runs of the reaction of diphenylsilanediol and tetrabutoxytitanium indicated that a chemical reaction took place, since heat was evolved. However, attempts to separate the reaction mixture by fractional distillation failed. Therefore, the reaction was repeated under mild conditions. These were obtained by the use of the low boiling solvent, diethyl ether.

Diphenylsilanediol (0.658 mole), tetrabutoxytitanium (0.33 mole), and 300 ml. of anhydrous diethyl ether were placed in a three-neck, one-liter flask. This flask was equipped with a reflux condenser and a Trubore stirrer. The slurry was stirred for a period of two hours. Some reflux of ether, due to the heat of the reaction, was observed. Eight hours later, the reaction mixture was found to contain a heavy white precipitate and a pale yellow liquid. Rapid filtration, under an atmosphere of dry nitrogen, gave a quantity of large, white, opaque, rhombic crystals. The precipitate was washed with ether and dried.

Recrystallization of the rhombic crystals from toluene gave colorless, square plates. The melting point of these plates was 297–303°. The melting point varied from sample to sample, but was reasonably sharp for each sample. Recrystallization of the rhombic crystals from diethyl ether yielded square, colorless plates having a melting point of 314–314.5°.

The results of the analyses of the plates crystallized from ether were: Ti, 3.23, 3.14; Si, 13.71, 13.62; C, 69.28; H, 4.93. Calcd. for $Ti[O_5Si_4(C_6H_5)_8]_2$: Ti, 2.88; Si, 13.49; C, 69.20; H, 4.84.

The molecular weight of the compound which was recrystallized as plates from ether was determined in the ebulliometer in benzene with a benzene thermometer. Hexaphenyldisiloxane was used for the standard. The molecular weight values obtained were 1676 and 1637. On the other hand, samples of the rhombic opaque crystals gave molecular weights of 1320, 1480 and 1510. The calculated molecular weight for $Ti[O_5Si_4(C_6H_5)_8]_2$ is 1666.

When the opaque crystals were crushed, the odor of butyl alcohol was very strong. Either butyl alcohol, *per se*, was present, or the butyl alcohol was formed by the hydrolysis of traces of titanium ester. The plates, recrystallized from either toluene or ether, did not give evidence of the presence of butyl alcohol. In the reaction of diphenylsilanediol and tetrabutoxytitanium, the mole ratio of silicon to titanium was 2:1. From the analyses, a much higher silicon to titanium ratio is evident for the product. It is therefore certain that a considerable excess of titanium ester was present. It is felt that the rhombic crystals contained absorbed or trapped ester.

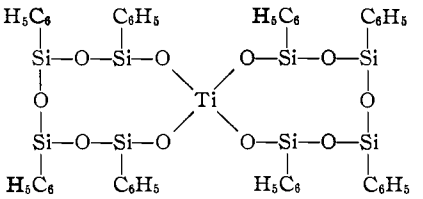
The infrared spectra[9] of the opaque crystals and the colorless plates crystallized from ether were identical. Neither the peaks belonging to butyl alcohol nor the peaks of tetrabutoxytitanium were detected in either sample. Three strong peaks at 739, 717 and 696 cm.$^{-1}$, correspond in intensity and position to three peaks attributed by Young[10] to diphenyl substitution in octaphenylcyclotetrasiloxane. Hexaphenylcyclotrisiloxane can be differentiated from the tetramer by the intensity pattern of these three peaks. In addition, octaphenylcyclotetrasiloxane has a strong absorption at 1079 cm.$^{-1}$; but the trimer absorbs at 1013 cm.$^{-1}$. These peaks are due to the Si–O–Si stretch vibration and are distinctive features of the two cyclosiloxanes. The spectrum of $Ti[O_5Si_4(C_6H_5)_8]_2$ has a strong absorption doublet at 1093 and 1066 cm.$^{-1}$, but no absorption in the vicinity of 1013 cm.$^{-1}$. This doublet corresponds to the

(8) A. Nesmeyanov, E. Braĭnina and R. Friedlina, *Doklady Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **94**, 249 (1954); *C. A.*, **49**, 3000*f* (1955).

(9) V. A. Zeitler and C. A. Brown, to be published.

(10) C. W. Young, *et al.*, THIS JOURNAL, **70**, 3762 (1948).

1079 cm.$^{-1}$, peak of octaphenylcyclotetrasiloxane. On the basis of this additional evidence, the colorless plates are believed to consist of molecules which contain two rings of four diphenylsiloxy groups with each ring bonded to a central titanium atom. This compound probably has the structural formula



From these structural features, the name 16-phenyloctasiloxyspiro(9.9)titanate appears appropriate.

Discussion

It was found that hexakistriphenylsiloxydititoxane could not be produced from the corresponding condensed ester. Although Boyd[4] and Ishino[5] reported preparations of hexabutoxydititoxane, careful repetition of their work has indicated that their syntheses do not yield the desired compound. In their studies of the condensation of titanium esters, analyses for titanium and the absence of the initial monomer during distillation were cited as evidence for the formation of dimers, trimers and other molecular species. In their preparations, the titanium analysis for a mixture containing the simple ester and more highly condensed materials would be the same value as that of the dimer. Although Boyd did not obtain tetrabutoxytitanium the present work demonstrates that this substance is present in the distillation. Ishino and Minami's analyses were not in good agreement with theory and the cryoscopic molecular weights were far from the calculated values. On the other hand, even if hexabutoxydititoxane were available, it has been established that triphenylsilanol would react with this substance with the splitting of the Ti–O–Ti bonds.

None of the Karl Fischer titrations on the problematic hexabutoxydititoxane gave any indication of "apparent water" content. The material definitely contained Ti–O–Ti bonds, but molecular weights did not indicate the principal species to be hexabutoxydititoxane. For such a polymer, two types of Ti-O-Ti bonds are possible. These are (1) the normal covalent bond, Ti–O–Ti; or (2) the dative bond, Ti–O → Ti. Both types of bonds would lead to types of cross-linking. Although Bradley claimed the ability to differentiate between the various types of Ti–O–Ti bonding in condensed ethoxytitanium materials, the experimental work described here demonstrates that the K-F reagent will not identify any Ti–O–Ti bonds in condensed butoxytitanium materials.

The product of the reaction of diphenylsilanediol and tetrabutoxytitanium is a unique compound, $Ti[O_5Si_4(C_6H_5)_8]_2$. The molecular weight determinations and the results of the analyses indicated that this was a simple molecule rather than a polymeric material. In addition, the high solubility, definite crystalline structure, and the sharp melting point indicated a monomer. The preparation from diphenylsilanediol, a bifunctional molecule, and tetrabutoxytitanium, a tetrafunctional molecule, indicated the general type of the product to be expected. Bridged ring structures were less probable than spiro structures. There are five reported spirosiloxanes.[11–13] Three of these possess structures containing two rings of different size. One of the remaining spiro compounds, octamethylspiro[5,5]pentasiloxane, is known to have two rings of equal size. These spirosiloxanes were produced by the cohydrolysis of silicon tetrachloride and dimethyldichlorosilane. In addition, they were subjected to conditions favoring thermal rearrangement. The fifth compound, $(CH_3)_{12}Si_7O_8$, may have a (7.7) spiro structure or it may have a bridge structure. The bridge structure would be obtained by a shift of methyl groups from the dimethyldichlorosilane to the silicon tetrachloride molecule. $Ti[O_5Si_4(C_6H_5)_8]_2$ was produced under such mild conditions that a shift of phenyl groups was unlikely. Hence a bridged structure has been excluded from consideration.

The possibility that the colorless plates (recrystallized from ether) are mixtures of siloxyspirotitanates is not completely ruled out. The sharp melting point is not necessarily a criterion of purity. A solid solution of similar spiro compounds is possible. However, the data provided by the infrared spectrum of these crystals has confirmed the analytical results and the molecular weight determinations. In addition, the spectrum tends to indicate the ring size. Furthermore, the spectrum failed to indicate a mixture of spirotitanates in the opaque rhombic crystals or in the purified colorless plates.

Acknowledgment.—We wish to gratefully acknowledge the financial support of the Office of Naval Research during this investigation.

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(11) D. W. Scott, THIS JOURNAL, **68**, 356 (1946).

(12) D. W. Scott, U. S. Patent 2,418,051.

(13) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 92.