

THE ORGANIC CHEMISTRY OF TITANIUM

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I. INTRODUCTION

The best introduction to a subject such as the organic chemistry of titanium comes from a reading of those contributions which come under the heading of general summaries or short reviews. Among these should be listed two anonymous articles published in 1955 (20) and 1956 (21). A review by Wardlaw and Bradley (395) is especially noteworthy. Pfeiffer (316) has described molecular compounds, and a later paper by Jones and Gilman (178) on organometallic compounds has added more information. Both of these include material on titanium compounds. Pilcher and Skinner (319) have presented a thorough study of the valence states of titanium and vanadium from the physical-chemical point of view. A published index of compounds for which infrared data are available includes many organic compounds of titanium (156).

A monograph by Post (322) on aliphatic ortho esters contains a small section on alkyl orthotitanates. Cotton (87) has included mention of titanium compounds in a review of certain phases of organometallic chemistry. An account of a recent conference on organosilicon chemistry lists several titanium compounds as well (392). Ishino and Minami (168) have presented a review of the organic compounds of titanium. Theoretical considerations on the stability of organic compounds of titanium have been discussed by Jaffe and Doak (174). Other reviews devoted to the subject of alkyl orthotitanates include those of Yoshida (405) and of Ishino and Minami (169), as well as *Metal-Organic Compounds* (5), published by the American Chemical Society.

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II. THE ZIEGLER-NATTA TYPE OF POLYMERIZATION CATALYST

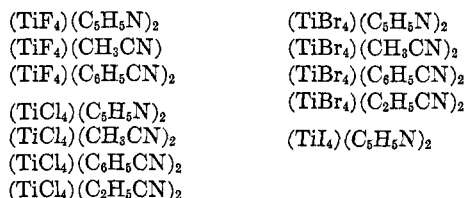
Undoubtedly, action on the part of the Ziegler-Natta catalyst is preceded by the formation of some sort of coordination or "double" compound involving the titanium halide. Wöhler (401) in 1850 reported the isolation of $(\text{TiCl}_4)(\text{ClCN})$ and of $(\text{TiCl}_4)(\text{HCN})_2$. Oberhauser (295) has reported the isolation of $(\text{TiCl}_4)(\text{BrCN})_2$. Henke (147) in 1858 prepared $(\text{TiCl}_4)(\text{CH}_3\text{CN})$ and $(\text{TiCl}_4)(\text{C}_2\text{H}_5\text{CN})_2$ (see also reference 30). Demarcay (98) synthesized $(\text{TiCl}_4)(\text{C}_2\text{H}_5\text{SC}_2\text{H}_5)$ and its 1:2 analog in 1873, and Bertrand (40, 41, 42) in 1880 reported the preparation of $(\text{TiCl}_4)(\text{CH}_3\text{COCl})$. Beilstein (39) records the preparation of $(\text{TiCl}_4)(\text{C}_6\text{H}_5\text{CN})_2$.

Hamilton, McBeth, Bekebrede, and Sisler (140) have prepared six additional compounds: one mole of titanium(IV) chloride combining with one each of dioxane, oxacyclohexane, oxacyclopentane, and methyl phenyl ether and with two moles of oxacyclohexane and oxacyclopentane. These compounds, which were prepared in carbon tetrachloride solution, are all yellow solids. In addition, titanium(IV) chloride was found to react with trioxane to give formaldehyde and polymerized formaldehyde. Ralston and Sisler (326) have prepared $(\text{TiBr}_4)[(\text{CH}_2\text{CH}_2)_2\text{O}]$, $(\text{TiBr}_4)[(\text{CH}_2\text{CH}_2)_2\text{O}]_2$, and $(\text{TiBr}_4)[(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{O}]$. Titanium(IV) iodide did not form double compounds. The titanium compound seemed to have a rupturing effect on the ethers.

Lysenko and Osipov (201, 202) have prepared 1:1 molar double compounds of titanium(IV) chloride and trichloroacetic acid, benzoic acid, and isopropyl formate. The last-named compound was subjected to pyrolysis at 70°C., yielding titanium(IV) chloride,

titanium(IV) oxide, hydrogen chloride, carbon monoxide, and isopropyl chloride. A 1:1 molar compound of titanium(IV) chloride and dimethyl ether has also been reported (37, 195).

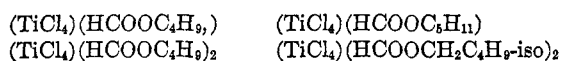
Emel us and Rao (115) have prepared a series of coordination compounds involving titanium(IV) halides:



Those of titanium(IV) iodide are least stable. Dissociation pressures at 80–130°C. under comparable conditions are greatest for fluorides, next for iodides, then bromides and chlorides. Schmitz-Dumont and Motzkus (349) have prepared a 1:2 double compound of titanium(IV) chloride and indole. Titanium(IV) chloride forms a 1:1 double compound with vinyl acetate (78), which on standing polymerizes to a brittle solid foam with loss of hydrogen chloride. The complex reacts with methyl alcohol to form a clear viscous liquid.

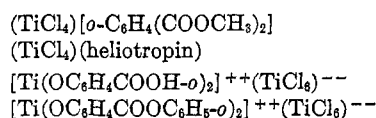
Sumarokova and Nevskaya (371, 372) have reported the preparation of a 1:2 molar coordination compound for titanium(IV) chloride and cineole.

Lysenko (199, 200) has reported the preparation of the following complexes:



The complexes involving acetates with the ratio 1:2 were more stable than the 1:1 analogs. Bradley, Hancock, and Wardlaw (61) have reported that $(\text{TiCl}_4)(\text{CH}_3\text{COOC}_2\text{H}_5)$ can be distilled without decomposition or disproportionation.

Scagliarini and Tartarini (348) have prepared several more coordination compounds containing titanium(IV) chloride:



Additional compounds to be found in earlier literature include $(\text{TiCl}_4)(\text{C}_2\text{H}_5\text{SH})$ and $(\text{TiCl}_4)(\text{R}'\text{COOR})$ (79, 99). Aubin and Rivest (25) have reported the preparation of $(\text{TiCl}_4)[(\text{COOC}_2\text{H}_5)_2]$.

Sutton (375) has prepared the following complexes:



where I is *o*-bis(dimethylarseno)benzene and II is water. Double compounds formed from amines and the tetrachlorides of titanium, zirconium, and silicon have been reported by the Titanium Alloy Manufacturing Company (385).

Titanium(III) reacts with 5,8-dihydroxyquinoxaline to give a red precipitate from acetone, probably a coordination type of compound (1). From other sources has come a series of papers devoted to the preparation of similar compounds, usually as means to the identification of titanium (27, 296, 297, 298, 299, 345, 362, 363, 364, 365).

Prasad and Tripathi (323) have reported the preparation of double compounds containing titanium(IV) bromide and a number of amines.

Majundar and Banajee (205) have reported the determination of tetravalent titanium by its precipitation with 5,6-benzoquinaldinic acid at pH 3.0 or above. Dogani and Bhattacharya (104) have made use of 1-(*p*-chlorophenyl)-3-hydroxy-3-phenyltriazine for the same purpose. Elving and Olson (114) have presented a study of the chelates of tetravalent titanium with cupferron, etc. Osipov (304) has determined dipole moments for five double compounds of titanium(IV) chloride with ethyl butyrate (1:1 and 1:2), with butyl butyrate (1:1 and 1:2), and with amyl butyrate (1:1). Two recent patents (243, 244) have covered the preparation of titanium salt complexes.

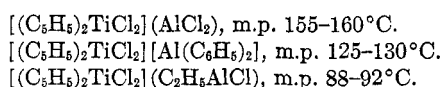
Natta, Corradini, and Bassi (252) have reported as a result of x-ray studies of single crystals of the catalyst $[(\text{C}_6\text{H}_5)_2\text{TiCl}_2][\text{Al}(\text{C}_2\text{H}_5)_2]$ that the dimensions of the unit cell are $a = 15.77 \pm 0.08$ A., $b = 14.24 \pm 0.07$ A., and $c = 7.54 \pm 0.04$ A. There are four molecules in the unit cell and titanium is connected directly to aluminum. Mackey (204) and Ziegler (411) have obtained varying analytical results. Natta (245) finds that some compounds vary in composition. As the aluminum:titanium ratio increases, the chlorine:titanium ratio decreases.

Shiihara (355), Mosevichkiĭ (228), Murahashi (229), Furukawa and Tsuruta (129), and Aggarwal and Sweeting (3) have presented overall summaries of the functions of the titanium chloride-aluminum type of catalyst.

Saltman, Gibbs, and Lal (346) believe that in the complex $(\text{TiCl}_4)[\text{Al}(\text{iso-C}_4\text{H}_9)_3]$ the titanium is actually in the reduced state. With increase in the aluminum content, brown titanium(IV) chloride gives way to replacement of chlorine by isobutyl. The rate of polymerization of isoprene is proportional to the aluminum:titanium ratio. When the ratio is unity, the product is elastomeric; when it is one-third, the product is resinous. The reaction is first order in isoprene; the activating energy is 14,400 cal. per gram-molecule at a constant aluminum:titanium ratio.

Feldman, Arnold, and McDonald (118) have studied the kinetics attendant on the catalytic action of a mixture of titanium(IV) chloride and triisobutyl-aluminum, including the rapid reduction of titanium to the trivalent state.

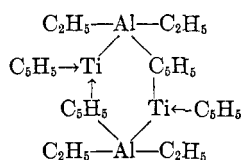
Natta (248) has published a review dealing with stereospecific polymerization, while Werber and Hoeg (398) have presented a very timely summary of isotactic and related types of polymerization. A general review of the Ziegler-Natta type of catalyst appeared in 1957 (259), calling attention to the higher degree of stereospecificity for ethylene than for higher olefins. Natta (246) has presented a general discussion showing that the catalytic complexes are "electron deficient complexes containing bridge-bonds between very electropositive transition metals with valence less than the maximum and very electropositive metals with very small ion diameter to which the electronegative carbon atoms are co-ordinated." At low pressures in the course of olefinic polymerizations, the following have been isolated in the crystalline state:



The radicals come off in a free state and have a tendency to undergo disproportionation to hydrocarbons (262).

Cooper and Rose (85) believe that contact between titanium(IV) chloride and the aluminum alkyl results first in the formation of a complex involving a lower titanium chloride. This reduction is accompanied by the formation of hydrocarbons, coming probably from the disproportionation of free radicals. It is believed that hydrocarbon formation from free methyl involves abstraction of hydrogen from the solvent.

Terenitsinia and Farberov (379) believe that the trialkylaluminum reduces titanium from its tetravalent state, the extent varying inversely as the titanium:aluminum ratio. Titanium becomes bivalent if the ratio is less than 1. These workers propose, as a measure of reactivity, the measure of the ability of the trialkylaluminum to reduce titanium. Natta (245) has observed that an increase in chlorine content causes a decrease in the anionic activity of the catalyst. Natta and Corradini (250) have suggested the following as the structure of the Ziegler catalyst of bis(cyclopentadienyltitanium):



Malatesta (207) has found that the catalytic rates of polymerization induced by a mixture of titanium(IV) chloride and ethylaluminum dichloride are independent of the ratios of the reactants. Groenewege (137) has reported an infrared spectroscopic study of the components of the Ziegler catalyst prepared from titanium(IV) chloride and dimethylaluminum chloride offering evidence for the existence of an equilibrium involving

titanium tetrachloride, methyltitanium trichloride, tetramethyldialuminum dichloride, and dimethyldialuminum tetrachloride. Raman data were also reported. Uelzmann (388, 389) has reported a theoretical study on the mechanism of the Ziegler-Natta type of polymerization, explaining the active units as $(TiCl_3)^+-(R_3AlCl)^-$, $(TiCl_2)^+(R_3AlCl)^-$, etc. The mechanism of polymerization then involves addition of the olefin to the catalytic cation with perhaps a shift to $(TiCl_2)^+(RCH_2CH_2AlR_2Cl)^-$. Polymerization is retarded by the formation of MCH_2CH_2R , thereby taking radicals from the aluminum. The stereospecific polymerization of propylene has been explained through the formation of hydrogen bonds between methyl and chlorine.

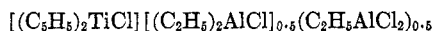
McGowan and Ford (215) have polymerized ethylene, using a mixture of titanium(IV) chloride and butyllithium or dibutylzinc. The velocity of polymerization was proportional to the square of the ethylene pressure. Friedländer and Otia (126) attribute the reaction involving titanium(IV) chloride, ethyllithium, and ethylene to surface-bound ion-pair radicals. Nenitzescu, Huch, and Huch (269, 270, 271) have polymerized ethylene using titanium(IV) chloride and isoamylsodium (see also reference 272). Dialkylzinc compounds are also satisfactory. Natta, Pino, Mazzanti, Giannini, Mantica, and Peroldo (263) have prepared a stable, soluble, and recrystallizable compound containing cyclopentadienyltitanium and aluminum which was satisfactory for the polymerization of ethylene (412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422).

Ludlim, Anderson, and Ashby (198) have shown that ethylene is polymerized at atmospheric pressure to a high-molecular-weight linear polymer by the catalytic activity of titanium(IV) chloride and metallic alkyls such as hexyllithium, lithium aluminum tetraphenyl, triisobutylaluminum, triethylaluminum, and trihexylaluminum. Production of polymer was directly proportional to the concentration of titanium(IV) chloride and of ethylene. Mechanisms were proposed. Natta, Valvassori, Mazzanti, and Sartori (266) have presented additional data on the polymerization of ethylene. Ethylene is polymerized under the influence of titanium(IV) and tetrabutylzinc at a rate which is proportional to the square of the ethylene concentration (132). Orzechowski (303) has found that the most efficient catalyst ratio for a mixture of titanium(IV) chloride and isobutylaluminum is between 1.4 and 2.8 (aluminum:titanium). Additional work has been carried out by Kocheshkov, Kargin, Palev, Talalaeva, and Sogolova (187), using Ziegler-type catalysts containing alkyl derivatives of lithium, magnesium, sodium, cadmium, and zinc. Bawn and Symcox (33) have successfully used $Ti(OC_4H_9\text{-}sec)_4$ and triethylaluminum as a soluble Ziegler catalyst mixture. Maximum rate was attained with an aluminum:titanium ratio of 2.4. Frankel, Rabani, and Zihka (123) have used butyllithium and

isoamylolithium with titanium(IV) chloride for the polymerization of ethylene.

Crystalline organometallic complexes containing titanium and aluminum have been prepared by Natta and coworkers (261) in Italy. It was found that if triethylaluminum is added to a suspension of bis(cyclopentadienyl)titanium dichloride in hexane, a blue mixture forms, from which a blue crystalline solid can be isolated. Analysis showed the compound to be $[(C_5H_5)_2TiCl_2][Al(C_2H_5)_2]$.

A solution of ethylene in heptane in the presence of the titanium-aluminum complex after 20 hr. at 40 atm. and 95°C. yielded 8.4 g. of crystalline polymer. Under the same conditions, bis(cyclopentadienyl)titanium dichloride, when used alone, was reported to be inactive, while triethylaluminum alone gave oily polymers of low molecular weight. Bis(cyclopentadienyl)titanium dichloride-alkylaluminum complexes were used by Breslow and Newburg (70) as catalysts for the polymerization of ethylene. Diethylaluminum chloride reacts with bis(cyclopentadienyl)titanium dichloride in toluene with the evolution of ethylene. From the resulting blue solution a crystalline blue solid was obtained. It melted at 80–90°C. Analysis indicated it to be a complex of bis(cyclopentadienyl)titanium(III) chloride with aluminum sesquichloride.



This was found to be a poor polymerizing agent.

X-ray studies of sky-blue crystals of $[(C_5H_5)_2TiCl_2][Al(C_2H_5)_2]$ have been carried out by Corradini, Bassi, and Natta (86), and the cell constants have been determined.

TABLE 1
Coordination compounds with titanium halides

Formula	Melting Point	Boiling Point	Reference
	°C.	°C.	
TiCl ₄		136.5	(12)
(TiCl ₄)[(C ₂ H ₅) ₂ O].....	42–45	118–120	(34)
(TiCl ₄)(CH ₃ COCl).....	65		(39)
(TiCl ₄)(CH ₃ COOC ₂ H ₅).....		80/0.2 mm.	(421)
(TiCl ₄)(CH ₃ COOCH=CH ₂).....	34		(264)
[(C ₅ H ₅) ₂ TiCl ₂](C ₂ H ₅ AlCl).....	88–92		(253)
[(C ₅ H ₅) ₂ TiCl ₂](C ₂ H ₅) ₂ Al].....	125–130		(253)

However, a freshly prepared solution of bis(cyclopentadienyl)titanium dichloride and diethylaluminum chloride was found to be a highly active catalyst if the ethylene contained traces of oxygen. It was thought that oxygen functions to re-form the tetravalent titanium compound.

With 0.003 per cent oxygen present, ethylene, when bubbled into a solution of bis(cyclopentadienyl)titanium dichloride and diethylaluminum chloride, turns the solution green, indicating the presence of titanium-

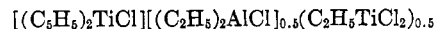
(III) compounds. Thirteen grams of polyethylene was formed in 1 hr. Under the same conditions, but with 0.025 per cent oxygen present in the ethylene, 174 g. of polymer was formed in 1 hr. The solution turned red, owing to the formation of titanium(IV) compounds. The product differs from Ziegler-type polyethylene in that the polymers are more linear and are higher melting.

Badin (28, 29) has found that in the polymerization of ethylene at atmospheric pressure and 10–70°C. with titanium(IV) chloride and triisobutylaluminum, the products are linear with molecular weights between 3500 and 940,000. Raising the reaction temperature decreases the molecular weight. Increasing the titanium:aluminum ratio and increasing the quantity of catalyst have the same effect. At a ratio of 2:1 the activation energy is 10 kcal. per mole. Using the same catalysts, 1-hexene at atmospheric pressure between 10° and 50°C. gave products of low molecular weight. The rate of polymerization was found to be of first order with respect to the olefin concentration. The activation energy was 9.5 kcal. per mole for a titanium:aluminum ratio of 2. Triethylamine stops the reaction, but it can be started again by the addition of more catalyst.

Ziegler and Martin (423) have described the preparation of (TiCl₄)[Al(C₂H₅)₃] and (TiCl₄)[(C₂H₅)₂AlCl] for the polymerization of ethylene at low pressures.

Crystalline polymers are obtained from ethylene, propylene, and isoprene (107), using titanium(IV) chloride catalysts. The isoprene polymer was 100 per cent trans.

Highly crystalline, high-molecular-weight solids are prepared from ethylene in heptane at 90°C. and 30 p.s.i., using zinc or aluminum and TiCl₄, TiBr₄, Ti(OC₄H₉)₄, Ti(OC₃H₇-iso)₄, or Ti[OCH₂CH(C₂H₅)-C₄H₉]₄, or a mixture of titanium stearate and aluminum chloride. Propylene can also be polymerized in this manner (354). Breslow and Newburg (71) have reported the preparation of a liquid Ziegler catalyst and have isolated crystalline



The polyethylene obtained by the use of this catalyst is a linear polymer. The fact that polymerization was catalyzed by a liquid is cited as evidence against the concept that a solid surface is necessary.

Complexes of aluminum chloride and methylaluminum dichloride with bis(cyclopentadienyl)titanium dichloride are good catalysts for the polymerization of ethylene (196).

Kocheshkov, Kargin, Talalaeva, Sogolova, and Palev (188) have used mixtures of organolithium compounds and titanium(IV) chloride as polymerizing agents with ethylene. The catalyzing compounds were used in a 1:1 molar ratio in hexane, at temperatures

between -20° and 60°C . The polyethylenes were highly crystalline with very little branching and had molecular weights of the order of 300,000. Good tensile values were observed, varying, along with elongation values, with the nature of the radical attached to lithium. Twelve different organolithium compounds were used.

Société belge du titane S.A. (359) has prepared a polymerization catalyst, suitable for action with ethylene or propylene, by adding titanium(IV) chloride to powdered aluminum in kerosene at 200°C . The black crystals thus obtained are assumed to be "aluminum chlorotitanates." Furukawa, Tsuruta, Fueno, Sakata, and Ito (130) have investigated the efficacy of a mixture of diethylcadmium and titanium(IV) chloride as used with various olefinic monomers.

Ethylene forms solid polymers under the influence of titanium(IV) chloride and aluminum chloride (121).

Natta, Pasquon, and Giachetti (256, 257) have studied the kinetics of the polymerization of propylene with a mixture of titanium(III) chloride and triethylaluminum and reported that the velocity is dependent on the concentration of the titanium compound and independent of the titanium:aluminum ratio. However, variations in the yields of polypropylene can be dependent on the value of the titanium:aluminum ratio and the nature of the alkyl radical attached to the aluminum (212, 213). Stereospecificity decreases with an increase in the size of the radical. The optimum titanium:aluminum ratio is 0.5. The use of lithium, zinc, and beryllium in place of aluminum has also been discussed. A rise in reaction temperature decreases the tendency toward a stereospecific reaction (214). Additional data with regard to the polymerization of propylene have been presented by Natta, Pino, Mazzanti, and Longi (264).

An attempt to polymerize 3,3,3-trifluoropropylene was unsuccessful (305).

Isotactic polymerized 1-butene has been prepared by the catalytic action, on the monomer, of a mixture of titanium(IV) chloride and triethylaluminum (251). The product can be obtained in the crystalline state. The elementary cell is rhombohedral and the general structure is similar to that of polypropylene and polystyrene. Indeterminate results are obtained with titanium(IV) bromide and iodide (258, 259, 260), and none at all with the fluoride. Alkyl orthotitanates are of no value but as the alkoxyl groups are progressively replaced by chlorine atoms, the solid phase forms and becomes more active. 1-Butene can be polymerized in dry heptane under nitrogen with the aid of 5 per cent $(\text{TiCl}_4)\text{-}[(\text{C}_2\text{H}_5)_2\text{Al}]$ (386). The highest viscosity is attained with a titanium:aluminum ratio of 1:8.3, and the best yields at 25°C . Crystals (80 per cent yield) appear at a titanium:aluminum ratio of 3.1:13.

The rate of polymerization of isoprene is proportional

to the aluminum:titanium ratio (346). When the ratio is 1, the product is elastomeric. Other contributions to the study of this compound have come from Adams, Stearns, Smith, and Binder (2) and from Natta, Porri, and Mazzanti (265). A solution of milled rubber in gasoline, treated with a mixture of titanium(IV) chloride and tributylaluminum or bis(2-phenylbutyl)ethylaluminum, shows an increase in trans links and a decline in unsaturation (105, 106). Ethylaluminum dichloride was also used.

When titanium(IV) chloride and triisobutylaluminum were employed as catalysts, 1-hexene at atmospheric pressure and between 10° and 50°C , gave products of low molecular weight. The rate of polymerization was found to be of first order with respect to olefin concentration. The activation energy was 9.5 kcal. per mole for a titanium:aluminum ratio of 2. Triethylamine stops the reaction, but it is started again by the addition of more catalyst.

Overberger (305) has successfully used a mixture of titanium(IV) chloride and triisopropylaluminum to catalyze the polymerization of 3-methyl-1-vinylcyclohexane to a crystalline product. Oxygen and water affected the reaction. Vinylcyclopentane also gave a crystalline polymer, but no isolable products were obtained from methylenecyclohexane or from methylenecyclopentane. Methylenecyclobutane underwent polymerization but probably with some ring opening.

Copolymers of ethylene and bicyclo[2.2.1]hept-2-enes are synthesized by the catalytic action of titanium(IV) chloride and $\text{LiAl}(\text{C}_7\text{H}_{15})_4$ on the monomers (6). Ethyl β -phenoxyethyl carbonate and similar compounds undergo polymerization under the influence of titanium catalysts such as $\text{NaH}[\text{Ti}(\text{OC}_2\text{H}_5)_6]$ (331-334). Esters of orthotitanic acid are also of value as polymerization catalysts (77).

Certain polyfunctional isocyanates and organic titanium compounds find use as cross-linking agents for cellulose derivatives (158). Triisopropoxyphenyltitanium is used for the polymerization of styrene (152).

Danusso, Sianessi, and Calcagno (94, 96) found that the isotactic polymerization of styrene in benzene by a mixture of titanium(IV) chloride and triethylaluminum is first order in styrene and catalyst with apparent degradation of the latter. The titanium:aluminum ratio varied from 1:2.75 to 1:4. Temperature effects were also discussed. The work was continued by Natta, Danusso, and Sianessi (253) and later by Danusso and Sianessi (95), who discussed the influence of the titanium:aluminum ratio in particular.

A mixture of one mole of titanium(IV) chloride and 1.5 moles of triisopropylaluminum acts as a good polymerizing catalyst for diphenylacetylene, dimethylacetylene, and diethylacetylene (125).

Natta, Mazzanti, Longi, and Bernardini (254) have made use of a mixture of titanium(IV) chloride and

triethylaluminum to polymerize allyltrimethylsilane and trimethyl- γ -vinylpropylsilane. These polymers were linear entities of high molecular weight which could be fractionated to give both amorphous and crystalline materials, the latter having high melting points, some above 350°C. The same catalyst has been used by Topchiev, Nametkin, Durgar'yan, and Dyakov (387) to bring about the polymerization of diallyl-dimethylsilane to various types of liquids and solids, oily and viscous trimers, tetramers, and pentamers. Again, using the same catalyst, Murahashi, Nozakura, and Tadokoro (231) have polymerized *p*-methylstyrene, *m*-methylstyrene, and *p*-trimethylsilylstyrene, with yields of 43, 21, and 13 per cent, respectively. The silicon compound gave an amorphous acetone extract of the polymer, a partially crystalline ether extract, and a highly crystalline benzene extract melting at 124°C.

It is reported that titanium(IV) chloride acts on compounds such as toluene, isopropyl chloride, isobutyl chloride, and *tert*-butyl chloride, as well as the corresponding alcohols, to cause isomerization somewhat after the manner of the standard Friedel-Crafts catalysts (324).

The polymerization of trimethylvinylsilane with a mixture of titanium(IV) chloride and triethylaluminum gives a small yield, after extraction with toluene, of a polymer melting at 340°C. (230). Similarly, slightly higher yields were obtained from allyltrimethylsilane and 3-butenyltrimethylsilane. The polymers, crystalline in nature, melted at 258° and 206°C., respectively.

Natta (247) has differentiated α -, β -, and γ -forms of titanium(III) chloride. The β -form gives 1,4-*cis* polymers with diolefins, while the α - and γ -forms give *trans*.

Using the Ziegler catalyst, Lal (192) has successfully polymerized isobutyl vinyl ether to products of high molecular weight. Allyl vinyl ether gave a soluble, low-molecular-weight polymer, whose infrared spectrum indicated that polymerization had taken place on the vinyl groups to the exclusion of the allyl. Natta, Mazzanti, Longi, and Bernardini (255) have prepared isotactic polymers of allylsilane and allyltrimethylsilane, using $(\text{TiCl}_3)[(\text{C}_2\text{H}_5)_3\text{Al}]$. Some of the highly crystalline fractions melted between 350° and 360°C.

III. ALKOXIDES AND AROXIDES OF TITANIUM

Since titanium(IV) chloride is essentially an acid chloride, it is not at all surprising that it should be found to react easily with water, alcohols, etc.

Razivaev, Bobinova, and Etlis (328) have prepared isopropoxytitanium, isobutoxytitanium, and *sec*-butoxytitanium trichlorides by the interaction of the proper alcohol with titanium(IV) chloride in yields of 75, 56, and 43 per cent, respectively. Titanium(IV) chloride reacts with isopropyl ether to form isopropoxytitanium

trichloride (140).

Relative to compounds of the type ROTiCl_3 , Razivaev, Bobinova, and Etlis (327) have shown that if the radical is secondary or tertiary, decomposition is spontaneous even at low temperature, giving hydrogen chloride, olefins, alkyl chlorides, and polymeric oxyti-

TABLE 2
Properties of ROTiX_3 compounds

Formula	Melting Point	Boiling Point	References
	°C.	°C.	
$\text{C}_2\text{H}_5\text{OTiCl}_3$	76-78 80-81	186-188	(34) (275, 327) (280)
$\text{C}_3\text{H}_7\text{OTiCl}_3$	66-67	185-186 25/0.1 mm. 83-85/11 mm.; 100-102/23 mm.	(327) (275) (280)
<i>iso</i> - $\text{C}_4\text{H}_9\text{OTiCl}_3$	78-79	65/1 mm.	(327, 328) (275)
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OTiCl}_3$	164-166		(280)
$\text{C}_4\text{H}_9\text{OTiCl}_3$	67.5-70.0	124-127/40.5- 42.5 mm.	(224) (280)
<i>iso</i> - $\text{C}_4\text{H}_9\text{OTiCl}_3$	45-55	104	(122) (280)
<i>sec</i> - $\text{C}_4\text{H}_9\text{OTiCl}_3$	81-83 82-83	92-94/9 mm.	(280) (328)
<i>sec</i> - $\text{C}_4\text{H}_9\text{OTiCl}_3$	54-56		(327, 328)
<i>iso</i> - $\text{C}_6\text{H}_{13}\text{OTiCl}_3$	50-60	110-111/17 mm.	(280)
$\text{C}_6\text{H}_{13}\text{OTiCl}_3$	47.5-49.0	120-122/8 mm.	(280)
$\text{C}_6\text{H}_{11}\text{OTiCl}_3$	75-76		(327, 328)

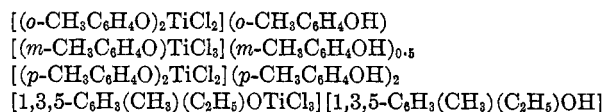
tanium chlorides. The latter are good polymerization catalysts. Reported were isopropoxytitanium, *sec*-butoxytitanium, cyclohexoxytitanium, ethoxytitanium, isobutoxytitanium, and propoxytitanium trichlorides.

Phenoxytitanium trichloride is prepared by the action of phenol on titanium(IV) chloride (172). The interaction of titanium(IV) chloride and acetylacetone forms acetylacetonyltitanium trichloride (335).

Minami and Ishino (224) have reported the formation and isolation of butoxytitanium trichloride, dibutoxytitanium dichloride, and tributoxytitanium chloride as a result of the action of butyl alcohol on titanium(IV) chloride in different molar proportions. Heats of evaporation were calculated.

Funk, Schlegel, and Zimmerman (127) have prepared bis(*o*-chlorophenoxy)titanium dichloride by the interaction of titanium(IV) chloride and *o*-chlorophenol as dark red plates, easily hydrolyzable and undergoing decomposition at the melting point. With an excess of the phenol, $\text{Ti}(\text{OC}_6\text{H}_4\text{Cl-}o)_4$ is formed, which can also be prepared by the action of *o*-chlorophenol on the first product. The reaction is apparently reversible, as tetrakis(*o*-chlorophenyl) orthotitanate is converted to titanium(IV) chloride by the action of dry hydrogen chloride in carbon tetrachloride solution. Radical interchange between chloride and ortho ester takes place with the formation of $(o\text{-ClC}_6\text{H}_4\text{O})_2\text{TiCl}_2$. Using the

meta isomer, a double compound was isolated, $[(m\text{-ClC}_6\text{H}_4\text{O})_2\text{TiCl}_2](m\text{-ClC}_6\text{H}_4\text{OH})$, while the para compound formed $[\text{Ti}(\text{OC}_6\text{H}_4\text{Cl-}p)_4](p\text{-ClC}_6\text{H}_4\text{OH})\text{-}(\text{C}_6\text{H}_{12})$. From benzene solution, the following were also isolated:



In benzene, pyrocatechol reacts with titanium(IV) chloride to form in 90 per cent yield a product reported as $\text{H}_2[\text{Ti}(\text{O}_2\text{C}_6\text{H}_4)_3]$. The diammonium, disodium, barium, magnesium, zinc, nickel(II), diguanidinium, dipyridinium, dipiperidinium, and dianilinium salts were reported. The free dibasic acid loses pyrocatechol at $170\text{--}180^\circ\text{C}$., giving $\text{Ti}(\text{O}_2\text{C}_6\text{H}_4)_2$. The interaction of titanium(IV) chloride and resorcinol did not lead to any isolable product. Hydroquinone reduces titanium(IV) chloride to titanium(III) chloride and is itself oxidized to quinone.

The preparation of a crystalline compound containing one part each of triisopropoxyphenyltitanium, lithium isopropoxide, lithium bromide, and diethyl has been reported by Herman (152).

Dibutoxytitanium dichloride has been prepared by Lowe (197) as the result of the action of butyl alcohol on titanium(IV) chloride. Bradley, Hancock, and Wardlaw (61) prepared diethoxytitanium dichloride and dibutoxytitanium dichloride by the same method.

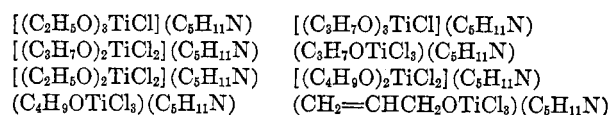
TABLE 3
Properties of the (RO)₂TiX₂ compounds

Formula	Melting Point	Boiling Point	References
	$^\circ\text{C}$.	$^\circ\text{C}$.	
$(\text{C}_2\text{H}_5\text{O})_2\text{TiCl}_2$	40-50		(275)
$(\text{C}_2\text{H}_5\text{O})_2\text{TiBr}_2$	47-50	142/18 mm.	(175)
$(\text{C}_3\text{H}_7\text{O})_2\text{TiCl}_2$		159/18 mm.	(276, 277)
(iso-C ₃ H ₇ O) ₂ TiCl ₂		160/18 mm.	(89, 275)
(C ₄ H ₉ O) ₂ TiCl ₂		182/17 mm.	(175)
		150-151/7.5 mm.	(89)
$(\text{C}_4\text{H}_9\text{O})_{1.46}\text{TiCl}_{2.46}$		123-126	(224)
(i β -C ₄ H ₉ O) ₂ TiCl ₂		184/18 mm.	(409)
			(175)

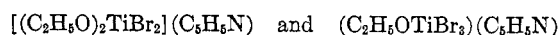
In addition, there were isolated ethoxytitanium trichloride, triisobutoxytitanium chloride, and butoxytitanium trichloride. Trimethyl orthotitanate reacted with titanium(IV) chloride to form methoxytitanium trichloride. Nesmeyanov, Brařnina, and Freřdlina (276, 277) have reported the preparation of tributoxytitanium chloride by the heating of hexabutoxydichlorotrititanoxane and trihexoxytitanium chloride by an analogous reaction. Disproportionation, under heat, of a mixture of tetraethyl orthotitanate and titanium(IV) bromide gave a mixture of diethoxytitanium dichloride and ethoxytitanium tribromide. Ishino, Minami, and Asada (171) allowed acetyl chloride to

react with tetraamyl orthotitanate to form triamoxytitanium chloride, diamoxytitanium dichloride, and a double compound of amoxytitanium trichloride and amyl alcohol in 1:1 molar ratio. The interaction of titanium(IV) chloride and butyl alcohol has been found by Minami and Ishino (224) to yield butoxytitanium trichloride, dibutoxytitanium dichloride, and tributoxytitanium chloride. Hydrochloric acid reacts with tetraethyl orthotitanate and with tetraisopropyl orthotitanate to form diethoxytitanium dichloride and diisopropoxytitanium dichloride (219).

Nesmeyanov, Brařnina, and Freřdlina (275) have found that dipropoxytitanium dichloride, prepared from the alcohol and titanium(IV) chloride, could be readily distilled but when prepared from acetyl chloride and the alcohol could only be isolated as the piperidine double salt, recrystallizable from a petroleum ether-benzene mixture but quite hygroscopic. This work stems from an earlier publication by the same authors (278), in which it was reported that triethoxytitanium chloride and piperidine formed a 1:1 addition compound, which could also be prepared by the interaction of tetraethyl orthotitanate and titanium(IV) chloride. Similar reactions were observed concerning tripropoxytitanium chloride, tetrapropyl orthotitanate, tetrabutyl orthotitanate, tributoxytitanium chloride, and tetraallyl orthotitanate with formation of the following:



The same authors (276, 277) also reported the formation of



In syntheses using acetyl chloride, Ishino, Minami, and Asada (171) have isolated $(\text{C}_3\text{H}_7\text{O})\text{TiCl}_3(\text{C}_6\text{H}_{11}\text{OH})$.

Acetyl chloride reacts with tetraethyl titanate to form triethoxytitanium chloride (89). The yield was considerably less when benzoyl chloride was used. Tripropoxytitanium, tributoxytitanium, triisobutoxytitanium, triamoxytitanium, and trihexoxytitanium chlorides were similarly prepared. In general these compounds easily underwent hydrolysis. Titanium(IV) chloride was found to react with propyl alcohol under anhydrous conditions to form dipropoxytitanium dichloride and with butyl alcohol to give dibutoxytitanium dichloride. Acetyl chloride was found to react with tripropoxytitanium chloride to form the corresponding dichloride but in small yields. The double compound $[(\text{C}_2\text{H}_5\text{O})_2\text{TiCl}_2](\text{C}_3\text{H}_7\text{OH})$ was also prepared. Jennings, Wardlaw, and Way (175) have synthesized triethoxytitanium chloride by the action of acetyl chloride on tetraethyl titanate, which went on to form diethoxytitanium dichloride. The latter was also

TABLE 4
 Properties of the $(RO)_3TiX$ compounds

Formula	Melting Point	Boiling Point	Other Properties	References
	°C.	°C.		
$(C_2H_5O)_3TiCl$		187	$d(25^\circ/4^\circ) = 1.1348$	(89, 175) (89) (293) (290) (275) (275) (294)
$(CH_2ClCH_2O)_3TiCl$		147.5-150.0/2 mm. 174-176/18 mm. 177.0-177.5/19 mm. 136-137/2 mm.		(275) (294) (89) (275) (279) (89)
$(C_2H_5O)_3TiCl$		175-180/1.5 mm. 168/12 mm. 136-137/1 mm. 148-150/1.5 mm. 199/13 mm.	$n(20^\circ/D) = 1.5192$	(276, 277) (131) (224) (294) (409) (131) (131) (131) (90) (294)
$(C_4H_9O)_3TiCl$		156.5/2.5 mm. 160-190/1.0-1.5 mm. 170-174/3 mm. 154-155/2 mm. 155-158/3 mm.	$n(20^\circ/D) = 1.5169$; $d(20^\circ/4^\circ) = 1.0985$	(294) (131) (131) (131) (131) (90) (294)
$(C_4H_9O)_3TiCl$		140-160/1.0-1.5 mm. 152-154/0.8 mm. 162-180/1.5-2.0 mm. 166/11 mm. 147-148/6 mm.; 125.0-125.5/2 mm.	$n(20^\circ/D) = 1.5158$; $d(20^\circ/4^\circ) = 1.1043$	(294) (89) (294) (89) (294) (89) (276, 277) (294) (127)
$(C_2H_5OCH_2CH_2O)_3TiCl$		182-183/1 mm. 214/20 mm. 173.5-175.5/2 mm. 233/18 mm. 198-200/2 mm. 182.0-182.5/1 mm.	$n(20^\circ/D) = 1.5178$; $d(20^\circ/4^\circ) = 1.2035$ $n(20^\circ/D) = 1.5092$; $d(20^\circ/4^\circ) = 1.6000$ $n(20^\circ/D) = 1.5060$ $n(20^\circ/D) = 1.5050$; $d(20^\circ/4^\circ) = 1.0039$	(294) (89) (294) (89) (276, 277) (294) (127)
$(o-ClC_2H_4O)_3TiCl$	115			

prepared directly by the action of ethyl alcohol on titanium(IV) chloride, as was diisobutoxytitanium dichloride. Minami and Ishino (224) have prepared several chlorobutoxy compounds of titanium from titanium(IV) chloride and butyl alcohol.

Nogina, Freidlina, and Nesmeyanov (294) have prepared the following compounds by the action of an alcohol of higher molecular weight on triethoxytitanium chloride: tri(*tert*-amoxy)titanium chloride, tris(β -chloroethoxy)titanium chloride, tributoxytitanium chloride, triisobutoxytitanium chloride, trihexoxytitanium chloride, and tris(β -ethoxyethoxy)titanium chloride.

Bradley, Gaze, and Wardlaw (58, 59, 60) have studied the hydrolysis of tetraalkyl orthotitanates and have recorded the conclusion that hexavalent titanium is undoubtedly an intermediate in the formation of the "oxide ethoxides" which are the end products. A low degree of polymerization is obtained using aqueous alcohol.

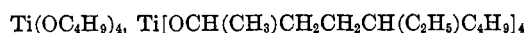
Triethoxytitanium chloride can be prepared by the action of pyridine hydrochloride on tetraethyl orthotitanate (293), and tripropoxytitanium chloride from tetrapropyl orthotitanate (279). Chlorination of tetra-butyl orthotitanate forms dibutoxytitanium dichloride (279) and similarly diethoxytitanium dichloride and dipropoxytitanium dibromide. Corresponding action on the part of bromine gives rise to diethoxytitanium dibromide, dipropoxytitanium dibromide, and dibutoxytitanium dibromide. Nesmeyanov, Freidlina, and No-

gina (280) have prepared $ROTiCl_3$ by the action of the alcohol on titanium(IV) chloride, where R is ethyl, propyl, isobutyl, isoamyl, hexyl, and β -methoxyethyl.

Details have been presented by Andreev and Nidolskiĭ (7) for the preparation of tetraethyl orthotitanate in good yields by the interaction of alcohol and titanium(IV) chloride with sodium or with the bubbling of ammonia gas through the system.

Cullinane, Chard, Price, and Millward (90) have reported their inability to use this method, even making use of the sodium alkoxide, in the preparation of products of tertiary radicals. A mixture of benzene and pyridine is satisfactory however, followed by treatment with ammonia. In this manner Cullinane, Chard, Price, and Millward (90) prepared $Ti(OR)_4$, where R is ethyl, propyl, butyl, isobutyl, *tert*-butyl, amyl, hexyl, and allyl.

Jennings, Wardlaw, and Way (175) have prepared analogous and identical compounds in which R is methyl and ethyl, by the action of titanium(IV) chloride on the sodium alkoxide. By the same reaction, using ammonia as a proton acceptor, Herman (151) has prepared



and



Additional compounds of the formula $Ti(OR)_4$ have

TABLE 5
 Properties of the $Ti(OR)_4$ compounds

Formula	Melting Point °C.	Boiling Point °C.	Other Properties	References
$Ti(OCH_3)_4$	209-210 Sublimes at 300/18 mm.	243/9 mm.		(45) (172)
$Ti(OC_2H_5)_4$		40/0.1 mm. 145-146/7 mm.; 126-128/2 mm. 205/156 mm. 112/1 mm. 103/0.1 mm. 104/1 mm.; 146/8 mm.; 153/12 mm.; 158/20 mm.; 161/24 mm.; 178/44 mm.; 203/222 mm.; 236/760 mm. 156/16 mm. 122-125/1-4 mm. 260; 177-179/44 mm. 150-155/12 mm. 142/18 mm. 150-155/2 mm. 150-152/10 mm. 130-132/2 mm.; 236-237 174-176/1 mm. 128-129/1.5 mm. 104/1 mm.	$n(20^\circ/D) = 1.5085$ $d(20^\circ/20^\circ) = 1.107$ $d(25^\circ/4^\circ) = 1.1044$ $n(35^\circ) = 1.4815-1.501$	(122) (7) (45) (49) (64) (91) (90) (157) (165) (268) (175) (189, 192) (51) (291) (292) (293) (367) (279)
$Ti(OCH_2CH_2Cl)_4$		180-182/2 mm.; 177-178/3 mm. 171/4 mm.	$n(35^\circ/D) = 1.5051$; $d(35^\circ) = 1.107$	(11) (64) (91)
$Ti(OC_3H_7)_4$		124/0.1 mm. 171/14 mm.; 188/64 mm.; 203/ 13 mm.; 223/220 mm.; 237/ 345 mm.; 265/760 mm. 162/12 mm. 130/0.2 mm. 170/3 mm. 137-140/3 mm. 230/740 mm. 49/0.1 mm.	$d(25^\circ/4^\circ) = 1.0329$ $n(35^\circ/D) = 1.4803$; $d(35^\circ) = 0.9970$ $d(35^\circ) = 1.0358$; $n(35^\circ/D) = 1.4907$	(89) (218) (367) (377) (45) (63) (191)
$Ti(OC_3H_7\text{-iso})_4$	20 15	58/1 mm.; 116/10 mm.; 175/100 mm.; 212/760 mm. 97-98/8 mm. 97/7.5 mm. 182.5-183.0/3 mm. 132/0.6 mm.	$d(25^\circ) = 0.9550$ $d(20^\circ/4^\circ) = 0.9711$; $n(20^\circ/D) = 1.4678$	(377) (122) (279) (131)
$Ti(OCH_2CH_2OCH_3)_4$		185/12 mm. 141-142/1 mm. 156-158/2.5 mm. 203-204/30 mm. 166/6.5 mm. 185-187/10 mm. 142/0.1 mm.	$d(25^\circ/4^\circ) = 1.1138$	(91) (90) (292, 293) (293)
$(C_3H_7O)_2Ti(OC_3H_7\text{-iso})_2$		203-204/30 mm. 166/6.5 mm. 185-187/10 mm. 142/0.1 mm.	$n(20^\circ/D) = 1.3915$ $d(20^\circ/4^\circ) = 1.0051$; $n(20^\circ/D) = 1.4925$ $d(20^\circ/20^\circ) = 0.993$	(10) (23) (45) (64) (91)
$Ti(OC_4H_9)_4$		151/1 mm.; 189/16 mm.; 206/33 mm.; 219/49 mm.; 228/96 mm.; 240/145 mm.; 247/197 mm.; 258/262 mm.; 268/375 mm.; 281/491 mm.; 281/760 mm. 189/13 mm. 185-188/11 mm. 134-136/0.5-1.0 mm. 162/1.0 mm. 160-162/3 mm. 134-136/0.5-1.0 mm. 160-162/2 mm. 160-162/3 mm. 152-154/1 mm. 180/8 mm. 160/0.8 mm. 160/2.5 mm.	$d(25^\circ/4^\circ) = 0.9932$ $n(35^\circ/D) = 1.4863$; $d(35^\circ) = 0.9927$	(90) (268) (53) (150) (151) (367) (293) (380) (49) (161) (122, 150) (131)
$(C_4H_9O)_2Ti(OC_3H_7)OCH_3$		131/0.3 mm. 156/0.8 mm.		(131) (131)
$C_4H_9OTi(OC_3H_7)_3$		141/1 mm.; 163/13 mm.; 197/61 mm.; 210/105 mm.; 218/143 mm.; 228/199 mm.; 236/252 mm.; 242/299 mm.; 244/344 mm.; 256/507 mm.	$d(25^\circ/4^\circ) = 0.9601$	(91)
$(C_4H_9O)_3TiOC_3H_7$		163/13 mm. 141/1 mm.	$n(54^\circ/D) = 1.4749$; $d(35^\circ/4^\circ) = 1.0358$	(90) (377)

TABLE 5—Continued

Formula	Melting Point °C.	Boiling Point °C.	Other Properties	References
Ti(OC ₄ H ₉ - <i>sec</i>) ₄		81/0.1 mm. 120-125 124/4.0 mm. 90-92/0.5-1.0 mm. 107-108/3 mm.	$n(35^\circ) = 1.4515$ $n(35^\circ/D) = 1.4550$; $d(45^\circ/4^\circ) = 0.9196$ $d(35^\circ/4^\circ) = 0.9463$; $n(35^\circ/D) = 1.4587$	(63) (157) (218) (367) (376)
Ti(OC ₄ H ₉ - <i>tert</i>) ₄		93.8/5 mm. 122/2 mm. 102/1 mm.; 113/13 mm.; 134/33 mm.; 154/66 mm.; 168/110 mm.; 181/165 mm.; 198/250 mm.; 201/352 mm.; 213/519 mm. 114/11 mm. 62-63/1 mm.	$d(25^\circ/4^\circ) = 0.8832$ $n(20^\circ/D) = 1.4436$, 1.4368 ; $d(20^\circ/4^\circ) = 0.8917$	(62) (63) (91) (90) (377)
Ti(OCH ₂ CH ₂ OC ₂ H ₅) ₄		187-188/3 mm.	$n(18^\circ/D) = 1.4920$; $d(28^\circ/4^\circ) = 1.1106$	(279)
Ti(OC ₅ H ₁₁) ₄		158/0.1 mm. 211/1 mm.; 224/27 mm.; 239/64 mm.; 259/140 mm.; 270/209 mm.; 281/313 mm.; 314/760 mm. 215/12 mm. 340; 206-208/2 mm. 182-183/3 mm. 130-132/1 mm. 105/0.05 mm. 81/2.0 mm. 106/0.3 mm. 129-130/2 mm. 98/0.1 mm.	$d(25^\circ/4^\circ) = 0.9735$, 0.9648 $d(35^\circ) = 0.9703$; $n(35^\circ/D) = 1.4813$	(64) (91) (11) (166) (369) (92) (395) (218) (122) (377) (395) (281)
Ti(OC ₅ H ₁₁ - <i>tert</i>) ₄	58-60	150-151/1 mm. 160.0-161.5/1 mm. 162.5-163.5/1.5 mm.; 157.5-158.0/1 mm. 154-155/1.5 mm. 151-153/2 mm. 149.5-151.0/1.5-2.0 mm. 127-130/1 mm.; 128-130/1 mm.	$n(20^\circ/D) = 1.5222$ $n(20^\circ/D) = 1.5050$ $n(20^\circ/D) = 1.4960$ $n(20^\circ/D) = 1.4570$ $n(20^\circ/D) = 1.4910$ $n(20^\circ/D) = 1.4893$ $n(20^\circ/D) = 1.4940$	(281) (281) (281) (281) (281)
Ti[OC(CH ₃) ₂ C ₂ H ₅] ₄		112/0.1 mm. 112/0.5 mm. 118/0.1 mm. 115/0.1 mm. 135/0.1 mm. 154/0.8 mm.	$d(20^\circ/4^\circ) = 0.9118$; $n(20^\circ/D) = 1.4543$	(63) (395) (63) (63) (395) (395)
(CH ₂ =CHCH ₂ O) ₂ TiOC ₅ H ₁₁ - <i>iso</i>		150-151/1 mm.	$n(20^\circ/D) = 1.5222$	(281)
(CH ₂ =CHCH ₂ O) ₂ Ti(OC ₅ H ₁₁ - <i>iso</i>) ₂		160.0-161.5/1 mm.	$n(20^\circ/D) = 1.5050$	(281)
(<i>iso</i> -C ₅ H ₁₁ O) ₂ TiOCH ₂ CH=CH ₂		162.5-163.5/1.5 mm.; 157.5-158.0/1 mm.	$n(20^\circ/D) = 1.4960$	(281)
(<i>iso</i> -C ₅ H ₁₁ O) ₂ TiOC ₇ H ₁₃ - <i>iso</i>		154-155/1.5 mm.	$n(20^\circ/D) = 1.4570$	(281)
(<i>iso</i> -C ₅ H ₁₁ O) ₂ TiOC ₂ H ₅		151-153/2 mm.	$n(20^\circ/D) = 1.4910$	(281)
(<i>iso</i> -C ₅ H ₁₁ O) ₂ TiOC ₂ H ₅		149.5-151.0/1.5-2.0 mm.	$n(20^\circ/D) = 1.4893$	(281)
<i>iso</i> -C ₅ H ₁₁ OTi(OC ₅ H ₁₁) ₂		127-130/1 mm.; 128-130/1 mm.	$n(20^\circ/D) = 1.4940$	(281)
Ti[OCH(C ₂ H ₅) ₂] ₄		112/0.1 mm. 112/0.5 mm. 118/0.1 mm. 115/0.1 mm. 135/0.1 mm. 154/0.8 mm.		(63) (395) (63) (63) (395) (395)
Ti[OCH(CH ₃)C ₂ H ₅ - <i>iso</i>] ₄		118/0.1 mm.		(63)
Ti[OCH(CH ₃)C ₂ H ₅] ₄		115/0.1 mm.		(63)
Ti(OCH ₂ C ₄ H ₉ - <i>sec</i>) ₄		135/0.1 mm. 154/0.8 mm.		(395) (395)
Ti(OC ₆ H ₄ CH ₃ - <i>o</i>) ₄	103.0-105.6	220/5 mm.		(406) (165)
Ti(OC ₆ H ₄ CH ₃ - <i>m</i>) ₄		220/5 mm.		(165)
Ti(OC ₆ H ₄ CH ₃ - <i>p</i>) ₄	47.9-51.4	255-258/2 mm. 219/1 mm. 214/0.1 mm. 214/0.1 mm.; 228/0.5 mm.	$d(20^\circ/4^\circ) = 0.9339$; $n(20^\circ/D) = 1.4810$ $n(35^\circ/D) = 1.4762$ $d(25^\circ/4^\circ) = 0.935$ $d(25^\circ/4^\circ) = 0.9351$	(406) (23) (367) (91) (64) (63) (91)
Ti(OC ₆ H ₁₇ - <i>iso</i>) ₄		214/0.1 mm. 214/0.1 mm.; 228/0.5 mm.	$d(25^\circ/4^\circ) = 0.9351$	(63) (23) (63) (91)
Ti[OCH(CH ₃)C ₂ H ₅] ₄		182/0.1 mm.		(63)
Ti(OC ₆ H ₁₃) ₄		264-265/1.5 mm.	$d(20^\circ/4^\circ) = 0.9241$; $n(20^\circ/D) = 1.4785$	(23)
Ti[OCH(C ₄ H ₉) ₂] ₄		195/0.1 mm.		(63)
Ti[OCH(CH ₃)CH ₂ CH ₂ CH(C ₂ H ₅)C ₄ H ₉] ₄		225/<1 mm. 255/21 mm.	$d(26^\circ/4^\circ) = 0.9012$ $d(26^\circ/4^\circ) = 0.9012$	(380) (151)
Ti{OCH ₂ CH[CH(CH ₃)CH ₂ C ₄ H ₉ - <i>tert</i>]-CH ₂ CH ₂ CH(CH ₃)CH ₂ C ₄ H ₉ - <i>tert</i>] ₄		305/<1 mm.		(151, 380)
(<i>iso</i> -C ₅ H ₁₁ O) ₂ Ti[OC(CH ₃)=CHCOCH ₃] ₂		123/0.5-0.8 mm. 138-139/0.4-0.5 mm.		(307) (69) (403)
(C ₂ H ₅ O) ₂ TiOC(CH ₃)=CHCOCH ₃	59-65			(403)
(C ₂ H ₅ O) ₂ TiOC(CH ₃)=CHCOOC ₂ H ₅	89-92			(403)
(C ₂ H ₅ O) ₂ TiOC(CH ₃)=CHCOOC ₂ H ₅	87.0-90.5			(170)
(C ₂ H ₅ O) ₂ Ti[OC(CH ₃)=CHCOCH ₃] ₂	48-52			(403)
(C ₂ H ₅ O) ₂ Ti[OC(CH ₃)=CHCOOC ₂ H ₅] ₂	40-45			(403)
(C ₂ H ₅ O) ₂ TiOC(CH ₃)=CHCOOC ₂ H ₅	38-42			(403)
(C ₂ H ₅ O) ₂ Ti[OC(CH ₃)=CHCOCH ₃] ₂		138-139/0.4-0.5 mm.	$d(25^\circ/4^\circ) = 1.125$; $n(25^\circ/D) = 1.554$	(403) (69)
(C ₄ H ₉ O) ₂ Ti[OC(CH ₃)=CHCOOC ₂ H ₅] ₂			$d(25^\circ/4^\circ) = 1.117$; $n(25^\circ/D) = 1.526$	(403)
(C ₄ H ₉ O) ₂ Ti[OCH(CH ₃)=CHCOCH ₃] ₂			$d(25^\circ/4^\circ) = 1.089$; $n(25^\circ/D) = 1.542$	(403)
(C ₄ H ₉ O) ₂ Ti[OCH(CH ₃)=CHCOOC ₂ H ₅] ₂			$d(25^\circ/4^\circ) = 1.090$; $n(25^\circ/D) = 1.519$	(403)
(C ₂ H ₅ O) ₂ Ti OC(CH ₃) ₂ CH ₂ OCHCH ₃		137-138/0.025 mm.	$d(25^\circ/4^\circ) = 1.115$; $n(25^\circ/D) = 1.517$	(40)

TABLE 5—Concluded

Formula	Melting Point °C.	Boiling Point °C.	Other Properties	References
$\begin{array}{c} \text{OC(CH}_3)_2 \\ \diagdown \quad \diagup \\ (\text{C}_2\text{H}_5\text{O})_2\text{Ti} \quad \text{CH}_2 \dots \dots \dots \\ \diagup \quad \diagdown \\ \text{OCHCH}_3 \\ \text{OC(CH}_3)_2 \end{array}$		140–142/0.025 mm.	$d(25^\circ/4^\circ) = 1.067$; $n(25^\circ/\text{D}) = 1.506$	(40)
$\begin{array}{c} \text{OCHCH}_3 \\ \diagdown \quad \diagup \\ (\text{C}_4\text{H}_9\text{O})_2\text{Ti} \quad \text{CH}_2 \dots \dots \dots \\ \diagup \quad \diagdown \\ \text{OC(CH}_3)_2 \\ \text{OCHCH}_3 \end{array}$		150–152/0.025 mm.	$d(25^\circ/4^\circ) = 1.505$; $n(25^\circ/\text{D}) = 1.506$	(40)
$\begin{array}{c} \text{OCHCH}_3 \\ \diagdown \quad \diagup \\ (\text{C}_8\text{H}_{17}\text{O})_2\text{Ti} \quad \text{CH}_2 \dots \dots \dots \\ \diagup \quad \diagdown \\ \text{OC(CH}_3)_2 \\ \text{OCHCH}_3 \end{array}$		174–175/0.025 mm.	$n(25^\circ/\text{D}) = 1.505$	(40)
OTi(OC ₂ H ₅) ₂	100–113			(283)
OTi(OC ₄ H ₉) ₂	112–115			(283)

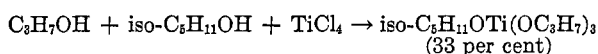
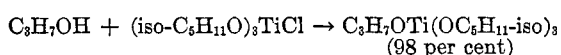
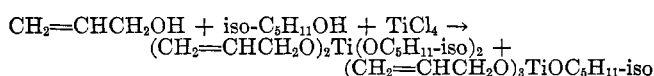
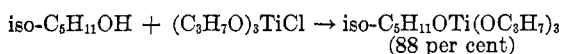
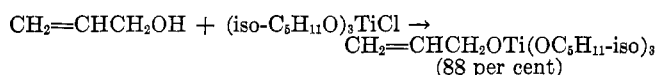
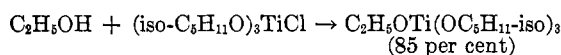
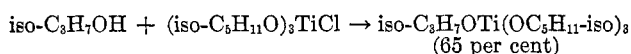
been prepared by Bradley, Hancock, and Wardlaw (61), where R is ethyl, isopropyl, butyl, and *tert*-amyl.

Methyl alcohol reacts with tetraisopropyl orthotitanate to form tetramethyl orthotitanate (61).

A patent obtained by Hill (157) covers the preparation of ortho esters of titanium by the conventional action of alcohol on titanium(IV) chloride but with increased yields owing to the presence, in the reaction mixture, of a sodium–calcium sludge. Ethyl, isopropyl, and *sec*-butyl alcohols are used (see also Meerwein and Bersin (216)).

Herman (150) has prepared tetra(2-ethylbutyl) orthotitanate by the interaction of 2-ethylbutanol and titanium(IV) chloride. The system is cooled by an ice bath and hydrogen chloride is removed by blowing air through the mixture. Similar reactions led to the formation of tetrabutyl and tetraoctadecyl titanates. Other reactions made use of several proton acceptors, such as dimethylformamide, ammonia, adiponitrile, iminodipropionitrile, and oxydipropionitrile, for tetraisopropyl orthotitanate and for tetraoctyl orthotitanate.

Nesmeyanov and Nogina (281) have reported the following reactions:



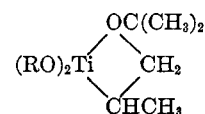
Bischoff and Adkins (45) have prepared several

alkyl orthotitanates and have found that methyl alcohol will react with a higher alkyl orthotitanate to form tetramethyl orthotitanate. Starting with tetraethyl orthotitanate, three by-products were isolated: namely, C₂H₅OTiOOH, OTi(OC₂H₅)₂, and (C₂H₅O)₃TiOTi(OC₂H₅)₃. Meerwein and Bersin (216) have prepared tetraethyl orthotitanate. Carpmael (79) and I. G. Farbenindustrie A.-G. (164) have continued the work, using ammonia as a proton acceptor. Plets (320) has reported the inability of triethoxytitanium chloride and diethoxytitanium dichloride to form alkyltitanium compounds with alkyl halide and lithium. Meerwein, von Brock, Kirschnik, Lenz, and Migge (217) have used tetraethyl orthotitanate in the reduction of aldehydes to alcohols, while MacCorquodale and Adkins (203) have prepared triethoxytitanium by the action of sodium on orthotitanate.

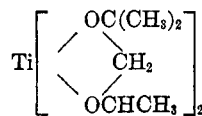
In 1940 Nelles (268) described the preparation of orthotitanates by standard means. Titanium(IV) chloride was found to react successfully with ethyl alcohol, butyl alcohol, and phenol in the presence of ammonia. For phenol, butylamine or aniline could be used in place of ammonia. Phenylpropylcarbinol also reacted well. Tetraphenyl orthotitanate was also obtained by heating tetraethyl orthotitanate with phenol.

Cullinane, Chard, Price, Millward, and Langlois (91) have prepared tetraethyl, tetraallyl, tetrapropyl, tetrabutyl, tetraisobutyl, tetra(*tert*-butyl), tetraamyl, tetrahexyl, and tetraisoöctyl orthotitanates by the action of a selected alcohol on another orthotitanate and also from titanium(IV) chloride.

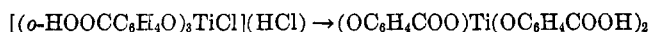
Yamamoto and Kambara (404) allowed 2-methyl-2,4-pentanediol to react with tetraethyl, tetrapropyl, tetrabutyl, and tetraamyl orthotitanates to form compounds of this type:



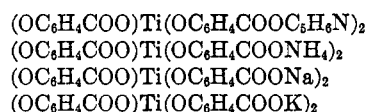
The products can be further heated with the diol to form the completely alcoholized ester:



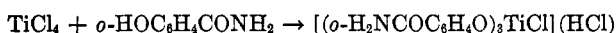
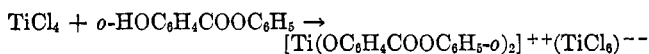
and the chelated compound in which three diol radicals are attached to titanium, two attachments being through the medium of coordinate valence. Rosenheim and Sorge (339) carried out the reaction:



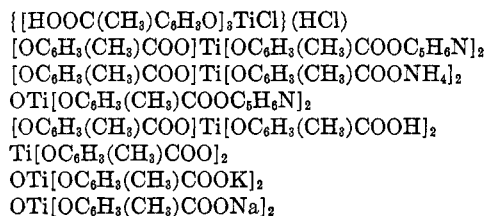
The product reacted with bases to form



A stream of carbon dioxide, passing through the hydrochloric acid double compound above, forms $\text{Ti}(\text{OC}_6\text{H}_4\text{COO})_2$ and this, with selected bases, formed $\text{OTi}(\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_5\text{N})_2$, $\text{OTi}(\text{OC}_6\text{H}_4\text{COONH}_4)_2$, and $\text{OTi}(\text{OC}_6\text{H}_4\text{COO})_2\text{Hg}$. In addition the following reactions were carried out:



By analogous reactions, the following were also reported:



Rosenheim, Raibmann, and Schendel (336) have prepared $(\text{C}_6\text{H}_4\text{O}_2)\text{Ti}(\text{OC}_6\text{H}_4\text{ONH}_4)_2(\text{HOH})$ from pyrocatechol. Other metals and radicals found satisfactory included K, Rb, Mg, Zn, Mn, Co, Ni, Ba, $\text{C}_5\text{H}_5\text{N}$, $(\text{CH}_3)_2\text{CH}_6\text{H}_3\text{NH}_3$, $\text{C}_6\text{H}_5\text{NH}_3$, and $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_3$.

Herman (148) has covered the preparation of tetra-(2-methylbutyl), tetrabutyl, tetraisopropyl, and tetraoctyl orthotitanates by the action of the proper alcohol on titanium(IV) chloride. Hydrogen chloride is swept out by the passage of an inert gas or is absorbed by ammonia.

Tetraisopropyl orthotitanate reacts with butyl acetate to form tetrabutyl orthotitanate (113, 143) and dibutyldiisopropyl orthotitanate. Similarly, tetraisopropyl orthotitanate reacts with *o*-methoxyphenyl acetate and with phenyl benzoate to form, respectively, tetra(*o*-methylphenyl) orthotitanate and tetraphenyl orthotitanate. In addition, Mehrotra (218) has reported the interaction of an alkyl orthotitanate with an ester of a carboxylic acid with resultant interchange of alkyl groups. Using acetates throughout, tetraethyl orthoti-

tanate was converted to the tetrapropyl and tetrabutyl homologs and tetrapropyl orthotitanates to the tetrabutyl, tetra(*sec*-butyl), and tetra(*tert*-butyl) compounds. Yields ranged between 90 and 94 per cent.

Titaan N. V. has described the preparation of tetra-butyl orthotitanate, tetrakis(5-ethyl-2-nonyl) orthotitanate, and tetrakis[2-(1,3,3-trimethylbutyl)-5,7,7-trimethyloctyl] orthotitanate by the action of the proper alcohol on titanium(IV) chloride (380).

Ortho esters of titanate are prepared on a commercial scale by the action of ethanol (95 per cent yield), 2-ethylhexanol (80 per cent yield), phenol (80 per cent yield), and many others on titanium(IV) sulfide (51). These esters are used as mordants and water repellants for textiles.

Mixed ortho esters have been prepared by Ghosh, Ghosh Mazundar, Bose, and Sen Gupta (131) utilizing the sodium alkoxides. They prepared tripropylbutyl orthotitanate, tributylpropyl orthotitanate, dibutyl methylpropyl orthotitanate, and isopropyltripropyl orthotitanate.

The interaction of acetaldehyde and tetraisopropyl orthotitanate results in the formation of diisopropyl divinyl orthotitanate (142). In addition, phenylacetaldehyde when similarly treated forms tetrasteryl orthotitanate and heptaldehyde yields tetrakis(β -amylvinyl) orthotitanate. When an analogous product from mesityl oxide was heated, polymers were formed. Several other aldehydes and ketones are listed as undergoing this type of reaction with alkyl orthotitanates.

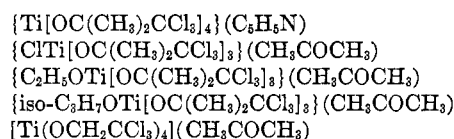
Yoshino, Kajima, Ochi, Sampei, and Sei (406) reported that tetrabutyl orthotitanate reacts with phenyl acetate to form tetraphenyl orthotitanate. Similarly, from tetrabutyl orthotitanate, these workers have prepared tetra(*o*-tolyl), tetra(*p*-tolyl), tetra(*o*-chlorophenyl), tetra(*p*-chlorophenyl), tetra(*o*-nitrophenyl), and tetra(*p*-nitrophenyl) orthotitanates. The combustibility of fuels is said to be increased by the addition of 0.1 per cent of dicyclopentadienyltitanium dichloride or dibutoxycyclopentadienyltitanium chloride (383).

Caughlan, Smith, Katz, Hodgson, and Crowe (81) report that tetraethyl, tetrapropyl, and tetrabutyl orthotitanates as well as triethoxytitanium chloride are associated in benzene solution as dimers and trimers. This is made possible by the increase in covalence of the titanium atom.

Bradley, Mehrotra, and Wardlaw (62, 63) have prepared additional series of titanium alkoxides, mainly with the view of determining whether or not molecular association takes place. The conclusion is that tetra(*tert*-butyl), tetra(*tert*-amyl), tetra(3-methylamyl), and tetra(1,1-dimethylbutyl) orthotitanates are monomeric as judged by boiling-point data. Entropies of vaporization showed little variation with change in molar

size, but boiling points and latent heats rose. Steric effects were in general assumed to be of considerable effect in determining the physical properties of tetra-isopropyl, tetra(diethylmethyl), tetra(dipropylmethyl), tetra(di-1-methylbutyl), tetra(1,2-dimethylpropyl), tetra(diisopropylmethyl), tetra(dibutylmethyl), tetra(*sec*-butyl), and tetra(1-methylheptyl) orthotitanates.

Bradley, Mehrotra, Swanwick, and Wardlaw (64) extended the studies on molecular complexity to cover tetraethyl, tetrapropyl, tetrabutyl, tetraamyl, tetrahexyl, tetraheptyl, and tetraoctyl orthotitanates. Their conclusion is that molecular complexity is practically independent of chain length. Entropies of vaporization increase with chain length however, a development which is probably connected with molecular entanglement. Bradley, Sircha, and Wardlaw (65) have prepared the following:



Boyd (49) has prepared tetrabutyl orthotitanate and tetraethyl orthotitanate by the action of the proper alcohol on titanium(IV) chloride. The former can be hydrolyzed to bis(tributoxytitanium) oxide, and this will react with stearic acid with replacement of several butoxy groups.

Nesmeyanov, Nogina, and Freĭdlina (283) have reduced tetrapropyl orthotitanate to tripropoxytitanium by the action of metallic potassium in propyl alcohol. Tetrabutyl orthotitanate underwent the same reaction. Both products were hydrolyzed and oxidized in air, however, to dibutyl metatitanate.

By means of the action of the proper alcohol on tetraethyl orthotitanate, Arbusov and Isaeva (23) have prepared tetrabutyl, tetrahexyl, tetraoctyl, and tetranonyl orthotitanates. Similarly, Nesmeyanov, Freĭdlina, and Nogina (279) have prepared tetra(β -chloroethyl), tetra(β -methoxyethyl), and tetra(β -ethoxyethyl) orthotitanates from the tetraethyl ester and tetrabenzyl orthotitanate from tetrabutyl orthotitanate. Speer (367) has prepared tetra(*tert*-butyl) orthotitanate by the action of *tert*-butyl alcohol on tetraethyl orthotitanate. Tetraethyl, tetrabutyl, and tetraisomyl orthotitanates have similarly been prepared by Kraitzer, Taggart, and Winter (189). With the aid of ammonia, tetraethyl, tetrabutyl, tetraphenyl, and tetra(1-phenylbutyl) orthotitanates were obtained (165).

Watanabe, Shiozawa, and Yanokura (397) have prepared thirty organic orthotitanates, reporting that secondary esters underwent hydrolysis faster than primary. Hydrolyses were also carried out on titanium salts of organic acids. Takatani (377) has prepared tetrapropyl, tetraisopropyl, tetra(*sec*-butyl), and tetra-

butyl orthotitanates by the interaction of the proper alcohol and tetraethyl orthotitanate. Ide (163) has covered the preparation of new organic orthotitanates by the reaction of resorcinol and *o*-dihydroxybenzene with tetraalkyl orthotitanates. Similarly, by the interaction of tetraethyl orthotitanate and esters of acetic acid, there were prepared tetraphenyl, tetra(*o*-nitrophenyl), tetraallyl, and tetrabutyl orthotitanates (161).

Triethoxytitanium chloride and tetraethyl orthotitanate have been prepared by the action of ethyl alcohol on titanium(IV) chloride in the presence of pyridine (290, 293). Similarly, tetraallyl (292), tetraethyl (291), and tetrabutyl, tetraallyl, and tetracyclohexyl (293) orthotitanates were obtained by the use of ammonia. Speer (367) has reported the preparation of tetra(*sec*-butyl), tetraethyl, tetrapropyl, tetrabutyl, tetraisobutyl, and tetraoctyl orthotitanates by the action of the proper alcohol on titanium(IV) chloride.

Bistan and Gömöry (46) have studied the relative rates of hydrolysis of ortho esters of titanate acid in which the radicals are butyl, heptyl, cetyl, benzyl, phenyl, and *m*-tolyl with titanium ratios of 0.5:1.0, 1:1, and 2:1. Resistance to hydrolysis varied as the length of the aliphatic chain and much greater resistance was exhibited by the compounds containing aromatic radicals. Hydrolysis in water of tetra α -pentyl orthotitanate yielded neopentyl alcohol (92). This led the authors to conclude that hydrolysis proceeds "along the coordinate axis of titanium with subsequent cleavage of the TiO bond." It is felt that cleavage of the carbon-oxygen bond would have led to the formation of isoamyl alcohol by rearrangement.

Bradley and Swanwick (66) have reported studies on the vapor pressures of tetra(*tert*-butyl) orthotitanate and tetra(*tert*-amyl) orthotitanate between 0.05 mm. and 50 mm. These values conform to the general formula:

$$\log P = C - \frac{x}{T} - y \log T$$

Infrared curves of alkyl orthotitanates and their hydrolysis products have been reported by Takatani, Yoshimoto, and Masuka (378). Kriegsmann and Licht (190) have determined similar infrared data as well as Raman data for tetramethyl, tetraethyl, tetrapropyl, tetraisopropyl, and tetrabutyl orthotitanates as well as for tetrakis(trimethylsilyl) orthotitanate. The addition of tetrabutyl orthotitanate to certain oil paints has been described by Nippon Telegraph and Telephone Company (288).

Electric moments of triethoxytitanium chloride, phenoxytitanium trichloride, tetraethyl orthotitanate, tetrapropyl orthotitanate, and tetrabutyl orthotitanate have been determined by Crowe and Caughlan (88) and by Caughlan, Katz, and Hodgson (80).

Takatani (377) has established the bond refraction values for the titanium-oxygen bond and its application to some of the alkyl orthotitanates. The value given is 4.08. Molar refractions of tetrapropyl, tetraisopropyl, tetra(*sec*-butyl), tetra(*tert*-butyl), tetraamyl, tetra(*tert*-amyl), tetracyclohexyl, and tetraheptyl orthotitanates were calculated using this value and were found to check satisfactorily.

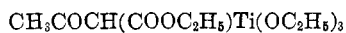
Ishino and Minami (167) have studied the hydrolysis of tetrabutyl orthotitanate. Franklin (124) has determined the dipole moments of tetraethyl orthotitanate, triethoxytitanium chloride, and phenoxytitanium tetrachloride. Takatani, Yoshimoto, and Masuka (378) have studied the infrared spectra of alkyl orthotitanates.

Acetylacetone reacts with well-cooled tetraisopropyl orthotitanate in heptane to give $(\text{iso-C}_3\text{H}_7\text{O})_2\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$ (119) and a polymer $[\text{OTi}(\text{C}_5\text{H}_7\text{O}_2)_2]_x$. Treated similarly, tetramethyl orthotitanate reacted but rather inconclusively. Tetrabutyl, tetra(*sec*-butyl), tetrakis(2-ethylbutyl), and tetrakis(2-ethylhexyl) orthotitanates formed compounds of the general formula $(\text{RO})_2\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$. Tetraacetylene reacted with tetrabutyl orthotitanate to yield products of the general formula $\text{C}_{12}\text{H}_{17-18}\text{TiO}_6$ and $\text{C}_{12}\text{H}_{17}\text{TiO}_{4.5}$. Tetraacetylene reacted with $(\text{iso-C}_3\text{H}_7\text{O})_2\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$ to form $\text{C}_{16}\text{H}_{26}\text{TiO}_6$ and $\text{C}_{11}\text{H}_{17-18}\text{TiO}_{6.4}$. (See also the work of Breed (69).)

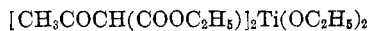
Reid, Bish, and Brenner (330) have studied the electrolysis of nonaqueous solutions of titanium compounds.

Orthotitanates with chlorine in the alkyl radical may be prepared by the action of a compound containing TiCl on ethylene oxide or a derivative (343). By this means there have been prepared $\text{Ti}(\text{OCH}_2\text{CH}_2\text{Cl})_4$, $\text{Ti}(\text{OCH}_2\text{CHClCH}_3)_4$, and $\text{Ti}(\text{OCH}_2\text{CHClC}_2\text{H}_5)_4$. The position of the chlorine atom in the last two products is assumed. Pechukas (313) has prepared $\text{Cl}_3\text{TiOCH}_2\text{CH}_2\text{Cl}$ by the same method. This product reacts further with vinylethylene oxide to form $\text{CH}_2=\text{CHCHClCH}_2\text{OTiCl}_2(\text{OCH}_2\text{CH}_2\text{Cl})$, and at 5°C, this compound interacts with 1,3-butadiene dioxide and the first product to form a solid resinous material. The ester containing the vinyl group can be copolymerized with other vinyl monomers under peroxide catalysis.

Ishino and Minami (170) have allowed tetraethyl orthotitanate and ethyl acetoacetate to interact with the formation of



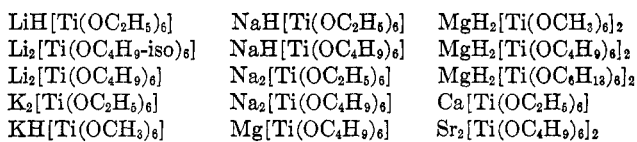
and



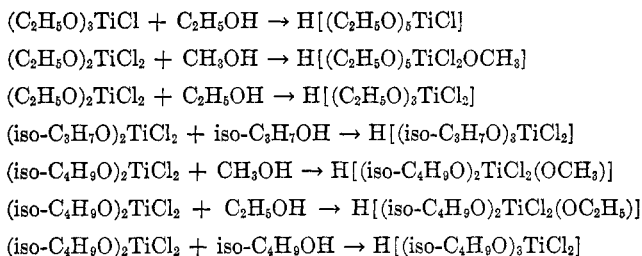
and with probable formation also of the tri- and tetrasubstituted compounds. It is probable also that the first two products exist as chelates of the enol form of ethyl acetoacetate, as evidenced by ultraviolet

and infrared data.

Two patents from the laboratories of Eastman Kodak Company (74, 75) report the preparation of addition compounds resulting from the union of titanium ortho esters, alcohols, and metallic alkoxide, such as:

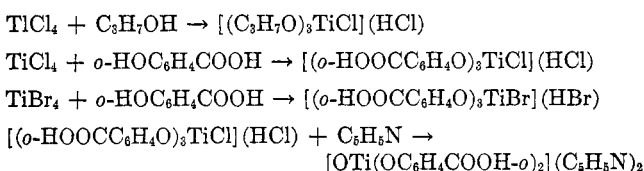


These compounds are used as catalysts in the condensation of esters of dicarboxylic acids and polyhydroxy compounds. Jennings, Wardlaw, and Way (175) have carried out the following reactions:



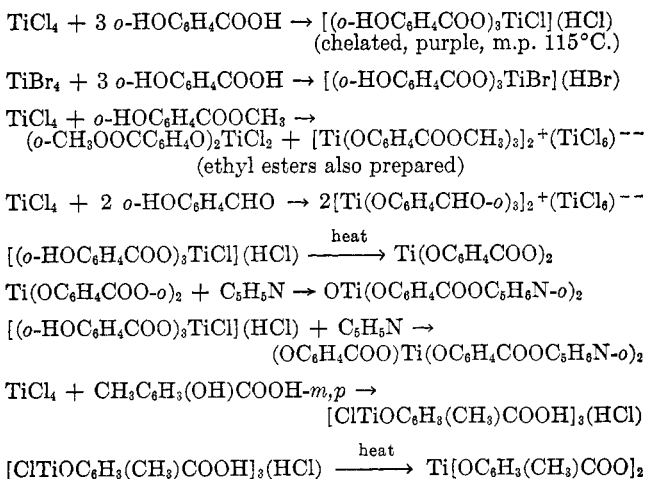
Formulas such as the above are given added weight by the work of Bradley, Hancock, and Wardlaw (61), who report the preparation of $\text{H}[\text{Ti}(\text{OC}_2\text{H}_5)_6]$.

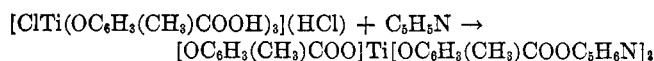
Coördination compounds containing hydrohalogen acids were reported as early as 1905 by Rosenheim and Schnabel (337):



The last product resulted from the action of pyridine on the coördination compound with hydrogen bromide.

Rosenheim, Schnabel, and Bilecki (338) continued the work, repeating some of the above reactions and adding the following:





$\text{Ti}(\text{OC}_6\text{H}_4\text{COO})_2$ has been prepared by Levi (193).

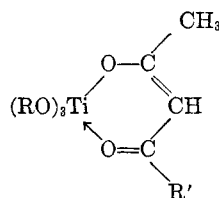
Scagliarini and Tartarini (348) have prepared several more coordination compounds involving titanium(IV) chloride and also some of the alkoxy derivatives of titanium:



Analogous compounds, prepared by Rosenheim and Sorge (339), have already been mentioned.

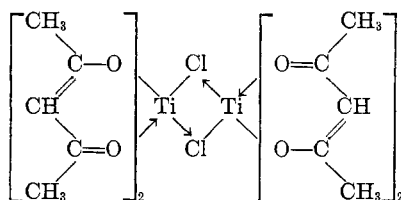
Ishino, Minami, and Asada (171) have isolated a double compound of amoxytitanium trichloride and amyl alcohol in 1:1 molar ratio. Reeves and Mazzeno (329) have shown by cryoscopic data that tetra(*tert*-butyl) orthotitanate in *tert*-butyl alcohol, ethylene glycol, octamethylene glycol, or tetramethylene glycol forms aggregates with a titanium:glycol ratio of 2:3, perhaps even 4:6, with some evidence favoring the existence as 2:2, 2:4, and 3:6. With ethyl acetoacetate, the orthotitanate forms 1:1 and 1:2 double compounds. Coordinated titanium is favored.

When equimolar parts of acetylacetone or ethyl acetoacetate and an alkyl orthotitanate are brought together, a pentacoordinated compound is produced (403), such as



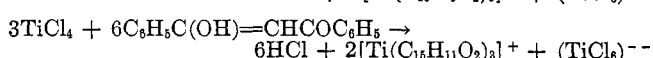
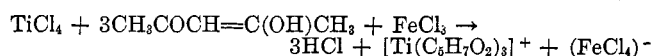
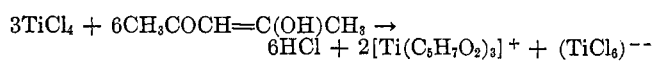
$\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{or } \text{C}_4\text{H}_9; \text{R}' = \text{CH}_3 \text{ or } \text{C}_2\text{H}_5\text{O}.$

and with two equivalents of the former, hexacoordinated products. These compounds are monomeric in benzene. Hydrolysis of dialkoxytitanium bisacetylacetonate yields a "new type of titanium complex," $\{\text{OTi}[\text{CH}(\text{COCH}_3)_2]_2\}_2$. Titanium(III) chloride reacts with acetylacetone to form a compound of molecular weight 490-540 (318), to which the following structure has been assigned:



Minami, Talano, and Ishino (225) have reported that tetraethyl orthotitanate reacts with ethyl acetoacetate to form the compounds $(\text{C}_2\text{H}_5\text{O})_3\text{TiCH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$ and $(\text{C}_2\text{H}_5\text{O})_2\text{Ti}[\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5]_2$.

Dilthey (102) has reported the following interesting syntheses:



It is to be assumed that these diketones are enolized and that the products are TiOC -containing compounds with chelation to hexavalent titanium.

Bis(acetylacetonyl)titanium dichloride is formed by the action of titanium(IV) chloride on diacetyl-methane; it is monomeric in boiling benzene (307). In isopropyl alcohol the chlorine atoms are replaced by isopropoxy groups. With ferric chloride a double compound is formed of the formula $(\text{TiCl}_4)[\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2]$. It is probably chelated in some manner. Chakravarti (82) has reported the synthesis of the compound $\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_3$, probably also chelated, by the interaction of titanium(III) chloride and diacetyl-methane in the presence of dry ammonia and in benzene solution.

Formulas such as the preceding are given added weight by the work of Bradley, Hancock, and Wardlaw (61), who report the preparation of $(\text{C}_2\text{H}_5\text{OTiCl}_3)(\text{CH}_3\text{COOC}_2\text{H}_5)$ and $(\text{iso-C}_3\text{H}_7\text{OTiCl}_3)(\text{CH}_3\text{COOC}_2\text{H}_5)$.

TABLE 6
Coordination compounds

Formula	Melting Point °C.	Boiling Point °C.	Reference
$(\text{C}_5\text{H}_7\text{OTiCl}_3)(\text{C}_5\text{H}_{11}\text{OH})$		105-110/0.5 mm.	(171)
$\text{H}[(o\text{-HOC}_6\text{H}_4\text{COO})_2\text{TiCl}_2]$	115		(338)
$(\text{C}_2\text{H}_5\text{OTiCl}_3)(\text{CH}_3\text{COOC}_2\text{H}_5)$		90/0.5 mm.	(122)
$(\text{iso-C}_3\text{H}_7\text{OTiCl}_3)(\text{CH}_3\text{COOC}_2\text{H}_5)$		70/0.1 mm.	(122)
$[\text{Ti}(\text{OC}_6\text{H}_4\text{Cl-}o)_4](\text{HOC}_6\text{H}_4\text{Cl-}o)$ - (C_6H_5)	90.5		(127)

These compounds can be distilled without decomposition or disproportionation, a result which leads to the assumption of strong bonds of chelation or secondary valence. (See also the work of Bourne, Nery, and Weigel (48).)

IV. TITANIUM ALKOXIDES AND AROXIDES OF HIGHER MOLECULAR WEIGHT, INCLUDING POLYMERS

Lowe (197) has described the interaction of dibutoxytitanium dichloride, 2-ethyl-1,3-hexanediol, and pyridine to form, eventually, highly viscous, tacky products, insoluble in water but soluble in ethyl alcohol and hydrocarbons. Synthetic naphthenate catalysts are used and other glycols are listed.

Nesmeyanov, Brañina, and Freidlina (274) have hydrolyzed tetraethyl orthotitanate in aqueous ethyl alcohol to form octaethoxytritanoxane in 70-75 per cent yields. The product very easily undergoes

further hydrolysis. Only in very dilute benzene solutions is this compound monomeric. When heated in a vacuum it polymerizes further to a material of molecular weight 750-770, probably a pentamer. Under different conditions, an octamer is obtained and an amorphous polymer, melting at 185-190°C.

Dibutoxytitanium dichloride reacts with aqueous butyl alcohol in toluene below 10°C. to give a straw-colored liquid polymer. Ammonia gas is bubbled through the system (55). This polymer is distillable without decomposition. Diethoxytitanium dichloride and distearoxytitanium dichloride may also be used and tributoxytitanium chloride as a chain stopper. Diethylamine is satisfactory as a proton acceptor.

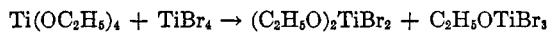
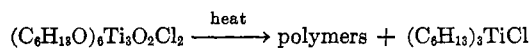
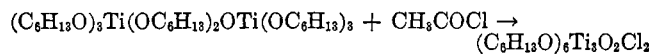
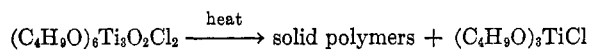
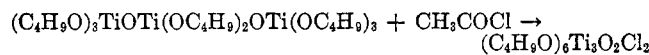
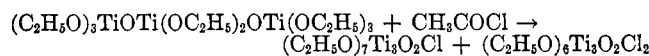
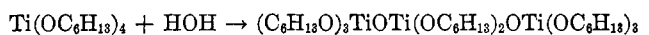
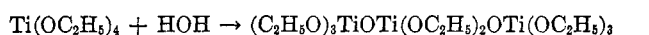
Under an atmosphere of nitrogen, potassium reacts with tetraethyl orthotitanate in ether to form the unstable product triethoxytitanium (284, 286). This compound is easily oxidized to hexaethoxydititanoxane, which in turn is capable of reacting with propyl alcohol with subsequent replacement of all ethoxy groups by

TABLE 7
Esters of higher molecular weight

Formula	Melting Point °C.	References
$(C_2H_5O)_2Ti[Ti(OC_2H_5)_2O]_2C_2H_5$	165-170	(247)
$(C_2H_5O)_3TiOTi(OC_2H_5)_2OTi(OC_2H_5)_3$	90-100	(274)
	75-85	(276, 277)
$(C_2H_5O)_3TiOTi(OC_2H_5)_3$	132-134	(275, 284)

propoxy. The reaction with butyl alcohol is analogous.

Nesmeyanov, Braunina, and Freidlina (276, 277) have presented the following reactions:



Resins are formed by the interaction of titanium(IV) chloride and glycol (407). Polymeric compounds of titanium are produced by the hydrolysis of TiOM monomers, where M is a metallic element (15).

Tetrabutyl orthotitanate in butyl alcohol solution can be hydrolyzed by the addition of water at 30°C. to a polytitanate with a viscosity of 5 to 25 centipoises

(53). Tetraphenyl and tetra(2-ethylhexyl) orthotitanates are also effective.

Nippon Telegraph and Telephone Company (287) has prepared coating materials from $Ti(OC_3H_7)_4$ and $Ti(OC_4H_9)_4$. Plastic fibers have been formed from tetraoctyl orthotitanate with coconut oil and "Syntex 120" (113). In addition, it is reported that tetraisopropyl orthotitanate is hydrolyzed to hexaisopropoxydititanoxane which, in turn, reacts with benzyl acetate to form 1,2-dibenzoyloxytetraisopropoxytetraitanoxane. Andrianov and Zhdanov (14) produced polymeric substances by the hydrolysis of tetrakis(trimethylsilyl) orthotitanate and tetrakis(triethylsilyl) orthotitanate.

Tetraoctadecyl, tetradodecyl, and tetrabutyl orthotitanates are used in the waterproofing of fabrics, probably through their hydrolysis (56). Other fabrics have also been treated with varying amounts of titanium compounds for water repellancy (83). Among the compounds used were tetrabutyl orthotitanate, titanium(IV) oxide, tetra(*p*-tolyl) orthotitanate, and titanium ethylhexanoate.

Esters of orthotitanic acid are of value as polymerization catalysts (77). Thus, tetrabutyl, tetraethyl, tetrapropyl, and tetraamyl orthotitanates catalyze the polymerization of compounds such as dibutyl *p,p'*-sulfonyldibenzoate, among nineteen compounds listed. Other catalysts of analogous types are $[(CH_3)_4N]^+(H) + [Ti(OC_4H_9)_6]^-$ and $[(C_2H_5)_4N]^+(H) + [Ti(OC_2H_5)_6]^+$, as well as several more.

Natural and artificial fibers, including glass, are coated with titanium(IV) oxide prior to further processing, by the use of alkyl orthotitanates or esters of organic acids, probably through their slow hydrolysis (350). Sidlow (357) has reviewed the use of orthotitanates in paints.

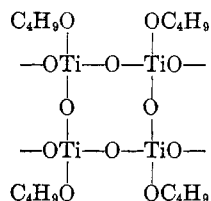
The partial hydrolysis of $Ti(OC_3H_7\text{-iso})_4$ and of $Ti[OCH_2CH(C_2H_5)C_4H_9]_4$ in acid solution gives products of good gelling ability (112, 352).

Tetraethyl orthotitanate has been recommended as an ingredient in the waterproofing of paper (393).

Gelled compositions are formed by adding orthotitanates to oxidized glycerides (34).

To accelerate the drying of oils (after oxidation), 0.1 to 0.5 part of tetraalkyl orthotitanates is added (57). Treatment to form a chelated titanium compound renders cotton and viscose nonflammable (139).

Minami, Akiyama, and Ishino (221) hydrolyzed tetrabutyl orthotitanate with aqueous butyl alcohol to obtain polybutyl titanates, which were liquid when the water:titanium ratio was 0.5, gelatinous when it was 1.0, and solid when it was 1.5. The same workers also found (222) that the viscosity of the resultant product increases with increasing water:titanium ratio. Minami and Ishino (223) later found evidence for the formation of a cyclic tetramer with later condensation to form:



Takatani, Yoshimoto, and Masuka (378) have studied the infrared spectra of complex polytitanates.

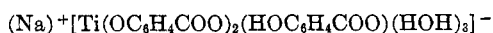
Speer and Carmody (368) have reported the synthesis of waterproofing agents prepared by the hydrolysis of tetraalkyl orthotitanates and useful in connection with cotton, felt, wood, and suede leather. Complex alcohols such as 2-ethyl-1,3-dihydroxyhexane, 1,3-dihydroxy-2-methylpentane, and 2-butyl-1,3-dihydroxybutane react with certain tetraalkyl orthotitanates with radical interchange. These product orthotitanates are then hydrolyzed to polymers (47). Polymeric titanium esters are also prepared by the action of organic acids on certain polymeric orthotitanates (52). Ide (162) has patented a method for the preparation of organotitanium resins by treating titanium(IV) chloride with a bifunctional alcohol at temperatures below 10°C. and with a mole ratio of 1:1. Gelatinous products were obtained; a solution of the product in ethyl alcohol was found useful as an adhesive for glass, wood, and polystyrene.

Interpolymers have been prepared of tricetoxytitanium and vinyl acetate giving enamel-like surfaces (340). Partial hydrolysis of tetrabutyl orthotitanate gives high-molecular-weight butoxytitanium polymers (376). Some of the butoxyl groups can be replaced by cinnamoyl and the resulting resin copolymerized with styrene and benzoyl peroxide. Tetra-β-aminoethyl orthotitanate when treated with sorbitol or a similar reactant yields products of high molecular weight (341). Titanium reacts with triacetyllevoglucosan to form the 1-chloro derivative (410)

V. TITANIUM SALTS OF ORGANIC ACIDS

Pande and Mehrotra (308) have prepared dichlorotitanium diacetate by the action of a mixture of acetic acid and acetic anhydride on titanium(IV) chloride. On distillation, the product undergoes disproportionation and loses acetic anhydride to form hexaacetoxydititanoxane and 1,3-dichlorotetraacetoxydititanoxane. Dichlorotitanium diacetate has also been prepared by Fichter and Reichert (120) by the action of acetic acid on titanium(IV) chloride.

Sudarikov and Smirnov (73) have prepared a coordinated sodium titanium salt of the formula



from sodium salicylate. Pyatnitskiĭ (325) has reported the preparation of certain coordinated titanium tartrates.

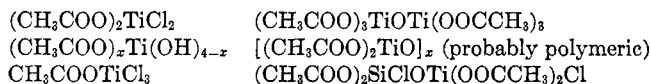
A complex oxalate has been reported by Subbanna,

Rao, and Bhattacharya (370).

Diethoxytitanium dibenzoate and a 1:1 double compound between ethoxytitanium tribenzoate and oxytitanium dibenzoate have been prepared by the action of benzoic acid on tetraethyl orthotitanate (391).

Titanium(IV) sulfide reacts with acetic acid to form, probably, titanium(IV) acetate. When this compound is heated in aqueous butyl alcohol a white, waxy, polymeric titanate is formed (53). The reaction with phthalic acid is similar.

Titanium(IV) chloride reacts with organic acids with formation of the following isolable products (179):

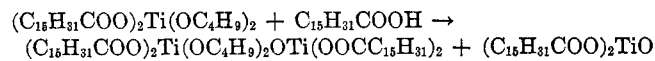
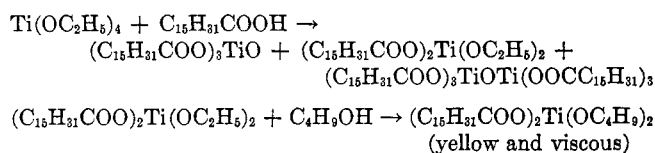


Treatment of alkyl orthotitanates with an organic acid produces $(\text{RCOO})_x\text{Ti}(\text{OR}')_{4-x}$ from linoleic, oleic, methacrylic, acrylic, and propionic acids. (R' is butyl or isoamyl (382).) Titanium(IV) oxide reacts similarly (144, 145).

Interchange between chlorine and acyloxy has been extended into the field of the carbohydrates. Pacsu (306) treated pentaacetylglucose with titanium(IV) chloride and obtained α-acetylchloroglucose. This reaction was extended to the preparation of α-aceto-chloromannose, heptaacetyl-α-chlorolactose, heptaacetyl-α-chlorogentiobiose, and tetraacetyl-β-salicin chloride. It was found that titanium(IV) chloride converted tetraacetyl-β-methylglucoside to its α-isomer. Zemlen and Csürös (410) treated triacetyllevoglucosan with titanium(IV) chloride and obtained 2,3,4-triacetyl-1-chloroglucose.

Giua and Monath (134, 135) have studied the reaction of formic, acetic, and isovaleric acids with titanium(IV) chloride. A mixture of acetic acid and acetic anhydride gave $[\text{Ti}(\text{OOCCH}_3)_2]^+ \text{Cl}^-$.

Pande and Mehrotra (311) have reported the following reactions:



Stearic acid is also satisfactory and isopropyl alcohol may be used.

Kiselev and Ermolaeva (184, 185, 186) have obtained polymeric products containing acyl radicals by the interaction, for instance, of tetrabutyl orthotitanate and fatty acids such as oleic, with dry carbon dioxide passing through the system. Titanium(IV) oleate is thus prepared, also butoxytitanium trioleate and bis-(trioleyl)titanium oxide. These polymers are capable

of forming films. Plastic films have been prepared from titanium(IV) stearate, pentaerythritol phthalate, and "Syntex 120" (113).

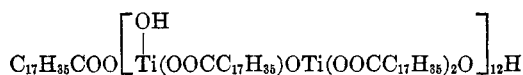
Triisopropoxytitanium reacts with butyric acid to form hexabutyroxydititanoxane (309), and a similar compound is formed by the action of valeric acid. Palmitic acid forms a double compound of hexapalmitoxydititanoxane and titanyl dipalmitate. Similar reactions are reported using tetraethyl orthotitanate (310), the two isolable products being triethoxytitanium acetate and diethoxytitanium diacetate.

Tetraethyl orthotitanate reacts with acetic acid with the formation of a solid product. Tetrabutyl orthotitanate and stearic acid form a coordination product containing three moles of oxotitanium distearate and one of tributoxytitanium hydroxide, as well as another consisting of butoxyoxotitanium stearate and bis(tributoxytitanium) oxide, in 1:1 molar ratio. Polymers can be formed from these and their isopropyl homologs, also using oleic acid (141, 194).

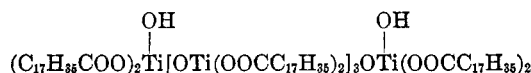
TABLE 8
Titanium salts of organic acids

Formula	Melting Point °C.	Reference
$(C_{17}H_{35}COO)_2Ti[OTi(OH)_2]_2OTi(OH)_2$	54-55	(62)
$[(C_{17}H_{35}COO)_2TiO]_2[(C_4H_9O)_2TiOH]$	51.6-52.4	(419)
$[C_{17}H_{35}COOTi(O)OC_4H_9]_2[(C_4H_9O)_2TiOTi(OC_4H_9)_2]$	69.5-72.1	(419)
$(C_{17}H_{35}COO)_4Ti$	64	(64)

In heptane solution, and in the presence of triethylamine, stearic acid reacts with titanium(IV) chloride to give a product which, when thrown into water, forms



and



Similarly, lauric acid gives a polymer of the formula $(C_{11}H_{23}COOTiOOH)_x$ (31).

Polymeric ester-impregnated wood has been prepared by the action of a 10 per cent toluene or xylene solution of polymeric isopropyltitanium stearate on wood blocks (191). This action results in impregnation and is followed by evaporation of the solvent. Other alkoxy and acyloxy groups are also satisfactory, for instance, oleate, "linseed acylate," and "soya acylate" as well as butoxy, "octylene glycol," acetylphenyl, and octyl. Tests showed a substantial increase in water repellancy as a result of this treatment.

National Lead Company (239) and Russell (341, 342) have covered the stabilization of titanium salts of certain

organic hydroxy acids by the addition of polyols.

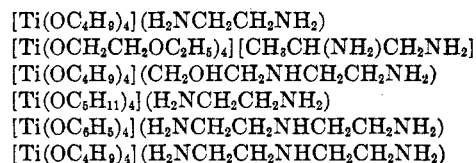
Titanium soaps, useful in waterproofing, are prepared by the interaction of titanium(IV) chloride and a selected calcium salt (344). The complex, probably an ester, which is formed by the interaction of lactic acid and tetraisopropyl orthotitanate, is useful as a gelling mixture (353). Titanium chelates of hydroxy acids are stabilized to a high pH by addition of a polyol to form "solutions useful in dyeing." Sorbitol added to the monolactate, dilactate, mandelate, citrate, malate, or tetralactate is useful. Mannitol and other sugar alcohols may be used in place of sorbitol.

Other titanium soaps have been prepared by the interaction of titanium(IV) chloride and sodium stearate (240). The titanium(IV) stearate thus formed reacts with 2-methyl-2,4-pentanediol with the production of a waxy solid. Use of tetrabutyl orthotitanate instead of titanium(IV) chloride gives the same type of product. Other compounds reacting with titanium include 2-methyl-2,4-pentanediol, 2-ethylhexanol, 1,4-butanediol, oleic acid, 1,2-propanediol, 1-butanol, 3,6-dimethyloctadiol-3,6-ene-4, benzoic acid, acetic acid, 4-ethyl-3-hexanol, myristic acid, 2,2,4-trimethyl-2-pentanol, 2,5-dimethyl-2,4-hexanediol, and 3-hexenediol-2,5.

Oxalato complexes of titanium have been reported by Babko and Dubovenko (26). Varma and Mehrotra (390) have prepared trichlorotitanium benzoate and dichlorotitanium dibenzoate by the interaction of titanium(IV) chloride and benzoic acid.

VI. TITANIUM COMPOUNDS CONTAINING NITROGEN

Coördinating compounds in which nitrogen could be attached to titanium by secondary valence include $(TiCl_4)[(CH_2)_6N_4]_{12}(CHCl_3)_3$ and $(TiI_4)[(CH_2)_6N_4]_4-(CHBr_3)_5$ (347). Beacham and Merz (36) report the synthesis of the following:



Tetrabutyl orthotitanate reacts with triethanolamine to form a reddish brown solid which softens at 70°C. (361). Tetraisopropyl orthotitanate also reacts with triethanolamine (341). The nitrogen:titanium ratio is 0.38:1.00. Alkyl orthotitanates with aqueous aminoalcohols are effective gelling catalysts, for instance, for linseed oil (149). In carbon tetrachloride, titanium(IV) chloride and *N,N*-dimethylformamide unite with the formation of a 1:1 compound, melting at 220-225°C. In dichloromethane, titanium(IV) chloride and formamide unite in a 1:2 ratio, losing hydrogen chloride on heating. At 0°C. the ratio is 1:3 (24). The interaction of tetraisopropyl orthotitanate and ethylamine is

TABLE 9
Titanium compound containing nitrogen

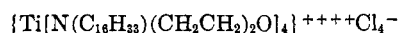
Formula	Melting Point	Reference
	°C.	
(TiCl) ₂ [HCON(CH ₃) ₂]	220-225	(24)

slight (84). Farbenfabriken Bayer A.-G. (117) has described a process for the preparation of a product from the interaction of an alkyl orthotitanate and cellulose nitrate. When tetrabutyl orthotitanate is used, for instance, gelling occurs immediately. Other hydroxy compounds found acceptable included diacetone alcohol, ethyl acetoacetate, and "polyglucose ethyl ether." A mixture of tetrabutyl orthotitanate and ethylenediamine in isobutyl alcohol is recommended as a curing agent for certain resins (234). Propylenediamine, tetraethoxyethyl orthotitanate, 1,3-diamino-2-propanol, tetramethyl orthotitanate, diethylenetriamine, and tetraphenyl orthotitanate may also be used.

One mole of titanium(IV) sulfide in benzene reacts with four moles of aniline at 50°C. to form, after 2 hr., Ti(NHC₆H₅)₄ (50). Conditions must, of course, be anhydrous. Butylamine or dibutylamine may also be used. Jacini (173) has prepared similar compounds from titanium(IV) chloride. The aniline derivative mentioned above can be hydrolyzed in aqueous butyl alcohol and carbon tetrachloride to give a waxy solid (53). Ti(NHC₄H₉)₄ reacts similarly. Other similar compounds have been reported, after polymerization, as coatings against rust (128).

Derner and Fernelius (100) allowed titanium(IV) chloride to react with *N*-potassiodiphenylamine and with *N,N*-dibenzylthiocarbamic acid to form Ti-[N(C₆H₅)₂]₄ and [(C₆H₅CH₂)₂NCSS]₄Ti, respectively. Several other derivatives were similarly prepared.

When *N*-cetylmorpholine in toluene is treated with titanium tetrachloride there is formed an ammonium type of product (366):



Tetraisopropyl orthotitanate reacts with "Aquadrol," *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine, with evolution of isopropyl alcohol (35, 233, 267). The product is probably polymeric and is used as a dispersing agent in aqueous media. Other examples are also given.

A patent issued to Titan Company (384) has covered the use of stabilizers for aminoalkyl orthotitanates.

Diethyl 4,4'-methylenedicarbamate reacts with tetrabutyl orthotitanate in butyl alcohol to give a polymeric substance, probably with N=C(O)OTi linkages (76). This polymer possesses strong elastic properties when extruded in the molten state through a spinneret. When extruded through a die, clear tough films result.

Other properties of a similar nature have been reported. Orthotitanates of aminoalcohols are described by the National Lead Company (236) and by Titaan N. V. (380).

VII. TITANIUM COMPOUNDS CONTAINING SILICON

Orlov, Dolgov, and Voronkov (301, 302) have reviewed the reactions of disiloxanes with titanium(IV) chloride. In the presence of aluminum chloride the products correspond to the formula (R₃SiO)_zTiCl_{4-z}, while tetraalkyl orthotitanates react with trialkylsilanes in the presence of metallic sodium to form Ti(OSiR₃)₄ (300).

Sodium trimethylsilanolate reacts with titanium(IV) chloride to give tetrakis(trimethylsilyl) orthotitanate, tris(trimethylsiloxy)titanium chloride, and trimethylsiloxytitanium trichloride in relative proportions of 66:53:27 (9). The first compound undergoes disproportionation with titanium(IV) chloride to form bis(trimethylsiloxy)titanium dichloride. Butyl alcohol reacts with tris(trimethylsiloxy)titanium dichloride and pyridine in benzene to form butyltris(trimethylsilyl) orthotitanate. Titanium(IV) chloride reacts with trimethylsilanol and ammonia to form tetrakis(trimethylsilyl) orthotitanate (116). Sodium triethylsilanolate reacts with titanium(IV) chloride to form tetrakis(triethylsilyl) orthotitanate (13). Trimethylsilanol reacts with tetraisopropyl orthotitanate to form tetrakis(trimethylsilyl) orthotitanate, triisopropyl trimethylsilyl orthotitanate, and diisopropyl bis(trimethylsilyl) orthotitanate (93). Bradley and Thomas (68) have reported the action of tetraisopropyl orthotitanate on trimethylsilyl acetate to form tetrakis(trimethylsilyl) orthotitanate in 95 per cent yields. In similar manner a 93 per cent yield of tetrakis(triethylsilyl) orthotitanate was obtained.

The reaction between sodium and trimethylsilanolate and titanium(IV) chloride to form tetrakis(trimethylsilyl) orthotitanate has also been reported by Andrianov and Zhdanov (14) and by Andrianov, Zhdanov, Kurasheva, and Dulova (18, 19). Tetrakis(triethylsilyl) orthotitanate was similarly prepared. Hydrolysis of these two compounds produces polymers.

Diethylmethylsilanol reacts with titanium(IV) chloride and pyridine to form tetrakis(diethylmethylsilyl) orthotitanate (109, 110). Tetrakis(triethylsilyl) and tetrakis(triphenylsilyl) orthotitanates are similarly prepared. Andrianov and Delazari (8) have synthesized several additional orthotitanates in a corresponding manner, using sodium dimethylphenylsilanolate and diphenylmethylsilanol, the latter with ammonia. Titanium(IV) chloride reacts with bis(trimethylsiloxy)lead to form tetrakis(triethylsilyl) orthotitanate (16, 17). Tetrakis(triethylsilyl) orthotitanate is also formed by the action of triethylsilanol and tetraethyl ortho-

TABLE 10
 Compounds containing titanium and silicon

Formula	Melting Point °C.	Boiling Point °C.	Other Properties	References
Ti[OSi(CH ₃) ₃] ₄		69-74/1-2 mm. 110/10 mm. 110/10 mm. 106/7 mm. 112/11 mm. 100/2 mm. 62/1 mm. 110/10 mm.	$n(20^\circ/D) = 1.4275$; $d(20^\circ) = 0.9044$ $n(20^\circ/D) = 1.4278$; $d(20^\circ) = 0.9078$ $n(20^\circ/D) = 1.4277$; $d(0^\circ) = 0.9051$ $n(22^\circ/D) = 1.4300$ $n(20^\circ/D) = 1.4292$	(220) (108) (18, 248) (116, 408) (9) (369) (68) (14)
[(CH ₃) ₃ SiO] ₂ TiCl ₂		67/3 mm.		(9)
[(CH ₃) ₃ SiO] ₂ TiCl.....		103-105/10 mm.		(9)
(CH ₃) ₃ SiOTi(OC ₂ H ₅ -iso) ₃		114/13 mm.	$n(22^\circ/D) = 1.4490$	(93)
[(CH ₃) ₃ SiO] ₂ TiOC ₂ H ₅		76-77/2 mm.	$n(20^\circ/D) = 1.4317$; $d(20^\circ) = 0.9070$	(9)
[(CH ₃) ₃ SiO] ₂ Ti(OC ₂ H ₅ -iso) ₂		120/14 mm.	$n(22^\circ/D) = 1.4408$	(93)
(CH ₃) ₃ SiOTiCl ₂		67/3 mm.		(9)
Ti[OSi(C ₂ H ₅) ₂] ₄	96	176-178/2.5 mm.; 169-171/1.5 mm. 199-202/3.5 mm.	$d(20^\circ) = 0.9809$; $n(20^\circ/D) = 1.4812$ $d(20.5^\circ) = 0.917$	(16) (402)
	96	221-222		(13)
	95	204/4 mm.		(14)
	96	176-178/2-3 mm.		(17)
	95-97	227-230/7 mm.		(109, 110)
	99-101	195/3.5 mm.		(108)
Ti[OSi(C ₂ H ₅) ₂ CH ₃] ₄		196/6 mm. 154/3 mm.	$n(20^\circ/D) = 1.4565$; $d(20^\circ) = 0.9248$ $n(20^\circ/D) = 1.4545$; $d(20^\circ) = 0.9244$	(109, 110) (108)
Ti[OSi(C ₂ H ₅) ₂ CH ₃] ₄		186/3 mm.	$n(20^\circ/D) = 1.4570$; $d(20^\circ) = 0.9044$	(108)
(C ₂ H ₅ O) ₂ TiOSi(OC ₂ H ₅) ₂		125-126/1 mm.; 66-69/10 ⁻⁵ mm.	$n(20^\circ/D) = 1.4647$	(391)
(C ₂ H ₅ O) ₂ TiOSi(OC ₂ H ₅) ₂ O Ti(OC ₂ H ₅) ₃		78-81/10 ⁻⁵ mm.	$n(20^\circ/D) = 1.4910$	(282)
(iso-C ₄ H ₉ O) ₂ TiOSi(OC ₂ H ₅ -iso) ₃		75-78/10 ⁻⁵ mm.	$n(20^\circ/D) = 1.4610$	(282)
Ti[OCH ₂ CH(C ₂ H ₅)C ₂ H ₅] ₄		194/0.25 mm.	$d(25^\circ) = 1.0711$	(191)
Ti[OSi(C ₂ H ₅) ₂] ₄	501-505 ca. 480	370/1 mm.	$d(29^\circ) = 1.215$; $n(114^\circ) = 1.6488$	(408) (109, 110)
Ti[OSi(CH ₃) ₂ C ₂ H ₅] ₄		274-275/7 mm.	$n(20^\circ/D) = 1.5392$; $d(20^\circ) = 1.0533$	(8)
Ti[OSi(C ₂ H ₅) ₂ CH ₃] ₄		370-374/6 mm.	$n(20^\circ/D) = 1.5960$; $d(20^\circ) = 1.1248$	(8)
Ti[OsSi ₄ (C ₂ H ₅) ₂] ₂	214.0-214.5			(409)

titanate (402); tetrakis(trimethylsilyl) orthotitanate can be similarly prepared (111, 220).

Titanium(IV) chloride reacts with ethyltriethoxysilane to form tetrakis(ethyldiethoxysilyl) orthotitanate (4). Similarly, tetrakis(hexyldiethoxysilyl), tetrakis(diethoxydecylsilyl), and tetrakis(triethoxysilyl) orthotitanates are synthesized (5).

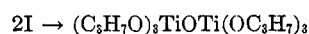
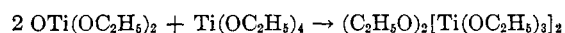
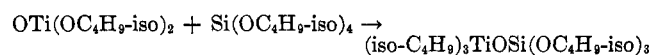
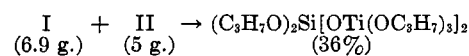
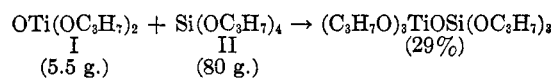
Zeitler and Brown (408, 409) have prepared tetrakis(triphenylsilyl) orthotitanate by two methods. Reaction of tetrabutyl orthotitanate with triphenylsilanol yielded a quantitative amount of the desired product. Similarly, titanium(IV) chloride and triphenylsilanol in the presence of ammonia also gave tetrakis(triphenylsilyl) orthotitanate. This compound is slightly soluble in organic solvents at their boiling points. It melts with decomposition at 460-470°C. Titanium(IV) chloride reacts with dimethylphenylsilanol and with sodium diphenylmethylsilanolate to form, respectively, tetrakis(dimethylphenylsilyl) and tetrakis(methylphenylsilyl) orthotitanates (8).

Tetrabutyl orthotitanate reacts with trimethylsilyl acetate to form [(CH₃COO)₂TiO]₄ and [(CH₃COO)₂TiO]₃[CH₃COOTi(O)OSi(CH₃)₃] (10). Titanium(IV) chloride reacts with the same silicon compound with the formation of chlorotrimethylsilane.

In the presence of a proton acceptor such as pyridine,

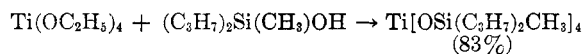
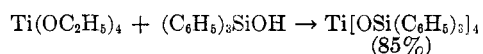
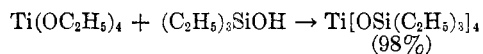
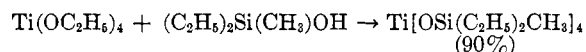
titanium(IV) chloride reacts with the corresponding silanol to form tetrakis(triphenylsilyl), tetrakis(triethylsilyl), and tetrakis(diethylmethylsilyl) orthotitanates (109, 110). Bradley and Thomas (67) have prepared tetrakis(trimethylsilyl) orthotitanate in 100 per cent yield from the reaction of trimethylsilanol and tetraisopropyl orthotitanate in benzene. Isopropyl alcohol was removed as formed by azeotropic distillation. Similarly, tetrakis(triethylsilyl) orthotitanate was formed from triethylsilanol and tetraisopropyl orthotitanate.

Compounds of the type OTi(OR)₂ have been shown to be monomeric in benzene, when R is propyl or butyl (282). This is shown by the following reactions:



Silicon-substituted orthotitanates have been prepared by Dolgov and Orlov (108) from a series of tetraalkyl orthotitanates and substituted silanols.

These reactions were carried out in benzene with 0.01 per cent of sodium present:



Warrick (396) has covered the preparation of titanium dioxide-reinforced liquid polymeric siloxane containing mostly methyl groups but some phenyl and ethyl. Essentially analogous procedures have also been described by Nitzsche and Wick (289). Dibutyltin oxide is included, however, in the last-named compound. Tetrabutyl orthotitanate and tetrakis(β -aminoethyl) orthotitanate are incorporated into coating compositions containing a wax and a methyl polysiloxane (351). Hormats (160) has described the moisture-proofing of masonry by the application of mixtures containing polysiloxanes and titanium(IV) oxide. A combined silicon-titanium cure can be applied to butadiene resins (146). A sample "compound" is listed below:

Ingredient	Per Cent
Butadiene polymer.....	42.50
Mineral spirits.....	56.63
Ti[OCH ₂ CH(C ₂ H ₅)C ₄ H ₉] ₄	0.85
Silicone-GE, SF-03.....	0.02

Octyleneglycol orthotitanate and polymeric isopropoxytitanium oleate may also be used.

At room temperatures, polymerized dimethyloxosilane is hardened by the addition of tetraethyl, tetrapropyl, or tetrabutyl orthotitanates and certain dialkyl tin salts (32). Kienle, Eates, and Cooke (181, 182) have covered the use of titanium(IV) oxide in polysiloxanes. In the preparation of waterproofing materials, organopolysiloxanes with Si—H linkages are used along with organotitanium halides (166). A formula which includes organopolysiloxanes and tetrabutyl orthotitanate is useful in the treatment of paper to produce sensitive adhesives (360). Titanium(IV) oxide is a filler ingredient for certain polysiloxane elastomers (72).

Mamitov and Voronkov (208) list thirteen organosilicon compounds, including certain polymers, which along with tetraethyl orthotitanate enter into the composition of materials with waterproofing properties.

The orthotitanate of triethanolamine combines with methylpolysiloxanes to form heat-resistant resins (314). Silicon compounds are used in which the silicon:methyl ratio varies from 1.0 to 1.3. Tetrabutyl orthotitanate acts in the same manner with the silicon polymers.

Titanium(IV) chloride, triisobutylaluminum, and diallyldimethylsilane interact to form polymeric oils or solids of high molecular weight with 6 per cent of the units retaining their unsaturation (211). Ziegler-type catalysts have been used by others for the same purpose (387). *p*-(Trimethylsilyl)styrene is polymerized by a mixture of titanium(IV) chloride and triethylaluminum (231).

Silicone elastomers can be strengthened by a load of from 60 to 70 per cent of titanium(IV) oxide (22). In other instances silicone elastomers containing vinyl groups are compounded, first with ferric chloride, then with titanium(IV) oxide and benzoyl peroxide (209). According to another patent (369), silicone elastomers are cured by milling 100 parts with 20 parts of titanium(IV) oxide and 2.5 parts of benzoyl peroxide. Pfeiffer, Savage, and White (317) have investigated the general problem of compounding silicone rubbers with titanium(IV) oxide, and additional data on the reinforcing action have been furnished by Pfeiffer (315). Doede and Panagrossi (103) have also reported increases in the tensile strength of silicone rubbers on the admixture of titanium dioxide. As a binder for attaching silicone rubber to "solid materials" a solution of tetrabutyl orthotitanate in naphtha can be applied and then air dried (180). Instead of a butyl ester, Kiel has found 2-ethylhexyl, octylene glycol, isopropyl, methyl, dodecyl, and γ -vinylpropyl orthotitanates satisfactory. Other compounding materials are also listed.

Tetrabutyl orthotitanate and dibutyldiethoxysilane condense in a 4:1 molar ratio with benzene, water, and butyl alcohol to form a viscous copolymer (54). Other monomers are likewise acceptable such as titanium diphthalate, tetrakis(butylamino)titanium, and tetrabutoxysilane.

Cockett, Evans, and Landells (83) have covered a treatment for water repellancy which can be applied to fabrics and which includes as ingredients silicones and tetrabutyl orthotitanate. Resins are formed by the interaction of a polymethylsiloxane and a tetraalkyl orthotitanate (183). Tetraethyl orthotitanate can also be used with polysiloxanes in which the organic radical is methyl, ethyl, or phenyl (138).

Copolymers of titanium compounds containing C—O or C—N bonds have been prepared with $\text{R}_2\text{Si}(\text{OR})_{4-x}$ by cohydrolysis (227).

Nikishima, Shiihara, and Ichiki (286) have presented a new method for the preparation of silicones which contain TiO groups. By the reaction of $(\text{RO})_n\text{TiX}_{4-n}$ with $\text{R}'_m\text{H}_n\text{Si}(\text{OM})_{4-m-n}$ there are formed resinous or oily products with TiOSi bonds. (R is alkyl or aryl, R' the same, M is hydrogen or alkali metal, n' is between 1 and 0, and $3n'$ is greater than m , which in turn is greater than 1.) Titanium(IV) chloride and diphenyldisilanol give a hard resinous product, titanium(IV) chloride and triethylsilanol an oily material, and

TABLE 11
 Compounds containing carbon-titanium bonds

Formula	Melting Point °C.	Boiling Point °C.	Other Properties	References
CH ₃ TiCl ₃	28.5			(38)
(CH ₂ =CH) ₂ TiCl.....		47/2 mm.	<i>n</i> (20°/D) = 1.5920; <i>d</i> (20°) = 2.1924	(273)
C ₆ H ₅ Ti(OC ₃ H ₇ -iso) ₃	88-90			(152, 154, 234)
C ₆ H ₅ TiCl ₂	145-147 (d.)			(358)
C ₆ H ₅ TiBr ₃	174.5-175.5 (d.)			(358)
C ₆ H ₅ TiI ₃	184-186 (d.)			(358)
C ₆ H ₅ Ti(OC ₂ H ₅) ₂ Cl.....		145-150/2-3 mm.		(241)
(C ₆ H ₅) ₂ TiCl ₂	285-287			(71)
	240-243			(400)
	287.0-287.5 (d.)			(358)
(C ₆ H ₅) ₂ TiBr ₂	Decomposes at 265	29-34/1 mm.		(237)
	309-310 (d.)			(236)
	317-318 (d.)			(358)
(C ₆ H ₅) ₂ TiI ₂				(358)
(C ₆ H ₅) ₂ Ti(OC ₂ H ₅) ₂		136-145/0.8 mm.		(237)
Ti(C ₆ H ₅) ₄	Sublimes 120-180			(202)
[(C ₆ H ₅) ₂ TiCl ₂](AlCl ₃).....	155-160			(246, 262)
[(C ₆ H ₅) ₂ TiCl ₂][Al(C ₂ H ₅) ₂].....	125-130			(262)
[(C ₆ H ₅) ₂ TiCl ₂](C ₂ H ₅ AlCl).....	88-92			(262)

ethoxytitanium trichloride with disodium diphenyldisilanolate and with sodium triethylsilanolate gives hard resinous compounds.

Resinous copolymers of SiO₂ and (R₂SiO)_x with as much as 10 per cent tetraisopropyl orthotitanate have been found useful for bonding polyfluoroethylene polymers to metals, silicone resins, and other plastics (101).

Andrianov, Ganina, and Khrustalev (11, 12) have prepared polymeric compounds containing Si—O—Ti bonds from the reaction of dimethyl dichlorosilane, phenyltrichlorosilane, and tetrabutyl orthotitanate. A glassy product is formed.

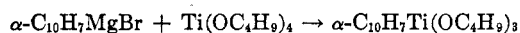
Tetrabutyl orthotitanate is used for adhering silicone rubber enclosures to small transformers for airborne equipment (312). It is converted by air to titanium(IV) oxide, which forms a birefringent film on the surface before the silicone rubber is applied.

VIII. COMPOUNDS WITH TITANIUM-CARBON BONDS

Gilman and Jones (133), Jones (177), Plets (320), and Cotton (87) have contributed to the early chemistry of this subject. In addition, compounds of the type R₂TiCl_{4-x} have been covered as aids in the coating of plastic and nonplastic organic surfaces (210).

Methyltitanium trichloride was synthesized by Beerman (38) as a result of the action of dimethylaluminum chloride on titanium(IV) chloride.

A National Lead Company patent (235) issued on the preparation of phenyltitanium triisopropoxide has shown this compound to be stable indefinitely at 10°C. The patent also covers the following preparation:

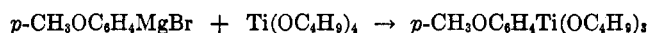
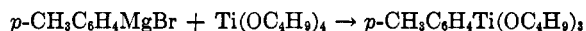
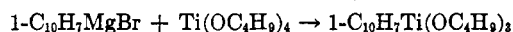


The resulting tributoxy- α -naphthyltitanium has been used without further purification for the polymerization of styrene.

Indenyltitanium tributoxide has been prepared from

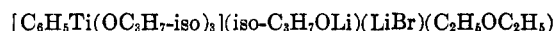
the corresponding Grignard reagent. All these compounds act as catalysts for vulcanization and polymerization.

Herman (152) has reported the following reactions:



Walter (394) has described the interaction of titanium dihydride and azobutane to form dibutyltitanium.

A coordination compound has been isolated (153) with the formula



which, however, decomposes spontaneously. Certain phenyltitanium compounds, when treated with nitrous anhydride, form diazonium salts (206).

The National Lead Company (237, 238) has synthesized several titanium derivatives of cyclopentadiene:



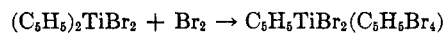
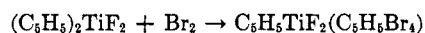
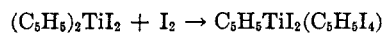
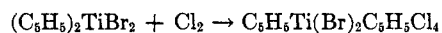
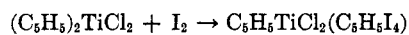
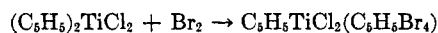
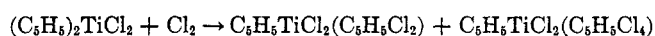
In similar manner, dicyclopentadienyltitanium dibromide and dicyclopentadienyltitanium dichloride were formed. The dibutoxy compound above easily underwent hydrolysis to a polymer. Hydrogen chloride gas reacted with dicyclopentadienyltitanium dichloride to form C₅H₇C₅H₄Ti(Cl)₂C₅H₅. Similar reactions were noted with the dibromide, diiodide, and difluoride.

Again, the National Lead Company (241) has reported a reaction between titanium(IV) chloride, tetrabutyl orthotitanate, and cyclopentadiene in benzene to form dibutoxycyclopentadienyltitanium chloride. The presence of a base such as piperidine prevents the polymerization of the product.

Titanium(IV) chloride undergoes disproportionation with dicyclopentadienyltitanium dichloride to

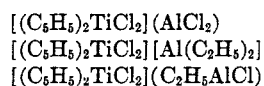
form cyclopentadienyltitanium trichloride (136) with or without a solvent. Dicyclopentadienyltitanium dichloride undergoes fission with chlorine with the formation of titanium(IV) chloride, cyclopentadienyltitanium trichloride, and $(\text{CHCl})_5$. Cyclopentadienyltitanium trichloride reacts with $\text{C}_6\text{H}_5\text{Na}$ to form dicyclopentadienyltitanium dichloride.

The National Lead Company (242) has covered several additional reactions:



Sloan and Barber (358) have prepared cyclopentadienyltitanium trichloride as orange crystals by the interaction of titanium(IV) chloride and magnesium dicyclopentadienyl. Dicyclopentadienyltitanium dichloride was also formed. The latter compound was found capable of reacting with titanium(IV) chloride to form the first. The corresponding bromides and iodides were also prepared.

Natta, Pino, Mazzanti, and Giannini (262) have isolated the following compounds:



Nesmeyanov, Borisov, Sevel'eva, and Golubeva (273) have carried out a reaction between vinylmagnesium chloride and titanium(III) chloride by which divinyltitanium monochloride is formed. A similar reaction is given for titanium(II) bromide. Tetrahydrofuran is the solvent, along with ether, at 5°C .

Dicyclopentadienyltitanium dichloride is treated with pentadienylsodium and then with carbon monoxide to form dicyclopentadienyldicarbonyltitanium (232).

The reaction of bis(cyclopentadienyl)titanium dibromide with lithium chloride and with benzyldimethyloctadecylammonium chloride is first order with respect to chloride (176).

Cotton (87) included compounds of titanium in a review of certain classes of organometallic compounds.

Holm and Ibers (159) have studied the nuclear magnetic resonance of titanocene dichloride. Breslow and Newburg (71) have prepared titanocene dichloride and found it useful as a part of the Ziegler catalyst.

Birmingham, Fischer, and Wilkinson (43) have found that bis(cyclopentadienyl)titanium dichloride can be reduced to bis(cyclopentadienyl)titanium(III) chloride by the action of zinc dust in either tetrahydrofuran, dimethylcellosolve, methanol, or acetone. Moffitt (226) has presented data covering the electronic

structures of cyclopentadienyl compounds, including those of titanium.

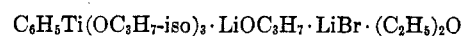
Bis(cyclopentadienyl)titanium was prepared by Fischer and Wilkinson (122) from the reaction of cyclopentadienylsodium and titanium(II) chloride in tetrahydrofuran. The green crystalline product was obtained in 40 per cent yield by vacuum sublimation ($120\text{--}180^\circ\text{C}$. at 10^{-3} mm.). It is exceedingly reactive in air and decomposes below its melting point. The compound when placed in concentrated hydrochloric acid forms bis(cyclopentadienyl)titanium dichloride.

Summers, Uloth, and Holmes (374) have prepared several diaryl compounds of bis(cyclopentadienyl)titanium dichloride. They are diphenyl-, di(*p*-tolyl)-, di(*m*-tolyl)-, and di(*p*-dimethylaminophenyl)bis(cyclopentadienyl)titanium. Preparation of the naphthyl and the *o*-tolyl derivatives was attempted, but the products decomposed before they could be isolated.

In a review of ferrocene and other metallocenes, Wardlaw and Bradley (395) mention the preparation of bis(cyclopentadienyl)titanium dichloride from cyclopentadienylsodium and titanium(IV) chloride. They also discuss the formation of various alkyl orthotitanates from alcohols and titanium(IV) chloride in the presence of ammonia.

Further work was done by Herman and Nelson (155) in an attempt to determine the order of stability in organotitanium compounds. In compounds of the type $\text{R}_n\text{TiX}_{4-n}$, variations in R, *n*, and X were made and observed. As the electronegativity of R was increased the stability of the compound increased. The stability of the compound decreased as *n* increased from 1 to 4. Investigation into the effect of X showed that butoxy groups stabilized the compound to a greater extent than methoxy groups. Similarly, chloro organotitanium compounds show a higher degree of stability than the corresponding fluoro compounds.

The first organotitanium compound containing a titanium-carbon bond was prepared in 1953 by Herman and Nelson (154). They found that a 1:1 molar ratio of phenyllithium and triisopropyl orthotitanate gave a 76 per cent yield of a crystalline complex:



Treatment of this complex with anhydrous titanium(IV) chloride gave a 50 per cent yield of triisopropoxyphenyltitanium.

The reaction of phenylmagnesium bromide and triisopropyl titanate gave no isolable product. However, further investigation showed the reaction of the Grignard reagent to be essentially complete.

Bis(cyclopentadienyl)titanium dibromide was prepared by Wilkinson, Pauson, Birmingham, and Cotton (400) from the reaction of cyclopentadienylmagnesium bromide and titanium(IV) chloride in toluene. Recrystallization from toluene yielded dark red crystals

melting at 240–243°C. The compound is diamagnetic and hydrolyzes in water to give a yellow solution. Bis(cyclopentadienyl)titanium dichloride forms a crystalline picrate, (C₂₂H₁₄N₆O₁₄Ti), which explodes at its melting point.

Summers and Uloth (373) prepared bis(cyclopentadienyl)titanium dichloride in 72 per cent yield from cyclopentadienyllithium and titanium(IV) chloride. Reaction of this dichloride with phenyllithium yielded as much as 81 per cent diphenylbis(cyclopentadienyl)titanium. It is an orange-yellow crystalline solid which decomposes on heating. In like manner, di(*p*-tolyl)bis(cyclopentadienyl)titanium (yellow orange) and di(*p*-dimethylaminophenyl)bis(cyclopentadienyl)titanium (maroon) were prepared.

Owing to the slight acidity of the methylene hydrogen atoms in cyclopentadiene, which is evidenced by its reaction with sodium to evolve hydrogen and its reaction with ethylmagnesium bromide to evolve ethane, Birmingham, Seyferth, and Wilkinson (44) attempted the reaction of cyclopentadiene and titanium(IV) chloride in the presence of some proton acceptor such as triethylamine, pyridine, or sodium methoxide. Competing reactions between the amine and the titanium(IV) chloride prevented good yields. However, without the proton acceptor present, no product could be isolated. Approximately a 3 per cent yield of bis(cyclopentadienyl)titanium dichloride was obtained.

Wilkinson and Birmingham (399) prepared both the bis(cyclopentadienyl)titanium dichloride and the dibromide from either cyclopentadienylmagnesium bromide and titanium(IV) chloride in benzene, or cyclopentadienylsodium and titanium(IV) chloride in tetrahydrofuran. After removal of the solvent, the residue was extracted with chloroform saturated with hydrogen chloride for the preparation of the chloride and with hydrogen bromide for the preparation of the bromide. The chloride melts at 289°C., whereas the bromide melts at 314°C.

Bis(cyclopentadienyl)titanium dibromide, when heated in 12 *N* hydrofluoric acid, yields yellow crystals of bis(cyclopentadienyl)titanium difluoride. Similarly, when refluxed in acetone with excess potassium iodide, the bromide yields purple crystals of bis(cyclopentadienyl)titanium diiodide melting at 319°C.

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