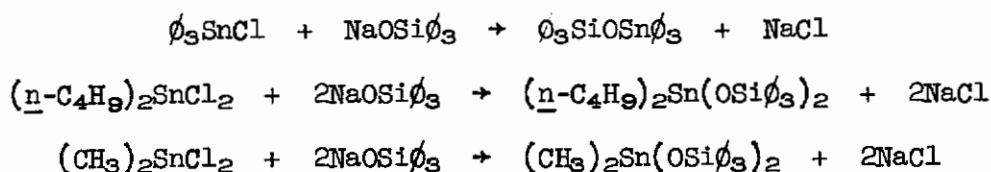


METAL-SILOXY CONDENSATION REACTIONS

Robert N. Hammer and Jack B. Kinsinger
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Abstract

In search for a prototype inorganic condensation reaction that could be used later for study of inorganic polycondensation reactions, it was found that the reaction of $\text{NaOSi}\phi_3$ with $\phi_3\text{SnCl}$, $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$, and $(\text{CH}_3)_2\text{SnCl}_2$ in an aprotic solvent is consistent with the overall equations:



with no evidence that significant side reactions occur. These reactions appear to go to completion as shown by quantitative determination of NaCl and the stannosiloxane product. The sodium chloride by-product forms immediately, indicating that these reactions at room temperature in benzene are extremely rapid. Quantitative rate measurements could not be made but the stoichiometry of the reaction was established. In the course of the study, several new stannosiloxanes were prepared and characterized by infrared spectroscopy and elemental analysis.

The preparation, characterization, and some properties are reported for siloxy derivatives of bis(cyclopentadienyl)titanium(IV). Monosiloxy derivatives were prepared by the reaction of the appropriate 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, methyl-diphenylsiloxybis(cyclopentadienyl)titanium chloride, and triphenylsiloxybis(cyclopentadienyl)titanium chloride. These Ti-O-Si compounds are orange crystalline substances; the triphenylsiloxy derivative melts at 201-204°C. Replacement of C_6H_5 by CH_3 groups markedly lowers the melting points and thermal stabilities.

Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was prepared in toluene at 75-90°C from bis(cyclopentadienyl)titanium dihalide and sodium triphenylsilanolate or triphenylsilanol. $(\text{C}_6\text{H}_5)_2\text{Ti}[\text{OSi}(\text{C}_6\text{H}_5)_3]_2$ is a white crystalline substance melting at 202-204°C.

An orange crystalline substance identified as 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dioxane was isolated from reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate or sodium dimethylphenylsilanolate.

The stabilities of the siloxy derivatives of bis(cyclopentadienyl)titanium(IV) and the yields of these compounds 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. Reaction paths are

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14. ABSTRACT

In search for a prototype inorganic condensation reaction that could be used later for study of inorganic polycondensation reactions, it was found that the reaction of $\text{NaOSi}(\text{C}_4\text{H}_9)_2$, $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$, and $(\text{CH}_3)_2\text{SnCl}_2$ in an aprotic solvent is consistent with the overall equations: $\text{SnCl}_4 + \text{NaOSi}(\text{C}_4\text{H}_9)_2 + \text{SiOSn}(\text{C}_4\text{H}_9)_2 + \text{NaCl} \rightarrow (\text{C}_4\text{H}_9)_2\text{SnCl}_2 + (\text{CH}_3)_2\text{SnCl}_2 + 2\text{NaOSi}(\text{C}_4\text{H}_9)_2 + (\text{C}_4\text{H}_9)_2\text{Sn}(\text{OSi}(\text{C}_4\text{H}_9)_2)_2 + 2\text{NaCl}$ $2\text{NaOSi}(\text{C}_4\text{H}_9)_2 + (\text{CH}_3)_2\text{Sn}(\text{OSi}(\text{C}_4\text{H}_9)_2)_2 + 2\text{NaCl}$ with no evidence that significant side reactions occur. These reactions appear to go to completion as shown by quantitative determination of NaCl and the stannosiloxane product. The sodium chloride by-product forms immediately, indicating that these reactions at room temperature in benzene are extremely rapid. Quantitative rate measurements could not be made but the stoichiometry of the reaction was established. In the course of the study several new stannosiloxanes were prepared and characterized by infrared spectroscopy and elemental analysis. The preparation, characterization, and some properties are reported for siloxane derivatives of bis(cyclopentadienyl)titanium(IV). Monosiloxane derivatives were prepared by the reaction of the appropriate sodium silanolate with bis(cyclopentadienyl)titanium dichloride in toluene at 75-90°C under anhydrous conditions. The compounds prepared and characterized were trimethylsilylbis(cyclopentadienyl)titanium chloride, methylphenylsilylbis(cyclopentadienyl)titanium chloride, and triphenylsilylbis(cyclopentadienyl)titanium chloride. These Ti-O-Si compounds are orange crystalline substances; the triphenylsilyloxy derivative melts at 201-204°C. Replacement of C₅H₅ groups by CH₃ groups markedly lowers the melting points and thermal stabilities. Bis(triphenylsilyloxy)bis(cyclopentadienyl)titanium was prepared in toluene at 15-90°C from bis(cyclopentadienyl)titanium dihalide and sodium triphenylsilanolate or triphenylsilanol. $(\text{C}_6\text{H}_5)_2\text{Ti}[\text{OSi}(\text{C}_6\text{H}_5)_2]_2$ is a white crystalline substance melting at 202-204°C. An orange crystalline substance identified as 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dioxane was isolated from reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate or sodium dimethylphenylsilanolate. The stabilities of the siloxy derivatives of bis(cyclopentadienyl)titanium(IV) and the yields of these compounds 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. Reaction paths are postulated for the formation of these compounds. The preparation and properties are reported for a series of compounds containing the Si-O-Cr linkage. A series of bis(triorganosilyl)chromates was obtained by the reaction $\text{CrO}_3 + 2\text{R}_3\text{SiOH} + (\text{AsSi})_2\text{CrO}_4 + \text{H}_2\text{O}$ in methylene chloride.

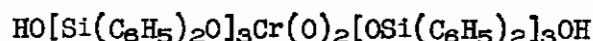
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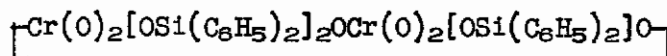
postulated for the formation of these compounds.

The preparation and some properties are reported for a series of compounds containing the Si-O-Cr^{VI} linkage. A series of bis(triorganosilyl) chromates was obtained by the reaction $\text{CrO}_3 + 2\text{R}_3\text{SiOH} \rightarrow (\text{R}_3\text{Si})_2\text{CrO}_4 + \text{H}_2\text{O}$ in methylene chloride. The silyl chromates prepared and characterized were bis(*p*-tolyl-diphenylsilyl) chromate, bis(tricyclohexylsilyl) chromate, bis(cyclohexyldiphenylsilyl) chromate, and bis(triphenylsilyl) chromate. These compounds are light-sensitive and decompose when heated above their melting points. The most stable is bis(triphenylsilyl) chromate; aliphatic groups reduce the thermal stability.

Reaction of either chromium(VI) oxide or chromyl chloride with diphenylsilanediol gives a mixture of two siloxy-chromium compounds which are difficult to separate. Compound I is believed to have the linear structure:



whereas compound II is apparently the cyclic structure:



Compound I is a yellow-orange oil and compound II is a yellow-orange crystalline solid with a sharp decomposition point at 169°C. Elemental analysis, infrared and ultraviolet spectra, molecular weight data, and chemical behavior support the postulated structures. Reaction schemes for the formation of these compounds are suggested.

INTRODUCTION

Within the past decade many attempts have been made to synthesize high molecular weight organometallic oxide polymers containing a metal-oxygen-metal backbone to which are attached "plasticizing" organic groups. The only high molecular weight polymers of this type which have been prepared are the organosiloxane compounds. Various workers claim to have made stannosiloxane, borosiloxane, arsenosiloxane, antimonosiloxane, aluminosiloxane, titanosiloxane, and aluminoxane compounds. However in all cases where molecular weights have been determined such "polymers" were found to be telomers with less than fifty repeating units in the chain. Little effort has been made to establish the nature and mechanism of even simple inorganic condensation reactions, and in too many cases the reactants and reaction products have not even been precisely characterized. Because high molecular weight organometallic oxide polymers have not been obtained, a careful study has been undertaken of the nature of the reactions involved in two siloxane-transition metal systems, and a kinetic and stoichiometric study of the mechanism of the formation of stannosiloxanes has been initiated.

Siloxy-Titanium Chemistry

James S. Skelcey

Because titanium alkoxides are polymeric and give rise to polymeric hydrolysis products which are heat resistant¹ and because of the well-known thermal stability of organosiloxanes, it is of interest to attempt to combine the structures of these two and compare the properties of the Ti-O-Si system with those of the Ti-O-C and Si-O-Si systems. Known siloxy-titanium compounds, their properties, and methods of preparation which are recorded in the literature have been reviewed in a WADD Technical Report². Bradley³ reviewed the physical and chemical properties of the tetrakis(trialkylsiloxy)titanium compounds; all are liquids except tetrakis(triethylsiloxy)titanium and tetrakis(dibutylmethylsiloxy)titanium. The siloxy-titanium compounds are perceptibly more resistant to hydrolysis and show greater thermal stability than the titanium alkoxides.

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, but in 1960 Gutmann and Meller⁴ described the isolation of tetrakis(triphenylsiloxy)titanium 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 both mono- and di-substituted triphenylsiloxy compounds of bis(cyclopentadienyl)titanium(IV) can be prepared along with tetrakis(triphenylsiloxy)titanium.

Van der Kerk and Noltes^{5,6} have 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 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 is 28.75 and that in bis(triphenylsiloxy)bis(cyclopentadienyl)titanium is 27.32, conclusive identification cannot be based on this information.

In this laboratory the preparation, characterization, and some properties have been studied in detail for 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)ditiotaxane was isolated and characterized as a side product in the reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate.

Experimental

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 obtained by the reaction of bis(cyclopentadienyl)titanium dichloride and triphenylsilanol in the presence of triethylamine. Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was 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.

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)ditiotaxane, $[(C_5H_5)_2ClTi]_2O$, are crystalline orange solids, while bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$, is a white crystalline solid.

The siloxy compounds are all soluble in benzene, toluene, chlorobenzene, nitrobenzene, acetone, chloroform, and carbon tetrachloride. They are slightly soluble in ether, petroleum ether, and aliphatic hydrocarbons. The ditiotaxane has a lower solubility in all of these solvents but 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 a red solution results, presumably with the formation of $(C_5H_5)_2TiCl_2$. All of the compounds are hydrolyzed by sodium hydroxide dissolved in an acetone-water

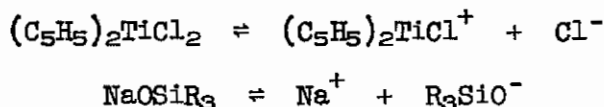
mixture; however $[(C_5H_5)_2ClTi]_2O$ appears to be much more stable towards alkaline hydrolysis than the siloxy compounds. Solutions of all compounds decompose with formation of titanium dioxide when exposed to atmospheric moisture for long periods of time.

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 $(C_5H_5)_2TiCl[OSi(CH_3)(C_6H_5)_2]$ and $(C_5H_5)_2TiCl[OSi(C_6H_5)_3]$ at $500^\circ C.$, while for $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$ this occurs at approximately $425^\circ C.$ The dititoxane slowly turns dark above $200^\circ C.$ and rapidly decomposes above $225^\circ C.$ The overall stability of $(C_5H_5)_2TiCl[OSi(CH_3)_3]$ is much lower than that of the phenylsiloxy derivatives.

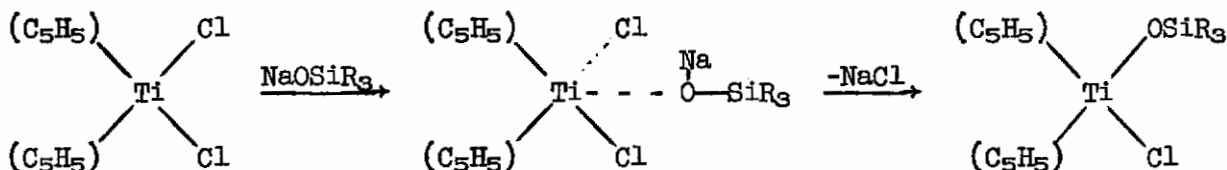
Infrared, visible, and ultraviolet spectra as well as molecular weight, x-ray diffraction, and complete elemental analytical data are reported and discussed in a thesis by J. S. Skelcey⁷.

Discussion

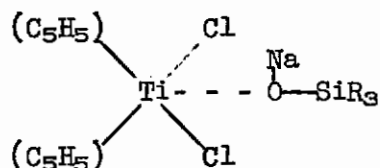
The formation of these siloxy compounds can be visualized as occurring either by a dissociation process or a bimolecular displacement reaction. A dissociation reaction involving one of the following processes seems unlikely in a solvent such as toluene.



A bimolecular displacement process seems more probable:



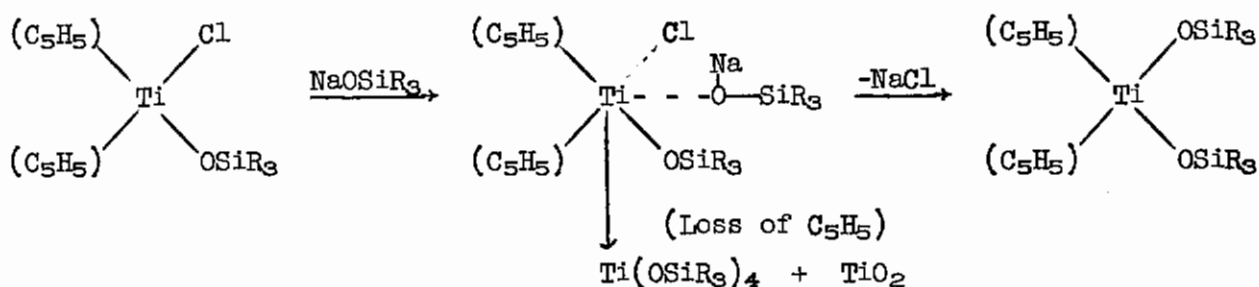
Bis(cyclopentadienyl)titanium dichloride has an essentially tetrahedral arrangement of cyclopentadienyl rings and chlorine atoms about the titanium atom. The primary bonding involves a set of tetrahedral orbitals of the titanium atom derived by a mixing of the $3d^34s$ and $4s4p^3$ hybrids. π -Bonding 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:



Conclusions

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.

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 removal occurs with formation of the tetrasubstituted compound or titanium dioxide. The penta-coordination 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) moiety 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.

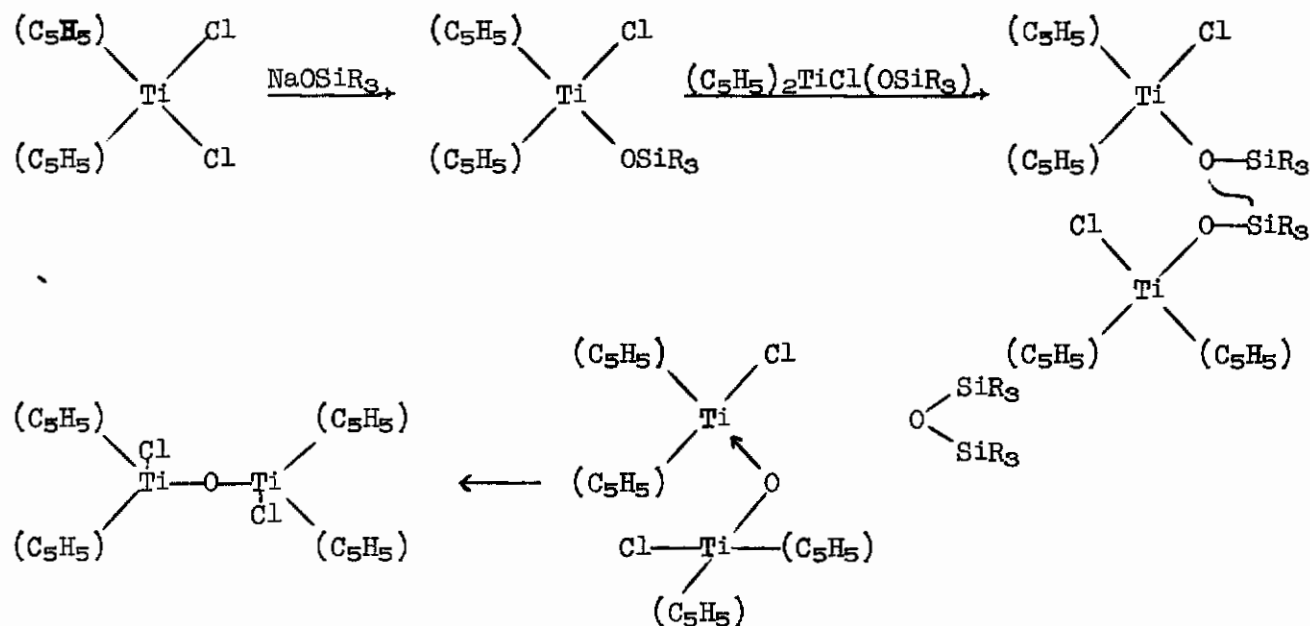
On this basis it is easy to visualize why such low yields of the monosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) have been obtained. Consideration of the fact that the only disubstituted compound isolated was bis(triphenylsiloxy)bis(cyclopentadienyl)titanium and that only very small amounts of trimethylsiloxybis(cyclopentadienyl)titanium chloride were isolated leads 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 loss of cyclopentadienyl groups to occur. This is observed to be the case. Differences in the steric effects between the cyclopentadienyl rings and trimethylsiloxy or triphenylsiloxy

Contrails

groups apparently is not significant; basicity of the siloxy groups 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 the open 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 hygroscopic 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 proceed by 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)ditiioxane in the reaction of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate is not at first easily understood. However, consideration of the greater stabilities of hexamethyldisiloxane and tetramethyldiphenyldisiloxane in comparison to the respective silanols suggests a plausible mechanism for the formation of the ditiioxane. This is illustrated by the following scheme:



The first step of such a reaction might be the formation of the monosubstituted siloxy compound of bis(cyclopentadienyl)titanium(IV). Release of electrons by the trimethylsilyl or dimethylphenylsilyl group should make the electrons of the oxygen atom more available for coordination and also should oppose the $d - p_\pi$ bonding between 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 titanium-oxygen-titanium bond of the dititoxane.

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 organo-silicon compounds. Thus, in many cases repeated recrystallizations were necessary for purification.

The thermal stabilities of the siloxy derivatives of bis(cyclopentadienyl)titanium(IV) are lower than the tetrasubstituted siloxy compounds of titanium(IV). This is especially noted in the comparison of triphenylsiloxybis(cyclopentadienyl)titanium chloride and bis(triphenylsiloxy)bis(cyclopentadienyl)titanium with tetrakis(triphenylsiloxy)titanium. Furthermore, 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.

Inorganic Condensation Reactions. I. Preparation of Some Stannosiloxanes

Curt Thies

Within the past decade many workers have attempted to synthesize polymers with elements other than carbon in the chain backbone. A majority have followed the simple and classical route to polymer formation by mixing bifunctional reactants which polycondense. While there is ample information on the products formed from a large variety of different elemental systems, little effort has been made to establish the nature and mechanism of simple inorganic condensation reactions. Because of their commercial interest, the only inorganic polycondensation process studied quantitatively is the polymerization of difunctional silanols. Thus a prototype condensation reaction, carefully characterized in stoichiometry and rate, is needed to understand the details of inorganic condensation reactions. Once a prototype system is established, variations with respect to the influence of pendant substituents and other elements on the condensation reaction can be evaluated. In addition it will be possible to determine whether or not the theory of polycondensation as developed by Flory, Carrothers and others for simple organic condensation reactions can be applied to inorganic systems as well.

Since the silanediol system has been studied in detail, a prototype copolycondensation reaction with difunctional siloxy compounds was chosen for investigation. For the other comonomer, difunctional compounds of tin were chosen because of the availability of commercially pure monomers and the reported stability of Sn-O-Si bonds. As the first step in this study, the preparation and characterization of dimeric and trimeric species was undertaken.

Experimental

Sodium triphenylsilanolate ($\text{NaOSi}\phi_3$) was prepared by the cleavage of $\phi_3\text{SiOSi}\phi_3$ with a stoichiometric amount of sodium hydroxide.⁸ The equilibrium is forced to the right by removing the water formed from the reaction mixture.

All organotin chlorides were obtained from commercial sources. Triphenyltin chloride ($\phi_3\text{SnCl}$), diphenyltin dichloride ($\phi_2\text{SnCl}_2$), and dimethyltin dichloride [$(\text{CH}_3)_2\text{SnCl}_2$] were recrystallized from toluene at -14°C . Dibenzyltin dichloride [$(\phi\text{CH}_2)_2\text{SnCl}_2$] was recrystallized from toluene at -4°C while dibutyltin dichloride [$(\text{n-C}_4\text{H}_9)_2\text{SnCl}_2$] was recrystallized from 30-60° petroleum ether at -4°C .

Preparation of stannosiloxane compounds. Several stannosiloxane compounds were prepared by dissolving $\text{NaOSi}\phi_3$ in dry benzene and adding to this solution a stoichiometric amount of the appropriate organotin chloride also dissolved in benzene. After mixing, the reaction mixture was allowed to stand five to fifteen minutes at room temperature before the sodium chloride precipitate was removed by filtration. The clear filtrate was taken to dryness in vacuo and the product recrystallized.

Stoichiometry. Stoichiometry of the reaction of $\text{NaOSi}\phi_3$ with $\phi_3\text{SnCl}$, $(\text{CH}_3)_2\text{SnCl}_2$, and $(\text{n-C}_4\text{H}_9)_2\text{SnCl}_2$ in benzene was established by obtaining closed material balances about reaction systems involving semi-micro quantities of reactants. In

order to obtain sufficient material for analysis, 5 ml. aliquots of the reactant solutions were pipetted into the reactor, a 50 ml. Erlenmeyer. The solutions ranged in concentration from 0.007 to 0.05 M. After mixing, the reaction mixture was kept in the reactor for a known period at room temperature before being filtered into a tared 50 or 125 ml. filter flask. The clear filtrate was temporarily set aside.

All traces of benzene in the reactor and filter were removed by drying at 90°C. Upon cooling, the reactor was extracted with 10 ml. of distilled water. This solution was transferred to the filter and drawn into a clean 125 ml. filter flask. A second extraction with 5 ml. of water was used to insure complete removal of sodium chloride from the reactor and filter. Chloride present in the combined water extract (15 ml.) was determined by titration with 0.0200 N standard silver nitrate using dichlorofluorescein as the indicator.

Several standard chloride analyses were carried out to establish the effectiveness of the above extraction and titration method. The results indicate that in the presence of $\phi_3\text{SiOSn}\phi_3$ the average recovery is 99.0% with a standard deviation (σ) of $\pm 0.21\%$. The presence of organotin chlorides did not appear to affect chloride recovery significantly except in the case of $(\text{CH}_3)_2\text{SnCl}_2$ where the effect is small.

After the water extraction, the reactor and filter were dried at 105°C. Upon cooling, the reactor was extracted with 10 ml. benzene. The extract was transferred to the filter and drawn into the tared 125 ml. filter flask containing the original benzene filtrate. A second 10 ml. benzene extraction was used to assure complete removal of solids from the walls of the reactor and filter. The combined benzene filtrate was taken to constant weight in vacuo and the weight of the solid residue determined by difference. The amount of stannosiloxane compound present in this residue was measured spectrophotometrically using the characteristic Si-O-Sn peak for identification. Examination of infrared spectra of the reactants and products established that only the intense Si-O-Sn peak in the various stannosiloxane compounds absorbed significantly in the 10.40 to 10.60 μ region.

In order to carry out spectrophotometric determinations of various stannosiloxanes, it was first necessary to prepare calibration plots for each compound. Solutions of known concentrations ranging from 0.0055 to 0.0091 M were prepared using purified $\phi_3\text{SiOSn}\phi_3$, $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$, and $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$ samples. Cyclohexane was used as a solvent for $\phi_3\text{SiOSn}\phi_3$ and $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$, while carbon disulfide was employed for $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$. Eight and one-half microns was selected as the 100% transmission reference point. In all cases, Beer's Law was obeyed over the concentration range investigated.

The yield of a stannosiloxane compound in a given reaction mixture was determined by preparing a solution (cyclohexane or carbon disulfide) of the solid residue with a known concentration (c_0 , M). Absorbancy of the Si-O-Sn peak was then measured as outlined above, and the concentration (c , M) of the stannosiloxane compound actually present in the solution taken from the appropriate Beer's Law calibration plot. The yield (%) was calculated from the relation:

$$Y = (c/c_0) \times 10^2$$

Results

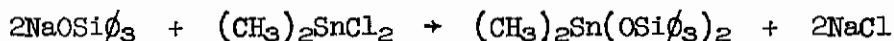
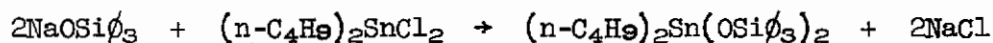
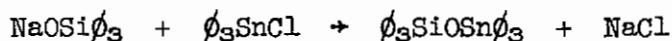
A. Stannosiloxane formation. A series of stannosiloxane compounds was synthesized by the procedure outlined above. Pertinent data are listed in Table I. Only carbon-hydrogen data are reported here. Combined Si-Sn oxides, determined by the method of Gilman and King, were within $\pm 1.0\%$ of the theoretical value.⁹

TABLE I

Stannosiloxane Compounds Prepared by Silanolate Condensation Reaction in Benzene

| Compound | Moles of NaOSi ϕ_3 Used | M.P., °C | Yield, % | Analytical | | | |
|---|---------------------------------|-------------|-------------|------------|------|-------|------|
| | | | | Calculated | | Found | |
| | | | | C,% | H,% | C,% | H,% |
| $\phi_3\text{SiOSn}\phi_3$ | 0.00612 | 139-140 | 59.7 | 69.15 | 4.80 | 69.33 | 4.84 |
| $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$ | 0.00708 | 155-156 | 64.9 | 65.26 | 6.01 | 65.44 | 5.9 |
| $(\text{n-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$ | 0.00677 | 69-70 | 79.5 | 67.46 | 6.90 | 67.61 | 6.57 |
| $\phi_2\text{Sn}(\text{OSi}\phi_3)_2$ | 0.00758 | 148.5-149.5 | 40.2 | 70.01 | 5.83 | 70.05 | 5.64 |
| $(\phi\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$ | 0.00958 | 122-123 | 78.3 | 70.36 | 5.39 | 70.41 | 5.31 |

B. Stoichiometry and rate of stannosiloxane formation. Representative stoichiometric results for the reaction of NaOSi ϕ_3 with $\phi_3\text{SnCl}$, $(\text{CH}_3)_2\text{SnCl}_2$, and $(\text{n-C}_4\text{H}_9)_2\text{SnCl}_2$ in benzene are presented in Table II. The NaCl, $\phi_3\text{SiOSn}\phi_3$, $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$, and $(\text{n-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$ yields are consistent with the overall equations:



There is no evidence that significant side reactions occurred. Although a few relatively low $(\text{n-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$ and $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$ yields were observed, a frequency plot of data from 42 runs shows the results cluster about a central value of 96%. Since the NaOSi ϕ_3 used was only 96-98% pure, this is the expected range for total consumption of reactants.

TABLE II

Representative Stoichiometric Data for Stannosiloxane Formation

| Initial Reactant Concn. (g. equiv./l) | Sodium Chloride Yield (%) | Stannosiloxane Yield (%) |
|--|---------------------------------|-----------------------------|
| $\phi_3\text{SiOSn}\phi_3$: | | |
| 0.0127 | 96.2 | 96.7 |

continued

Table II - continued

| Initial Reactant Concn. (g. equiv./l) | Sodium Chloride Yield (%) | Stannosiloxane Yield (%) |
|---|---------------------------------|-----------------------------|
| $\phi_3\text{SiOSn}\phi_3$: | | |
| 0.0127 | 99.6 | 100.2 |
| 0.0127 | 98.0 | 103.2 |
| 0.0345 | 97.4 | 99.4 |
| 0.0345 | 97.6 | 98.5 |
| 0.0345 | 96.0 | 98.7 |
| $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$: | | |
| 0.026 | 96.8 | 89.3 |
| 0.026 | 96.7 | 93.6 |
| 0.026 | 95.8 | 89.5 |
| 0.049 | 96.8 | 89.3 |
| 0.049 | 98.3 | 97.5 |
| 0.049 | 97.9 | 100.0 |
| 0.049 | 97.3 | 97.1 |
| $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$: | | |
| 0.0127 | -- | 88.5 |
| 0.0136 | 98.6 | 98.7 |
| 0.0136 | 90.9 | 97.8 |
| 0.0136 | 99.0 | 87.1 |
| 0.049 | 94.7 | 97.0 |
| 0.026 | 97.2 | 96.4 |

Sodium chloride formation is rapid when stoichiometric amounts of $\text{NaOSi}\phi_3$ are mixed in benzene with $\phi_3\text{SnCl}$, $(\text{CH}_3)_2\text{SnCl}_2$, $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$, or $\phi_2\text{SnCl}_2$. Representative data are shown in Table III. Since the $\text{NaOSi}\phi_3$ used in this study was 96-98% pure, the observed sodium chloride recoveries correspond to total $\text{NaOSi}\phi_3$ consumption. Variation in the sodium chloride yields is within experimental error.

TABLE III
Representative Sodium Chloride Recovery Data

| Initial Reactant Concn. (g. equiv./l) | Reaction Time (minutes) | Sodium Chloride Recovery (% theoretical) |
|---|-------------------------------|--|
| $\phi_3\text{SiOSn}\phi_3$: | | |
| 0.0127 | 1.1 | 96.2 |
| 0.0127 | 51.3 | 99.6 |
| 0.0127 | 2796.0 | 98.0 |
| 0.0345 | 0.9 | 96.0 |
| 0.0345 | 27.8 | 97.4 |
| 0.0345 | 2994.0 | 97.6 |
| $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OSi}\phi_3)_2$: | | |
| 0.0147 | 4.0 | 95.2 |
| 0.0147 | 9.0 | 100.9 |
| 0.0147 | 148.1 | 99.8 |
| 0.0147 | 1207.0 | 99.7 |
| 0.0490 | 0.8 | 94.6 |
| 0.0490 | 50.4 | 95.1 |
| 0.0490 | 1560.0 | 94.9 |
| $(\text{CH}_3)_2\text{Sn}(\text{OSi}\phi_3)_2$: | | |
| 0.0136 | 3.8 | 98.4 |
| 0.0136 | 12.5 | 99.0 |
| 0.0136 | 61.8 | 98.6 |
| 0.0136 | 682.0 | 90.9 |
| 0.0490 | 1.0 | 95.0 |
| 0.0490 | 50.2 | 95.5 |
| 0.0490 | 2190.0 | 94.7 |

The rapid rate of sodium chloride formation found in this study indicates that $\text{NaOSi}\phi_3$ -organotin chloride condensation processes carried out at room temperature in benzene are extremely fast. Such reactions are complete in less than a minute, so quantitative rate data could not be obtained.

Since quantitative rate measurements were not made, elucidation of a reaction mechanism for the $\text{NaOSi}\phi_3$ -organotin chloride condensation process in benzene is not possible. However, certain inferences may be drawn from the stoichiometric and qualitative rate data which were obtained. One of these is that pure $\text{NaOSi}\phi_3$ will react in benzene with a stoichiometric amount of R_3SnCl or R_2SnCl_2 to give quantitative yields of the corresponding stannosiloxane compound. Side reactions do not occur under the mild reaction conditions employed in this study

This is significant since conventional polycondensation processes must utilize reactions which are free of undesirable side reactions. Extrapolation of the above results to bifunctional systems which are capable of polymer formation might seem precarious, but syntheses of organic condensation polymers are based on simple reactions of multifunctional groups. The fact that these reactions were free of secondary processes was established from studies of the corresponding monofunctional systems. The lack of such knowledge has been one of the handicaps in syntheses of organometallosiloxane polymers. Results of the present investigation indicate the reaction of pure $(\text{NaO})_2\text{SiO}_2$ with R_2SnCl_2 in an aprotic solvent should yield stannosiloxane polymers having a regular alternating $(-\text{Si}-\text{O}-\text{Sn}-\text{O}-)$ structure. If cyclic compounds are formed, it should be possible to isolate and identify these. The important point is Si-O-Si or Sn-O-Sn bonds should not be formed by various side reactions under normal reaction conditions if pure reactants are employed.

It is significant that the reaction of NaOSiO_3 with organotin chlorides in benzene is extremely fast and irreversible. The sodium chloride byproduct precipitates immediately thereby forcing the reaction to completion. This distinguishes such reactions from those commonly employed to synthesize organic condensation polymers. Organic polycondensation processes, in general, have utilized slow, reversible organic reactions which require elevated temperatures and reduced pressure for high polymer formation. A notable exception is the interfacial polycondensation technique which has recently been developed. In this method a fast, irreversible polymerization of two fast-reacting intermediates occurs near the interface between phases of a heterogeneous liquid system.^{10,11} Characteristic features of ordinary melt and interfacial polycondensation processes are compared in Table IV.¹⁰ The interfacial method is obviously the simplest since impurities, stoichiometric imbalance of reactants, and even side reactions do not necessarily limit polymer formation. All of these factors drastically limit the molecular weight of polymers formed by the melt condensation process.

Since reactions ordinarily used in interfacial polycondensations are similar to the NaOSiO_3 -organotin chloride reaction (fast and irreversible), it appears that regular alternating stannosiloxane polymers could be prepared by the interfacial method. The only difficulty seems to be lack of a suitable heterogeneous solvent system since relatively pure $(\text{NaO})_2\text{SiO}_2$ has already been isolated.

TABLE IV
Comparison of Interfacial and Melt Polycondensation

| | Interfacial | Melt |
|-------------------|-------------------------|-------------|
| Intermediates | | |
| Purity | moderate to high (90%) | high (98%) |
| Balance | unnecessary | necessary |
| Stability to heat | unnecessary | necessary |

continued

Table IV - continued

| | Interfacial | Melt |
|---------------------------|-----------------|---|
| Polymerization conditions | | |
| Time | several minutes | several hours |
| Temperature | 0-40°C | >200°C |
| Pressure | atmospheric | high and low |
| Equipment | simple, open | special, sealed |
| Products | | |
| Yield | low to high | high |
| Structure | unlimited | limited by stability to heat and fusibility |

C. Polymer formation. Several stannosiloxane polymers were synthesized by the in situ condensation of $(\text{NaO})_2\text{Si}\phi_2$ with $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$. The polymers have not been fully characterized as to their hydrolytic and thermal stability, molecular weight, or various other physical properties. Attention was focused on determining if the silanolate-organotin chloride reaction involving bifunctional reactants proceeded in the same manner as the monofunctional systems. The polymerizations were carried out under a variety of reaction conditions. Complete material balances were established about each reaction system and the sodium chloride recovery data taken as a measure of the extent of reaction.

The results (Table V) show there is essentially no difference in the extent of reaction of each polymerization process. Similar sodium chloride recoveries were obtained for the polymerization carried out at -14°C for two hours and that carried out at reflux temperature for 24 hours.

TABLE V

Material Balance Data for In Situ Preparation of Stannosiloxane Polymers

| Sample | $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$ Added, Mole | Reaction Time, Min. | Reaction Tem- perature, °C. | Sodium Chloride Recovery, % | Total Bulk Polymer Recovered, % |
|----------|--|------------------------|--------------------------------|-----------------------------------|---------------------------------------|
| ϕ-Bu I | 0.0250 | 108 | -4 | 98.0 | 99.2 |
| ϕ-Bu II | 0.0226 | 30 | reflux | 97.4 | 98.2 |
| ϕ-Bu III | 0.0249 | 3042 | -14 | 97.7 | -- |
| ϕ-Bu IV | 0.2026 | 1440 | reflux | 97.1 | 87.4 |

Undesirable side reactions in the in situ $(\text{NaO})_2\text{Si}\phi_2-(\text{n-C}_4\text{H}_9)_2\text{SnCl}_2$ polycondensation process were detected by fractionating the bulk stannosiloxane polymers into a methanol-soluble and methanol-insoluble fractions as outlined previously. Carbon, hydrogen, and chlorine analyses for each methanol-insoluble fraction are shown in Table VI. Calculated carbon-hydrogen values are for the $[\text{O-Si}\phi_2\text{-O-Sn}(\text{n-C}_4\text{H}_9)_2]$ unit.

Although none of the fractions had carbon-hydrogen analyses which agreed well with the calculated values, carbon-hydrogen analyses for the ϕ -Bu I and ϕ -Bu II fractions are extremely close. This indicates, but does not prove, the ϕ -Bu I and ϕ -Bu II polymerizations were relatively free of side reactions. In contrast, carbon-hydrogen analyses for the ϕ -Bu III and ϕ -Bu IV fractions differ significantly from the calculated values. In these cases the Si-Sn ratio is 1 indicating significant side reactions have occurred. It is interesting to note reaction times for ϕ -Bu III and ϕ -Bu IV are much greater than those for ϕ -Bu I and ϕ -Bu II. Infrared spectra for all methanol-soluble fractions were essentially identical.

TABLE VI

Analytical Data for Methanol-Insoluble Stannosiloxane Polymer Fractions

| Polymer | Analytical | | | | |
|----------------|------------|-------|----------------|--------------|--------|
| | Calculated | | Found | | |
| | C (%) | H (%) | C (%) | H (%) | Cl (%) |
| ϕ -Bu I | 53.73 | 6.27 | 53.33 53.22 | 6.20 2.24 | 0.0 |
| ϕ -Bu II | 53.73 | 6.27 | 53.43 53.37 | 6.36 6.25 | 0.0 |
| ϕ -Bu III | 53.73 | 6.27 | 48.42 48.62 | 6.60 6.52 | 0.0 |
| ϕ -Bu IV | 53.73 | 6.27 | 44.64 44.72 | 6.86 6.92 | 0.0 |

The above results show the in situ $(\text{NaO})_2\text{Si}\phi_2-(\text{n-C}_4\text{H}_9)_2\text{SnCl}_2$ polymerization process is rapid and yields polymers which contain Si-O-Sn bonds. However, further conclusions about these polymers cannot be made at present since they have not been properly characterized. Such characterization will be the subject of a future study. In addition it will be necessary to perform the polymerization with highly purified monomers under conditions more conducive to high polymer formation than those attempted to date.

Summary

A series of stannosiloxane compounds has been prepared by the condensation of sodium triphenylsilanolate with various organotin chlorides in benzene. Infrared and elemental analyses were employed to characterize the reaction products.

Conclusions

The stoichiometry of the reaction of sodium triphenylsilanolate with triphenyltin chloride, dimethyltin dichloride, and dibutyltin dichloride in benzene has been established. Sodium chloride byproduct yields were obtained by standard silver nitrate titration. Stannosiloxane yields were determined spectrophotometrically using the characteristic Si-O-Sn peak for identification. Results obtained using these techniques show the sodium chloride-organotin chloride condensation reaction in benzene goes to completion and is free of significant side reactions.

Sodium chloride formation has been found to be rapid when sodium triphenylsilanolate is caused to react at room temperature in benzene with a stoichiometric amount of an organotin chloride. Such reactions are complete in less than a minute, so quantitative rate data could not be obtained. For this reason, a mechanism cannot be postulated for the sodium triphenylsilanolate-organotin chloride condensation process in benzene. However, the lack of side reactions in such processes is significant since this implies the reaction of pure $(\text{NaO})_2\text{Si}\phi_2$ with organotin dichlorides in an aprotic solvent will yield high molecular weight stannosiloxane polymers having a regular alternating $(-\text{Si}-\text{O}-\text{Sn}-)$ structure.

Several stannosiloxane polymers have been prepared under a wide range of reaction conditions by the in situ condensation of $(\text{NaO})_2\text{Si}\phi_2$ with dibutyltin dichloride. The polymers were not fully characterized, but it has been established that the polymerization process is rapid. Highly purified $(\text{NaO})_2\text{Si}\phi_2$, which is soluble in absolute ethanol, has been isolated and will be used in future stannosiloxane polymerizations.

Infrared spectra and complete analytical data of some eighty preparations and additional experimental detail are available in the dissertation of C. Thies, Department of Chemistry, Michigan State University.

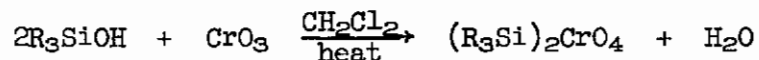
Silyl Chromates

Curtis R. Hare

Recent interest in polymeric inorganic molecules has lead to consideration of the possibility of incorporating the difunctional and approximately tetrahedral chromyl group into siloxy compounds. In this laboratory an investigation has been undertaken of the synthesis and properties of compounds in the general class $(R_3Si)_2CrO_4$. The methods developed for the preparation, isolation, purification, and characterization of these compounds were then used in studying the more complex reactions of chromium(VI) compounds with the silanediols. Simple $(R_3Si)_2CrO_4$ compounds also were used to observe the effects of different organic groups (R) on the properties of silylchromates.

When this investigation was undertaken in 1958, no information was available on the chemistry of the $Cr^{VI}-O-Si$ linkage. Schmidt and Schmidbaur¹² recently reported the preparation of bis(trimethylsilyl)chromate from hexamethyldisiloxane and chromium(VI) oxide. This compound also was prepared as a part of this investigation. Granchelli and Walker¹³ have patented a method of preparation for bis(triphenylsilyl) chromate by the reaction of triphenylsilanol with chromium(VI) oxide in glacial acetic acid or xylene. Preparation of the compound was carried out independently in this investigation.

Bis(triorganosilyl)chromates were synthesized by condensation of the appropriate silanol with chromium(VI) oxide in chlorinated-methane solutions in which the silanols are soluble but chromium(VI) oxide is not.



Solutions of the silanol immediately took on a yellow-orange color when chromium(VI) oxide was added, and in all cases the reaction mixtures were highly colored within thirty minutes. After 0.5-3.0 hours of refluxing, the reaction mixture was filtered to remove excess chromium(VI) oxide and the solvent was removed with a rotary evaporator. The crude product, obtained in 94-97% yield (based on the silanol), was then purified by recrystallization from an appropriate solvent. Characterization of the products was based upon analytical and spectrophotometric data. Complete experimental details, including infrared, visible, and ultraviolet spectra as well as molecular weight, x-ray diffraction, and complete elemental analytical data are reported and discussed in a thesis by Curtis R. Hare¹⁴.

Experimental

Bis(triphenylsilyl) chromate. Three types of reactions were used under varying conditions to prepare bis(triphenylsilyl) chromate: (a) the reaction of triphenylsilanol with chromium(VI) oxide, (b) the reaction of triphenylsilanol with chromyl chloride, and (c) cohydrolysis of triphenylechlorosilane and chromyl chloride. The first general reaction was studied most extensively because any excess chromium(VI) oxide is easily removed by filtration and a high yield (96-97%) of crude product is obtained regardless of the solvent used or the

presence of base.

Crude bis(triphenylsilyl) chromate from reactions (a) and (b) was recrystallized from methylene chloride and an 85% yield of orange-colored crystals (m.p. 153.5-154°C) was obtained. This compound decomposes above its melting point. Analytical data are recorded in Table I.

Bis(p-tolyldiphenylsilyl) chromate. This compound was prepared by the general method. After removal of the solvent, a red, uncrystallizable oil was obtained. It was dissolved in methylene chloride, hexane was added, and the solution was boiled to remove methylene chloride. A yellow crystalline product was obtained from the cooled solution. After recrystallization from hexane, the melting point was 98.5-99°C; decomposition occurs above the melting point. Analytical data are recorded in Table I.

Bis(cyclohexyldiphenylsilyl) chromate. The preparation of bis(cyclohexyldiphenylsilyl) chromate was effected by the general method. Purified material is an orange solid melting at 84-85°C. Solid bis(cyclohexyldiphenylsilyl) chromate does not appear to decompose at its melting point but it is unstable at 100°C. Analytical data are recorded in Table I. The purity of the silyl chromate is 96% based on chromium content and 107% based on silicon content. These data, along with the low molecular weight, indicate that separation of the silanol from the silyl chromate was not complete. Since this product is highly soluble in common organic solvents and a good recrystallization technique for its purification could not be developed, further effort did not seem justified.

TABLE I
Some Properties of Silyl Chromates

| Compound | Composition (%) | | | | Molecular Weight | Melting Point (°C) |
|---------------------------------------|-----------------|------|-------|------|------------------|--------------------|
| | Cr | Si | C | H | | |
| bis(triphenylsilyl) chromate | | | | | | 153.5-154 |
| Calculated | 8.19 | 8.84 | 68.11 | 4.76 | 634 | |
| Found | 8.20 | 8.91 | 68.04 | 4.80 | 626 ± 10 | |
| bis(p-tolyldiphenylsilyl) chromate | | | | | | 98.5-99 |
| Calculated | 7.85 | 8.47 | 68.50 | 5.17 | 664 | |
| Found | 7.76 | 8.55 | 68.51 | 5.22 | 644 ± 10 | |
| bis(cyclohexyldiphenylsilyl) chromate | | | | | | 84-85 |
| Calculated | 8.04 | 8.68 | 66.84 | 6.55 | 647 | |
| Found | 7.72 | 9.25 | 66.56 | 6.52 | 633 ± 10 | |
| bis(tricyclohexylsilyl) chromate | | | | | | 125-126 |
| Calculated | 7.76 | 8.37 | 64.43 | 9.91 | 671 | |
| Found | 7.68 | 8.40 | 64.22 | 9.78 | 643 ± 10 | |

Bis(tricyclohexylsilyl) chromate. This compound was also prepared by the general method previously described. The recrystallized red-orange solid had a melting point of 125-6°C. It is unstable above its melting point and has a different absorption spectrum from the other compounds in this series.

Bis(trimethylsilyl) chromate. Hexamethyldisiloxane was refluxed with chromium(VI) oxide in methylene chloride, and after 12 hours the mixture was filtered and solvent removed. The resulting red oil was not distilled owing to its explosive character. Vacuum evaporation into a bath at -78°C was used to isolate the compound. The product is stable when stored at -78°C in the dark, but at room temperature and in the absence of light it shows appreciable decomposition within three hours. The infrared, visible, and ultraviolet spectra of this compound were recorded without isolation of the substance from solution. An attempt to determine the molecular weight of bis(trimethylsilyl) chromate in benzene failed because of reaction of the silyl chromate with benzene.

Properties of silyl chromates. All of the silyl chromates described in the previous section decompose into a black amorphous solid on prolonged exposure to light. Bis(tricyclohexylsilyl) chromate is less light sensitive than the other silyl chromates, while bis(trimethylsilyl) chromate decomposes most rapidly on exposure to light. All except the aliphatic silyl chromates may be safely stored in the dark at room temperature.

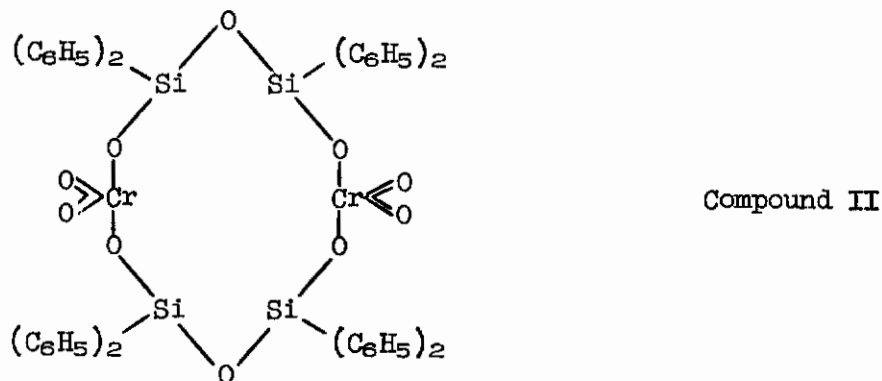
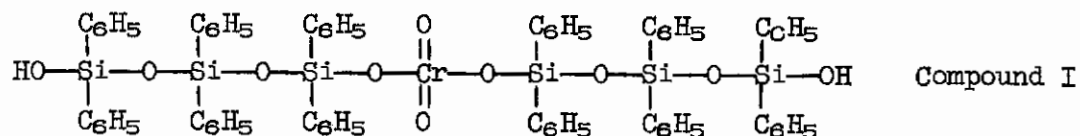
The aliphatic silyl chromates and bis(cyclohexyldiphenylsilyl) chromate are decomposed by concentrated nitric acid, and all are decomposed by a mixture of concentrated sulfuric and nitric acids. Both bis(trimethylsilyl) chromate and bis(methyldiphenylsilyl) chromate are decomposed by water. In the case of bis(trimethylsilyl) chromate, the disiloxane is formed on hydrolysis. All the silyl chromates are decomposed by homogeneous hydrolysis in an acetone-water solution. Homogeneous hydrolysis of bis(triphenylsilyl) chromate by addition of water to an acetone solution gives the silanol in a nearly quantitative yield, and about half of the chromium remains in the hexavalent state, most likely as chromic acid.

The silyl chromates are very soluble in methylene chloride, carbon tetrachloride, chloroform, acetone, and ethanol. With the exception of bis(cyclohexyldiphenylsilyl) chromate and the aliphatic silyl chromates, they are all only slightly soluble in cyclohexane and aliphatic hydrocarbons.

Of the compounds prepared, thermal stability is greatest for bis(triphenylsilyl) chromate which decomposes above its melting point of 153.5-154°C. All of the organosilyl chromates decompose above their melting points except for bis(cyclohexyldiphenylsilyl) chromate which is stable to about 15° above its melting point of 84-85°C.

Condensation products of diphenylsilanediol with chromium(VI) compounds. The reaction of diphenylsilanediol with chromium(VI) oxide or chromyl chloride in methylene chloride or carbon tetrachloride has been carried out under various conditions. Two compounds tentatively believed to be represented by the structures I and II below are obtained, but compound I is very difficult to separate in pure form.

Contrails



Characterization of compounds I and II. Numerous determinations of molecular weight and elemental analysis of compound I have been made. Although complete removal of impurities (hexaphenylcyclotrisiloxane, compound II, and solvent) is difficult, the most nearly pure product has a silicon-chromium ratio approaching six to one and a molecular weight of about 1300. These data are consistent with structure I. The infrared spectrum of this compound shows weak OH, strong Si-O-Si, and strong Cr=O absorptions. The product repels cold water but is slowly attacked by hot water; it is rapidly hydrolyzed with acetone-water solution. In the latter case, the only product isolated was hexaphenylcyclotrisiloxane. Compound I is sticky when freshly prepared, but on standing it hardens into a yellow-brown glassy substance. It is quite stable at room temperature in the dark, but in light it slowly decomposes to a black mass from which hexaphenylcyclotrisiloxane has been isolated. Even in the glassy state compound I is easily melted with the heat of the hand. Differential thermal analysis shows that it begins to decompose at about 275°C; the thermal effect reaches a maximum at 460°C.

Compound II has the following elemental analysis: carbon, 58.15% (calcd. 58.05%); hydrogen, 4.23% (calcd. 4.06%); chromium, 10.46% (calcd. 10.48%); and silicon, 11.47% (calcd. 11.30%). The molecular weight of compound II (calcd. 993) was found to be 1168 ± 100 using diphenyl as a cryoscopic solvent and 1030 ± 100 in benzene. The low precision of these determinations is due to the low solubility of compound II in these and all other solvents tried. Compound II is hydrolyzed by acetone-water to give tetraphenyldisiloxane-1,3-diol; this information suggests that the disiloxy group exists in compound II. The infrared spectrum shows no OH absorption, medium Si-O-Si absorption characteristic of strain-free siloxanes, and Cr=O absorptions. A model using bond angles and distance of strain-free cyclic siloxanes indicates that structure II is plausible in a crown conformation.

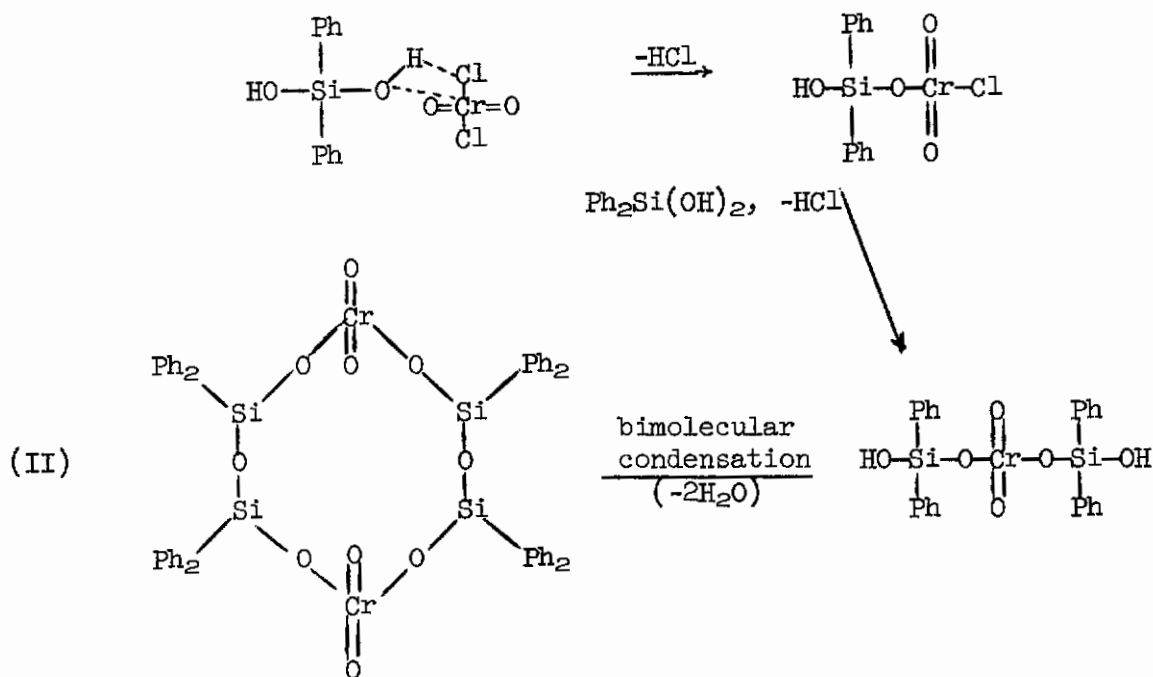
Compound II has a sharp decomposition point at 169°C which is unchanged by recrystallization. It slowly decomposes to a brown solid when exposed to light and is decomposed in hot acetone, ethanol, and benzene. It is sparingly soluble in cold methylene chloride, chloroform, carbon tetrachloride, carbon disulfide,

chromyl chloride is attributed to the tendency of the diol to undergo rapid self-condensation which is either acid or base catalyzed. This is illustrated by the observation that diphenylsilanediol is not soluble in pure methylene chloride, but in the presence of a trace of chromyl chloride it dissolves and forms hexaphenylcyclotrisiloxane and higher siloxanes. The condensation of diphenylsilanediol to form hexaphenylcyclotrisiloxane apparently does not participate in the overall formation of compound I. Compound I is produced only in poor yield by the reaction of hexaphenylcyclotrisiloxane and chromyl chloride or by the reaction of chromium(VI) oxide or chromyl chloride with hexaphenyltrisiloxane-1,5-diol. Compound II is not obtained at all from these reactions but is produced in good yield by the reaction of tetraphenyldisiloxane-1,3-diol and chromium(VI) oxide. Also, compound II undergoes a rapid reaction (15 minutes) with diphenylsilanediol in methylene chloride to give a product with the characteristics of compound I.

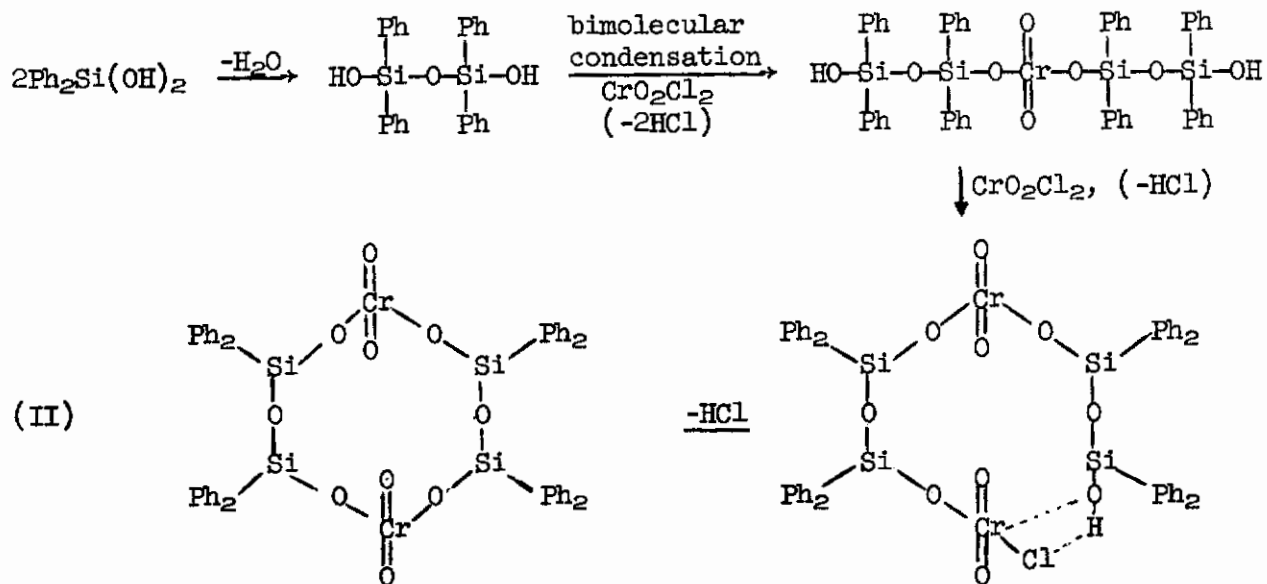
A possible mechanism for the formation of compound II from the reaction of diphenylsilanediol with chromyl chloride in methylene chloride is a reaction of the diol with chromyl chloride by elimination of hydrogen chloride to form $\text{Ph}_2(\text{OH})\text{SiOCr}(\text{O}_2)\text{Cl}$. This intermediate may react with a second molecule of the diol to form $\text{Ph}_2(\text{OH})\text{SiOCr}(\text{O}_2)\text{OSi}(\text{OH})\text{Ph}_2$, which may in turn undergo condensation with a similar molecule to form compound II. Compound II could also be produced by the formation of tetraphenyldisiloxane-1,3-diol by self-condensation of the diol, followed by successive reactions with chromyl chloride.

These two plausible mechanisms for the formation of compound II are illustrated by the following schemes B and C:

Reaction Scheme B

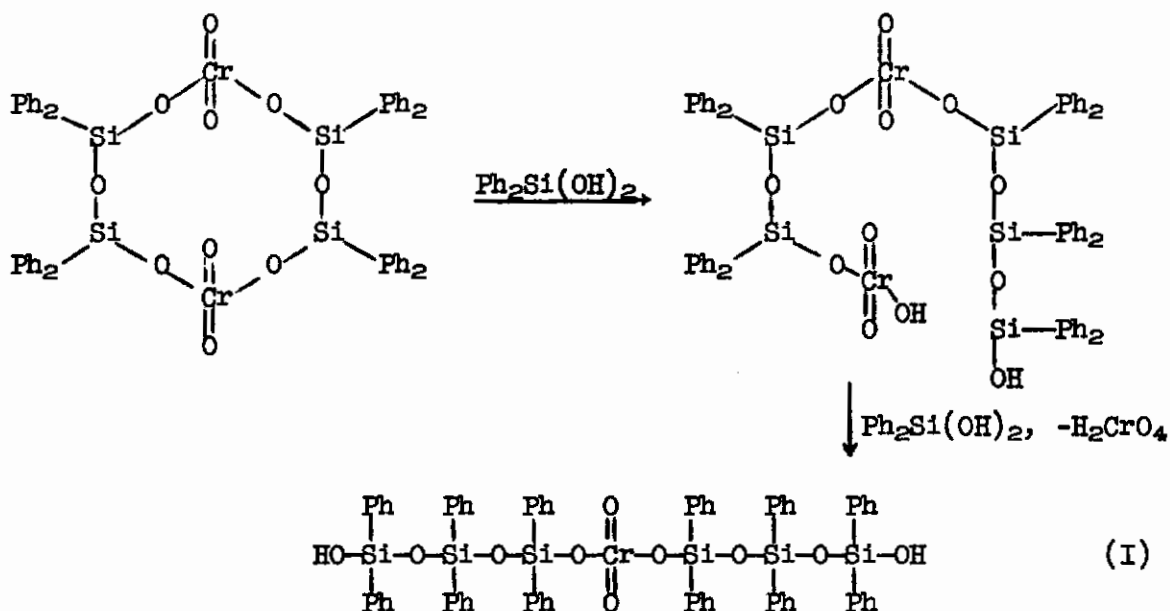


Reaction Scheme C



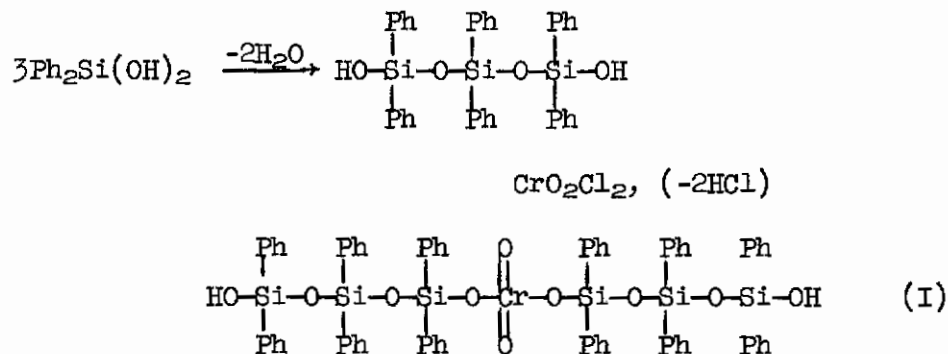
Compound I may be formed from the reaction of 2 molecules of diphenylsilanediol with compound II (Reaction Scheme D), hexaphenylcyclotrisiloxane with chromyl chloride, or hexaphenyltrisiloxane-1,5-diol with chromyl chloride (Reaction Scheme E). Only the first and last reactions seem plausible.

Reaction Scheme D



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Reaction Scheme E



The reaction of diphenylsilanediol with chromium(VI) oxide probably proceeds in a manner similar to Scheme A. Intermediates analogous to those of Schemes B and C may give compound II. Reaction Scheme D is favored over a reaction scheme analogous to E since combination of hexaphenyltrisiloxane-1,5-diol with chromium(VI) oxide failed to give compound I. The higher yield of compound II over compound I in the reaction of diphenylsilanediol with chromium(VI) oxide may be due to the fact that reactions of Scheme E do not occur with chromium(VI) oxide, or to a slower reaction due to the insolubility of chromium(VI) oxide in methylene chloride.

The thermal stability of the bis(triorganosilyl)chromates follows a definite pattern. The least stable is bis(trimethylsilyl)chromate which explodes when heated to about 80°C; the most stable is bis(triphenylsilyl)chromate which decomposes as it melts at 153.5-154°C. The effect of the presence of donor groups on the stability of the silylchromate is illustrated by the reduced stability of bis(*p*-tolyl-diphenylsilyl)chromate (m.p. 98.5-99°C, decomp.) or bis(methyldiphenylsilyl)chromate (decomp. 85°C) compared to bis(triphenylsilyl)chromate. Of the solid silylchromates prepared, only bis(cyclohexyldiphenylsilyl)chromate was stable above its melting point.

Compound I is the most thermally stable compound prepared in this investigation. It has no definite melting point but passes from a brittle glass into a viscous fluid by the heat of the hand. Differential thermal analysis of this material shows it begins to decompose at 275°C. Compound II decomposes very sharply at 169°C without melting. Its lower stability may be due to thermal cracking of the cyclic structure.

The toxicity of all known hexavalent chromium compounds warrants a word of caution concerning the silylchromates. The physiological properties of these compounds have not been investigated and more than normal care should be observed in handling them.

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