SILOXY-BIS(CYCLOPENTADIENYL)TITANIUM(IV) COMPOUNDS

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ABSTRACT

SILOXY-BIS(CYCLOPENTADIENYL)TITANIUM(IV) COMPOUNDS

by James S. Skelcey

The purpose of this investigation was the preparation, characterization, and a study of some of the properties of triorganosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) which have titanium-oxygen-silicon bonds. Monosubstituted siloxy derivatives were prepared by the reactions of the corresponding sodium silanolate with bis(cyclopentadienyl)titanium dichloride in toluene at 75-90°C. under anhydrous conditions. The compounds prepared and characterized were trimethylsiloxybis(cyclopentadienyl)-titanium chloride, methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, and triphenylsiloxybis(cyclopentadienyl)titanium chloride. This last compound was also prepared by the reaction of bis(cyclopentadienyl)-titanium dichloride, triphenylsilanol, and triethylamine in toluene at 80-90°C. These reactions are accompanied by extensive decomposition of the titanium starting material and formation of titanium dioxide. The reactions of triphenylsilanol and triphenylsilanolate also produced large quantities of tetrakis(triphenylsiloxy)titanium. The siloxybis(cyclopentadienyl)titanium chlorides are orange solid materials of which the triphenylsiloxy derivative is the most stable.

Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was prepared by the following reactions in toluene at 75-90°C.: bis(cyclopentadienyl)-titanium dichloride and sodium triphenylsilanolate, triphenylsiloxybis-(cyclopentadienyl)titanium chloride and sodium triphenylsilanolate, and bis(cyclopentadienyl)titanium diiodide and triphenylsilanol in the presence of triethylamine. This disubstituted triphenylsiloxy derivative of

bis(cyclopentadienyl)titanium(IV) could only be synthesized in very low yields. It is a white crystalline solid.

An orange crystalline solid identified as 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane was isolated from the reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate.

The stabilities of the siloxy derivatives of bis(cyclopentadienyl)-titanium(IV) and the yields of these compounds isolated from the reactions are directly related to the basicity or electron-donating properties of the siloxy group. The greater the basicity of the siloxy group, the more unstable is the silicon-titanium compound. Mechanisms were postulated for the formation of these compounds and for the decomposition of the titanium starting material.

It was observed that the reactivities of the two halogen atoms in bis(cyclopentadienyl)titanium dihalides are not the same. The second halogen is more difficult to replace than the first one. Bis(cyclopentadienyl)titanium diiodide was also observed to be more reactive than bis(cyclopentadienyl)dichloride.

Ultraviolet, visible, and infrared spectra of the compounds prepared in this investigation were recorded. Differential thermal analysis curves were determined for methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, triphenylsiloxybis(cyclopentadienyl)titanium chloride, and bis(triphenylsiloxy)bis(cyclopentadienyl)titanium. Crystallographic d-spacings for these three compounds and for the dititoxane were calculated from x-ray diffraction data.

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By

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INTRODUCTION

The field of inorganic chemistry is presently marked by a great amount of research in the synthesis of high temperature polymers. Investigations in this area have developed because of the demand by the military services for materials which are stable above 500°C. Because organic polymers composed of carbon chains are unstable at these temperatures, interest has shifted to inorganic materials which may resist breakdown and oxidation at elevated temperatures.

Totally inorganic substances such as metal silicates, titanates, and corundum exhibit extreme thermal stabilities, but they are hard, brittle materials which are insoluble in most solvents. When inorganic polymer chains of metal-oxygen atoms are framed by organic groups through the formation of metal-carbon bonds, the properties of these substances are greatly altered. Organometallic polymers of this type are marked by a flexibility of the molecular chains which is not characteristic of the metal silicates and other related substances. These organometallic polymers are soluble in many solvents and exhibit properties characteristic of plastics and elastomers. The silicones are an example of this type of material, and they offer an improvement in thermal stability over that of the common organic systems.

The preparation of new metal-oxygen-silicon chains by the reaction of certain transition metal compounds with difunctional organosilicon compounds may provide products which have a higher thermal stability than that of the silicones. The tetrahalides and tetraalkoxides of titanium are somewhat useful in preparing polymers of this type because of the stability of the tetravalent state of titanium and the ease with which these compounds undergo reactions. However, such compounds can form brittle cross-linked polymers not only because titanium (IV) is tetrafunctional but also because it can be hexacoordinated.

Bis(cyclopentadienyl)titanium dichloride, a titanium analogue of ferrocene, has been used extensively as a starting material in this research because of its high thermal stability and the fact that it has only two chlorine atoms which may participate in condensation reactions with difunctional silicon compounds to form linear polymers. The cyclopentadienyl rings of this titanium compound may also prevent hexacoordination of the titanium atom through intermolecular bonding. Conceivably this steric shielding of the titanium-oxygen bonds in the skeletal chain may reduce hydrolytic instability of the polymer. On the basis of these considerations it was decided that an attempt should be made to prepare organosiloxy derivatives of bis(cyclopentadienyl)titanium(IV).

The methods of preparation, the characterization, and a study of some properties of disubstituted triorganosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) are the subject of this investigation. Emphasis is placed upon the triphenylsiloxy derivatives since these organosilicon compounds are known to have higher thermal stabilities relative to the alkylsilicon compounds. The results of this thesis will then be useful in deciding whether or not the preparation of high molecular weight polymers of bis(cyclopentadienyl)titanium(IV) and organosilicon compounds is feasible and merits further investigation.

HISTORY

Chemistry of the Bis(cyclopentadienyl)titanium Halides.

In 1953 the first titanium sandwich-compound, bis(cyclopentadienyl)-titanium dibromide, was reported by Wilkinson, et al. (1), and since that time the other three halides have also been prepared (2, 3). Table I shows the melting points and appearances of these compounds.

Table I. Melting Points and Appearances of Bis(cyclopentadienyl)titanium Dihalide (3)

Compound	Melting Point, (°C.)	Appearance
$(C_5H_5)_2TiF_2$	not reported	yellow crystals
$(C_5H_5)_2TiCl_2$	289 ± 2	bright red crystals
$(C_5H_5)_2TiBr_2$	314 ± 2	dark red crystals
$(C_5H_5)_2TiI_2$	319 ± 2	dark purple crystals

The preparation of bis(cyclopentadienyl)titanium dihalides has been described by Wilkinson and Birmingham (3). Bis(cyclopentadienyl)-titanium dichloride was prepared in 90 percent yield by the reaction of cyclopentadienylsodium and titanium tetrachloride in tetrahydrofuran. Bis(cyclopentadienyl)titanium dibromide was prepared in 70 percent yield by the reaction of cyclopentadienylmagnesium bromide and titanium tetrachloride in benzene. Bis(cyclopentadienyl)titanium diflouride was obtained by allowing bis(cyclopentadienyl)titanium dibromide to react with hot 12<u>N</u> hydrofluoric acid. The reaction of bis(cyclopentadienyl)titanium dibromide and potassium iodide in refluxing acetone produced bis(cyclopentadienyl)titanium diiodide. Birmingham *et al.* (2), used the reaction of titanium tetrachloride, cyclopentadiene, and triethylamine in benzene to obtain bis(cyclopentadienyl)titanium dichloride in 3 percent yield. Summers, Uloth, and Holmes (4) prepared bis(cyclopentadienyl)titanium dichloride by the reaction of cyclopentadienyllithium and titanium tetrachloride in a petroleum ether-xylene mixture. Sloan and Barber (5) synthesized bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)-titanium dibromide, and bis(cyclopentadienyl)titanium diiodide by the reaction of magnesium cyclopentadienide with the corresponding titanium tetrahalide in xylene.

These compounds are soluble in acetone and acetonitrile, and are moderately soluble in toluene, benzene, chloroform, and methylene chloride. They are sparingly soluble in ether, carbon disulfide, carbon tetrachloride, petroleum ether, alcohols, and water. The fluoride is much more soluble in water than are the other halides. Purification of the bis(cyclopentadienyl)titanium dihalides is effected by recrystallization from toluene or chloroform. Bis(cyclopentadienyl)titanium dichloride sublimes at 190°C./2 mm., and bis(cyclopentadienyl)titanium dibromide sublimes above 160°C. *in vacuo*.

Natta and co-workers (6, 7) determined the arrangement of cyclopentadienyl rings and chlorine atoms about the titanium atom in bis(cyclopentadienyl)titanium dichloride by x-ray analysis of the bis(cyclopentadienyl)titanium dichloride-aluminum complex, $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$. Their examination of single crystals revealed that (a) both titanium and aluminum atoms have tetrahedral coordination and are joined by bridges of chlorine atoms forming a square ring; (b) the plane of a cyclopentadienyl group is perpendicular to the line joining titanium to the center of the group, the five titanium-carbon distances being all equal; (c) the ethyl groups are bonded to the aluminum atoms; and (d) the cyclopentadienyl groups are not parallel to each other as in ferrocene. Table II shows the bond lengths and bond angles for $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$.

Table II. Bond Lengths and Bond Angles in $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ (6, 7).

Bond	Bond Length (A)	Bond	Bond Angle
Ti-Cl	2.5	(C_5H_5)-Ti-(C_5H_5)	130^o
Ti-C	2.4	Cl-Ti-Cl	90^o
Ti-Al	3.5	Cl-Al-Cl	90^o
Al-Cl	2.5		
Al-C	2.5		

The distance between the titanium atom and the plane of the cyclopentadienyl ring is 2.1 A. Giddings and Best (8) measured the dipole moment of bis(cyclopentadienyl)titanium dichloride in benzene and report a value of 6.3 Debye units. They concluded that bis(cyclopentadienyl)-titanium dichloride has four essentially equivalent bond angles and that the structure is similar to the $[(C_5H_5)_2TiCl_2]$ grouping in $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$, i.e., approaching the tetrahedral configuration. This tetrahedral structure appears to be independent of the oxidation state of titanium since the formal oxidation numbers of this element in bis(cyclopentadienyl)-titanium dichloride and $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ are +4 and +3 respectively.

Wilkinson and Birmingham (3) concluded from the infrared spectra of the bis(cyclopentadienyl)titanium dihalides that the existence of a single carbon-hydrogen stretching frequency and of other bands in positions similar to those in neutral bis(cyclopentadienyl)compounds and the ferricinium ion provided evidence for the "sandwich" structure of the compounds. Sloan and Barber (5) also reached the conclusion from infrared spectra and nuclear magnetic resonance studies. Coates (9) explains the bonding in bis(cyclopentadienyl)titanium dichloride as follows:

> . . . it is regarded as having a roughly tetrahedral arrangement of cyclopentadienyl rings and chlorine atoms about the metal atom, the primary bonding being by the $(d^3s + sp^3)$ tetrahedral orbitals. . . . π-Bonding to the cyclopentadienyl *e* orbitals would then be possible by the d_{z^2} and $d_{x^2-y^2}$ metal orbitals (the d_{xy}, d_{xz}, and d_{yz} being used to form the tetrahedral set).

Further evidence for π-bonding between the cyclopentadienyl rings and the titanium atom is shown by the extreme stability and high melting points of the bis(cyclopentadienyl)titanium dihalides when compared with organotitanium compounds containing strictly σ-type carbon-metal bonds such as phenyltitanium triisopropoxide (10) and tetramethyltitanium (11). Wilkinson and Birmingham (3) also determined the molar magnetic susceptibility of bis(cyclopentadienyl)titanium dibromide and obtained a value of $-186 \pm 3 \times 10^{-6}$ c.g.s. units at 25°C. showing it to be diamagnetic.

Although bis(cyclopentadienyl)titanium dibromide is only slightly soluble in water ($\sim$0.5 g./100 ml. at 25°C.), the saturated solution is acidic (pH $\sim$1.8) because of hydrolysis to the $(C_5H_5)_2TiOH^+$ ion (3). When the solution is saturated with hydrogen bromide, bis(cyclopentadienyl)-titanium dibromide is precipitated. Orange crystals of bis(cyclopentadienyl)titanium hydroxybromide monohydrate are obtained when a solution of bis(cyclopentadienyl)titanium dibromide in boiling water is allowed to cool (3). Acidic solutions of these titanium compounds are stable, but when the pH is raised above four, complete hydrolysis occurs with the formation of titanium dioxide (3).

Bis(cyclopentadienyl)titanium hydroxypicrate is precipitated when a saturated solution of potassium picrate is added to a saturated aqueous solution of bis(cyclopentadienyl)titanium dibromide (3). The dipicrate is isolated by adding a saturated solution of picric acid to a saturated solution of the dibromide and recrystallizing the yellow precipitate from dilute picric acid solution. The bis(cyclopentadienyl)titanium cation is also precipitated by large anions such as silicotungstate, triiodide, mercuriiodide, ferrocyanide, and Reineckate (3). An aqueous solution of

bis(cyclopentadienyl)titanium dibromide can be converted to the perchlorate by passage through an anion exchange resin column (3). Reduction of the perchlorate solution at a dropping mercury electrode shows a cathodic wave with $E_{\frac{1}{2}}$ = -0.44 volt versus the saturated calomel electrode (3). When the perchlorate solution is passed through a Jones reductor, a green solution of $(C_5H_5)_2Ti^+$ ions is produced. Addition of this green solution to a picric acid solution precipitates a brown solid with a molar magnetic susceptibility of 2.3 Bohr magnetons. This suggests the presence of a single unpaired electron (3).

Many attempts have been made to acylate the cyclopentadienyl rings of the bis(cyclopentadienyl)titanium dihalides by Friedel-Crafts reactions, but they have proved unsuccessful (3, 12, 13, 14). Reynolds and Wilkinson (15) did succeed in preparing bis(methylcyclopentadienyl)titanium dichloride by the reaction of titanium tetrachloride and methylcyclopentadienylsodium. The product was isolated as brilliant red diamond-shaped leaflets which melt at 217-218°C. with decomposition. Gorsich (16) reported a compound which has only one cyclopentadienyl ring substituted with a methyl group. He treated cyclopentadienyltitanium trichloride with methylcyclopentadienylsodium in tetrahydrofuran to obtain scarlet needles of cyclopentadienyl(methylcyclopentadienyl)titanium dichloride which meets at 205-206°C.

Summers and co-workers (4, 17) prepared a series of tetraorganotitanium compounds by the action of aryllithium reagents on bis(cyclopentadienyl)titanium dichloride in diethyl ether. By this method they prepared the following compounds: diphenylbis(cyclopentadienyl)titanium, orange-yellow crystals, m.p. 146-148°C.; di-p-tolylbis(cyclopentadienyl)titanium, orange-yellow crystals; di-m-tolylbis(cyclopentadienyl)titanium, orange-yellow crystals, m.p. 135-140°C., and di-p-dimethylaminophenylbis(cyclopentadienyl)titanium, maroon crystals. Attempts to isolate di-o-tolylbis(cyclopentadienyl)titanium and di-α-naphthylbis(cyclopentadienyl)titanium failed. Piper and Wilkinson (18) prepared dimethylbis(cyclopentadienyl)titanium in one percent yield by treating bis(cyclopentadienyl)-titanium dichloride with methylmagnesium iodide in tetrahydrofuran at 25°C. The product is an orange-yellow waxy solid which decomposes at 100°C. The stabilities of these compounds depend upon the nature of the substituent. Compounds with electron-withdrawing groups, such as phenyl, are more stable than those with electron-releasing groups, i.e., dimethylaminophenyl and methyl. Failure to isolate the o-tolyl and α-naphthyl derivatives may be due to steric hindrance.

Murray (19, 20) prepared bis(cyclopentadienyl)titanium dicarbonyl by treating bis(cyclopentadienyl)titanium dichloride with carbon monoxide in the presence of a reducing agent such as cyclopentadienylsodium or butyllithium. The carbonyl was also prepared by the reaction of titanium tetrachloride, excess cyclopentadienylsodium, and carbon monoxide. The product is a dark reddish brown crystalline solid which is extremely sensitive to air and decomposes above 90°C. under nitrogen.

Because of the catalytic action of organoaluminum-titanium tetrachloride complexes in olefin polymerizations, much interest has been shown in these compounds. The research of Natta and co-workers (6, 7, 21) has been notable in this area. When a slurry of bis(cyclopentadienyl)-titanium dichloride in n-heptane at 70°C. is treated with triethylaluminum, gas evolution occurs and a blue solution is developed. From this solution the blue complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ can be isolated; it melts at 126-130°C. Its structure has been described in an earlier section. A complete list of other titanium-aluminum complexes which have been prepared by this group of workers is given in Table III. These complexes are sensitive to air. Treatment of the first three listed complexes with anhydrous hydrogen chloride produces bis(cyclopentadienyl)titanium dichloride in high yields. The same occurs when $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ is treated with hydrogen chloride and chlorine gas. The oxidation state of titanium in the

Table III. $(C_5H_5)_2TiCl_2$--Aluminum Complexes (6, 7, 21)

Compound	M.P. (°C.)	Magnetic Moment (Bohr Magnetons)	Preparation
$Cp_2TiCl_2AlEt_2$	126-130	1.70	$Cp_2TiCl_2 + Et_3Al$ $Cp_2TiCl + Et_2AlCl$
$Cp_2TiCl_2AlEtCl$	88-92	1.57	$Cp_2TiCl_2 + Et_2AlCl$ $Cp_2TiCl + EtAlCl_2$
$Cp_2TiCl_2AlCl_2$	155-160	1.72	$Cp_2TiCl_2 + EtAlCl_2$ $Cp_2TiCl + AlCl_3$
$[Cp_2TiAlEt_2]_2$	169-171	diamagnetic	Cp_2TiCl + excess Et_3Al

Cp = Cyclopentadienyl, Et = ethyl

monomeric complexes is +3, while in the case of $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ the oxidation state of titanium formally is +1. The structural details of the dimeric complex have been determined by Natta and Mazzanti (7). Breslow and Newburg (22), Chien (23), Long (24), Long and Breslow (25), Adema, Bos, and Vrinssen (26), and Zefianova and Shilov (27) have also described these complexes, the kinetics of their formation, and their catalytic activities in ethylene polymerizations.

Jensen and Basolo (28) conducted a detailed study on the kinetics of the reactions bis(cyclopentadienyl)titanium dibromide with different chlorides under various conditions to form bis(cyclopentadienyl)titanium dichloride. The rates were followed spectrophotometrically. Results indicated that during most of the reaction there was at no time any appreciable concentration of the intermediate $(C_5H_5)_2TiBrCl$. This indicated that the intermediate reacts rapidly and the rates observed were then essentially the rates of formation. The data show that the rate of reaction of bis(cyclopentadienyl)titanium dibromide with benzyldimethyloctadecylammonium chloride in tetrahydrofuran and in benzene is first order in bromide and first order in the quarternary ammonium chloride. At the concentration used in these studies the chloride must be present almost entirely in the form of ion pairs, and the first order dependence on the chloride then supports a direct displacement (S_{N2}) by the ion pair.

$$\begin{tikzcd}
Cp_2TiBr_2 + R^+Cl^- \arrow[r, shift left, "slow"] & Cp_2TiBr_2 \cdot R^+Cl^- \arrow[l, shift left] \arrow[r, shift left, "fast"] & Cp_2TiBrCl + R^+Br^- \arrow[l, shift left] \arrow[d, shift right, "fast"', "R^+Cl^-"] \\
 & & Cp_2TiCl_2 + R^+Br^- \arrow[u, shift right]
\end{tikzcd}$$

This mechanism was justified on the basis that titanium(IV) can have a coordination number of six; it is relatively large in size; and it has vacant 3d orbitals. These factors suggest attack by a Lewis base.

The same reaction with lithium chloride in tetrahydrofuran shows zero order dependence on the chloride. A solvent displacement mechanism was suggested which is analogous to the mechanism proposed for the quarternary ammonium chloride.

$$\begin{tikzcd}
Cp_2TiBr_2 + \text{solvent} \arrow[r, shift left, "slow"] & Cp_2TiBr_2 \cdot \text{solvent} \arrow[l, shift left] \arrow[r, shift left, "fast"] & Cp_2TiBr \cdot \text{solvent}^+ + Br^- \arrow[l, shift left] \arrow[d, shift right, "fast"', "Li^+Cl^-"] \\
 & & Cp_2TiBrCl + Li^+ \arrow[u, shift right] \arrow[d, shift right, "fast"', "Li^+Cl^-"] \\
 & & Cp_2TiCl_2 + Li^+Br^- \arrow[u, shift right]
\end{tikzcd}$$

Data show that the rate of reaction of bis(cyclopentadienyl)titanium dibromide with chlorides depends not only on the chloride but also on the solvent. In general, the reaction was faster in the more polar solvent.

The reverse reaction was also studied in tetrahydrofuran:

$$Cp_2TiCl_2 + 2LiBr \rightleftarrows Cp_2TiBr_2 + 2LiCl$$

The results show that even in the presence of a relatively large concentration of lithium bromide the concentration of bis(cyclopentadienyl)-titanium dichloride exceeds that of bis(cyclopentadienyl)titanium dibromide at equilibrium. These results indicate that the dichloride is more stable than the dibromide. These researchers have pointed out that in general the stability of metal halide complexes decrease with increasing atomic number of the halide ion for metal ions that do not tend to form π-bonds. Since titanium(IV) in bis(cyclopentadienyl)titanium dihalides do not contain d orbital electrons which could be used for π-bonding with the vacant d orbitals of the halide ions, the dichloride would be more stable than the dibromide.

Other Cyclopentadienyltitanium Compounds.

Bis(cyclopentadienyl)titanium(II) was prepared by Fischer and Wilkinson (29) by the reaction of cyclopentadientylsodium and titanium dichloride in tetrahydrofuran. This dark green solid is sensitive towards air and decomposes above 130°C. in an evacuated tube. Magnetic measurements showed that bis(cyclopentadienyl)titanium(II) is diamagnetic. This compound forms two tetrahydrofuran etherates: unstable green monoclinic crystals which are paramagnetic, and brown tetragonal crystals, m.p. 81°C. which are diamagnetic.

Fischer and Lochner (30) reported the synthesis of tris(cyclopentadienyl)titanium by the reaction of bis(cyclopentadienyl)titanium dichloride and excess cyclopentadienylsodium. The product was isolated in very low yield by sublimation at 125°C. *in vacuo*. The dark green sublimate was very sensitive to air and decomposed without melting at 130°C. Magnetic susceptibility studies showed the presence of one unpaired electron. A symmetrical arrangement of ligands about the central metal atom was indicated by infrared spectral studies.

Cyclopentadienyltitanium trichloride was prepared by Gorsich (16, 31) by treating bis(cyclopentadienyl)titanium dichloride with titanium tetrachloride in xylene at 140°C., and by the reaction of bis(cyclopentadienyl)titanium dichloride and chlorine gas at 60°C. in carbon tetrachloride. This orange crystalline solid melts at 208-211°C. Sloan and Barber (5) reported that cyclopentadienyltitanium trichloride prepared by the reaction of titanium tetrachloride and magnesium cyclopentadienide in refluxing xylene melts at 145.5-147°C. with decomposition. Table IV lists other monocyclopentadienyltitanium compounds.

Table IV. Monocyclopentadienyltitanium Compounds.

Compound	M.P. (°C.)	Preparation	Reference
$CpTiBr_3$	174.5-175.5	$TiBr_4 + MgCp_2$	5
$CpTiI_3$	184-186	$TiI_4 + MgCp_2$	5
$CpTiBrCl_2$	165-170	$Cp_2TiCl_2 + Br_2$	16
$CpTiCl_2(OCH_3)$	93-96	$CpTiCl_2 + CH_3OH$	16
$CpTiCl_2(OC_5H_{10}O)Cl_2TiCp$	157-159	$CpTiCl_3 + HOC_5H_{10}OH$	16
$(CpTiCl_2)_2O$	149-151	$CpTiCl_3 + H_2O$	16
$(CpTiClO)_3$	258-260	$CpTiCl_3 + H_2O$	16
$(CpTiClO)_n$	258	$CpTiCl_2(OC_5H_{10}O)Cl_2TiCp + H_2O$	16
$CpTi(CH_3)_3$	0	$CpTiCl_3 + LiCH_3$	32

Cp = cyclopentadienyl

The cyclopentadienyltitanium trihalides are fairly soluble in aromatic hydrocarbons and chloroform and are quite soluble in polar solvents such as tetrahydrofuran. In general, they are more soluble in a given solvent than the bis(cyclopentadienyl)titanium dihalides. The cyclopentadienyltitanium trihalides are more unstable to hydrolysis and heat than the bis(cyclopentadienyl)titanium dihalides. Molecular weight and conductivity measurements in chloroform showed that cyclopentadienyltitanium trichloride is monomeric and not $(C_5H_5)_2Ti(TiCl_6)$. The infrared spectra of bis(cyclopentadienyl)titanium dichloride and cyclopentadienyltitanium trichloride are very similar except that an intense broad band at 770 cm.$^{-1}$ is characteristic of each single ring compound. This and nuclear magnetic resonance studies show that all protons are equivalent in cyclopentadienyltitanium trichloride and that there is π-bonding between the metal and cyclopentadienyl ring.

Patented Cyclopentadienyltitanium Compounds.

The catalytic effect of organotitanium compounds in olefin polymerizations has stimulated the synthesis of many other cyclopentadienyltitanium compounds, mainly by industrial chemists. Unfortunately, only a small portion of the information on these compounds is given in patents and abstracted patents. Table V lists these patented compounds.

Table V. Patented Cyclopentadienyltitanium Compounds.

Compound	Properties	Reference
$CpTiCl_3$	b.p. 29-34°C./1.0 mm m.p. 140-42°C.	33 34
$CpTiBr_3$	m.p. 163-65°C	34
$CpTiI_3$	m.p. 185-90°C	34
$CpTiCl_2(OMe)$	m.p. 89-90°C	35
$CpTiCl(OBu)_2$	b.p. 145-50°C./2.3 mm	36, 37
$CpTiCl_2$(O-tert-Bu)	--	35
$(CpTiCl_2)OC_5H_{10}O(CpTiCl_2)$	m.p. 153-56°C.	35
$CpTiBr(OBu)_2$	b.p. 136-45°C./0.8 mm	33

continued

Table V - continued

Compound	Properties	Reference
$CpTiBr_2(OC_2H_4OCH_3)$	--	35
$CpTi(OBu)_2(O_2C_2Cl_3)$	--	38
$Cp_2Ti_2Cl_6$	m.p. 208-10°C.	37
$(C_6H_5COC_5H_4)TiBr_2(OC_6H_4Cl)$	--	35
$(C_5H_4)TiF_2$	--	39
$(C_5H_4)TiCl_2$	m.p. 167-69°C.	39
$(C_5H_4)TiBr_2$	--	39
Cp_2TiCl_2	red crystals	36
Cp_2TiBr_2	m.p. 265°C.	33
$Cp_2TiCl(Me)$	m.p. 168-70°C.	40
$Cp_2TiCl(Pr)$	decompose 160°C.	40
Cp_2TiMe_2	decompose 97°C.	40
$(CH_3C_5H_4)_2TiMe_2$	yellow crystals	40
$Cp_2Ti(OAc)_2$	--	38
$Cp_2Ti(O_2CCH_2Cl)_2$	--	38
$Cp_2Ti(O_2CCHCl_2)_2$	--	38
$Cp_2Ti(O_2CCCl_3)_2$	--	38
$Cp_2Ti(O_2C_{18}H_{35})_2$	--	38
$Cp_2Ti(O_2C_{18}H_{33})_2$	--	38
$Cp_2Ti(O_2CCH_2OH)_2$	--	38
$Cp_2Ti(O_2CCH_2SH)_2$	--	38
$Cp(C_5H_7C_5H_4)TiF_2$	yellow solid	41
$Cp(C_5H_7C_5H_4)TiCl_2$	reddish brown solid	41
$Cp(C_5H_7C_5H_4)TiBr_2$	pink solid	41
$Cp(C_5H_7C_5H_4)TiI_2$	red solid	41

continued

Table V - continued

Compound	Properties	Reference
$Cp(C_5H_5Cl_2)TiCl_2$	orange crystals	42, 43, 44
$Cp(C_5H_5Br_2)TiCl_2$	--	42
$Cp(C_5H_5Cl_4)TiCl_2$	--	44
$Cp(C_5H_5Cl_4)TiBr_2$	orange crystals	42
$Cp(C_5H_5Br_4)TiF_2$	yellow orange crystals	42, 44
$Cp(C_5H_5Br_4)TiCl_2$	orange-yellow crystals	42
$Cp(C_5H_5Br_4)TiBr_2$	orange crystals	42, 44
$Cp(C_5H_5I_4)TiCl_2$	--	44
$Cp(C_5H_5I_4)TiI_2$	--	42, 44
$inTiBr(OBu)_2$	--	33
$in_2Ti(O_2CCCl_3)_2$	--	38

Cp = cyclopentadienyl, Me = methyl, Bu = butyl, Pr = propyl, OAc = acetate, in = indenyl

Chemistry of Silanols and Silanolates.

Only a few generalizations will be made on the chemistry of the triorganosilanols and alkali metal triorganosilanolates since detailed information is compiled in Eaborn's Organosilicon Compounds (45). This reference has been used for the following discussion.

The hydrolysis of organosilicon halides results in the formation of silanols. These organosilicon halides are usually prepared by the action of organolithium and Grignard reagents on silicon halides. Silanols are also produced by the hydrolysis of organosilicon sulfides, amines, hydrides, alkoxides, phenoxides, and esters. The free silanol is not always isolated since self-condensation to the disiloxane can occur. Formation of the silanol or the disiloxane is often controlled by the conditions of the hydrolysis. The silanols vary from volatile liquids, e.g., trimethylsilanol, b.p. 98.6°C., to high melting solids, e.g., tri-α-naphthylsilanol, m.p. 208-209°C. Silanols dissolve in most common organic solvents and they are insoluble in water.

The trialkylsilanols are stronger acids than the corresponding carbon compounds. In view of the greater electronegativity of carbon, the silanols should be weaker acids than the carbinols. The greater acidity is attributed to $d\pi$-$p\pi$ bonding between the silicon and oxygen atoms. Such bonding will increase the protonic character of the hydrogen atom. Triphenylsilanol is a stronger acid than the trialkylsilanols. This increase of the acidity of triphenylsilanol is explained on the basis of an inductive electron withdrawal by the phenyl groups since it is known that relative to trialkylsilyl groups the triphenylsilyl withdraws electrons.

The stability of trialkylsilanols is dependent on the size of the alkyl groups. Trimethylsilanol is difficult to prepare, and it decomposes on heating or even on prolonged standing with formation of the disiloxane. Dimethylethylsilanol is somewhat more stable and triethylsilanol is distinctly more stable. Stability continues to increase with increasing size of the alkyl groups. The stability of triphenylsilanol compares with that of trialkylsilanols containing large alkyl groups. Highly hindered compounds such as tri-α-naphthylsilanol do not undergo self-condensation to the disiloxane.

Various catalysts and conditions will bring about condensation of silanols to disiloxanes. Triethylsilanol is largely unaffected by boiling with an equal volume of 0.1 N aqueous hydrochloric acid or alkali. Heating triethylsilanol with a few drops of concentrated hydrochloric acid causes about 50 percent of the material to condense, while concentrated alkali under the same conditions has little effect. Refluxing with twice its volume of 70 percent sulfuric acid gives the disiloxane in 85 percent yield in four hours, and refluxing the silanol with a small amount of iodine for half an hour brings about complete dehydration. Triphenylsilanol is condensed rapidly to hexaphenyldisiloxane by adding concentrated nitric acid to a solution in boiling glacial acetic acid. Refluxing a solution of triphenylsilanol in 98 percent formic acid for 15 hours gives the siloxane in quantitative yield. Dilute alcoholic alkali has also been used to bring about the condensation. Grubb (46) studied the kinetics of formation of disiloxanes from silanols and has shown that triphenylsilanol and triethylsilanol condense at a rate approximately 5×10^{-7} and 1.7×10^{-3} times as fast as trimethylsilanol under the same conditions.

Triorganosilanols react with alkali metals, usually in a solvent such as ether or benzene, to form alkali metal silanolates. Hyde <u>et</u> <u>al</u>. (47), have prepared several pure silanolates by alkali cleavage of hexaorganodisiloxanes in an alcoholic solvent by completely removing the water formed: $[(C_6H_5)_3Si]_2O + 2NaOH \longrightarrow 2\ NaOSi(C_6H_5)_3 + H_2O$. Sodium trimethylsilanolate is best prepared from the reaction of the disiloxane and sodium amide in liquid ammonia (47):

$$2[(CH_3)Si]_2O + NaNH_2 \longrightarrow 2\ NaOSi(CH_3)_3 + 2\ H_2NSi(CH_3)_3$$

The pure alkali metal silanolates are hygroscopic solids which sublime or decompose on heating without melting. They are strong bases which are readily hydrolyzed to the silanols or disiloxanes. The silanolates are usually employed as solutions in the solvents in which they are prepared. They react readily with silicon halides and metal halides such as stannic chloride, titanium tetrachloride, mercuric chloride, and boron trifluoride. Their coupling reactions with carbon halides are also notable, e.g.,

$$3\ NaOSi(C_6H_5)_3 + CHCl_3 \longrightarrow [(C_6H_5)_3SiO]_3CH + 3\ NaCl \quad (48)$$

$$4\ NaOSi(CH_2C_6H_5)_3 + CCl_4 \longrightarrow [(C_6H_5CH_2)_3SiO]_4C + 4NaCl \quad (49).$$

Siloxy Derivatives of Titanium Halides and Alkoxides.

Since 1955 when English and Sommer (50) reported the synthesis of terakis(trimethylsiloxy)titanium, a significant amount of work has been done on the silicon-titanium system of compounds. Because titanium alkoxides are polymeric and give rise to polymeric hydrolysis products which are heat resistant (51) and because of the well-known thermal stability of organosiloxanes, it was of interest to combine the structures of these two and compare the properties of the titanium-oxygen-silicon system with those of the titanium-oxygen-carbon and silicon-oxygen-silicon systems.

Organosiloxy-titanium compounds have been prepared by the following reactions in organic solvents.

1. Titanium halide and silanol in the presence of a proton acceptor (50).

   $TiCl_4 + 4HOSi(CH_3)_3 \xrightarrow{NH_3} Ti[OSi(CH_3)_3]_4 + 4NH_4Cl$

2. Titanium halide and alkali metal silanolate (52).

   $TiCl_4 + 4NaOSi(CH_3)_3 \longrightarrow Ti[OSi(CH_3)_3]_4 + 4NaCl$

3. Titanium halide and heavy metal silanolate (53).

   $TiCl_4 + 2Pb[OSi(C_2H_5)_3]_2 \longrightarrow Ti[OSi(C_2H_5)_3]_4 + 2\ PbCl_2$

4. Titanium halide and siloxane (54).

   $TiCl_4 + [(CH_3)_3Si]_2O \xrightarrow{AlCl_3} TiCl_2\ [OSi(CH_3)_3]_2.$

5. Titanium halide and siloxy-titanium compound (52).

   $TiCl_4 + Ti[OSi(CH_3)_3]_4 \longrightarrow 2TiCl_2[OSi(CH_3)_3]_2$

6. Titanium alkoxide and silanol (55).

   $Ti(OC_3H_7)_4 + 4HOSi(CH_3)_3 \longrightarrow Ti[OSi(CH_3)_3]_4 + 4HOC_3H_7$

7. Titanium alkoxide and silylcarboxylate (56).

   $Ti(OC_3H_7)_4 + 4(CH_3)_3SiO_2C_2H_3 \longrightarrow Ti[OSi(CH_3)_3]_4 + 4C_3H_7O_2C_2H_3$

8. Alkoxytitanium oxide and silicon alkoxide (57).

   $(C_3H_7O)_2TiO + (CH_3)_2Si(OC_3H_7)_2 \longrightarrow Ti(OC_3H_7)_3[OSi(CH_3)_2(OC_3H_7)].$

9. Tetrakis(alkylamido)titanium and silanol (58).

   $Ti[N(C_2H_5)_2]_4 + 4HOSi(C_2H_5)_3 \longrightarrow Ti[OSi(C_2H_5)_3]_4 + 4HN(C_2H_5)_2.$

Table VI tabulates the siloxy-titanium compounds, properties, and method of preparation which have been recorded in the literature.

Of these methods of preparation of the tetrakis(siloxy)titanium compounds, the raction of silanol and alkoxide results in quantitative yields when the silanol is slowly added to the alkoxide in benzene and the resulting alcohol is continuously removed by azeotropic distillation (61). Yields of 90 percent were obtained when titanium tetrachloride and the silanol were allowed to react in the presence of dimethylaniline; however, lower yields were obtained when pyridine was used as a proton acceptor (66). Good yields were also obtained by transesterification reactions involving the titanium alkoxide and organosilyl acetates (56). Reactions involving trimethylsilanol and its derivatives are complicated by the ease with which it condenses to the disiloxane. Preparation from other alkylsilanols and arylsilanols are easier because of the smaller tendency to form disiloxanes.

Bradley (77) reviewed the physical and chemical properties of the tetrakis(trialkylsiloxy)titanium compounds. All of the alkylsiloxy compounds of titanium are liquids except tetrakis(triethylsiloxy)titanium and tetrakis(dibutylmethylsiloxy)titanium. Ebullioscopic molecular weight determinations in benzene reveal that tetrakis(trimethylsiloxy)titanium is polymeric (degree of polymerization = 1.21) whereas the others are essentially monomeric. These siloxytitanium compounds are perceptibly resistant towards hydrolysis by water compared with the titanium alkoxides. In homogeneous solution, hydrolysis by water is fairly rapid and the greater resistance to hydrolysis by liquid water may be due to the heterogeneity of the system coupled with the water-repellent effect of the alkylsiloxy groups. Siloxytitanium compounds show greater thermal stability than the alkoxides.

The most stable of the silicon-titanium compounds is tetrakis(triphenylsiloxy)titanium which decomposes at 460°C. in the open and melts

Table VI. Siloxy-Titanium Compounds

Compound	M.P. (°C.)	B.P. (°C./mm.)	Index of Refraction $n_D^{(°C)}$	Density d (°C)	Preparation	Reference
Ti(OSiMe$_3$)$_4$	--	100/2	1.4300^{22}	--	6	55
	--	110/10	1.4275^{20}	0.9004^{20}	6	59
	--	106/7	1.4278^{20}	0.9078^{20}	1	50
	--	110/10	1.4292^{20}	--	2	60
	--	62/0.1	--	--	7	56
	--	60/0.1	--	--	6	61, 62
	--	--	--	--	6	63
	--	112/11	1.4277^{20}	0.9051	2	52
	--	125/8	1.4283^{25}	--	7	64
Ti(OSiMe$_2$Et)$_4$	--	140-2/5	1.4461^{20}	0.9237^{20}	6	65
	--	86/0.1	--	--	6	62
Ti(OSiMeEt$_2$)$_4$	--	186/6	1.4565^{20}	0.9248^{20}	1	66
	--	154/3	1.4545^{20}	0.9244^{20}	6	59, 65
	--	120/0.1	--	--	6	62
Ti(OSiMe$_2$Pr)$_4$	--	112/0.2	--	--	6	62
Ti(OSiMe$_2$-*iso*-Pr)$_4$	--	115/0.2	--	--	6	62
Ti(OSiMe-*iso*-Pr$_2$)$_4$	--	186-8/3	1.4570^{20}	0.9044^{20}	6	59
Ti(OSiMeBu$_2$)$_4$	99-101	195/3.5	1.4582^{20}	0.9056^{20}	6	65
Ti(OSiMe$_2$Ph)$_4$	--	274-5/7	1.5392^{20}	1.0533^{20}	2	67

continued

Table VI - continued

Compound	M.P. (°C.)	B.P. (°C./mm.)	Index of Refraction $n_D(^{\circ}C)$	Density $d(^{\circ}C)$	Preparation	Reference
$Ti(OSiMePh_2)_4$	--	370-4/6	1.5960^{20}	1.1248^{20}	2	67
		346-8/3	1.5988^{21}	1.1394^{20}	1	68
$Ti(OSiEt_3)_4$	95-7	227-30/7	--	--	1	66
	99-101	195/3.5	--	--	6	59, 65
	--	204/4	1.4689^{20}	0.9408^{20}	2	60
	110	150/0.1	--	--	6, 9	58, 62
	--	199-202/3.5	--	0.917^{20}	6	69
	96	176-8/2-3	--	--	3	53
	96	221-2/9	--	--	2	70
$Ti(OSiEt_2Ph)_4$	--	300-5/5	1.5455^{20}	1.0459^{20}	6	65
$Ti(OSiPh_3)_4$	480	--	--	--	1, 6	59, 65, 66
	501-5	--	1.6488^{114}	1.215^{29}	1, 6	63
$TiCl(OSiMe_3)_3$	--	103-5/10	--	--	2	52
Ti(O-$\underline{\text{iso}}$-Pr)$(OSiMe_3)_3$	--	107/8	1.4321^{25}	--	7	64
$Ti(OBu)(OSiMe_3)_3$	--	76-7/2	1.4317^{20}	0.9070^{20}	1	52
$Ti(OBu)(OSiEt_3)_3$	--	174-7/3	1.4687^{20}	0.9379^{20}	6	71
$TiCl_2(OSiMe_3)_3$	--	106-10/18	--	1.155^{20}	4	54
	--	87-8/8	--	--	4	72
	--	72-3/3	--	--	5	52

continued

Table VI - continued

Compound	M.P. (°C)	B.P. (°C./mm.)	Index of Refraction $n_D(^\circ C)$	Density $d(^\circ C)$	Preparation	Reference
$TiCl_2(OSiMe_2Et)_2$	--	114-18/9	--	1.111^{20}	4	54
$TiCl_2(OSiMeEt_2)_2$	--	127-35/2	--	1.068^{20}	4	54
$Ti(O\text{-}\underline{iso}\text{-}Pr)_2(OSiMe_3)_2$	-- --	120/14 103/9	1.4408^{22} 1.4379^{25}	-- --	6 7	55 64
$Ti(OPr)_2(OSiEt_3)_2$	--	144-6/1.5	1.4800^{20}	0.9680^{20}	6	71
$Ti(OBu)_2(OSiEt_3)_2$	--	182/4	1.4758^{20}	0.9517^{20}	6	71
$TiCl_3(OSiMe_3)$	32-2 -- --	82-8/17 62-3/8 67/9	-- -- --	-- -- --	4 4 2	54 72 52
$TiCl_3(OSiMe_2Et)$	--	94-8/17	--	1.305^{20}	4	54
$TiCl_3(OSiMeEt_2)$	--	122-6/9	--	1.217^{20}	4	54
$TiBr_3(OSiMe_3)$	32-4	102-4/10	--	1.807^{40}	4	54
$Ti(O\text{-}\underline{iso}\text{-}Pr)_3(OSiMe_3)$	-- --	114/13 91/5	1.4490^{22} 1.4509^{25}	-- --	6 7	55 64
$Ti(OPr)_3[OSiMe_2(OPr)]$	--	--	--	--	8	57
$Ti(OPr)_3[OSi(OPr)_3]$	--	125-6/1	1.4647^{20}	--	8	73
$Ti(OBu)_3(OSiMe_3)$	--	176-7/8	--	--	1	68

continued

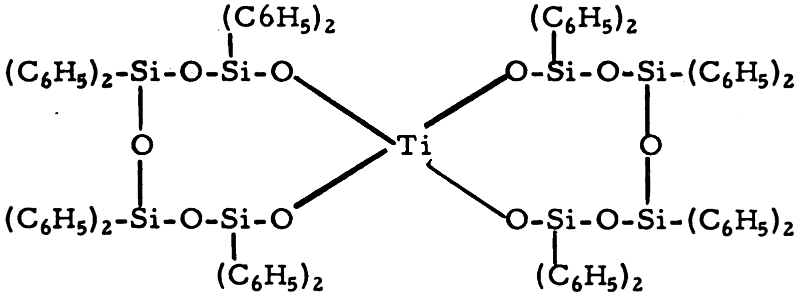
Table VI - continued

Compound	M.P. (^{o}C.)	B.P. (^{o}C./mm.)	Index of Refraction $n_D^{(^{o}C)}$	Density d(^{o}C.)	Preparation	Reference
$\mathrm{Ti(O\text{-}\underline{iso}\text{-}Bu)_3[OSi(O\text{-}\underline{iso}\text{-}Bu)_3]}$	--	$75\text{-}8/10^{-5}$	1.4610^{20}	--	8	73
$\mathrm{Ti(O_5Si_4Ph_8)_2}$	314	--	--	--	6	74
$\mathrm{TiCl_3[(OSiMe_2)_4Cl]}$	--	97-8/2	--	--	4	75
$\mathrm{TiCl_3[(OSiEt_2)_3Cl]}$	--	141-3/2	--	--	4	75
$\mathrm{[(PrO)_3TiO]_2Si(OPr)_2}$	--	$78\text{-}81/10^{-5}$	1.4910^{20}	--	8	73
$\mathrm{(PrO)_3TiOSiMe_2OTi(OPr)_3}$	--	--	1.5310^{20}	--	8	57
$\mathrm{[(AcO)_2TiO]_3OTi(OAc)OSiMe_3}$	--	--	--	--	--	76

Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Ph = phenyl, OAc = acetate.

at 501-505°C. in an evacuated sealed tube (63). It sublimes at 370°C. and 1 mm. Hg. This compound does not react with dilute alkaline or acid solutions, but it is decomposed by concentrated sulfuric and nitric acids. Tetrakis(triphenylsiloxy)titanium is only slightly soluble in benzene, toluene, chlorobenzene, and nitrobenzene at their boiling points, and it is insoluble in alcohols, ethers, acetone, carbon tetrachloride, and carbon disulfide. The insolubility of tetrakis(triphenylsiloxy)titanium in these solvents is remarkable when compared to the alkylsiloxytitanium compounds which are soluble in most organic solvents. Attempts to substitute less than four triphenylsiloxy groups on titanium have failed, and thus no mono-, bis-, and tris(triphenylsiloxy) derivatives of titanium halides and alkoxides are known.

Zeitler and Brown (74) isolated a phenylsiloxytitanium compound from the reaction of diphenylsilonediol and titanium butoxide in a 2:1 ratio in ether. This crystalline solid, m.p. 314-314.5°C., is soluble in most organic solvents. On the basis of its infrared spectrum, elemental analysis, and molecular weight, they have assigned the following cyclic structure for the compound:



Little has been reported on the chemical properties of the partially substituted alkylsiloxy derivatives of titanium, e.g., bis(trimethylsiloxy)-titanium diisopropoxide. Rust et al. (64), have described the syntheses of the trimethylsiloxytitanium isopropoxides in detail. The extent of substitution of trimethylsiloxy groups for the isopropoxide groups is controlled by the stoichiometry and order of addition of the reactants. Danforth (55) reported that bis(trimethylsiloxy)titanium diisopropoxide and trimethylsiloxytitanium triisopropoxide develop an intense blue color on standing in sealed capsules. Other work in this area of silicon-titanium chemistry is reported in the Russian literature; few translations are available and abstracts must be relied upon.

Silicon-Titanium Polymers.

Andrianov and co-workers (78) in 1956 prepared glassy silicon-titanium polymers by the cohydrolysis of alkyl and aryl chlorosilanes and titanium butoxide. The cohydrolysis of dimethyldichlorosilane, phenyltrichlorosilane, and titanium butoxide resulted in a polymer which was soluble in alcohol and acetone. Fractionation of the polymer according to the solubility in alcohol and acetone gave polymers with the following silicon to titanium ratios: alcohol fraction, 41:1; and acetone fraction, 25:1. The same reaction using diethyldichlorosilane instead of dimethyldichlorosilane gave the following results: alcohol fraction, 25:1; and acetone fraction, 18:1. Their experimental results indicated that the reactions proceeded according to the scheme:

$$R_2SiCl_2 + Ti(OC_4H_9)_4 + H_2O \longrightarrow (-OR_2Si-)_{\underline{n}}OTi(OC_4H_9)_2-O-$$

The dimethyldichlorosilane reaction was also carried out and followed by heating to 200°C. The alcohol fraction had a silicon:titanium ratio of 30:1, and the acetone fraction had a ratio of 5:1.

Andrianov *et al.* (79), prepared a silicon-titanium polymer containing titanium-oxygen-titanium bonds by acid hydrolysis of tetrakis(trimethylsiloxy)titanium. The initial polymer was soluble in organic solvents, but after heating with an excess of water, an insoluble polymer was formed. They proposed the following structure for the polymer:

$-Ti(OSi(CH_3)_3)_2-O-Ti(OSi(CH_3)_3)_2-O-$

Deposition of polymer solutions on a metal surface and evaporation of the solvent gave hard films.

Andrianov and Kurasheva (80) also prepared polymers by the reaction of bis(trimethylsiloxy)titanium dichloride and methylphenyldiethoxysilane for 4.5 hours at 150°C. and of bis(trimethylsiloxy)titanium dichloride and dimethyldibutoxysilane under the same conditions. The polymers were viscous materials which formed filaments on being hot-drawn.

Siloxy Derivatives of Bis(cyclopentadienyl)titanium Dichloride.

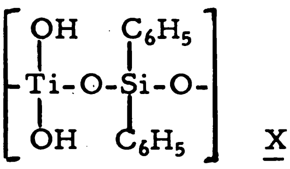
The first report of a reaction of bis(cyclopentadienyl)titanium dichloride and an alkali metal silanolate was made in 1960 by Gutmann and Meller (81). Since that time descriptions of work in this area have been found in progress reports to various governmental agencies who are supporting research in the field of high temperature materials.

Gutmann and Meller reported that the reaction of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate yields tetrakis-(triphenylsiloxy)titanium in 76 percent yield based upon the silanolate. The reaction was carried out in anhydrous toluene at reflux temperature for thirty minutes. The formation of this product was explained on the basis of the high stability and great tendency of formation of the tetrakis-(triphenylsiloxy)titanium molecule (82). During the course of the reaction the titanium-carbon bonds of bis(cyclopentadienyl)titanium dichloride are broken with the subsequent formation of titanium-oxygen-silicon bonds.

This same reaction of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate in toluene at 90°C. was described by van der Kerk and Noltes (83, 84) as yielding orange-yellow crystals of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, m.p., 203-205°C. This product is not susceptible to hydrolysis. The identification of this product was based upon the percentage of combined titanium and silicon oxides after ignition of a sample. These investigators also studied the reactions of bis(cyclopentadienyl)titanium dichloride with difunctional phenylsilicon compounds in an attempt to prepare polymeric materials (85). Addition of bis(cyclopentadienyl)titanium dichloride to a toluene solution of disodium diphenylsilanediolate at 90°C. resulted in an orange-yellow solid, m.p., 180°C. An analysis for total residue indicated the silicon:titanium ratio of the product to be greater than one. They concluded that the disodium diolate was not sufficiently pure from the reaction of diphenylsilanediol and sodium metal, and consequently it would not favor high polymer formation. On this basis, the reaction of bis(cyclopentadienyl)titanium dichloride and diphenylsilanediol was studied at 90°C. in toluene containing aniline as a proton acceptor. An orange-brown solid, m.p. 155°C., was isolated. Analysis indicated a silicon:titanium ratio greater than one, and this was explained on the basis of self-condensation of the diol in preference to titanium-oxygen-silicon bond formation. When the diol was added slowly to a solution of bis(cyclopentadienyl)titanium dichloride in the presence of a great excess of organic base and at a low temperature, a silicon-titanium polymer formed. This polymer did not melt or soften below 260°C.

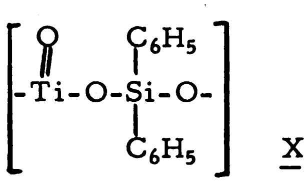
Schwartz and Post (86) observed no reaction between bis(cyclopentadienyl)titanium dichloride and dimethyldiethoxysilane in refluxing toluene. Ferric chloride had no catalytic effect. When dimethylsilanediol was treated with bis(cyclopentadienyl)titanium dichloride in refluxing tetrahydrofuran no apparent reaction occurred. Repetition of the reaction in the presence of pyridine yielded a solid product which was insoluble in all organic solvents and concentrated hydrochloric acid. The cohydrolysis of dimethyldichlorosilane and bis(cyclopentadienyl)titanium dichloride in benzene by treatment with concentrated ammonium hydroxide resulted in the formation of an orange plastic solid which was not characterized. These investigators (87) also prepared a brown resinous solid by the cohydrolysis of dimethyldiethoxysilane and bis(cyclopentadienyl)titanium dichloride in a mixture of tetrahydrofuran, water, and pyridine. Substitution of triethylamine for pyridine resulted in the formation of a similar product but in far less time. Hydrolysis of dimethyldichlorosilane in a benzene-concentrated ammonium hydroxide mixture followed by treatment with bis(cyclopentadienyl)titanium dichloride and water yielded a grey-brown plastic which had a silicon:titanium ratio of 6:1. It was concluded that the cohydrolysis product is a bouncing putty similar to that having silicon-oxygen-silicon bonds but inferior in quality. Therefore they felt that no advantages could be gained by preparing siloxy-cyclopentadienyltitanium polymers.

Morton and Harwood (88) prepared a brown, hard, brittle resin by the reaction of diphenylsilanediol and bis(cyclopentadienyl)titanium dichloride in a mixture of dioxane, pyridine, and finely ground calcium carbide maintained between 70°C and 75°C. The polymer was insoluble in aliphatic hydrocarbons and alcohols but soluble in benzene, pyridine, and dioxane. It had no melting point or softening point, but gradually decomposed above 300°C. The polymeric product did not contain cyclopentadienyl groups and was found to contain considerably more titanium than silicon. The following structures were proposed for the polymer:



$$\left[-\underset{OH}{\overset{OH}{Ti}}-O-\underset{C_6H_5}{\overset{C_6H_5}{Si}}-O-\right]_x$$

and



$$\left[-\overset{\overset{O}{\|}}{Ti}-O-\underset{C_6H_5}{\overset{C_6H_5}{Si}}-O-\right]_x$$

Because of the high titanium:silicon ratio (1.5-2.0), some titanium-oxygen-titanium linkages were believed to be present. The influence of reaction conditions were studied, and the following observations were made:

1. The self-condensation of diphenylsilanediol can be retarded by keeping the reaction mixture below 80°C. and by slowly adding the diol to the bis(cyclopentadienyl)titanium dichloride solution.

2. The optimum temperature range for condensation of bis(cyclopentadienyl)titanium dichloride with diphenylsilanediol is 70-80°C.
3. Organic bases must be used in the solvent system.
4. A drying agent, preferably calcium carbide, should be added to the reaction mixture to assure anhydrous conditions. Water in the system tends to destroy bis(cyclopentadienyl)titanium dichloride at 70-80°C.

When bis(cyclopentadienyl)titanium dichloride and triphenylsilanol were allowed to react under the same conditions, a product was obtained with an analysis corresponding reasonably well with $[(C_6H_5)_3SiO]_2TiO$ or $[(C_6H_5)_3SiO]_2Ti(OH)_2$.

A later investigation by Morton and Harwood (89) established that bis(cyclopentadienyl)titanium dichloride is decomposed by the reaction mixture in the absence of diphenylsilanediol and that pyridine was principally responsible for this decomposition. Further studies (90, 91) indicated that when bis(cyclopentadienyl)titanium dichloride was treated with pyridine at 75°C. the cyclopentadienyl groups were completely cleaved from titanium when the reaction time was sufficient. The formation of cyclopentadiene in the reaction occurred in the absence of moisture, and a product of the empirical formula, $(C_5H_5N)TiCl_2$, was isolated.

Other Properties of Siloxy Titanium Compounds.

Calculations of bond strengths by Zietter and Brown (63) indicate that the titanium-oxygen bond ($\sim$112 kcal./mole) and the silicon-oxygen bond ($\sim$103 kcal./mole) are approximately of the same strength. They also investigated the infrared spectra of titanium-silicon compounds and condensed titanium butoxides (92). Table VII lists their assignments for the titanium-oxygen-silicon and titanium-oxygen-titanium bonds.

Table VII. Infrared Absorptions of Titanium-Silicon Compounds (92)

Compound	Absorption (cm.$^{-1}$)	Intensity	Assignment
$Ti[OSi(CH_3)_3]_4$	919	very strong	Ti-O-Si stretch
$Ti[OSi(C_6H_5)_3]_4$	926	very strong	Ti-O-Si stretch
$Ti[O_5Si_4(C_6H_5)_8]_2$	925	very strong	Ti-O-Si stretch
Condensed titanium butoxides	820	strong	Ti-O-Ti
Condensed titanium butoxides	726	medium	Ti-O-Ti

Andrianov *et al.* (93), studied the infrared absorption spectra of poly(titanoorganosiloxanes) and reports that the characteristic bonds of the titanium-oxygen vibration in the titanium-oxygen-silicon grouping are in the 914-922 cm.$^{-1}$ region.

EXPERIMENTAL

Preparation of Reactants.

The organosilicon compounds which were used as starting materials were purchased from the Dow-Corning Corporation, Midland, Michigan, and Anderson Chemical Company, Weston, Michigan. These materials were used without further purification.

Sodium Trimethylsilanolate. This compound was prepared by the method of Hyde et al. (47). Sodium amide was prepared from 4.2 g. of sodium metal in 100 ml. of liquid ammonia at -33°C. To the resulting suspension, 45.9 g. of hexamethyldisiloxane was slowly added. The mixture was kept at -33°C. for two hours, and the ammonia was then evaporated with a stream of nitrogen gas. The residue was dissolved in anhydrous diethyl ether, filtered, and the solvent evaporated. The resulting solid was sublimed under vacuum at 140-150°C. to yield 10 g. of sodium trimethylsilanolate. A determination of its neutralization equivalent showed that the compound was 96.24 percent pure.

Sodium trimethylsilanolate was also prepared by the reaction of 2.8 g. of sodium metal and 9.5 g. of trimethylsilanol in 100 ml. of anhydrous benzene at room temperature overnight. The resulting solution was decanted from the excess sodium and evaporated to dryness. Sublimation under vacuum at 140-150°C. produced 2.5 g. of the silanolate.

Sodium dimethylphenylsilanolate. The method of Hyde et al. (47), was used to prepare this compound. The hydrolysis of 166 g. of dimethylphenylchlorosilane in 300 ml. of acetone was accomplished by addition of 100 ml. of water. The product, as an immiscible liquid, was separated from the aqueous layer and distilled through a Vigreux column. The fraction at 138.5-142°C. and 4-5 mm. Hg pressure was collected. An 85 g. yield of tetramethyldiphenyldisiloxane was obtained. A mixture of 8 g. of powdered sodium hydroxide, 70 ml. of isopropyl alcohol, and 30 ml. methanol was heated to 50°C., and 28.6 g. of tetramethyldiphenyldisiloxane was added. The resulting solution was filtered and then concentrated by azeotropic distillation at 115°C. using a Dean-Stark trap to collect the distillate. When the solution became viscous, 10 ml. of methanol was added. This procedure was repeated three times, and the solution was finally concentrated by heating to 135°C. under the reduced pressure produced by an aspirator. When the solution was cooled, the sodium silanolate failed to crystallize completely, and a gummy product was obtained. Drying at 80°C. and 3 mm. Hg pressure failed to give a solid product before decomposition began. This product was assumed to be a mixture of the sodium salt and starting materials. The neutralization equivalent of this material was not determined. The procedure for the preparation of this compound was repeated several times. Amounts of solvents and reaction temperatures were varied, but no crystalline sodium dimethylphenylsilanolate was ever isolated.

Sodium methyldiphenylsilanolate. Hyde's method (47) was also used in this preparation. Methyldiphenylchlorosilane (183 g.) in 300 ml. of acetone was hydrolyzed by treatment with 100 ml. of water and heating the solution on a steam bath. When the solution was cooled the crude disiloxane solidified out. After separation from the water this product was recrystallized from ethanol; 107 g. of dimethyltetraphenyldisiloxane was obtained. The procedure described for the preparation of sodium dimethylphenylsilanolate was repeated using 41 g. of the prepared disiloxane. The alcohol solution was concentrated by heating to 100°C., 30 ml. of tolune was added, and the temperature was raised to 130°C. As the solution cooled, a white solid formed which hardened on drying at 50°C. and 3 mm. Hg pressure. Because the product was insoluble in ethanol, the neutralization equivalent of sodium methyldiphenylsilanolate could not be determined.

Sodium triphenylsilanolate. Hexaphenyldisiloxane was prepared according to the method of Daudt and Hyde (94). Triphenylsilanol (25 g.) in 450 ml. of absolute ethanol at reflux temperature was treated with 0.1 g. of sodium hydroxide. After refluxing for four hours, the precipitate of hexaphenyldisiloxane was collected by filtration and recrystallized from cyclohexane to yield 17 g. of the pure product. By the method of Hyde (47), a mixture of 1.97 g. of sodium hydroxide, 20 ml. of methanol, 10 ml. of isopropanol, 15 ml. of toluene, and 13.2 g. of hexaphenyldisiloxane was treated as in the previous preparation. When the solution became viscous 10 ml. portions of isopropanol were added. As the solution cooled, white crystals of sodium triphenylsilanolate formed. After drying at 58°C. and 3 mm. Hg pressure for 10 hours the silanolate proved to be 96.3 percent pure by the determination of its neutralization equivalent.

Sodium triphenylsilanolate was also prepared by the reaction of sodium metal and triphenylsilanol. Thus, 15 g. of triphenylsilanol was slowly added to 2 g. of sodium metal in 130 ml. of toluene. After the vigorous evolution of hydrogen subsided, the solution was brought to reflux temperature and maintained there until the apparent completion of the reaction. Filtration through a funnel packed with glass wool and cooling to room temperature produced white crystals of sodium triphenylsilanolate. This product had a neutralization equivalent of 338.6 (theory, 298.4).

Sodium tri-α-naphthylsilanolate. A solution of 4 g. of tri-α-naphthylsilanol (supplied by Dr. C. R. Hare) in 120 ml. of mixed xylenes was treated with 0.22 g. of sodium metal and refluxed overnight. The hot solution was decanted from the unreacted sodium metal, cooled, and filtered. In this manner, 1.9 g. of sodium tri-α-naphthylsilanolate was isolated as a white solid.

Lithium triphenylsilanolate. This compound was prepared by treating 10 g. of triphenylsilanol with excess lithium metal in 150 ml. of refluxing toluene for 24 hours. After decanting the unreacted lithium metal from the solution and then cooling, 8.0 g. of fine white crystalline lithium triphenylsilanolate was isolated by filtration.

Lead trimethylsilanolate. This compound was prepared by the method of Patnode and Schmidt (95). Lead monoxide (2.0 g.) was treated with 15 ml. of trimethylsilanol. The mixture was stirred overnight at room temperature while lead trimethylsilanolate formed. The silanolate was isolated by evaporation of the excess silanol and drying under vacuum.

Bis(cyclopentadienyl)titanium dichloride. The method of Summers, Uloth, and Holmes (4) was used to prepare this compound. Cyclopentadiene was prepared by cracking dicyclopentadiene at 160°C; it was stored at -78°C. until used in the following preparation (96). A thoroughly dried three-neck three liter flask was equipped with a mechanical stirrer, nitrogen inlet, thermometer, condenser and addition funnel. The apparatus was swept with nitrogen while 700 ml. of petroleum ether and 13.88 g. of lithium shot were introduced. A solution of 92.57 g. of *n*-butyl chloride in 200 ml. of petroleum ether was added over a period of 3 hours. The reaction temperature was maintained at 0°C. while the n-butyllithium formed. A solution of 66.10 g. of cyclopentadiene in 150 ml. of xylene was added to the *n*-butyllithium over a period of one hour. As the thick slurry of cyclopentadienyllithium formed, 1 liter of petroleum ether was added. This mixture was stirred overnight at room temperature. Titanium tetrachloride (94.87 g.) in 200 ml. of xylene was then added over a period of 1.5 hours. The mixture was refluxed for 4 hours, and 1400 ml. of solvent was distilled off. The temperature of this mixture was then maintained at 60°C. for 16 hours. Filtration and evaporation of the solvent produced a large amount of dark brown solid which was extracted with chloroform. After evaporation of the chloroform and recrystallization of the residue from toluene, dark red crystals of bis(cyclopentadienyl)titanium dichloride were isolated, m.p. 279-280°C. (reported, 289-291°C). Analysis of the compound gave 48.21% C (theory, 48.23%) and 4.23% H (theory, 4.04%).

Bis(cyclopentadienyl)titanium diiodide. The method of Wilkinson and Birmingham was used (3). A solution of 4 g. of bis(cyclopentadienyl)-titanium dichloride in 180 ml. of acetone was treated with 5 g. of potassium iodide at reflux temperature for 1 hour. The hot solution was filtered, and the acetone was evaporated to yield bis(cyclopentadienyl)titanium diiodide which was recrystallized from toluene. The product was dark purple crystals melting at 310-316°C. (reported, 319 ± 3°C.).

Preparation of Siloxy Derivatives of Bis(cyclopentadienyl)-titanium (IV).

The following reactions of bis(cyclopentadienyl)titanium dichloride and bis(cyclopentadienyl)titanium diiodide with silanolates and silanols were carried out under anhydrous conditions. The reaction vessels, usually 300 ml. or 500 ml. three-necked flasks, were equipped with an addition pistol and condenser with a nitrogen inlet. This equipment was thoroughly dried in an oven at 110°C. before use. After being charged with the starting materials, the equipment was assembled and connected to the receiving end of a distilling head to receive freshly distilled solvent. The apparatus was evacuated and heated to exclude last traces of moisture before nitrogen was allowed to pass through the system. The solvent (toluene or benzene) was then distilled over sodium directly into the reaction flask. The temperature of the solution in the flask (bis(cyclopentadienyl)titanium dichloride in toluene) was then raised to 70-90°C. before the other reactant in the pistol was added. This reaction mixture was constantly stirred with a magnetic stirrer. After completion of the reaction the system was opened to the air to isolate the products.

Trimethylsiloxybis(cyclopentadienyl)titanium chloride. A solution of 2.22 g. (0.009 mole) of bis(cyclopentadienyl)titanium dichloride in 200 ml. of benzene was treated with 1.0 g. (0.009 mole) sodium trimethylsilanolate. The silanolate was not completely soluble in the benzene solution. The mixture was allowed to react at reflux temperature for one hour during which time the solution turned from deep red to an orange color. The mixture was filtered and the solvent was evaporated. The viscous residue from the evaporation was vacuum dried at room temperature and then was sublimed under vacuum as the temperature was slowly raised. At 80°C. and 0.1 mm. Hg pressure 0.32 g. of an orange material was collected. At 110-130°C. and 0.1 mm. Hg pressure 0.2 g. of a dark orange material collected on the cold finger. The fraction at 80°C. appeared wet and contaminated. After resublimation of this fraction, only about 0.05 g. of a bright yellow fluffy solid was collected owing to extensive decomposition of the material. From elemental analysis and the infrared spectrum, the material was identified as trimethylsiloxybis-(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl(OSi(CH_3)_3)$, m.p. 107°C. The analysis showed 51.81 and 51.67% C (theory, 51.58%), 6.57 and 6.42% H (theory, 6.34%), and 11.90 and 11.77% Cl (theory, 11.71%). Not enough product was isolated for titanium and silicon analyses or for a molecular weight determination.

An infrared spectrum of the 110-130°C. fraction indicated the presence of a titanium-oxygen-silicon bond (absorption in the 10.5 micron region). However, upon recrystallization of a portion of the material from toluene, bis(cyclopentadienyl)titanium dichloride was recovered. This 110-130°C. fraction was assumed to be a mixture of the titanium starting material and trimethylsiloxybis(cyclopentadienyl)titanium chloride. Pure trimethylsiloxybis(cyclopentadienyl)titanium chloride could not be recovered.

The synthesis of trimethylsiloxybis(cyclopentadienyl)titanium chloride was attempted six other times at temperatures ranging from 25 to 110°C.

Toluene or a petroleum ether-chloroform mixture was used as the solvent. In each case only milligram quantities of the product could be isolated by sublimation. In no instance was the desired product isolated by extraction with or recrystallization from diethyl ether, n-hexane, cyclohexane, cyclohexene, petroleum ether, toluene, or benzene.

The residue from the filtration of the reaction mixture after completion of the reaction appeared to contain an orange product. Extraction of this residue with toluene yielded approximately 0.05 g. of bright orange crystals. This product is described below. A large amount of titanium dioxide was also isolated from the filtration residue. Identification of titanium dioxide was based upon its x-ray diffraction pattern.

Reaction of Bis(cyclopentadienyl)titanium Dichloride and Sodium Dimethylphenylsilanolate. A solution of 2.86 g. (0.015 mole) of bis(cyclopentadienyl)titanium dichloride in 400 ml. of toluene was treated with 2.0 g. of the gummy product which was isolated in the synthesis of sodium dimethylphenylsilanolate. This material was added to the reaction flask through an open neck while a fast stream of nitrogen flowed through it. The mixture was allowed to react for one hour at 90°C. and slowly cooled with constant stirring overnight. Filtration yielded a brown residue and an orange colored filtrate. Extraction of the brown residue with toluene produced a large amount of titanium dioxide as insoluble material and 0.15 g. of bright orange crystals as soluble material. These orange crystals proved to be identical to that isolated from the reaction of sodium trimethylsilanolate by comparison of their infrared spectra. The orange solution from the filtration was reduced in volume to give a viscous red slurry. This slurry was treated with 5 ml. of diethyl ether and filtered to yield small amounts of bis(cyclopentadienyl)titanium dichloride and the orange material as solids. No compound was isolated which contained a titanium-oxygen-silicon bond. An attempt to isolate products by vacuum sublimation failed.

The bright orange crystals which were isolated in this reaction and in the previous reaction involving sodium trimethylsilanolate decomposed when heated above 200°C., and the infrared spectrum indicated no titanium-oxygen-silicon bonds. Decomposition of a sample in sulfuric acid gave no precipitate of silica, indicating that silicon was not present in the compound. Elemental analysis showed the following composition: 54.47 and 54.47% C, 4.81 and 4.67% H, 15.89, 16.25 and 16.11% Cl, and 21.55 and 21.45% Ti. This compound had a molecular weight of 411 by cryoscopic measurements in 1,4-dioxane. On the basis of elemental analysis, molecular weight determinations, and its infrared spectrum (vide infra) the compound has been identified as 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dititoxane, $[(C_5H_5)_2ClTi]_2O$, which contains 54.21% C, 4.55% H, 16.01% Cl, and 21.68% Ti. This compound has a formula weight of 443.

Methyldiphenylsiloxybis(cyclopentadienyl)titanium Chloride. In 200 ml. of toluene at 85°C., 2.10 g. (0.0085 mole) of bis(cyclopentadienyl) titanium dichloride and 2.0 g. (0.0085 mole) of sodium methyldiphenylsilanolate were allowed to react for one hour. The mixture was cooled, filtered, and the solvent was evaporated. Recrystallization from cyclohexene followed by recrystallization from toluene yielded 0.5 g. of orange crystals believed to be methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, m.p. 164-166°C. The material had a molecular weight of 433 by cryoscopic measurements in benzene (theory, 427). Elemental analysis showed 64.91 and 64.82% C (theory, 64.71%), 5.41 and 5.46% H (theory, 5.43%), 8.54 and 8.55% Cl (theory, 8.31%), 6.56% Si (theory 6.58%), and 10.31% Ti (theory, 11.22%). The residue from the filtration contained titanium dioxide.

Triphenylsiloxybis(cyclopentadienyl)titanium Chloride. A suspension of 4.84 g. (0.018 mole) of bis(cyclopentadienyl)titanium dichloride in 250 ml. of toluene at 85°C. was treated with 9.67 g. (0.036 mole) of sodium triphenylsilanolate. The mixture was cooled, filtered, and evaporated to produce an orange solid. Recrystallization from cyclohexane produced 2 g. of orange crystals believed to be triphenylsiloxybis(cyclopentadienyl)-titanium chloride, $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, m.p. 201-204°C. This material had a molecular weight of 497 by cryoscopic measurements in benzene (theory, 489). Elemental analysis showed 68.70 and 68.62% C (theory, 68.78%), 5.05 and 5.20% H (theory, 5.15%), 7.38 and 7.40% Cl (theory, 7.24%), 5.67 and 5.75% Si (theory, 5.75%), and 10.32 and 10.77% Ti (theory, 9.85%).

Other products isolated from the reaction were titanium dioxide, sodium chloride, and tetrakis(triphenylsiloxy)titanium in the residue from filtration, and hexaphenyldisiloxane and unreacted bis(cyclopentadienyl)-titanium dichloride from the recrystallization. Titanium dioxide and tetrakis (triphenylsiloxy)titanium were produced in large quantities.

When 1.23 g. (0.005 mole) of bis(cyclopentadienyl)titanium dichloride, 2.7 g. (0.01 mole) of triphenylsilanol, and 1.0 g. (0.01 mole) of triethylamine in 200 ml. of toluene at 80-90°C. were allowed to react for 70 hours, 0.55 g. of triphenylsiloxybis(cyclopentadienyl)titanium chloride was isolated by recrystallization from cyclohexene. Although considerable decomposition of the titanium starting material took place, as evidenced by the dark brown color of the reaction mixture, no titanium dioxide was isolated; however, tetrakis(triphenylsiloxy)titanium was present in the reaction products.

Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium. A solution of 0.1 g. (0.0004 mole) of bis(cyclopentadienyl)titanium dichloride in 60 ml. of toluene was treated with 0.24 g. (0.0008 mole) of sodium triphenylsilanolate at 80°C. for two hours during which time the solution turned from deep red to light yellow. The mixture was filtered and the solvent evaporated. The resulting residue was dissolved in boiling acetone and filtered. On cooling and slow evaporation of the acetone solution, light yellow crystals formed as well as a fine white powder.

This solid mixture was collected and treated with diethyl ether. The white powder was held in suspension in diethyl ether and was decanted from the light yellow solid which remained on the bottom of the mixture. This light yellow solid was then recrystallized from acetone to yield 0.05 g. of white crystals believed to be bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$, m.p. 202-204°C. The white powder suspended in diethyl ether was identified as hexaphenyldisiloxane by its melting point and infrared spectrum. In another synthesis in which 2.04 g. (0.007 mole) of sodium triphenylsilanolate and 0.83 g. (0.0035 mole) of bis(cyclopentadienyl)titanium dichloride were reacted, 0.25 g. of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was isolated. The reaction of bis(cyclopentadienyl)titanium dichloride and freshly prepared sodium triphenylsilanolate was also observed. The reaction of 5.53 g. (0.02 mole) of triphenylsilanol and 0.46 g. (0.02 g.-atom) of sodium metal in 400 ml. of toluene at 90°C. produced sodium triphenylsilanolate <u>in situ</u>. Treatment of this solution with 2.5 g. (0.01 mole) of bis(cyclopentadienyl)titanium dichloride followed by constant stirring at 90°C. for five hours and slow cooling to room temperature produced less than 0.1 g. of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium.

The reaction of 2.0 g. (0.008 mole) of bis(cyclopentadienyl)titanium dichloride and 4.5 g. (0.016 mole) of lithium triphenylsilanolate in 250 ml. of toluene at 90°C. for six hours yielded less than 0.05 g. of bis-(triphenylsiloxy)bis(cyclopentadienyl)titanium when isolated in the above manner.

When 0.33 g. (0.0007 mole) of triphenylsiloxybis(cyclopentadienyl)-titanium chloride and 0.20 g. (0.0007 mole) of sodium triphenylsilanolate were reacted in 200 ml. of toluene at 80°C. for one hour, 0.1 g. of bis-(triphenylsiloxy)bis(cyclopentadienyl)titanium was isolated by recrystallization from acetone.

A better yield of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was obtained when 2.33 g. (0.0054 mole) of bis(cyclopentadienyl)titanium diiodide and 2.95 g. (0.011 mole) of triphenylsilanol was allowed to react in 400 ml. of toluene at 80-85°C. for two days. Triethylamine (1.05 g.) was added as a proton acceptor. The product was isolated by recrystallization from acetone to yield 0.8 g. of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium. Elemental analysis showed 75.80 and 75.86% C (theory, 75.80%), 5.42 and 5.55% H (theory, 5.53%), 8.24% Si (theory, 7.71%), and 6.48% Ti (theory 6.57%). The material had a molecular weight of 765 by cryoscopic measurements in benzene (theory, 729). The infrared red spectrum of this compound is very similar to that of triphenylsiloxybis(cyclopentadienyl)titanium chloride. When an acetone solution of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was treated with hydrogen chloride gas, the solution turned orange, then red, and finally brown. Presumably the following reactions took place:

$$(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2 \xrightarrow{HCl} (C_5H_5)_2TiCl(OSi(C_6H_5)_3) \xrightarrow{HCl} (C_5H_5)_2TiCl_2 \xrightarrow{HCl}$$

decomposition.

Large amounts of tetrakis(triphenylsiloxy)titanium and titanium dioxide were isolated from the reactions of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate. Other products identified from the reactions were sodium chloride, hexaphenyldisiloxane, and triphenylsiloxybis(cyclopentadienyl)titanium chloride. The reaction of bis(cyclopentadienyl)titanium diiodide and triphenylsilanol yielded lesser amounts of titanium dioxide and tetrakis(triphenylsiloxy)titanium. No attempt was made to isolate the monosubstituted compound, triphenylsiloxybis(cyclopentadienyl)titanium iodide, which probably exists in the reaction mixture as a stable intermediate. Unreacted bis(cyclopentadienyl)titanium diiodide was also isolated from the acetone recrystallization.

Reactions of Bis(cyclopentadienyl)titanium Dichloride with Sodium Tri-α-naphthylsilanolate and Tri-α-naphthylsilanol. A solution of 1.06 g. (0.0043 mole) of bis(cyclopentadienyl)titanium dichloride and 250 ml. of toluene at 80°C. was treated with 1.90 g. (0.0043 mole) of sodium tri-α-naphthylsilanolate. The reaction mixture was stirred for three hours at this temperature during which time the color changed from deep red to orange. The mixture was cooled and filtered, and the solvent was evaporated to yield an orange residue. Recrystallizations from toluene, benzene, cyclohexene, and carbon tetrachloride produced no other products than tri-α-naphthylsilanol and titanium dioxide. Tri-α-naphthylsiloxybis(cyclopentadienyl)titanium chloride could not be isolated even though the change in color of the reaction mixture indicated that a reaction had taken place.

In another attempt to isolate the naphthylsiloxy derivative of bis-(cyclopentadienyl)titanium dichloride, 1.77 g. (0.004 mole) of tri-α-naphthylsilanol and 1.07 g. (0.004 mole) of bis(cyclopentadienyl)titanium dichloride in 250 ml. of toluene were treated with 1.5 ml. of triethylamine. The solution was kept at 90°C. for twenty hours. A color change from red to orange occurred. Cooling, filtration, and evaporation of the solvent yielded an orange solid. Treatment with 50 ml. of hot carbon tetrachloride followed by filtration and slow evaporation of the solvent yielded no product containing a titanium-oxygen-silicon bond.

Miscellaneous Reactions.

Previous to the development of the described method for carrying out the reactions of bis(cyclopentadienyl)titanium dihalides with alkali metal silanolates and silanols, many other reactions under various conditions were attempted. These reactions and their results are described in this section.

When no special precautions are taken to exclude moisture from the reaction system, bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate react to yield titanium dioxide and tetrakis(triphenylsiloxy)titanium as the main products. The odor of dicyclopentadiene is always detectable in these reactions when the decomposition of the organotitanium compound occurs.

A solution of 4.10 g. (0.018 mole) of bis(cyclopentadienyl)titanium dichloride and 10.0 g. (0.034 mole) of sodium triphenylsilanolate in 250 ml. of toluene was refluxed for ten hours, during which time the characteristic red color of the titanium starting material changed to a light orange and a light brown solid deposited from solution. Isolation by filtration and extraction of the solid with benzene yielded tetrakis(triphenylsiloxy)-titanium. The residue from the extraction was identified as a mixture of titanium dioxide and sodium chloride. The light orange filtrate contained unreacted bis(cyclopentadienyl)titanium dichloride and hexaphenyldisiloxane.

A solution of 1.0 g. (0.004 mole) of bis(cyclopentadienyl)titanium dichloride in 200 ml. of toluene at reflux temperature was prepared. A Soxhlet extractor containing 2.39 g. (0.008 mole) of sodium triphenylsilanolate was fitted to the flask containing the solution of titanium starting material, and the silanolate was slowly extracted into this solution. By this method the basicity of the reaction solution was kept low to minimize hydrolysis of bis(cyclopentadienyl)titanium dichloride. After introduction of all the silanolate, the solvent was evaporated and the residue extracted with benzene. The extracted products were tetrakis (triphenylsiloxy)-titanium and hexaphenyldisiloxane. Titanium dioxide and sodium chloride were also identified in the residue from the extraction.

In another attempt to bring about condensation, 250 ml. of toluene was distilled into a dry 300 ml. flask. While dry nitrogen was passed through the system, the flask was cooled in a cellosolve-dry ice bath.

To the flask was added 0.31 g. (0.0012 mole) of bis(cyclopentadienyl)-dichloride and 0.75 g. (0.0025 mole) of sodium triphenylsilanolate. After being stirred four days, the solution was filtered; no sodium chloride was isolated. The filtrate, which still had the red color of unreacted bis(cyclopentadienyl)titanium dichloride, was quickly transferred into a stoppered flask; however, upon standing for less than an hour precipitation of titanium dioxide occurred.

Reactions of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate carried out at room temperature in solvents such as toluene, benzene, and nitromethane also produced titanium dioxide and hexaphenyldisiloxane.

A solution of 1.8 g. (0.007 mole) of bis(cyclopentadienyl)titanium dichloride in 150 ml. of anhydrous xylene was prepared at reflux temperature. Ammonia was slowly bubbled into this solution while a solution of 4.0 g. (0.014 mole) of triphenylsilanol in xylene was added dropwise over a period of 1.5 hours. After complete addition, the mixture was refluxed for one hour longer and filtered. The filtrate contained unreacted titanium starting material and hexaphenyldisiloxane. The residue from the filtration was identified as a mixture of titanium dioxide and ammonium chloride.

A solution of 1.35 g. (0.008 mole) [$AgC_2H_3O_2$] in 90 ml. of water and 10 ml. of acetic acid was added to a solution of 1.0 g. (0.004 mole) of bis(cyclopentadienyl)titanium dichloride in 25 ml. of acetic acid. The silver chloride precipitate was filtered off, and the orange filtrate was extracted with five 50 ml. portions of chloroform. The chloroform solution was dried over calcium sulfate and filtered. No attempt was made to isolate the bis(cyclopentadienyl)titanium diacetate in solution. Triphenylsilanol (2.0 g.) was added to the solution, and the mixture was refluxed for one day without apparent reaction. The chloroform was evaporated, benzene was added, and the solution brought to reflux temperature. A Barrett distilling receiver was used to remove the benzene-acetic acid azeotrope at 80.0°C. After removal of the solvent, the residue was extracted with toluene to produce approximately 1 g. of tetrakis(triphenylsiloxy)titanium.

After investigating the reactions of bis(cyclopentadienyl)titanium dichloride with triphenylsiloxy compounds, it was believed at the time that possible steric hindrance between the cyclopentadienyl rings of the titanium compound and the phenyl rings of the siloxy compound prevented formation of the desired product and aided in the rupture of the titanium-carbon bonds. Therefore, attention was directed towards the preparation of the trimethylsiloxy derivatives of bis(cyclopentadienyl)titanium(IV).

A solution of 4.14 g. (0.017 mole) of bis(cyclopentadienyl)titanium dichloride in 250 ml. of anhydrous acetonitrile was prepared at reflux temperature. To this solution was added 10 ml. of pyridine; 3 g. (0.033 mole) of trimethylsilanol was then added dropwise over a period of one hour. The solution was refluxed for three days during which time the intense red color of the titanium compound changed to a light orange. A light brown solid which deposited from solution was isolated and identified as titanium dioxide. When the acetonitrile was evaporated titanium starting material and pyridine hydrochloride were isolated.

Sodium metal (1.02 g.) was treated with 4.0 g. (0.045 mole) of trimethylsilanol in 100 ml. of diethyl ether. After complete reaction the diethyl ether was replaced with 150 ml. of acetonitrile. To this solution was added 5.5 g. (0.022 mole) of bis(cyclopentadienyl)titanium dichloride at room temperature. A precipitate of titanium dioxide immediately formed.

When the sodium trimethylsilanolate produced by the reaction of 1.0 g. (0.043 g.-atom) of sodium metal and 3.94 g. (0.043 mole) of trimethylsilanol in 50 ml. of anhydrous diethyl ether was added dropwise to a slurry of 5.4 g. (0.022 mole) of bis(cyclopentadienyl)titanium dichloride in 100 ml. of diethyl ether at room temperature, and stirred for one day, titanium dioxide and sodium chloride were precipitated. Unreacted titanium starting material was also isolated.

Lead monoxide (1.0 g.) was treated with 25 ml. of trimethylsilanol, and the mixture was stirred over night at room temperature while lead trimethylsilanolate formed. Then 1.11 g. (0.0045 mole) of bis(cyclopentadienyl)titanium dichloride was added. Although this titanium compound is insoluble in trimethylsilanol, the red color of the suspension disappeared and a white suspension formed after two hours stirring at room temperature. Following evaporation of the solvent, the residue was extracted with benzene and then ethanol at their boiling points; however, no material was dissolved by either solvent.

In another attempt to effect condensation by precipitation of lead chloride, a solution of 1.30 g. (0.0052 mole) of bis(cyclopentadienyl)-titanium dichloride and 2.0 g. (0.0052 mole) lead trimethylsilanolate in 200 ml. of acetonitrile was prepared. While the solution was stirred over night, its color changed from red to orange. After filtration, the orange solution was evaporated to dryness and the residue was dissolved in hot benzene. Approximately 0.15 g. of an orange solid was precipitated by addition of petroleum ether. This material decomposed above 200°C. Because of the small amount of the product and the fact that its infrared spectrum indicated the absence of a titanium-oxygen-silicon bond no further time was spent trying to identify it.

Bis(cyclopentadienyl)titanium diacetate was prepared *in situ* by treating a solution of 2.0 g. (0.008 mole) of bis(cyclopentadienyl)-titanium dichloride in 150 ml. of acetic acid with a solution of 2.68 g. (0.016 mole) of silver acetate in 150 ml. of acetic acid and enough water to complete dissolution. The silver chloride precipitate was filtered off, and the acetic acid was removed by distillation and replaced with 25 ml. of sym-tetrachloroethane. Trimethylmethoxysilane (2.0 g.) in 60 ml. of chloroform was added, and the solution was refluxed at 68°C. in an attempt to bring about a transesterification by distilling off methyl acetate. After refluxing for one day the solvent was evaporated to leave a residue of titanium dioxide.

Preparation of tetrakis(triphenylsiloxy)titanium. According to the method of Zietler and Brown (63), a solution of 8.3 g. of triphenylsilanol in 100 ml. of anhydrous benzene was treated with 2.8 g. of titanium tetrabutoxide. The mixture was stirred for two hours at room temperature, and the solvent was evaporated to yield a quantitative amount of tetrakis-(triphenylsiloxy)titanium. A portion of this product was purified by extraction with toluene, and another portion was purified by vacuum sublimation at 340-360°C. This compound was used for comparative purposes with the products obtained from the reactions of bis(cyclopentadienyl)-titanium dichloride and triphenylsiloxy compounds.

Properties of Siloxy Derivatives of Bis(cyclopentadienyl)titanium(IV) and of 1, 3-Dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane.

Trimethylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl(OSi(CH_3)_3)$, methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, triphenylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, and 1, 3-dichloro-1, 1, 3, 3-tetrakis-(cyclopentadienyl)dititoxane, $[(C_5H_5)_2ClTi]_2O$, are crystalline orange solids. Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$, is a white crystalline material.

The siloxy compounds are all soluble in benzene, toluene, chlorobenzene, nitrobenzene, acetone, chloroform and carbon tetrachloride. They are slightly soluble in diethyl ether, petroleum ether, and aliphatic hydrocarbons. The dititoxane has a lower degree of solubility in all of these solvents. It is moderately soluble in toluene, nitrobenzene, and 1, 4-dioxane.

All of these compounds are decomposed by concentrated sulfuric acid. When acetone solutions of the siloxy derivatives are treated with hydrogen chloride gas red solutions result, presumably with the formation of bis(cyclopentadienyl)titanium dichloride. All of the compounds are hydrolyzed by sodium hydroxide dissolved in an acetone-water mixture; however, the dititoxane appears to be much more stable towards alkaline hydrolysis than the siloxy compounds. Solutions of all compounds decompose with formation of titanium dioxide when exposed to atmospheric moisture for long periods of time.

Differential thermal analyses of $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, and $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$ show that these compounds soon start to decompose above their melting points. Decomposition is essentially complete for the two monosubstituted siloxy compounds at 500°C., while for the disubstituted compound this occurs at approximately 425°C. The dititoxane slowly turns dark above 200°C and rapidly decomposes above 225°C. The differential thermal analysis curves for $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, and $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$ are shown in Figures I, II, and III. Enough samples were not available for the thermal analyses of $(C_5H_5)_2TiCl(OSi(CH_3)_3)$ and $[(C_5H_5)_2ClTi]_2O$.

Spectroscopic Data.

Ultraviolet and Visible Spectra.

These absorption spectra of the compounds were measured in cyclohexane solutions with a Beckman DK-2 recording spectrophotometer (Figures IV, V, VI, VII, VIII). The absorbancies are arbitrary. In the ultraviolet region bis(cyclopentadienyl)-titanium dichloride has a strong absorption in the 255-260 millimicron region. This absorption band is also present in the spectra of $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, and $(C_5H_5)_2TiCl(OSi(CH_3)_3)$. This band is shifted slightly to lower wavelengths as methyl

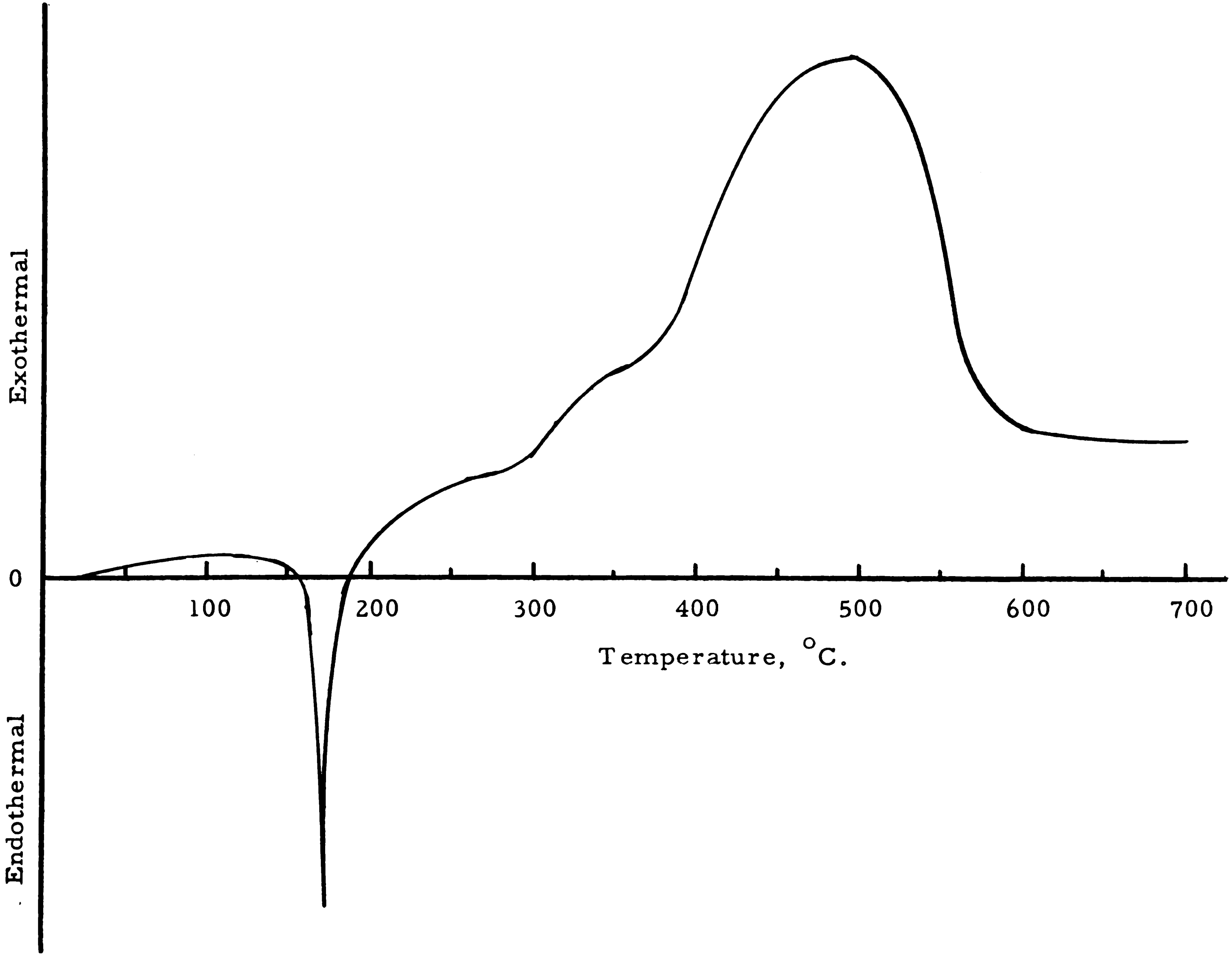


Figure I. Differential thermal analysis of methydiphenylsiloxybis(cyclopentadienyl)titanium chloride.

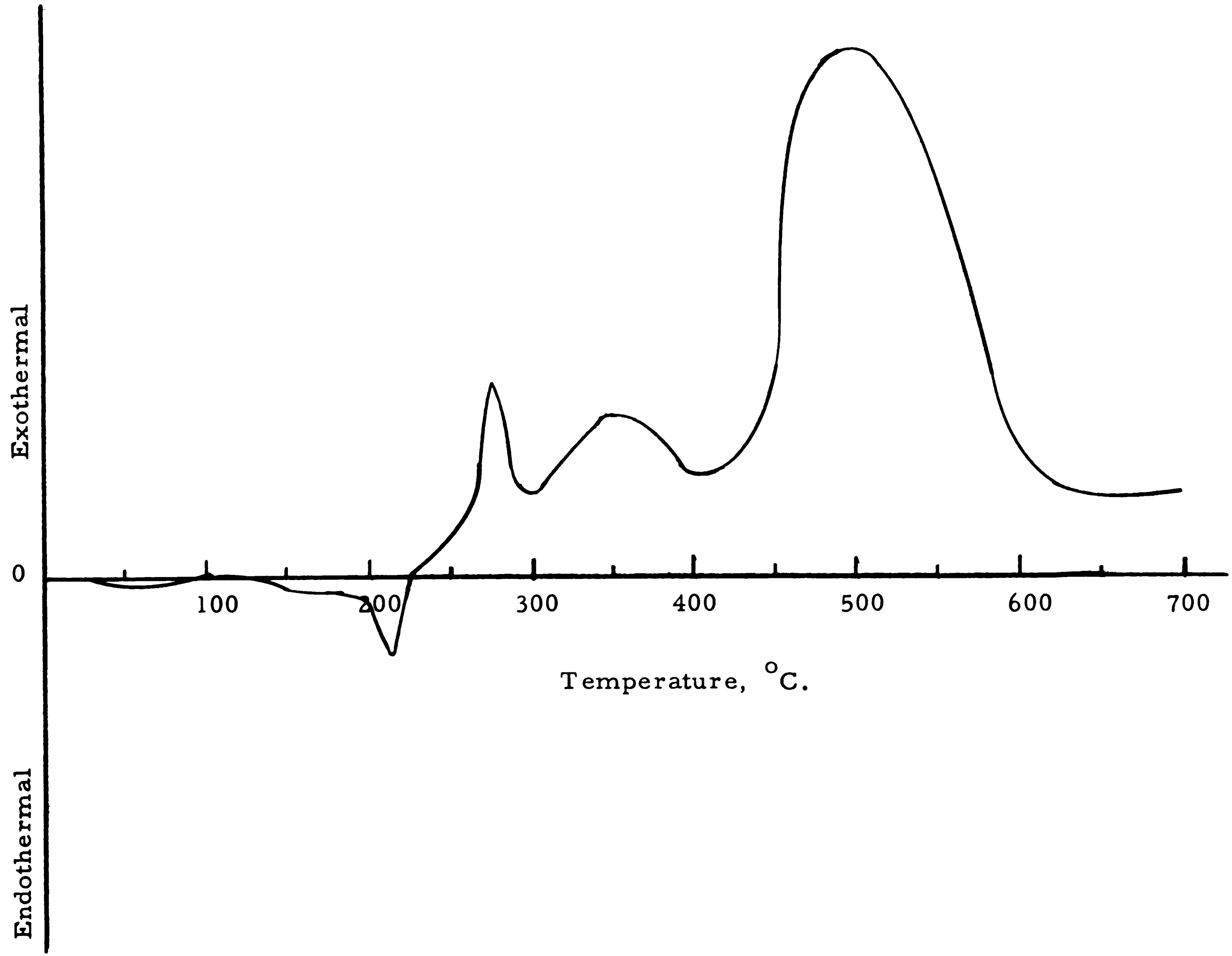


Figure II. Differential thermal analysis of triphenylsiloxybis(cyclopentadienyl)-titanium chloride.

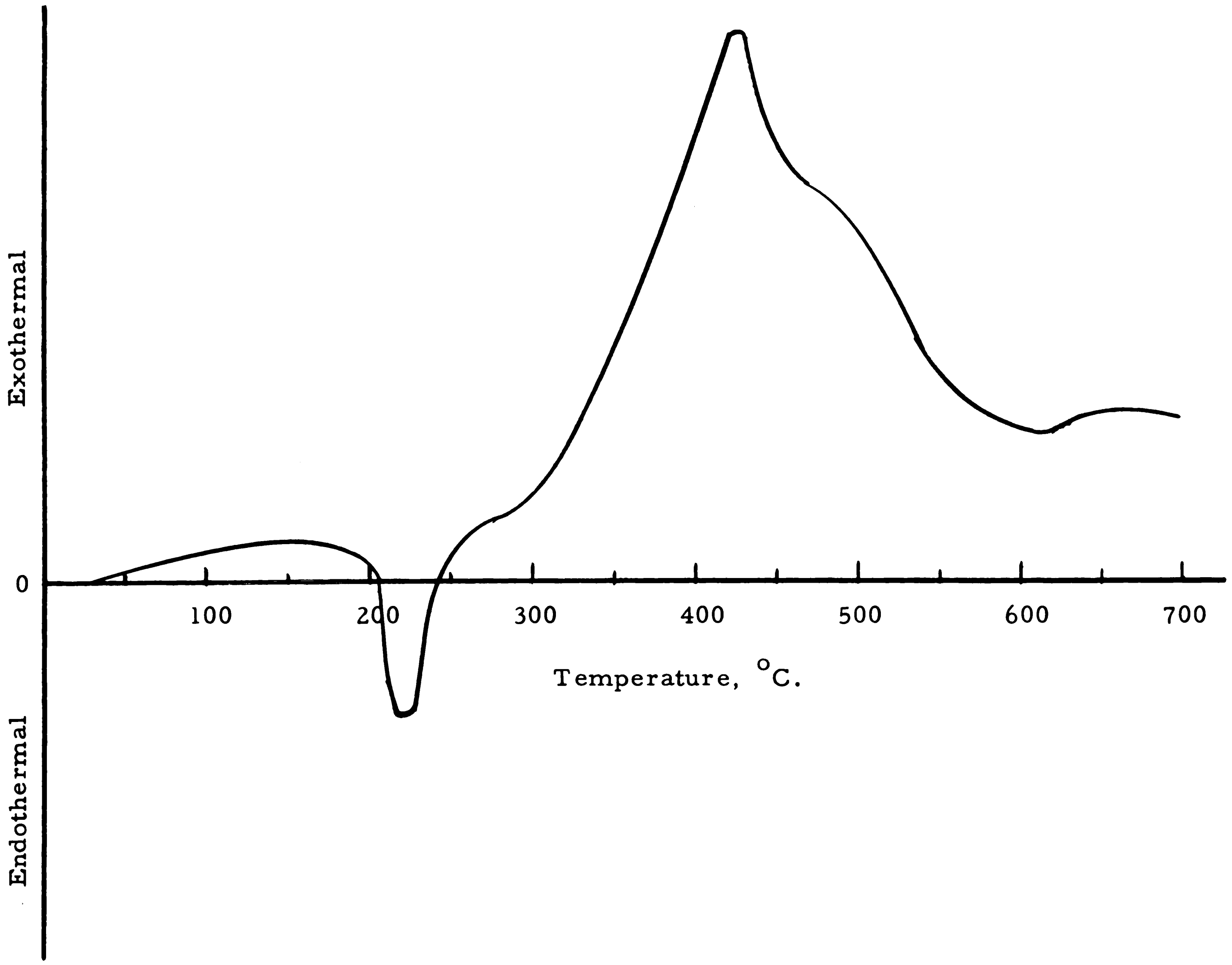


Figure III. Differential thermal analysis of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium.

groups are substituted for phenyl groups in these compounds. Thus for the triphenylsiloxy derivative the absorption maximum is at 259 millimicrons, for the methyldiphenylsiloxy compound it is at 258 millimicrons, and for the trimethylsiloxy compound it is at 256 millimicrons. The ultraviolet spectrum of $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$ shows an absorption in the 300-305 millimicron region, and in the region lower than 280 millimicrons the fine structure due to the phenyl absorptions of the triphenylsiloxy groups is observed (97). The compounds which have phenyl groups have high absorptions below 230 millimicrons. There are no prominent absorption bands in the ultraviolet spectrum of the dititoxane. There is only gradually increasing absorption as the wavelength is decreased from 340 to 220 millimicrons.

The visible spectra of the siloxy compounds show absorptions in the 340-350 millimicron region. Once again this band is shifted slightly to lower wavelengths as methyl groups are substituted for phenyl groups. The absorption maxima are: $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, 345 millimicrons; $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, 342 millimicrons; and $(C_6H_5)_2TiCl(OSi(CH_3)_3)$, 340 millimicrons. The visible spectrum of $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$ shows increasing absorption below 380 millimicrons which leads to the absorption maxima at 300 millimicrons in the ultraviolet region. Like the ultraviolet spectrum, the visible spectrum of $[(C_5H_5)_2ClTi]_2O$ shows increasing absorption as the wavelength decreases.

The molar extinction coefficients of the siloxy compounds in the 260 millimicron region are in the order of 4000-7500. For the 340 millimicron region the molar extinction coefficients are in the order of 1700-3400, at 300 millimicrons $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$ has a molar extinction coefficient of approximately 6400. These values were calculated from absorbancy measurements on chloroform solutions of the compounds.

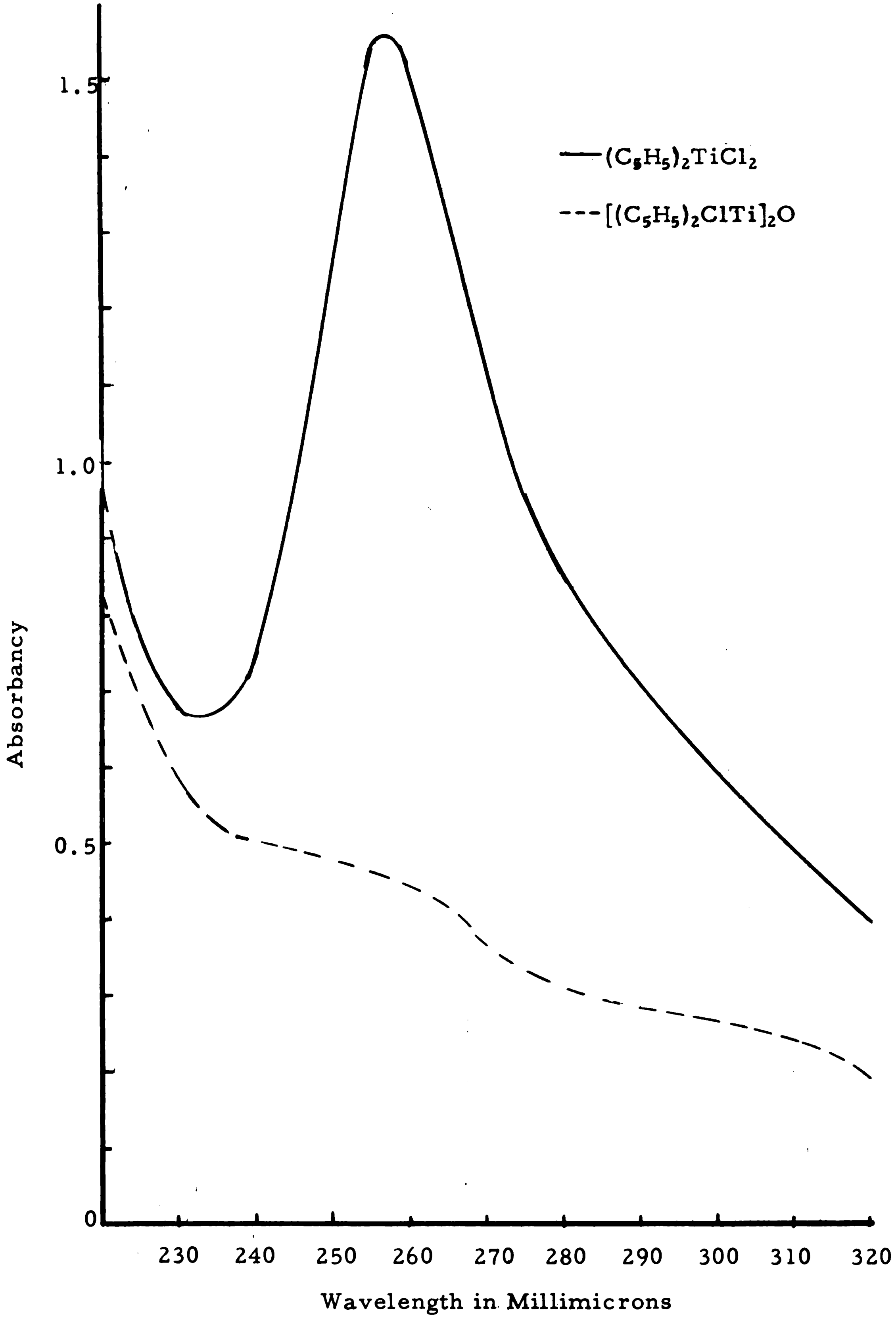


Figure IV. Ultraviolet spectra of bis(cyclopentadienyl)titanium dichloride and 1, 3-dichloro-1, 1, 3, 3-tetrakis-(cyclopentadienyl)dititoxane.

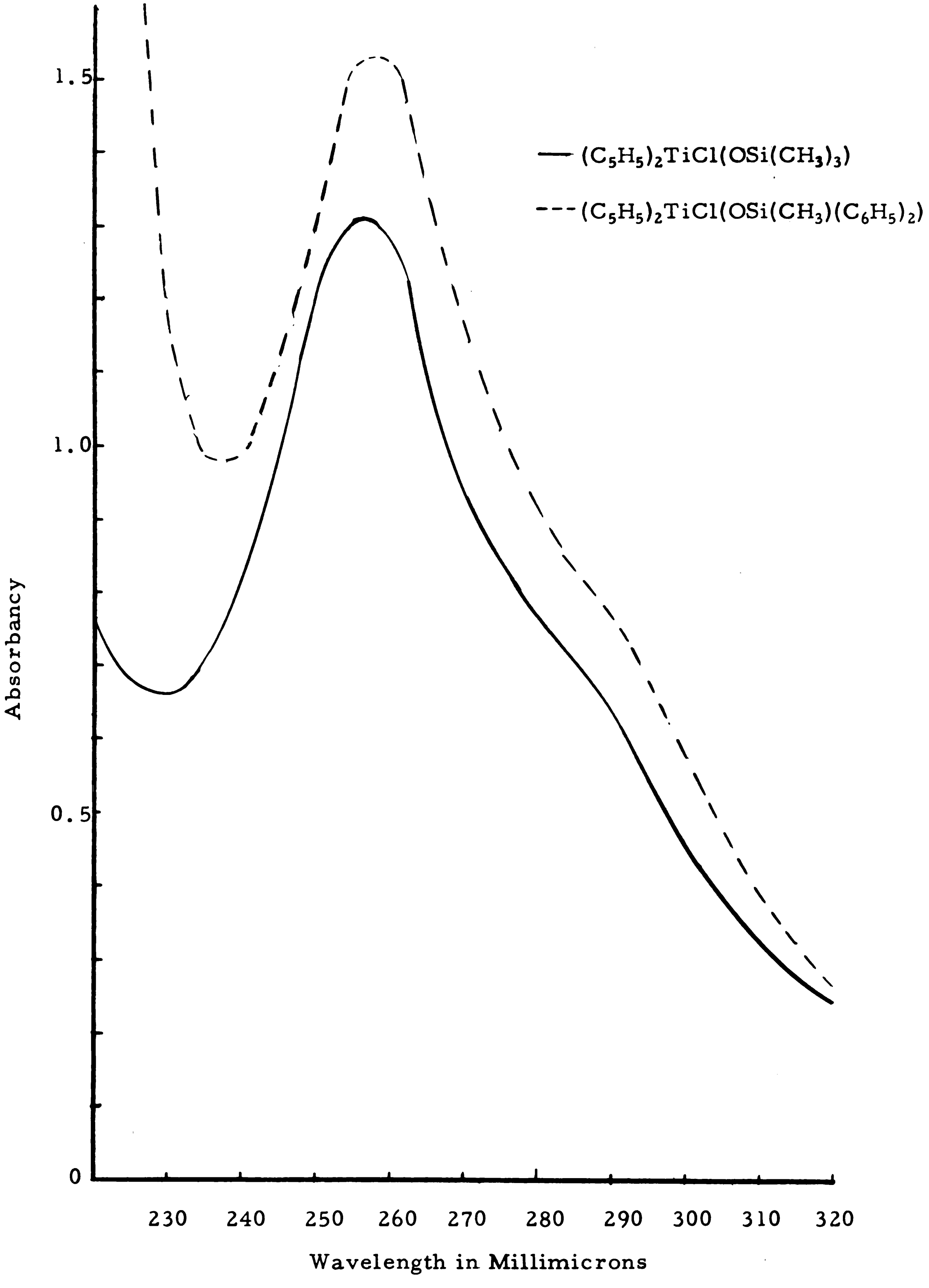


Figure V. Ultraviolet spectra of trimethylsiloxybis(cyclopentadienyl)titanium chloride and methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride.

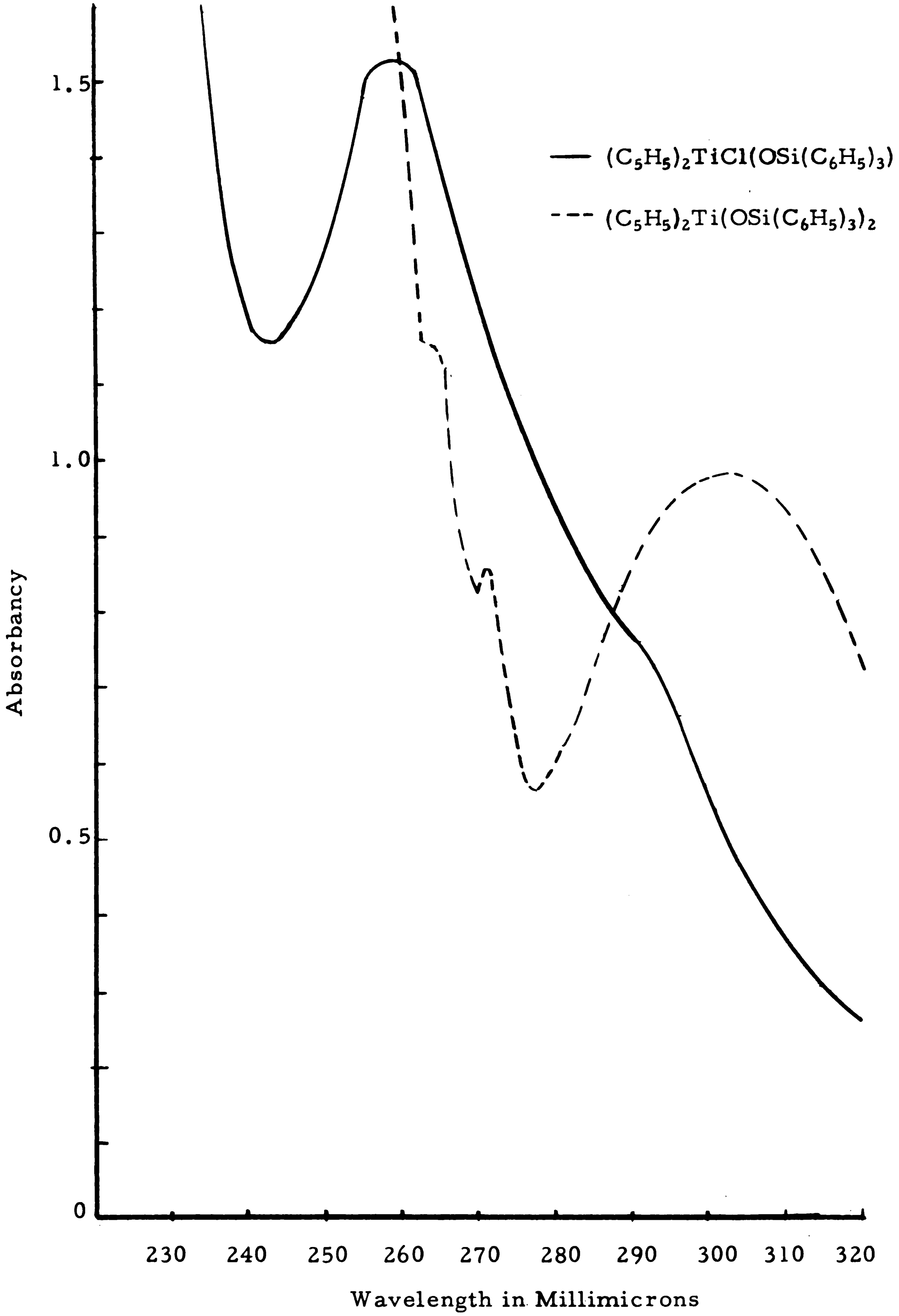


Figure VI. Ultraviolet spectra of triphenylsiloxybis(cyclopentadienyl)titanium chloride and bis(triphenylsiloxy)bis(cyclopentadienyl)titanium.

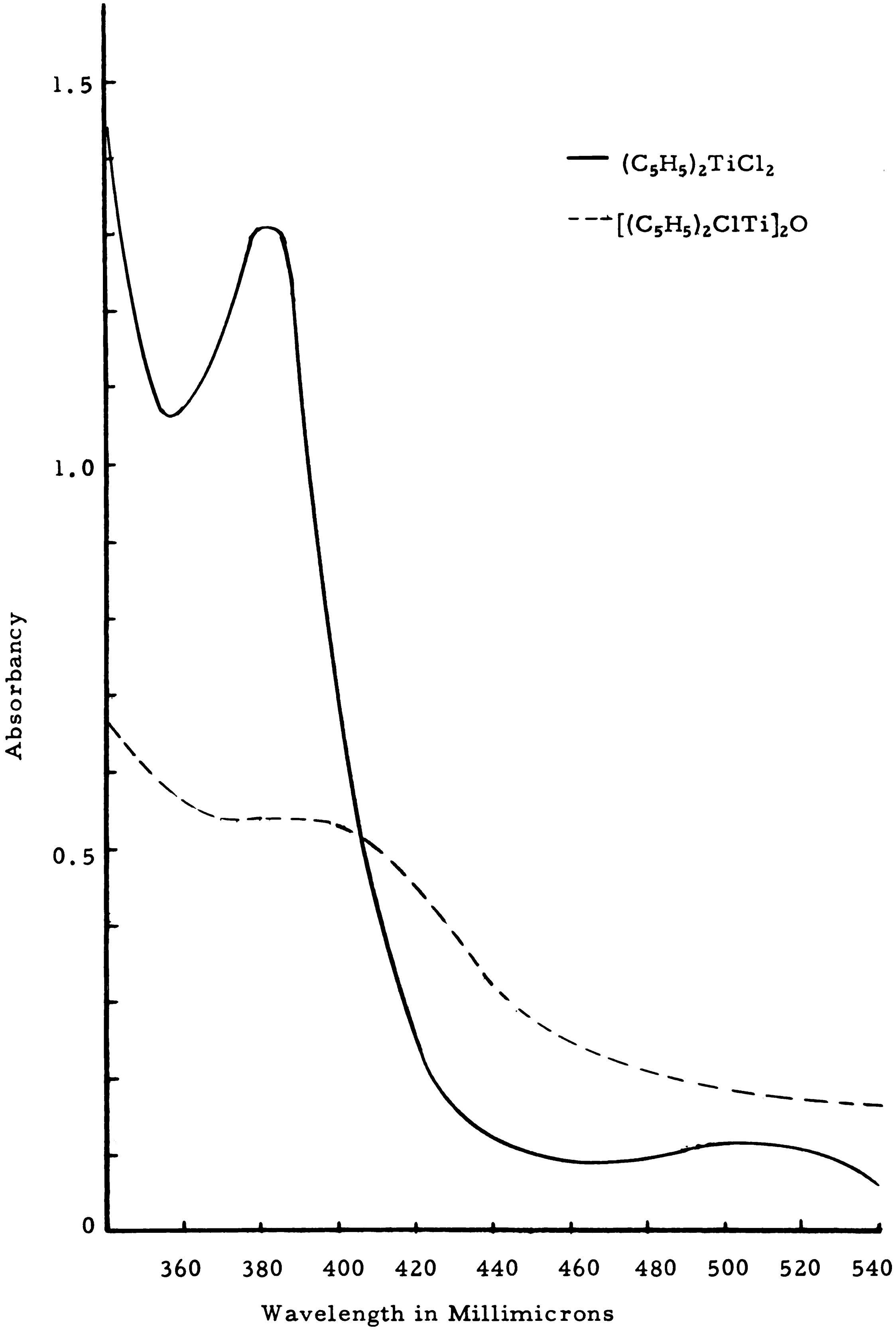


Figure VII. Visible spectra of bis(cyclopentadienyl)titanium dichloride and 1, 3-dichloro-1, 1, 3, 3-tetrakis-(cyclopentadienyl)dititoxane.

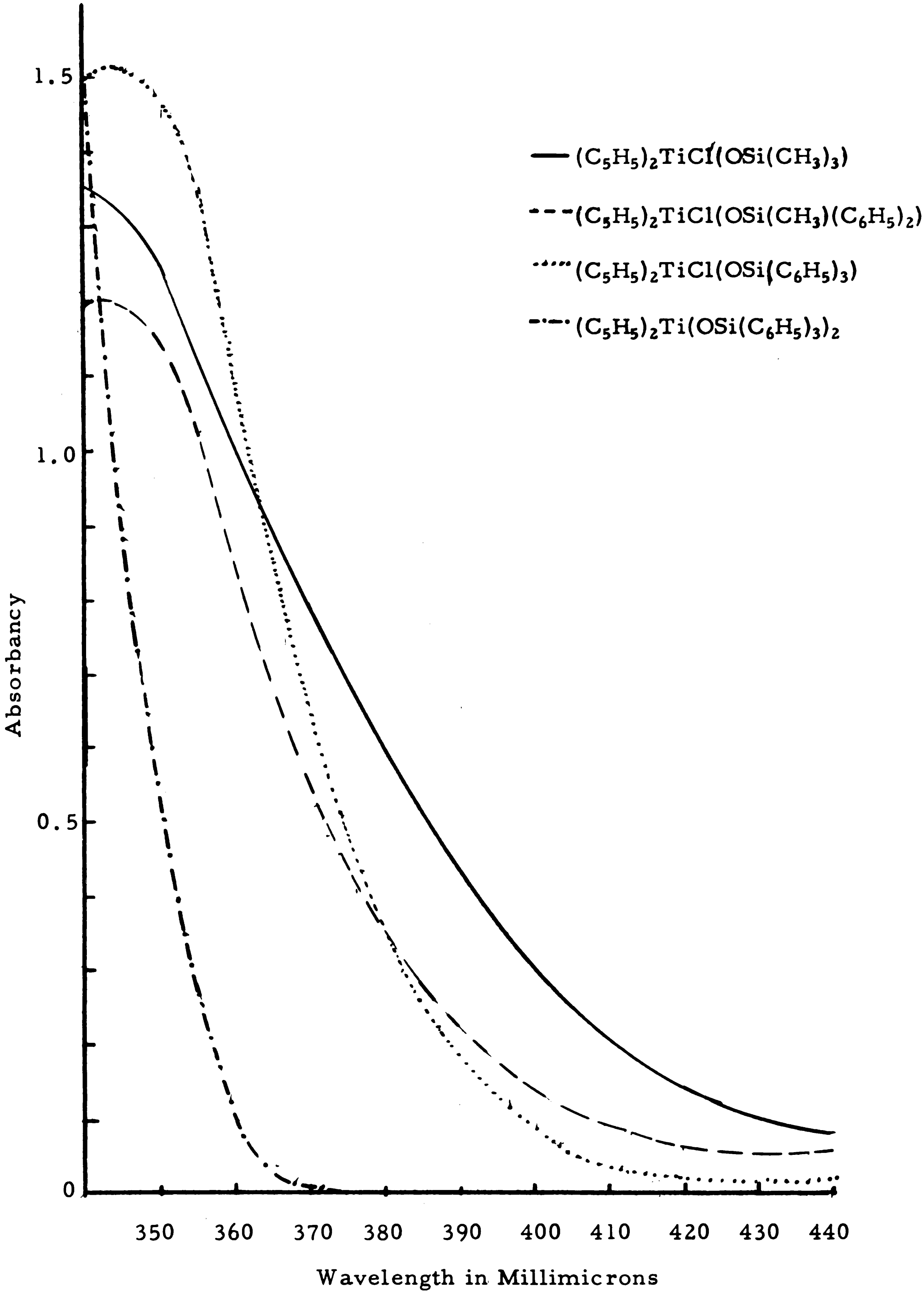


Figure VIII. Visible spectra of siloxy derivatives of bis(cyclopentadienyl)titanium(IV).

Infrared Spectra. The infrared spectra of the compounds (Figures IX-XVI) were recorded in potassium bromide pellets with a Perkin-Elmer Model 21 spectrophotometer. Concentrations of 2-3 mg. of sample in approximately 500 mg. of potassium bromide were used. The infrared spectra of bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)titanium diiodide, and tetrakis(triphenylsiloxy)titanium are also listed.

Compounds containing titanium-oxygen-silicon bonds have strong broad absorptions in the 10.25-11.25 micron region which Zietler and Brown (92) have assigned to the titanium-oxygen-silicon stretching frequency. As the electron-donating properties of the siloxy group is increased, e.g., substitution of methyl groups for phenyl groups, this absorption band is shifted to higher wavelengths. For $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$, which has two siloxy groups bonded to the titanium atom, the absorption band is located at 11 microns compared to 10.5 microns for $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$.

All of the siloxy derivatives of bis(cyclopentadienyl)titanium(IV) show the strong absorption in the 12.15 micron region which is present in the spectrum of bis(cyclopentadienyl)titanium dichloride. Absorptions at 6.95 and 9.85 microns present in the spectrum of bis(cyclopentadienyl)-titanium dichloride are masked by the stronger silicon-phenyl absorptions of $(C_5H_5)_2TiCl(OSi(CH_3)(C_6H_5)_2)$, $(C_5H_5)_2TiCl(OSi(C_6H_5)_3)$, and $(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$; however, they are evident in the spectrum of $(C_5H_5)_2TiCl(OSi(CH_3)_3)$.

The infrared spectrum of $[(C_5H_5)_2ClTi]_2O$ is similar to the spectrum of bis(cyclopentadienyl)titanium dichloride except that it has an additional intense broad absorption at 13.25-13.75 microns. Zeitler and Brown (92) have studied the spectra of condensed titanium butoxides and have assigned a strong absorption at 12.20 microns and a medium absorption at

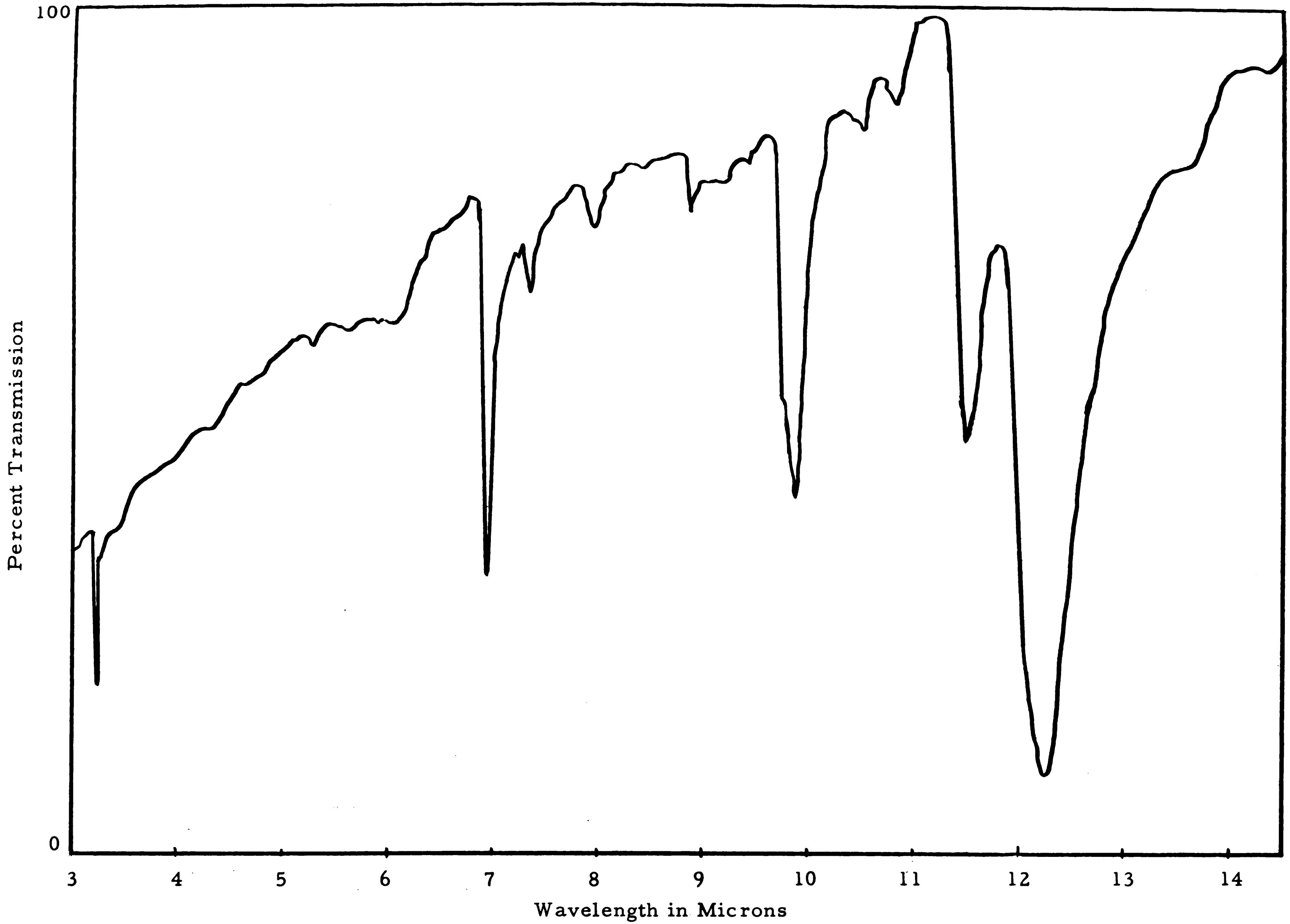


Figure IX. Infrared spectrum of bis(cyclopentadienyl)titanium dichloride.

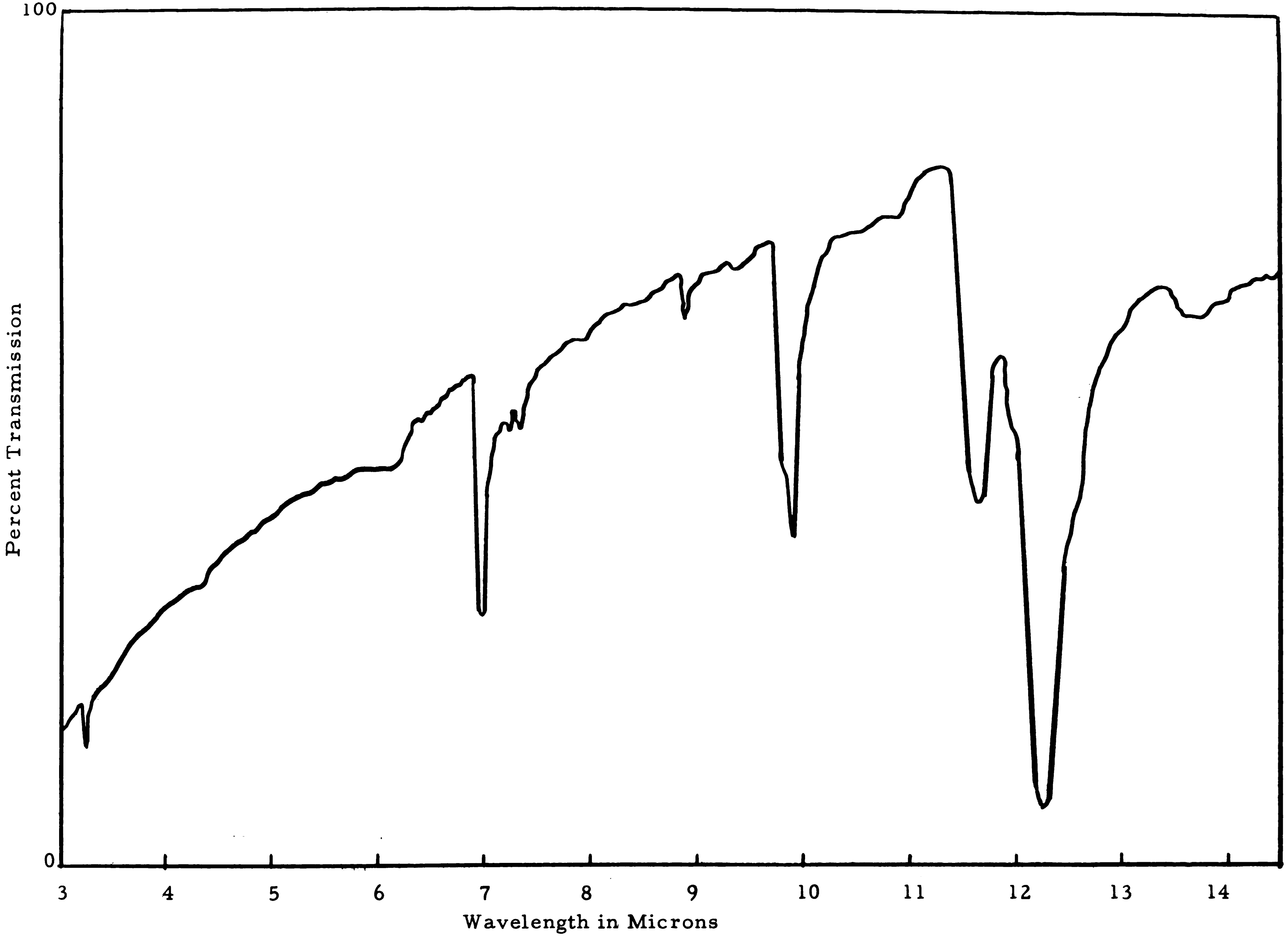


Figure X. Infrared spectrum of bis(cyclopentadienyl)titanium diiodide.

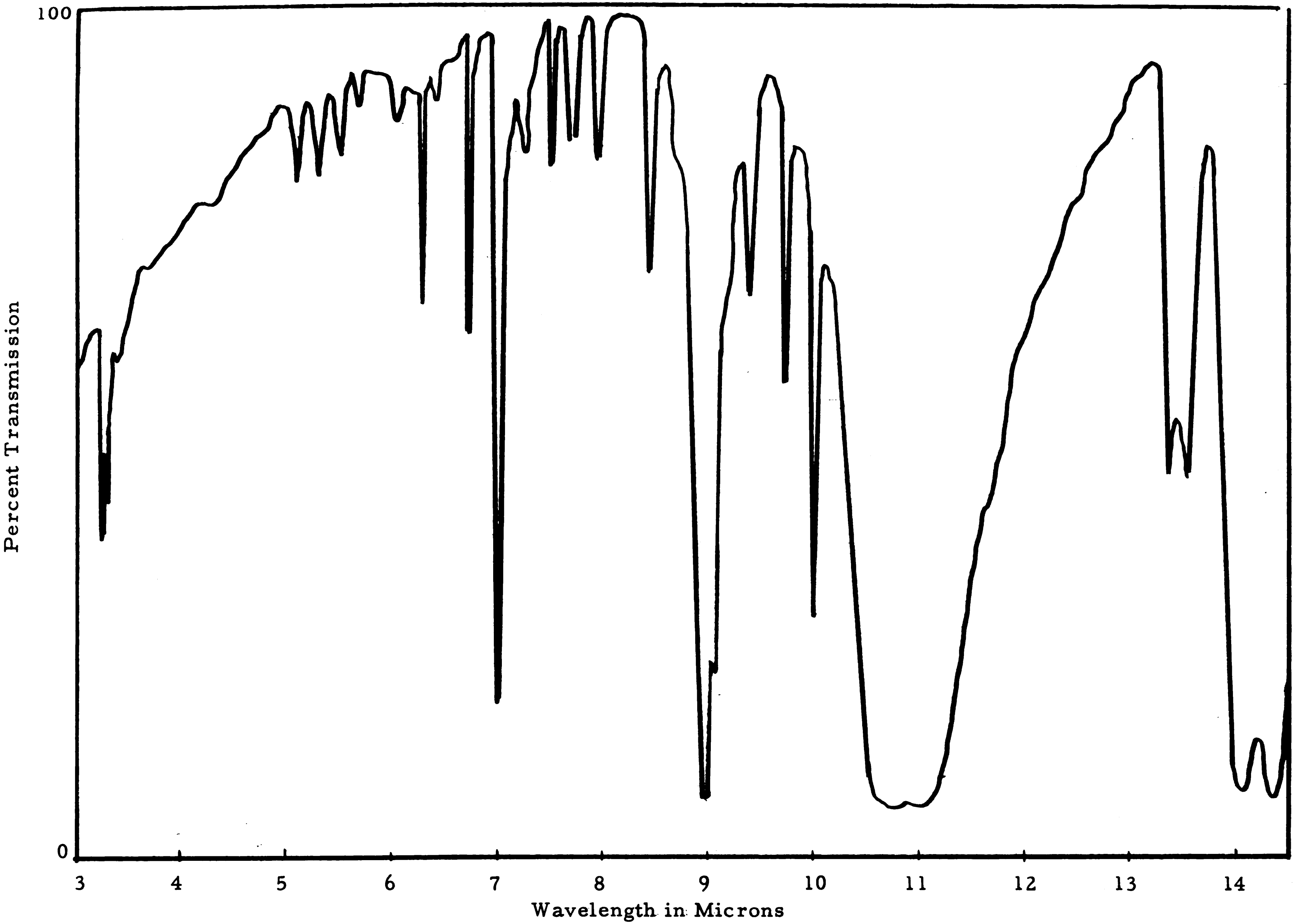


Figure XI. Infrared spectrum of tetrakis(triphenylsiloxy)titanium.

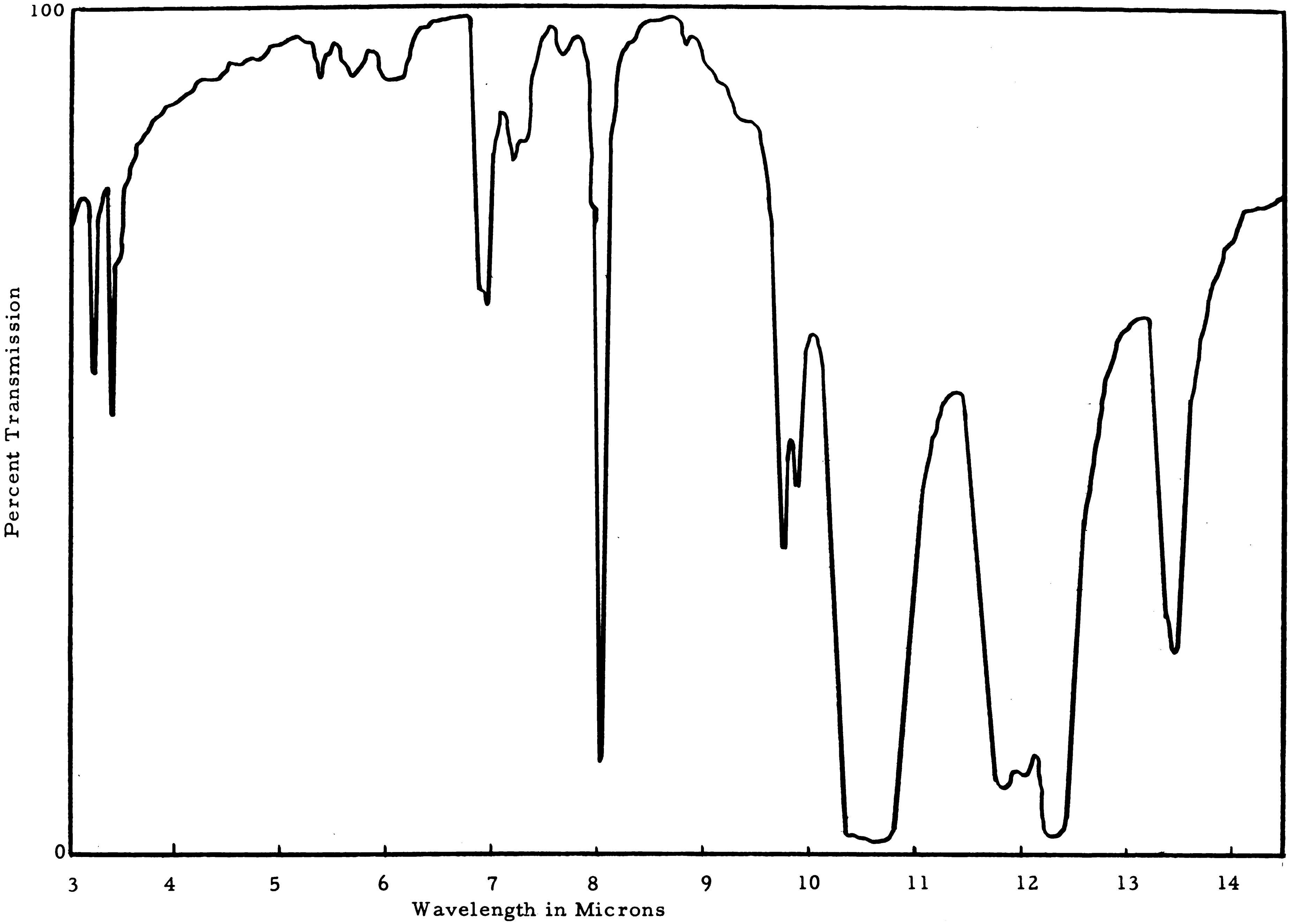


Figure XII. Infrared spectrum of trimethylsiloxybis(cyclopentadienyl)titanium chloride.

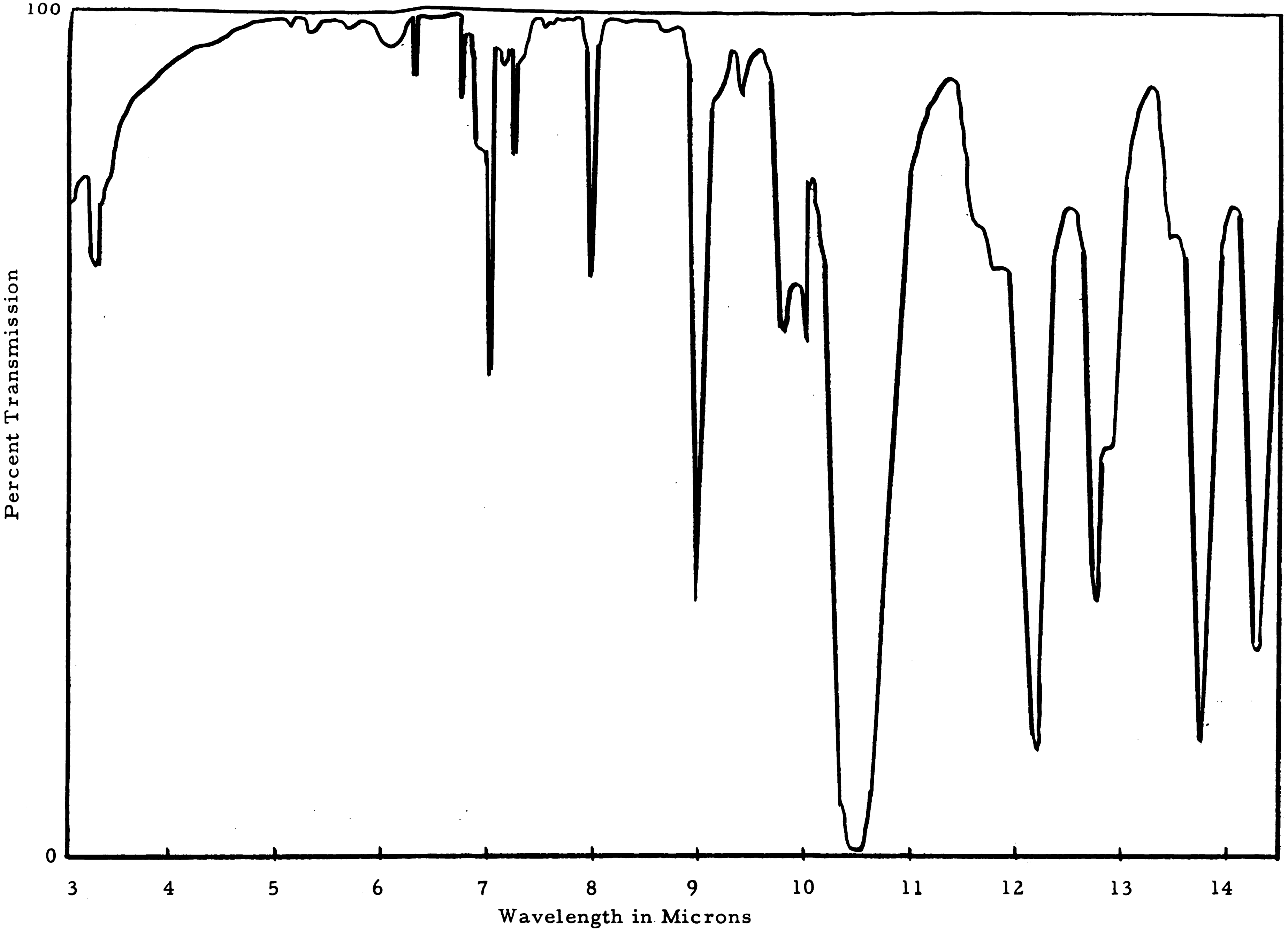


Figure XIII. Infrared spectrum of methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride.

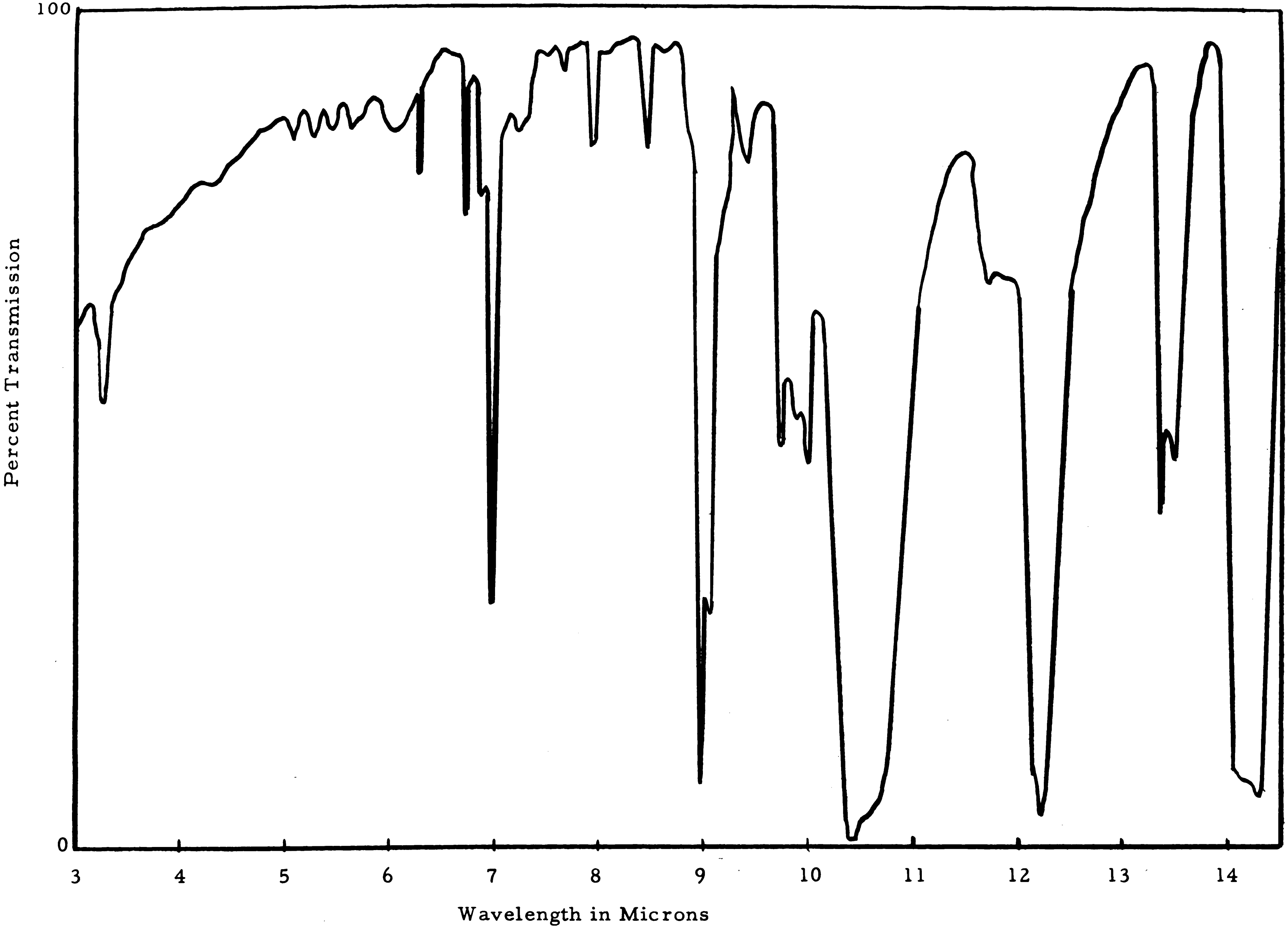


Figure XIV. Infrared spectrum of triphenylsiloxybis(cyclopentadienyl)titanium chloride.

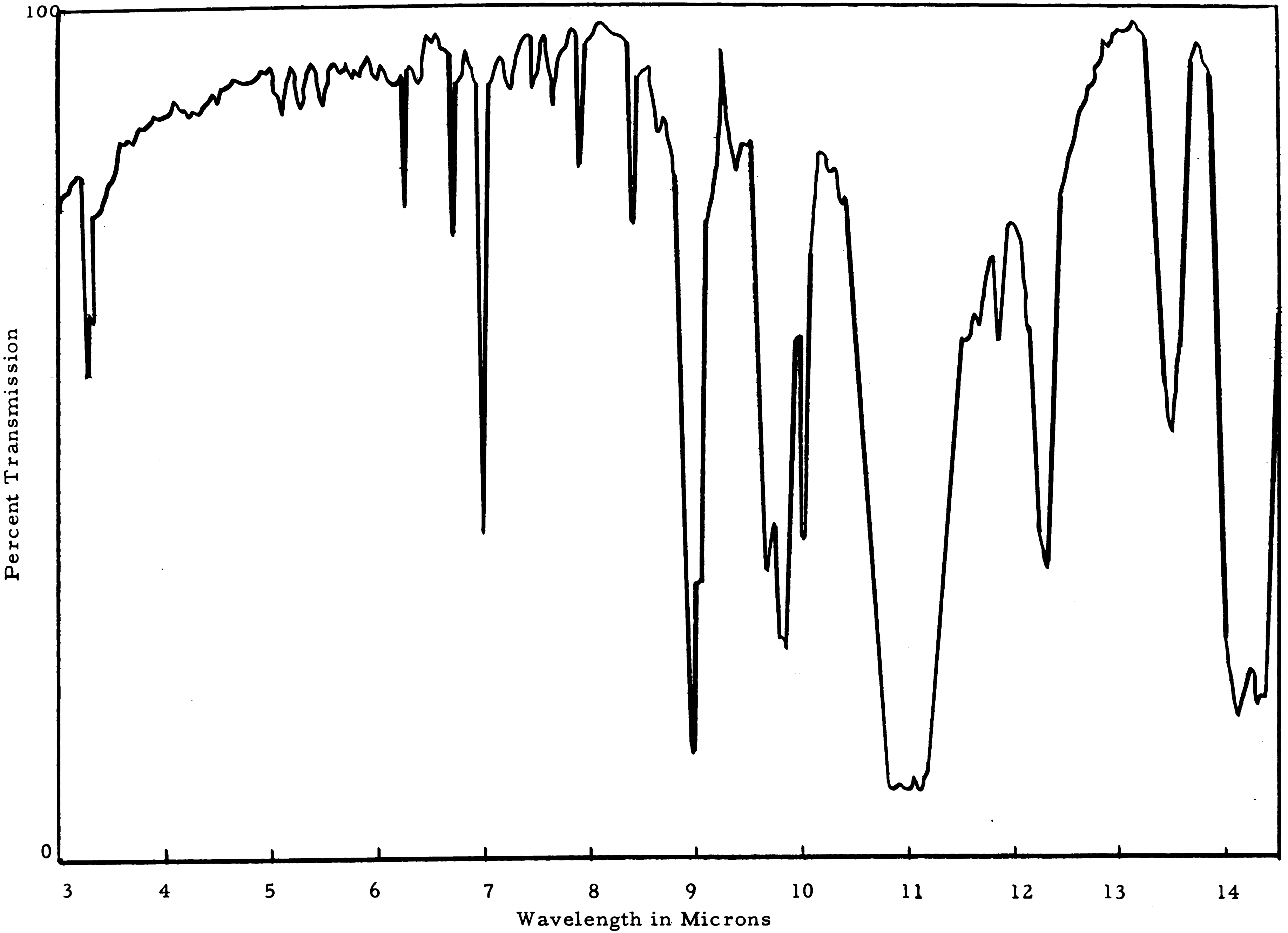


Figure XV. Infrared spectrum of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium.

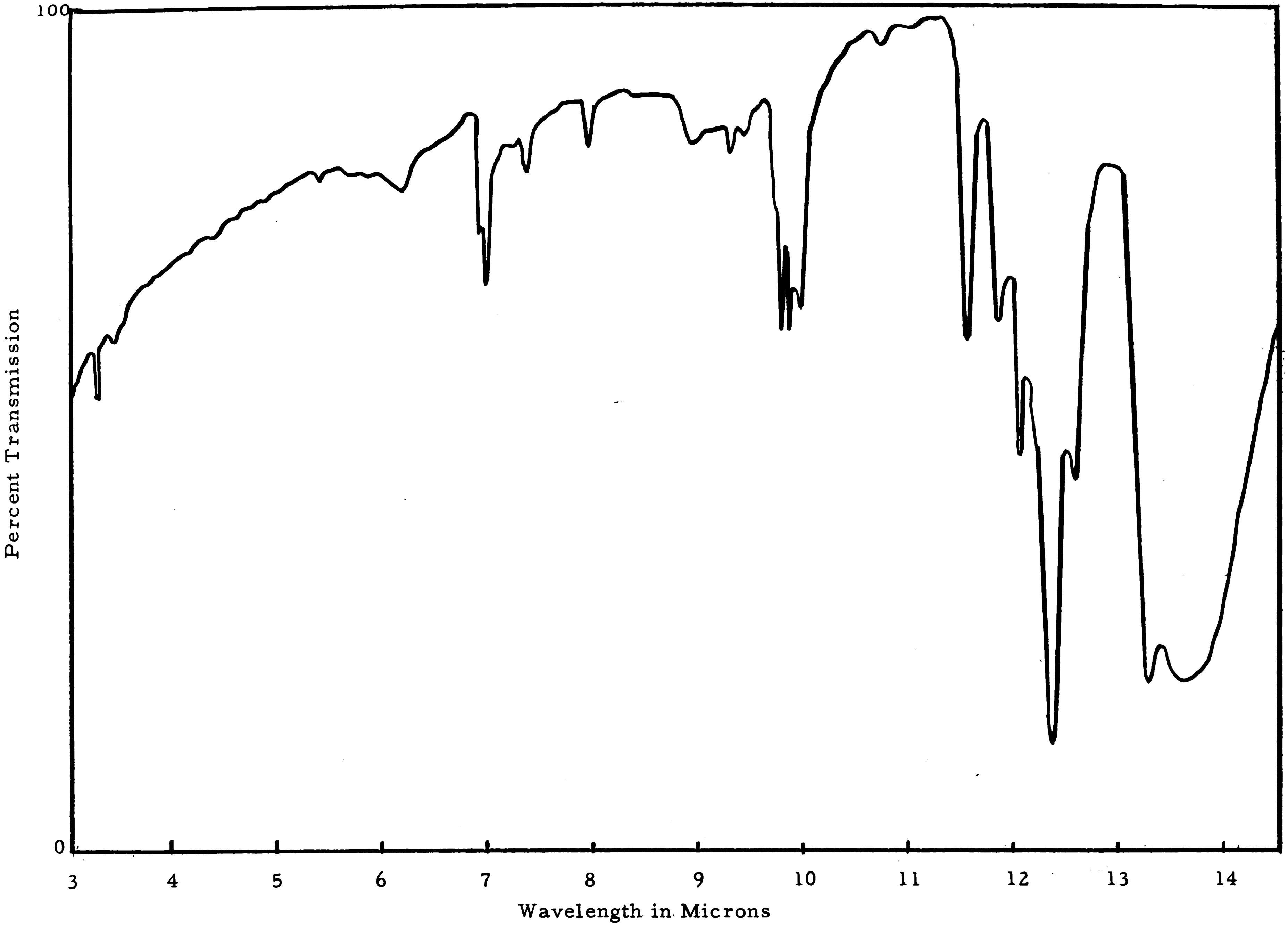


Figure XVI. Infrared spectrum of 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane.

13.11 microns to the titanium-oxygen-titanium bonds. If these assignments are correct, then the band at 12.20 microns is probably masked by the strong absorption at 12.25 microns which is characteristic of bis(cyclopentadienyl)titanium (IV) compounds. The intense broad band at 13.25-13.75 microns in the spectrum of the dititoxane would then correspond to the absorption at 13.11 microns which is observed in the condensed titanium butoxides. The absence of an intense broad band at 13.0 microns which is characteristic of monocyclopentadienyltitanium(IV) compounds (5) indicates the presence of two cyclopentadienyl rings bonded to the titanium atoms in the dititoxane.

Analytical Methods.

Carbon, hydrogen, and chlorine analyses and the titanium analysis for 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dititoxane were done by Spang Microanalytical Laboratory, Ann Arbor, Michigan. The following methods were used for the determination of silicon and titanium in the compounds prepared in this investigation and for the determination of the neutralization equivalents of the sodium silanolates.

Silicon and Titanium Analysis. A sample of the siloxy-titanium compound was weighed into a 100 ml. beaker and treated with 20 ml. of concentrated sulfuric acid and 0.1 g. of ammonium peroxydisulfate. After the decomposition had started, the mixture was slowly heated until fumes of sulfur trioxide were given off. Ammonium peroxydisulfate was added in approximately 0.1 g. portions until decomposition of the sample was complete. In this manner decomposition was accomplished in approximately one-half hour. The mixture was then diluted to 200 ml. and the silicon dioxide was filtered off. The filtrate was saved for titanium analysis. The silicon dioxide was ignited and brought to constant weight in a platinum crucible. This residue was then treated with five drops of water, 1 ml. of 18 M sulfuric acid, and 4 ml. of 49 percent hydrofluoric acid. After the volatile substances were evaporated off in an iron radiator, the crucible was brought to constant weight. Percent silicon was calculated from loss in weight.

Concentrated aqueous ammonia was added to the filtrate to precipitate the titanium. The titanium precipitate was filtered off and transferred to the platinum crucible. It was then ignited and brought to constant weight. From the weight of titanium dioxide the percentage of titanium was calculated.

Various reagents which facilitate the decomposition of siloxy-titanium compounds have been tried; however, the sulfuric acid-ammonium peroxydisulfate mixture is by far the most efficient. Reagents which have been tried include fused ammonium bisulfate, fused ammonium sulfate, fused ammonium bisulfate-sulfate mixture, sulfuric acid-ammonium bisulfate mixture, sulfuric acid-ammonium sulfate mixture, sulfuric acid-potassium iodate mixture, and fuming sulfuric acid-nitric acid mixture.

Neutralization Equivalents of Sodium Silanolates. The neutralization equivalents of the sodium silanolates were determined by dissolving weighed samples in 95 percent ethanol and titrating with standard hydrochloric acid to the end point of bromthymol blue.

Molecular Weights. Molecular weight determinations of the compounds were made by cryoscopic measurements on benzene solutions. The apparatus for this purpose consisted of a Wheatstone bridge in which a thermistor was used as the temperature sensing element. The bridge output was connected to a current-time recorder which automatically plotted the cooling curves of the solutions.

The Wheatstone bridge was constructed using a thermistor,[1] two 1000 ohm resistors, and a 100,000 ohm resistance box which was set a 5250 ohms for determination in benzene. Current for the bridge was supplied

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[1] Veco Number 33A7, Victory Engineering Corporation, Union, New Jersey.

by a 1.5 volt dry cell in series with a 10,000 ohm resistor. The current flowing through the bridge was recorded on a Sargent Model XXI Polarograph operating at a sensitivity of 0.003 or 0.004 microamperes per millimeter. Temperatures could be measured to $\pm 0.002^{\circ}C$.

The thermistor was silver soldered to platinum leads in a glass cell (Figure XVII) which contained the solution whose freezing point was to be measured. A motor operating at a constant 600 r.p.m. drove the stirrer for the cell. The cell was immersed in an ice bath up to the side arm.

The freezing point of purified benzene was established by pipetting 25 ml. into the cell and recording its freezing curve. Extrapolation of the freezing portion of the curve back to the cooling portion gave the freezing point. An average of five determinations was used as the freezing point. Next, pellets of a known weight of hexachlorobenzene were added to the benzene and five freezing curves were recorded. The cell was cleaned and dried. The above procedure was then repeated for the compound whose molecular weight was to be determined.

The freezing point depressions of the standard and unknown solutions were expressed in chart divisions, ΔD(mm.), which are directly related to ΔT. Assuming that the freezing point constant, K_f, was the same for both solutions, the molecular weight of the unknown was calculated from the following equation:

$$M_1 = M_2 \frac{\Delta T_2}{\Delta T_1} \frac{W_1}{W_2}$$

where: M_1 = molecular weight of unknown.

M_2 = molecular weight of hexachlorobenzene or any other standard.

ΔT_1 = freezing point depression of unknown solution.

ΔT_2 = freezing point depression of standard solution.

W_1 = weight of unknown.

W_2 = weight of standard.

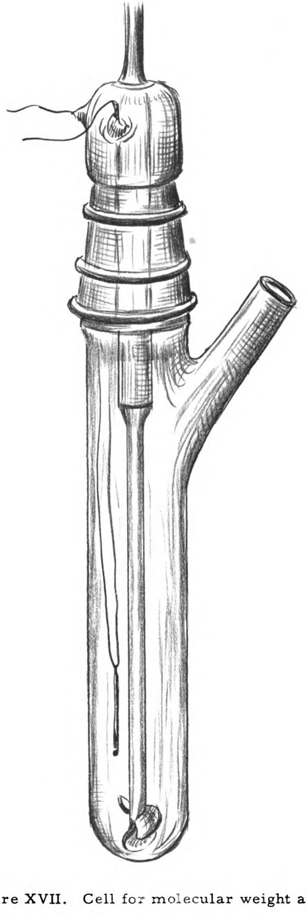


Figure XVII. Cell for molecular weight apparatus.

This instrument can easily be adapted for other solvents by simply setting the resistance box of the Wheatstone bridge to the approximate resistance of the thermistor at the freezing point of the solvent. The molecular weight of 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)-dititoxane was determined in 1, 4-dioxane (freezing point, 11.7°C.) because of its low solubility in benzene. The resistance box in the bridge was operated at 4125 ohms in this case.

For very precise determinations of molecular weights it is suggested that the freezing point depressions of a series of solutions at various concentrations, both standard and unknown, be determined. This can easily be accomplished by the successive addition of weighed solute pellets to the solvent, followed by the determination of the freezing point depression of each of these solutions. To calculate the molecular weight of the unknown, the quantity $\Delta T/C$ is plotted against C for the standard and unknown solutions. The quantity C is the concentration of the solution expressed in grams of solute per 25 ml. of solvent, and $\Delta T/C$ is the change in temperature expressed in millimeters divided by C. Extrapolation to infinite dilution gives ΔT at that concentration. The molecular weight can then be calculated from the previous equation except that the weight terms are dropped out.

X-Ray Diffraction Data.

Crystallographic d-spacings for methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, triphenylsiloxybis(cyclopentadienyl)titanium chloride, and bis(triphenylsiloxy)bis(cyclopentadienyl)titanium were calculated from x-ray diffraction data obtained with a Siemens Kristalloflex-4 diffractometer using copper K_{α_1} radiation (λ = 1.5405 A). The d-spacings for 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane were calculated from film data obtained with a North American Philips powder diffraction unit using copper K_α radiation (λ =1.5418 A). Tables VIII, IX, X, and XI list these data.

Table VIII. Interatomic Spacings for Methyldiphenylsiloxybis(cyclopentadienyl)titanium Chloride.

Line	θ (degrees)	d_{hkl} (A)	Relative Intensity
1	5.71	7.73	22
2	7.31	6.05	6
3	7.47	5.93	16
4	7.72	5.74	9
5	8.16	5.42	18
6	8.25	5.37	8
7	8.45	5.24	9
8	8.65	5.12	28
9	8.86	5.00	8
10	9.65	4.60	100
11	11.20	3.97	32
12	11.52	3.85	32
13	11.70	3.79	9
14	14.65	3.05	10
15	16.28	2.74	22
16	18.55	2.42	14
17	20.30	2.22	7
18	20.65	2.18	11
19	21.59	2.09	9
20	22.21	2.04	3
21	22.97	1.97	5
22	24.30	1.87	2
23	24.53	1.86	9
24	25.32	1.80	7
25	26.10	1.75	2
26	28.44	1.62	3
27	28.60	1.61	3
28	29.87	1.55	9
29	30.62	1.51	14
30	33.99	1.38	2
31	38.20	1.25	2

Table IX. Interatomic Spacings for Triphenylsiloxybis(cyclopentadienyl)-titanium Chloride.

Line	θ (degrees)	d_{hkl} (A)	Relative Intensity
1	5.22	8.47	100
2	6.02	7.35	8
3	6.54	6.77	10
4	7.18	6.16	5
5	7.93	5.58	5
6	8.35	5.31	5
7	8.83	5.01	5
8	9.20	4.82	18
9	9.96	4.45	32
10	10.34	4.29	8
11	11.01	4.03	8
12	11.78	3.77	5
13	14.89	3.00	13
14	15.75	2.84	2
15	16.42	2.73	2
16	16.77	2.67	2
17	17.71	2.53	15
18	17.98	2.50	2
19	19.44	2.32	5
20	24.39	1.87	15
21	29.55	1.56	2
22	31.21	1.49	13

Table X. Interatomic Spacings for Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium.

Line	θ (degrees)	d_{hkl} (A)	Relative Intensity
1	6.02	7.35	37
2	6.83	6.47	14
3	7.54	5.88	10
4	9.14	4.85	53
5	9.33	4.75	61
6	9.62	4.61	100
7	9.73	4.56	98
8	10.57	4.20	37
9	11.03	4.02	22
10	11.10	4.00	22
11	12.17	3.65	16
12	12.53	3.55	10
13	13.05	3.41	10
14	14.09	3.17	6
15	14.43	3.09	6
16	15.25	2.93	26
17	15.60	2.86	8
18	19.55	2.30	6
19	21.53	2.10	16
20	24.33	1.87	4
21	24.86	1.83	4
22	26.36	1.73	4
23	30.35	1.52	2
24	35.48	1.33	2
25	35.83	1.32	2

Table XI. Interatomic Spacings for 1, 3-Dichloro-1, 1, 3, 3-tetrakis-(cyclopentadienyl)dititoxane.

Line	θ (degrees)	d_{hkl} (A)	Relative Intensity
1	4.89	9.06	vw
2	6.78	6.53	vs
3	7.34	6.04	m
4	8.22	5.40	s
5	9.28	4.78	vw
6	9.82	4.52	s
7	10.52	4.22	vw
8	11.45	3.88	m
9	11.91	3.73	vw
10	12.51	3.56	vw
11	13.26	3.36	w
12	14.16	3.15	vw
13	17.77	2.53	w
14	18.40	2.44	m
15	18.90	2.38	w
16	20.40	2.21	vw
17	24.47	1.86	vw

Relative Intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

DISCUSSION

During the course of this investigation four siloxy derivatives of bis(cyclopentadienyl)titanium(IV) were prepared and characterized. These are the first well characterized silicon derivatives of ferrocene-type compounds which have metal-oxygen-silicon bonds. The compounds are trimethylsiloxybis(cyclopentadienyl)titanium chloride, methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, triphenylsiloxybis(cyclopentadienyl)titanium chloride, and bis(triphenylsiloxy)bis(cyclopentadienyl)-titanium. In addition 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)-dititoxane was isolated and characterized as a side-product in the reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate. The study of the reactions of bis(cyclopentadienyl)titanium dichloride with silanols and sodium silanolates yielded additional information on the properties of this organotitanium compound.

Prior to the start of this investigation in December, 1959, no reactions of bis(cyclopentadienyl)titanium dichloride and siloxy compounds were reported in the literature. In 1960 Guttmann and Meller (81, 82) reported the isolation of tetrakis(triphenylsiloxy)titanium in 76 percent yield from the reaction of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate in toluene at reflux temperature. The isolation of this product, rather than bis(triphenylsiloxy)bis(cyclopentadienyl)-titanium, was explained on the basis that the extreme stability of tetrakis(triphenylsiloxy)titanium favors its formation even though this involves the cleavage of the cyclopentadienyl rings from the titanium atom. Thus, the formation of compounds with less than four triphenylsiloxy groups bonded to titanium was believed to be unlikely. Although their reaction was carried out at a higher temperature than was used in this investigation, it has been shown that mono- and disubstituted triphenylsiloxy compounds of bis(cyclopentadienyl)titanium(IV) can be prepared along with tetrakis-(triphenylsiloxy)titanium.

van der Kerk and Noltes (83, 84) reported the synthesis of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium by the reaction of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate in toluene at 90°C. The product was described as orange-yellow crystals which melt at 203-205°C. Identification of this compound was based solely on the percentage of combined titanium and silicon oxides after ignition of a sample. Our investigation has now shown that the orange-yellow crystals which are isolated in this reaction are actually triphenylsiloxybis(cyclopentadienyl)-titanium chloride and not bis(triphenylsiloxy)bis(cyclopentadienyl)titanium. Since the percentage of combined metal oxides in triphenylsiloxybis(cyclopentadienyl)titanium chloride 28.75 and that in bis(triphenylsiloxy)bis(cyclopentadienyl)titanium is 27.32, conclusive identification cannot be based on this information.

The monosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) were prepared by the treatment of bis(cyclopentadienyl)titanium dichloride with the appropriate sodium silanolate in toluene or benzene solutions at 75-90°C. or at room temperature. The triphenylsiloxy derivative was also prepared by the reaction of bis(cyclopentadienyl)titanium dichloride and triphenylsilanol in the presence of triethylamine. Bis(triphenylsiloxy)-bis(cyclopentadienyl)titanium was also prepared by the reaction of bis-(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate, as well as by the reaction of bis(cyclopentadienyl)titanium diiodide and triphenylsilanol in the presence of triethylamine. The titanium starting material is moderately soluble in toluene in the 75-90°C. temperature range. Approximately 3 g. of bis(cyclopentadienyl)titanium dichloride can be dissolved in 300 ml. of toluene at 90°C.; it is less soluble in benzene.

Organic solvents of high dipole moments such as acetonitrile and nitromethane dissolve larger amounts of the titanium compound, but these solvents are more difficult to dry and seemed to increase the decomposition of the titanium compound in the presence of sodium silanolates. Chlorinated solvents such as chloroform and carbon tetrachloride will dissolve moderate amounts of bis(cyclopentadienyl)titanium dichloride, but these solvents are reported to react with sodium silanolates in the following manner:

$$3NaOSi(C_6H_5)_3 + CHCl_3 \longrightarrow HC(OSi(C_6H_5)_3)_3 + 3\ NaCl \qquad (48)$$

$$4NaOSi(CH_2C_6H_5)_3 + CCl_4 \longrightarrow C\ (OSi(CH_2C_6H_5)_3)_4 + 4NaCl \qquad (49).$$

The sodium silanolates have variable solubilities in toluene and benzene. The same silanolate prepared by two different methods often shows different solubilities in toluene. Even the same silanolate prepared by the same method at different times does not have the same solubilities. Sodium triphenylsilanolate prepared from sodium metal and triphenylsilanol in refluxing toluene, in which it is completely soluble, usually could not be redissolved in toluene after it had been isolated and dried. Sodium triphenylsilanolate prepared by the alkaline cleavage of hexaphenyldisiloxane was more soluble than that prepared from sodium metal and the silanol. Sodium trimethylsilanolate was the least soluble of the silanolates. Consequently, when solid sodium silanolates were added to toluene solutions of bis(cyclopentadienyl)titanium dichloride, a heterogeneous mixture resulted.

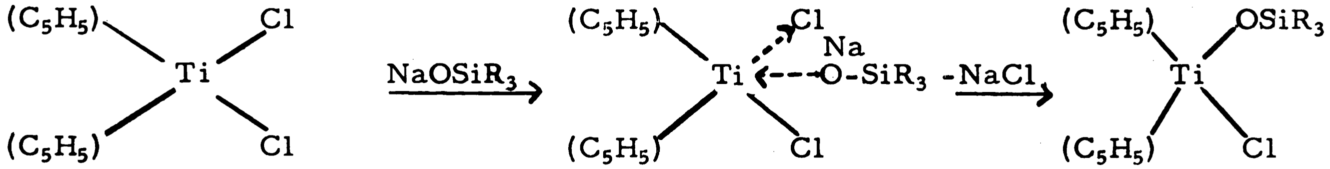
Reactions which were carried out at 75-90°C. were essentially complete after the final addition of the silanolate, as evidenced by a color change of the reaction mixture from deep red to orange. Reactions at room temperatures were observed to be complete within thirty minutes. The reaction of bis(cyclopentadienyl)titanium diiodide and triphenylsilanol in toluene and triethylamine at 90°C for two days yielded moderate amounts of the titanium starting material. This may indicate the unreactivity of the titanium compound under these conditions or the unavailability of the silanol for reaction due to its self-condensation; hexaphenyldisiloxane is isolated as one of the reaction products.

The formation of these siloxy compounds can be visualized as occurring either by a dissociation process or a bimolecular displacement reaction. A dissociation reaction which would involve one of the following processes is very unlikely to occur in a solvent such as toluene.

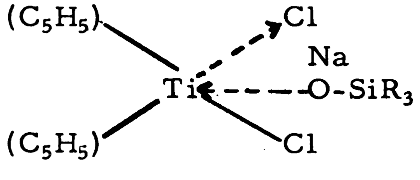
$$(C_5H_5)_2TiCl_2 \rightleftarrows (C_5H_5)_2TiCl^+ + Cl^-$$

$$NaOSiR_3 \rightleftarrows Na^+ + R_3SiO^-$$

A bimolecular displacement process seems more likely. This type of reaction might take place in the following steps:

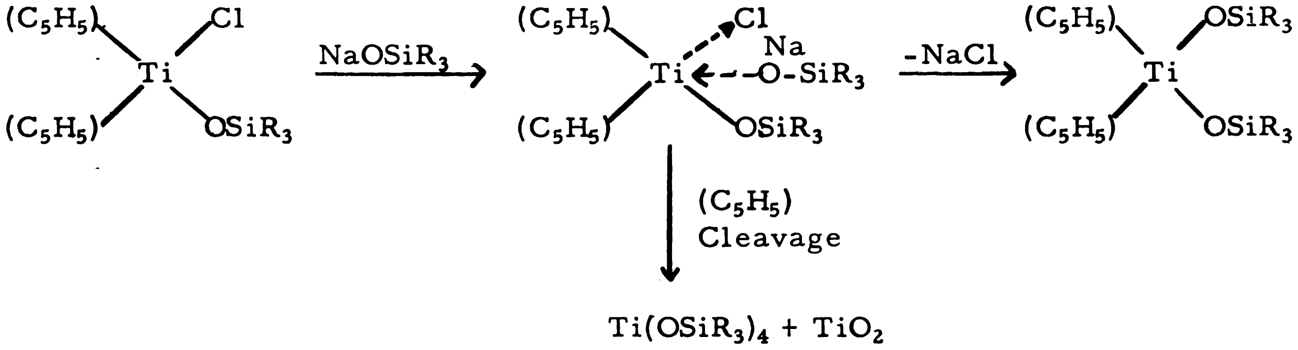


Bis(cyclopentadienyl)titanium dichloride has an essentially tetrahedral arrangement of cyclopentadienyl rings and chlorine atoms about the titanium atom. The primary bonding involves a set of tetrahedral orbitals of the titanium atom derived by a mixing of the $3d^34s$ and $4s4p^3$ hybrids (9). π-Bonding to the cyclopentadienyl rings then occurs through the d_{z^2} and $d_{x^2-y^2}$ orbitals of titanium. Since there is a mixing of the $3d^34s$ and $4s4p^3$ hybrids, 3d and 4p orbitals are still available to accept an electron pair from the oxygen of the silanolate and form the activated complex,



The coordination of the oxygen electron-pair to the titanium would favor the use of the titanium 3d orbitals since they are at a lower energy level than the 4p orbitals. Because of the steric hindrance of the cyclopentadienyl groups, attack by the silanolate should occur on the chlorine side of the molecule and simultaneous weakening of a titanium-chlorine bond may be expected to lead to formation of the siloxy-titanium compound and sodium chloride. The increase in electron density about the titanium atom in the activated complex is expected to weaken the bonding between titanium and the cyclopentadienyl rings and to make them more susceptible to cleavage.

Since sodium silanolates were added as solids and were not readily dissolved in the toluene solutions of bis(cyclopentadienyl)titanium dichloride, high concentrations of the silanolate, in relation to the titanium compound, existed at the surface of the solid in the reaction mixture. Therefore, the initial step in the formation of the monosubstituted compound is probably quickly followed by an attack by the silanolate on the second chlorine according to the following scheme; the reaction is driven by the formation of the less soluble sodium chloride.

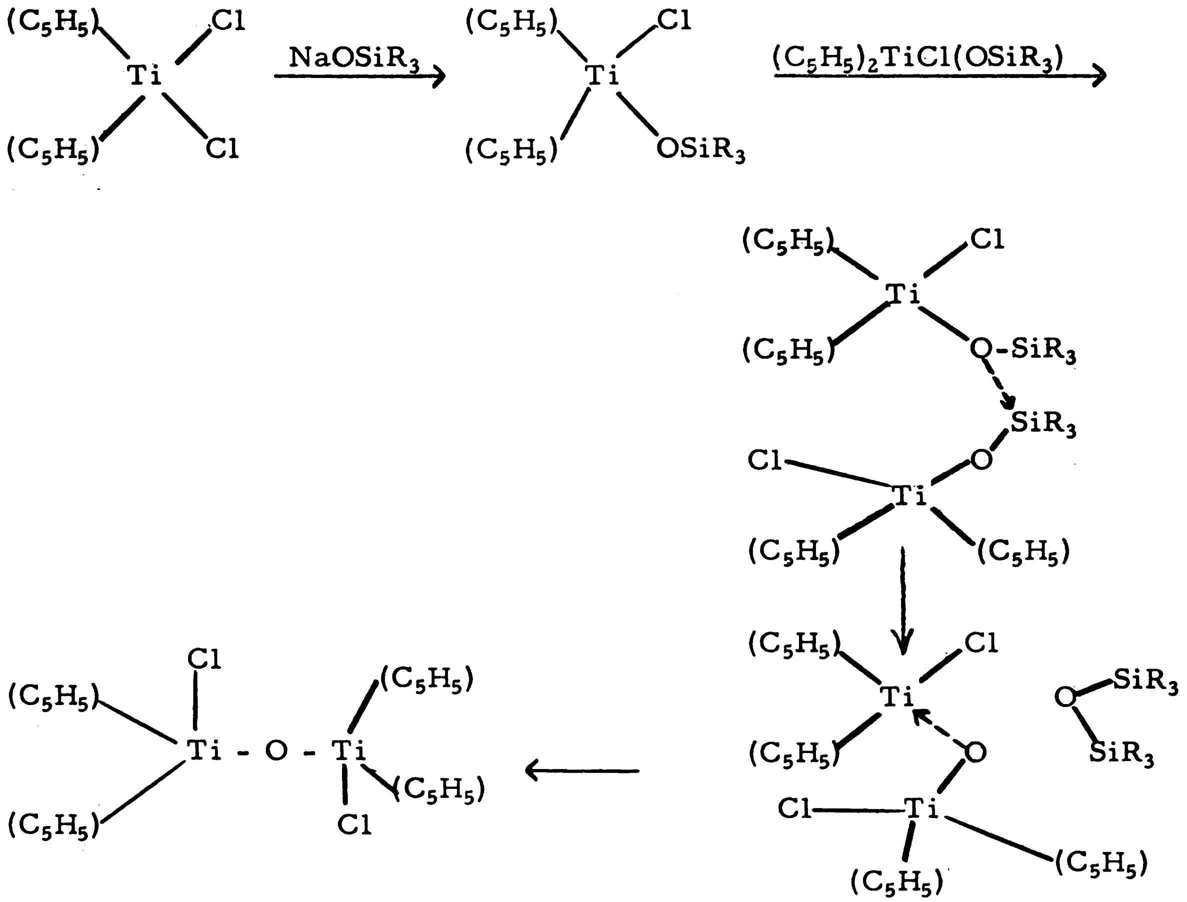


Formation of the activated complex in this case is a critical step in the reaction since either the disubstituted product is formed or ring cleavage occurs with formation of the tetrasubstituted compound or titanium dioxide. The pentacoordination of titanium in the complex weakens the bonds between titanium and the cyclopentadienyl rings because the increased electron density about the metal should decrease the π-bonding. Coupled to this may be a steric factor. The presence of two bulky triorganosiloxy groups as well as a chlorine atom around the bis(cyclopentadienyl)titanium(IV) moity may put an additional strain on the titanium-carbon bonds because of a crowding of these large groups about the metal atom. The formation of titanium dioxide is not completely understood; it may be the result of moisture in the reaction or an effect of the self-condensation of silanolates which would furnish the oxygen necessary for titanium dioxide formation.

On this basis it is easy to visualize why such low yields of the monosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) have been obtained. Consideration of the fact that the only disubstituted compound isolated was bis(triphenylsiloxy)bis(cyclopentadienyl)titanium and that only very small amounts of trimethylsiloxybis(cyclopentadienyl)titanium chloride were isolated leads one to the belief that the basicity or electron-pair donating properties of the siloxy group is a very important factor determining the stability of these compounds. If this is so, the greater basicity of the trimethylsiloxy group in comparison to the triphenylsiloxy group should further weaken the titanium-carbon bonds in the activated complex and increase the tendency for ring cleavage to occur. This is observed to be the case. Differences in the steric effects between the cyclopentadienyl rings and trimethylsiloxy or triphenylsiloxy groups apparently is not significant; basicity of the siloxy group appears to be the deciding factor which determines the stability of the activated complex and controls the subsequent formation of the siloxybis(cyclopentadienyl)titanium(IV) compound.

Moisture in the reaction mixture also enhances the cleavage of titanium-carbon bonds. The reactions of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate which were carried out in open air produced only titanium dioxide and tetrakis(triphenylsiloxy)titanium. The reactions involving sodium trimethylsilanolate yielded large amounts of titanium dioxide, but the presence of tetrakis (trimethylsiloxy)titanium in the reaction products was not confirmed. Sodium silanolates are hydroscopic solids which easily hydrolyze to the silanol and sodium hydroxide, and their handling in the open must be kept to a minimum. Reactions of bis(cyclopentadienyl)titanium dichloride with sodium silanolates in the presence of moisture probably result in a base-induced hydrolysis of the titanium compound which yields titanium dioxide as the main product.

The isolation of 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)-dititoxane in the reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate is not at first easily understood. However, when the greater stabilities of hexamethyldisiloxane and tetramethyldiphenyldisiloxane, in comparison to the respective silanols, are considered, a plausible mechanism can be proposed for the formation of the dititoxane. This is illustrated by the following scheme:



The first step of such a reaction scheme would be the formation of the monosubstituted siloxy compound of bis(cyclopentadienyl)titanium(IV). The inductive release of electrons by the trimethylsilyl or dimethylphenylsilyl group would make the electrons of the oxygen atom more available for coordination. Such an inductive release of electrons would also oppose the d_{π}-p_{π} bonding between the silicon and oxygen atoms in which an oxygen electron pair interacts with the empty d orbitals of silicon. Therefore, the d orbitals of silicon are more available to accept an electron pair. Two molecules of the monosubstituted compound can react by coordination of the oxygen atom of one siloxy compound to the silicon atom of the other compound. This might then be followed by the formation of the stable disiloxane and the formation of the titanium-oxygen-titanium bond of the dititoxane.

A less likely mechanism for the formation of the dititoxane would be the condensation of two molecules of the silanolate to form the disiloxane and sodium oxide. This might be followed by the reaction of the sodium oxide with two molecules of the titanium starting material to form the dititoxane and sodium chloride. The first step of this mechanism does not seem likely in a solvent such as toluene.

In summary, the reactions of bis(cyclopentadienyl)titanium dichloride and sodium silanolates were carried out in toluene or benzene at 75-90°C. At this temperature the reactions appeared to be instantaneous. A few reactions which were carried out at room temperature appeared to be complete within thirty minutes. Approximately the same yields of products were isolated from these reactions at room temperature as from those at higher temperatures.

Reactions of bis(cyclopentadienyl)titanium dichloride with sodium triphenylsilanolate yielded triphenylsiloxybis(cyclopentadienyl)titanium chloride in moderate amounts and bis(triphenylsiloxy)bis(cyclopentadienyl)-titanium in very small amounts. The major products of the reaction were tetrakis(triphenylsiloxy)titanium and titanium dioxide. Hexaphenyldisiloxane was also identified as a reaction product. The reaction of bis(cyclopentadienyl)titanium dichloride and sodium methyldiphenylsilanolate produced moderate yields of methyldiphenylbis(cyclopentadienyl)titanium chloride as well as large amounts of titanium dioxide. No attempt was made to establish the presence of the disubstituted methyldiphenylsiloxy compound of bis(cyclopentadienyl)titanium(IV) or the tetrasubstituted methyldiphenylsiloxy compound of titanium(IV) in the reaction products.

When bis(cyclopentadienyl)titanium dichloride and the gum-like product obtained in the preparation of sodium dimethylphenylsilanolate were mixed 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane was isolated in low yields. Large amounts of titanium dioxide were also produced. Although dimethylphenylbis(cyclopentadienyl)titanium chloride may have existed in the reaction medium, it could not be isolated by recrystallization techniques or by vacuum sublimation. The failure to isolate this compound may be due to some unique properties of this compound itself, or it may be due to the nature of the sodium silanolate that was used as a starting material.

The reactions of bis(cyclopentadienyl)titanium dichloride and sodium trimethylsilanolate produced only milligram quantities of trimethylsiloxybis(cyclopentadienyl)titanium chloride which was isolated by vacuum sublimation. This product could not be isolated by recrystallization from solution. Titanium dioxide and 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane were also identified as products.

Unreacted titanium starting material could usually be recovered from the reactions of bis(cyclopentadienyl)titanium dichloride and sodium silanolates. This is further proof that the silanolates and the titanium compound do not react in a one to one ratio and that more than one silanolate molecule attacks a bis(cyclopentadienyl)titanium dichloride molecule during the course of the reaction. This occurred even though small amounts of the silanolates were progressively added to the solutions of the titanium starting material.

The siloxy derivatives of bis(cyclopentadienyl)titanium(IV) were in general difficult to purify. The solubilities of these compounds in organic solvents are similar to those of bis(cyclopentadienyl)titanium dichloride and organosilicon compounds. Thus, in many cases repeated recrystallizations were necessary for purification.

The failure to isolate a tri-α-naphthylsiloxy derivative is not unexpected since tri-α-naphthylsilanol and sodium tri-α-naphthylsilanolate are known to be inert to condensation reactions with trimethylchlorosilane, triphenylchlorosilane, and tri-p-tolylchlorosilane (98). Such coupling reactions apparently are subject to steric hindrance. The failure to isolate tri-α-naphthylsiloxybis(cyclopentadienyl)titanium chloride is explained on this basis.

The reactions of bis(cyclopentadienyl)titanium dichloride and bis(cyclopentadienyl)titanium diiodide with triphenylsilanol show that the reactivities of the two halogen atoms of these titanium compounds are not the same. Others have made similar observations (99). Further evidence is given by the report of Wilkinson and Birmingham (3) that bis(cyclopentadienyl)titanium hydroxybromide monohydrate and not bis(cyclopentadienyl)titanium dihydroxide is the product when bis(cyclopentadienyl)titanium dibromide is dissolved in water.

Only triphenylsiloxybis(cyclopentadienyl)titanium chloride was isolated when bis(cyclopentadienyl)titanium dichloride and triphenylsilanol in a 1:2 ratio were stirred together in a toluene solution of triethylamine for 70 hours at 80-90°C. No disubstituted triphenylsiloxy compound was produced. Although considerable decomposition of the titanium starting material took place, as evidenced by the dark brown color of the reaction mixture, no titanium dioxide was isolated; however, tetrakis(triphenylsiloxy)titanium was present in the reaction products. The reaction of bis(cyclopentadienyl)titanium diiodide and triphenylsilanol under the same conditions for two days gave only low yields of bis(triphenylsiloxy)bis(cyclopentadienyl)titanium. The results of these reactions are an indication of the different reactivities of the two chlorine atoms or iodine atoms of the titanium starting materials. The fact that bis(triphenylsiloxy)bis(cyclopentadienyl)titanium is produced in the reaction of the iodide and not in the reaction of the chloride is also an indication of the greater stability of bis(cyclopentadienyl)titanium dichloride in comparison to the compounds which have halogen atoms of higher atomic numbers, as was shown by the kinetic studies of Jensen and Basolo (28). Reactions involving triphenylsilanol are complicated by the apparent triethylamine-catalyzed self-condensation of the silanol to the disiloxane.

The overall stabilities of the siloxy derivatives of bis(cyclopentadienyl)titanium(IV) are lower than the tetrasubstituted siloxy compounds of titanium(IV). This is expecially noted in the comparison of triphenylsiloxybis(cyclopentadienyl)titanium chloride and bis(triphenylsiloxy)bis-(cyclopentadienyl)titanium with tetrakis(triphenylsiloxy)titanium. These bis(cyclopentadienyl)titanium(IV) compounds have titanium-carbon bonds which are more susceptible to hydrolytic cleavage than the titanium-oxygen-silicon bonds of tetrasubstituted siloxy compounds of titanium. Thermal stabilities are also lower.

The infrared, ultraviolet, and visible spectra of the compounds prepared in this investigation were discussed in the experimental section dealing with these subjects.

CONCLUSIONS

Bis(cyclopentadienyl)titanium dichloride readily reacts with sodium silanolates at 70-90°C. in solvents such as benzene and toluene to produce monosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) which have titanium-oxygen-silicon bonds. These reactions are accompanied by extensive decomposition of the titanium starting material. The yields and stabilities of these silicon-titanium compounds are directly related to the basicities or electron-donating properties of the siloxy groups bonded to the titanium atom. The greater the basicity of a siloxy group the more unstable is the product and the smaller is the yield from the reaction.

Reactions of bis(cyclopentadienyl)titanium dichloride and bis(cyclopentadienyl)titanium diiodide with triphenylsilanol have shown that the two chlorine atoms or the two iodine atoms of these compounds do not have the same reactivities. After removal of the first halogen by reaction from the titanium compound, the second halogen is much more difficult to replace. Also the iodine atoms of bis(cyclopentadienyl)titanium diiodide undergo reactions with less difficulty than the chlorine atoms of bis(cyclopentadienyl)titanium dichloride.

Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, the only disubstituted siloxy derivative of bis(cyclopentadienyl)titanium(IV) isolated, can only be synthesized in very low yields by the methods employed in this research project. An investigation of a few of the properties of this compound indicates that it is less stable hydrolytically and thermally than tetrakis (triphenylsiloxy)titanium.

It was originally believed that disiloxy derivatives of bis(cyclopentadienyl)titanium(IV) could easily be prepared by metathesis reactions of sodium silanolates and bis(cyclopentadienyl)titanium dichloride, but it was found that these reactions are complicated processes in which cyclopentadienyl rings are cleaved from the titanium atom to a great extent. Therefore, only low yields of the desired products are obtained. It is highly doubtful that high molecular weight polymers can be prepared by the reactions of bis(cyclopentadienyl)titanium dihalides with diorganosilanediols or disodium diorganosilanediolates.

A compound identified as 1, 3-dichloro-1, 1, 3, 3-tetrakis(cyclopentadienyl)dititoxane was isolated from the reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate. This compound may be formed by an intermolecular rearrangement of two triorganosiloxybis(cyclopentadienyl) titanium chloride molecules.

Product identification was facilitated by the use of infrared spectroscopy. The absorptions of the titanium-oxygen-silicon bonds and of the bis(cyclopentadienyl)titanium(IV) group were particularly useful in determining their presence in reaction products.

RECOMMENDATIONS FOR FUTURE WORK

1. Better yields of disubstituted siloxy derivatives of bis(cyclopentadienyl)titanium(IV) might be obtained from reactions of bis(cyclopentadienyl)titanium dihalides with siloxy compounds having lesser electron-donating properties than those used in this investigation. Siloxy compounds which have highly electronegative groups bonded to the silicon atom are recommended. Fluorine, perfluoroalkyl groups, and phenyl rings substituted with electron-withdrawing groups would be useful in this respect.

2. The slow addition of dilute solutions of the silanolates to the reaction mixtures rather than the addition of solid silanolates might keep the decomposition of the titanium starting material to a minimum. Also, a more thorough investigation of the temperature-dependency of these reactions should be made.

3. Qualitative observations in this investigations indicates that bis(cyclopentadienyl)titanium diiodide is more reactive than bis(cyclopentadienyl)titanium dichloride and should be used as the titanium starting material.

4. Confirmation of 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)-dititoxane may be obtained by a more direct synthesis of this compound. The reaction of bis(cyclopentadienyl)titanium dichloride with silver oxide or an alkali metal oxide may yield this dititoxane. Another possible synthetic route to this compound would be the reaction of cyclopentadienyllithium and 1,1,3,3-tetrachloro-1,3-bis(cyclopentadienyl)dititoxane which is obtained from the partial hydrolysis of cyclopentadienyltitanium trichloride.

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