PREPARATION OF SILOXY-CHROMIUM COMPOUNDS

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Add

ABSTRACT

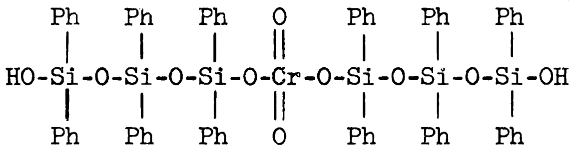
PREPARATION OF SILOXY-CHROMIUM COMPOUNDS

by Curtis Robert Hare

The purpose of this investigation was the preparation of inorganic heteropolymers containing silicon and hexavalent chromium. Prior to the preparation of the heteropolymers, a series of bis(triorganosilyl)chromates were prepared to study the effects of the silicon substituents on the stability of the silicon-oxygen-chromium(VI) linkage. The preparation of these silylchromates was carried out by reaction of the corresponding silanol with chromium(VI) oxide in methylene chloride. The silylchromates prepared and characterized were bis(p-tolyldiphenylsilyl)chromate, bis(tricyclohexylsilyl)chromate, and bis(cyclohexyldiphenylsilyl)chromate; the probable preparation of bis(methyldiphenylsilyl)chromate was also carried out. The compound bis(triphenylsilyl)chromate was prepared and characterized in this investigation prior to discovery of a brief description of its synthesis in the patent literature. These silylchromates decompose in light and when heated above their melting points. The most stable is bis(triphenylsilyl)chromate; aliphatic groups reduce the thermal stability. The new silanol cyclohexyldiphenylsilanol was prepared by the reaction of cyclohexyllithium and diphenyldichlorosilane in petroleum ether.

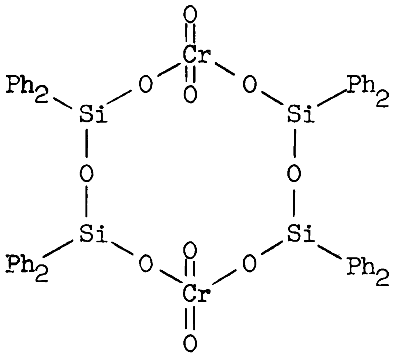
Reaction of either chromium(VI) oxide or chromyl chloride with diphenylsilanediol gives a mixture of two siloxy-chromium compounds and

siloxane impurities. The complete separation of the chromium compounds was difficult. Compound I is a yellow-brown, brittle, glassy solid which is easily melted to a viscous fluid. The structure of this compound is (Ph = phenyl):



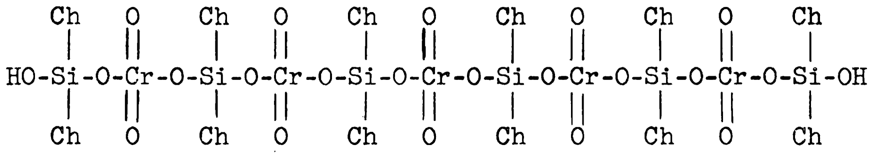
$$HO-SiPh_2-O-SiPh_2-O-SiPh_2-O-Cr(=O)_2-O-SiPh_2-O-SiPh_2-O-SiPh_2-OH \qquad (I)$$

Compound II is a yellow-orange, crystalline solid with structure:



(II)

Studies of the reactions of either chromium(VI) oxide or chromyl chloride with the siloxane condensation products of diphenylsilanediol as well as of the reaction of compound II with the diol enabled postulation of a mechanism for the formation of compounds I and II. Dicyclohexylsilanediol reacts with chromium(VI) oxide in methylene chloride to give a dark red, amorphous solid with the structure (Ch = cyclohexyl):



$$HO-SiCh_2-O-Cr(=O)_2-O-SiCh_2-O-Cr(=O)_2-O-SiCh_2-O-Cr(=O)_2-O-SiCh_2-O-Cr(=O)_2-O-SiCh_2-O-Cr(=O)_2-O-SiCh_2-OH \qquad (III)$$

Compounds I and III are believed to be the first compounds of their kind to be isolated and identified. Compound II is believed to be the first reported cyclic siloxane containing chromium. Compound III decomposes on standing, compound II has a sharp decomposition point at 169°C, and differential thermal analysis of compound I indicates decomposition at 275°C, which leads to the conclusion that increased chromium(VI)-to-silicon content in chromium(VI) heterosiloxanes brings on reduced thermal stability. Ultraviolet and visible spectra of the compounds prepared suggest an interaction involving the substituents of the silicon atom with the chromate group. The infrared absorption of the silylchromates in the 11.4-11.5μ region was tentatively assigned to the chromium-oxygen-silicon linkage.

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INTRODUCTION

Research in high temperature polymers recently has developed because of the growing need of industry and the military services for materials of construction which will endure temperatures of 500°C and above. Thermosetting and thermoplastic materials, elastomers, adhesives, coatings, and hydraulic fluids based on a carbon skeletal framework undergo oxidation and bond rearrangement at high temperatures.

The structural relationships between the metal silicates which compose the earth's crust and the man-made polysiloxanes (silicones) has led many investigators (1) to conclude that the introduction of metals into the siloxane moiety may produce polymers stable at high temperatures. A wide latitude for variation in obtaining optimal properties is available through the selection of functional groups which block valences of silicon and in the choice of metals for incorporation into the polysiloxane. The choice of metals or metal-containing reactants is considerably restricted when the requirement of difunctionality is imposed. Further, the metal reactant must conform to the tetracoordination of the polysiloxanes to produce high molecular weight linear polymers. Higher coordination will produce cross-linked resins which may lead to brittleness.

Several compounds of hexavalent chromium offer desirable properties which could be incorporated into the siloxane linkage. Hexavalent chromium is a powerful oxidizing agent and thus is resistant to oxidation. Hexavalent chromium compounds are difunctional reactants and show tetracoordination. Chromyl chloride and the chromates are known to undergo self-polymerization, and chromium(VI) oxide is composed of long tetrahedral CrO_4 chains in the solid state. Recent investigations of these compounds show that their bonding is considerably covalent, which is also the bonding of the siloxanes. Consideration of these properties leads to the conclusion that an attempt should be made to incorporate hexavalent chromium into the siloxane linkage. The primary reactants chosen for this study were chromyl chloride and chromium(VI) oxide.

When this investigation was undertaken in 1958, no information was available on the chemistry of the hexavalent chromium-oxygen-silicon linkage. The large variety of known silicon intermediates which are commercially available or relatively easy to prepare provided an opportunity to undertake a systematic study of the environmental effects on the chromium-oxygen-silicon linkage.

The methods of preparation and characterization of organosiloxy chromates, and also the properties of these compounds, are the subject of this investigation.

HISTORY

Chemistry of Hexavalent Chromium

The chemistry of hexavalent chromium is marked by a few general characteristics. All the compounds of hexavalent chromium are strong oxidizing agents. In general, the ultimate reduction product is trivalent chromium. Compounds of hexavalent chromium all exhibit approximately tetrahedral coordination in solution and in the solid state. These compounds also have a tendency to form higher aggregates. Two examples of this are the formation of polychromates in strongly acidic chromate solutions and self-association of chromyl chloride in non-aqueous solutions.

Chemistry of Chromyl Chloride. Chromyl chloride is a cherry-red transparent liquid having a boiling point of 115.7°C and a melting point of -96.5°C. The appearance and odor of this compound are similar to those of bromine. The compound was first prepared by Berzelius (2) by distilling a mixture of a chromate, sodium chloride, and sulfuric acid. Chromyl chloride is most conveniently prepared by the reaction of chromium(VI) oxide with concentrated aqueous hydrogen chloride in the presence of sulfuric acid as a dehydrating agent (3). Liquid chromyl chloride is easily separated and purified by distillation. Other methods are based on the reaction of chromium(VI) oxide, a chromate, or a dichromate with an acid chloride followed by separation and purification by distillation.

Hartford and Darrin in a recent review (4) have brought together the scattered information on chromyl compounds and report a large amount of unpublished information from their laboratory. Greater than half of the articles discussed in this review are from the nineteenth century. While much is known about the properties of the chromyl compounds, there is a definite need for more information on their chemistry.

The structure of chromyl chloride was determined by Palmer (5) by electron diffraction measurements. These data (Table I) show the structure to be approximately tetrahedral.

TABLE I

BOND LENGTHS AND BOND ANGLES IN CHROMYL CHLORIDE (5)

Bond	Bond Length in A	Bond	Bond Angle
Cr-O	1.57 ± 0.03	O-Cr-O	$105^{\circ}6' \pm 4^{\circ}$
Cr-Cl	2.12 ± 0.02	Cl-Cr-Cl	$113^{\circ}16' \pm 3^{\circ}$
Cl-O	3.03 ± 0.03	Cl-Cr-O	$109^{\circ}34' \pm 3^{\circ}$
Cl-Cl	3.54 ± 0.05		
O-O	2.49 ± 0.10		

The symmetric structure is also substantiated by the low dipole moment (0.47 D) and low dielectric constant (2.2-2.3) determined by Smyth, Grossman, and Ginsburg (6). Walden (7) has also determined the dielectric constant and obtained a value of 2.6. The specific conductivity is reported to be less than 10^{-10} ohm^{-1} (8). These data also suggest that the Cr-O and Cr-Cl bonds are nearly equivalent, which would account for the covalent and non-polar nature of this compound.

The density of chromyl chloride obeys the following equation:

$$d = 1.959 - 1.913 \times 10^{-3}t + 1.797 \times 10^{-6}t^2$$

in which t is the temperature in degrees centigrade. This gives a value of 1.912 g/ml at 25°C.

The vapor pressure may be calculated from

$$\log_{10}P(\text{mm}) = 7.723 - \frac{1883}{T}$$

This gives a value of 8620 cal/mole for the heat of vaporization and a Trouton's constant of 22.1. The viscosity is about that of water (0.8 centipoise) at room temperature, but it is less temperature dependent.

Chromyl chloride is highly soluble in most halogenated organic liquids and covalent halides such as stannic chloride. It is also soluble in common organic solvents, but chromyl chloride often reacts violently with them. In general, it dissolves in most non-polar compounds and is insoluble in most polar compounds. Tables II and III give the solubility and reactivity (qualitative) of various substances with chromyl chloride.

Several studies have been made of the molecular weight of chromyl chloride in various solvents by cryoscopic and ebullioscopic means (9, 10, 11, 12). In nearly all cases, the values of the molecular weight indicate a degree of polymerization of chromyl chloride from 1.5-3. Ebullioscopic measurements in carbon tetrachloride and carbon disulfide give the calculated value. Cryoscopic measurements in stannic bromide, stannic iodide, antimony trichloride, antimony triiodide, and arsenic triiodide give values of one-half that calculated for chromyl chloride.

The following is an example of the reaction proposed to take place in the latter solvents (13):

$$CrO_2Cl_2 + SnBr_4 \longrightarrow CrO_2^{++} + SnBr_4Cl_2^{=}$$

The vapor density of chromyl chloride indicates the presence of only the CrO_2Cl_2 molecule.

TABLE II

SOLUBILITY AND REACTIVITY OF CHROMYL CHLORIDE IN LIQUID SOLVENTS (4)

Miscible; No Reaction	Miscible; Slow Reaction	Miscible; Rapid or Violent Reaction	Essentially Immiscible
carbon tetrachloride	acetic anhydride	acetyl bromide	formic acid
1,2-dichloroethane	acetic acid	diethylsuccinate	hydrofluoric acid
1,2-dibromoethane	nitric acid (100%)	pyridine	phosphoric acid (85%)
thionyl chloride	n-hexane	sulfur monochloride	sulfuric acid (70%)
stannic chloride	benzene	toluene	mercury
acetyl chloride	cyclohexane	p-cymene	
methylene chloride	nitrobenzene	chlorosulfuric acid	
1,1,2,2-tetrachloroethane	carbon disulfide	oleum	
chloroform		aniline	
		tert-butylamine	
		triethanolamine	
		methanol	
		ethanol	

TABLE III

SOLUBILITY OF SOLIDS IN CHROMYL CHLORIDE (4)

Very Soluble	Slightly Soluble	Insoluble
iodine (reacts)	phenol (surface reaction)	zinc chloride
p-dichlorobenzene	pentachlorophenol	sodium chlorochromate
chromium(VI) oxide	aluminum chloride	sodium chromate
naphthalene (reacts)		ammonium hexachlorostannate sulfur
		metals (surface reaction)

Pure chromyl chloride may be stored in stainless steel, aluminum, or dark glass containers fitted with Teflon or Kel-F stoppers. In glass the material is stable if protected from light. When exposed to light, chromyl chloride decomposes into a black solid and chlorine gas. Schwab and Prakash (14) studied the photochemical decomposition of chromyl chloride in carbon tetrachloride solution and proposed the following mechanism:

$$CrO_2Cl_2 + h\nu \longrightarrow Cl\cdot + CrO_2Cl\cdot \qquad \text{(initiation)}$$

$$Cl\cdot + CrO_2Cl_2 \longrightarrow CrO_2Cl\cdot + Cl_2 \qquad \text{(propagation)}$$

$$CrO_2Cl\cdot + CrO_2Cl_2 \longrightarrow 2CrO_2 + Cl_2 + Cl\cdot \qquad \text{(propagation)}$$

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2 \qquad \text{(termination)}$$

$$CrO_2Cl\cdot \longrightarrow CrO_2 + Cl\cdot \qquad \text{(termination)}$$

Chromyl chloride is thermally stable to 180°. Above 180°C a dark decomposition product begins to form, and at 400°C a magnetic oxide having the composition Cr_5O_9 results. On further heating, chromium(III) oxide is formed (4).

Chromyl chloride is immiscible in water and hydrolyzes only slowly at the interface to form chlorides, chromates, and chlorochromates. It reacts with ammonia even in concentrated aqueous solution with incandescence to produce a brown solid which is apparently a mixture of chromium(III) oxide and chromium nitride. Hydrogen sulfide and sulfur monochloride are oxidized by chromyl chloride. Phosphorus trichloride reacts explosively with liquid chromyl chloride but it forms an addition compound with composition $CrOCl \cdot POCl_3$ when a carbon tetrachloride solution of chromyl chloride is used. Phosphorus pentachloride reacts with the liquid to give phosphorus oxychloride, chromium(III) chloride, and chlorine. It forms an addition compound of composition $CrO_2Cl_2 \cdot PCl_5$ with phosphorus pentachloride in carbon tetrachloride. Chlorochromates are produced by the action of chromyl chloride on concentrated chromate solutions. Chlorosulfuric acid and pyrosulfuric acid decompose chromyl chloride to produce a brown solid which has a composition corresponding to chromyl sulfate.

Except for tin and antimony which are readily attacked, most metals are only superficially attacked by chromyl chloride. It is reported that zinc and sodium react with chromyl chloride vapor to produce metallic chromium. Hydrogen reduces chromyl chloride to Cr_2O_3 (4) at elevated temperatures.

Graphite reacts with chromyl chloride to form intercalary compounds containing 36.3-40.4% CrO_2Cl_2. The interplanar spacing of the

graphite is increased from 4.5 A to 9 A. When the compound is heated to 200-300°C, the chromyl chloride is released and the graphite is exfoliated to many times its original volume (15). Up to 23% of the chromyl chloride is retained at 300°C.

Clean white phosphorus reacts vigorously with chromyl chloride, whereas sulfur reacts with less vigor. The products of these reactions are unknown.

The reactions of chromyl chloride with organic substances have received considerable attention (4). Historically, Étard was first to use this reagent to prepare benzaldehyde from toluene (16). In general, the Étard reaction involves the addition of chromyl chloride to an organic molecule at one or more hydrogen atoms. The addition product is separated and hydrolyzed to give aldehydes, ketones, and quinones. The addition compound is formed by adding a solution of chromyl chloride in an inert solvent (carbon disulfide or carbon tetrachloride) to an excess of the organic compound in the same solvent. The insoluble addition compound is separated after the disappearance of the red color of chromyl chloride. The addition compound is then decomposed with water or alcohol to give carbonyl compounds.

When chromyl chloride is reduced in an alcoholic solution in the presence of an organic acid, a trivalent chromium complex of the acid is formed. The complex is soluble in organic solvents and is water repellent if the organic acid consists of a long carbon chain. If the acid contains only a few carbon atoms, the complex is a repellent of fats and oils. Highly fluorinated organic acids give complexes which are repellent to water and oils (8).

Lastly, it should be pointed out that if the heat evolved from the oxidation of organic material by chromyl chloride is not dissipated, the kindling temperature is achieved and a violent explosion may result. Thus care should always be exercised in the use of chromyl chloride, and it is always best to use an inert solvent to reduce the reactivity.

Other Chromyl Compounds. Numerous other chromyl compounds have been described in the literature, but the chemistry of these compounds has not been studied as extensively as that of chromyl chloride. The chromyls that have been described are the fluoride, acetate, nitrate, perchlorate, bromide, thiocyanate (iso?), cyanate (iso?), sulfate, pyrosulfate, and azide. Of these, only the fluoride and the nitrate have been studied extensively.

The fluoride has been prepared in a very high state of purity by the reaction of anhydrous hydrogen fluoride and chromium(VI) oxide. This was purified by distillation or recrystallization in anhydrous hydrogen fluoride (17). It may also be prepared by the reaction of iodine pentafluoride with chromium(VI) oxide, antimony pentafluoride, or fluorine with chromyl chloride and anhydrous hydrogen fluoride with potassium dichromate. The violet-red solid sublimes at 29.6°C to a reddish-brown vapor. The chemistry of chromyl fluoride is similar to that of chromyl chloride. Chromyl fluoride exchanges its fluorine with metal oxides, forming boron trifluoride from boric oxide, silicon tetrafluoride from glass, and arsenic fluorides from arsenous oxide (4). The mixed halide CrO_2ClF has been prepared by Flesch and Svec (18) by mixing chromyl chloride and fluoride. The reactivity and oxidizing strength of chromyl fluoride is considered to be greater than that of chromyl chloride (4). This reagent may also be used for the Étard reaction.

Chromyl nitrate is obtained as a deep red liquid by the reaction of dinitrogen pentoxide on chromyl chloride or chromium(VI) oxide (19). The liquid is unstable and slowly decomposes on standing even in the absence of light. It is considered to be a stronger oxidizing agent than either chromyl fluoride or chloride. It also may be used for the Étard reaction.

Schmeissen has also reported (20) the preparation of chromyl perchlorate from dichlorine hexoxide and chromium(VI) oxide. This compound is very unstable and its existence has been questioned (4).

Chromyl bromide has been reported by Zellner (21) as the red-brown product of the reaction of chromyl chloride and anhydrous hydrogen bromide at -70°C. The product was contaminated with chromyl chloride and decomposed at room temperature.

Chromyl acetate has recently been prepared (22) by the reaction of chromium(VI) oxide with acetic anhydride in carbon tetrachloride in the absence of light and moisture. The red crystals can be distilled in high vacuum.

The other chromyl compounds that have been mentioned are reported to be the products of metathetical reactions with chromyl chloride. Since these compounds were never characterized, their existence is questionable.

Chromium(VI) Oxide, Chromates, and Polychromates. Chromium(VI) oxide is precipitated from alkali chromate or dichromate solutions by addition of a large excess of sulfuric acid. The dark red needles are

washed with concentrated nitric acid and dried at 70°C. The melting point is reported to be 197°C (23).

The structure of chromium(VI) oxide has been determined by Bystrom and Wilhelmi (24). Oxygen atoms form a distorted tetrahedron around each chromium atom, and the Cr-O distances are 1.79-1.81 A. The tetrahedra are linked into chains by sharing corners, but between CrO_3 chains probably only weak van der Waals bonds are operative. Many textbooks still report the erroneous structure of Brakken (25) which is based on CrO_6 octahedra. Crystalline chromium(VI) oxide is piezoelectric (26), indicating a permanent dipole exists in the crystal.

Chromium(VI) oxide is also paramagnetic (27), as are the chromates. This paramagnetism is attributed to imperfect pairing of the electrons in the ground state.

The differential thermal analysis of chromium(VI) oxide shows an endothermal reaction at 178-187°C which Vasenin (28) attributes to fusion, and an exothermal reaction at 267-348°C which is ascribed to decomposition.

Chromium(VI) oxide is a powerful oxidizing agent. It oxidizes alkali metals, sulfur, arsenic, phosphorus, hydrogen, ammonia, and hydrogen sulfide. Alcohols may be oxidized by aqueous solutions of chromium(VI) oxide to aldehydes, ketones, or acids, depending on the conditions. These oxidations may also be carried out in glacial acetic acid or acetic anhydride in which chromium(VI) oxide is only slightly soluble.

Chromium(VI) oxide also forms addition compounds with heterocyclic nitrogen bases such as pyridine (29, 30). The structure of the pyridine addition compound is considered to be trigonal bipyramidal with the pyridine molecules at the apexes. These compounds are insoluble in non-polar organic solvents but are slightly soluble in polar solvents. They dissolve in the parent nitrogen base. All are photo-sensitive and decompose when heated above 100°C.

The chemistry of the metal chromates is quite familiar. Alkali metal chromates are prepared commercially by fusion of chromite ore with alkali, followed by recrystallization. The principal uses of chromates are as oxidizing agents, in metal treatment, and for tanning leather. Acidic solutions of chromates have been shown to consist of the dichromate ion. Highly concentrated aqueous solutions of chromium(VI) oxide and highly acidic chromate solutions contain the trichromate and tetrachromate ions. The salts of these polychromates are prepared by the addition of chromium(VI) oxide to concentrated aqueous solutions of the metal dichromates. The color of the chromates passes from yellow for the monochromate to dark red for the tetrachromate. The following reactions illustrate aggregation of chromates in acidic solution:

$$\begin{array}{lcl}
CrO_4^{=} + H^+ & \longrightarrow & (HCrO_4^-) \\
2(HCrO_4^-) & \rightleftharpoons & Cr_2O_7^{=} + H_2O \\
Cr_2O_7^{=} + 2H^+ & \rightleftharpoons & Cr_3O_{10}^{=} + H_2O \\
Cr_3O_{10}^{=} + 2H^+ & \rightleftharpoons & Cr_4O_{13}^{=} + H_2O \\
\underline{n}CrO_4^{=} + 2\underline{n}H^+ & \rightleftharpoons & (CrO_3)_{\underline{n}} + \underline{n}H_2O
\end{array}$$

Chromate Esters. Gomberg (31) was the first to prepare a chromate ester. He prepared bis(triphenylcarbinyl)chromate by the reaction of silver chromate with triphenylmethyl chloride in benzene. Numerous other chromate esters have been prepared, but those which are insoluble are derived from tertiary alcohols only.

Several other methods have been described for the preparation of chromate esters. The most common method is to add chromium(VI) oxide to a solution of the alcohol in an inert solvent. The chromate esters may also be prepared by reaction of the alcohol with chromyl chloride in chloromethane solvent or sodium dichromate dihydrate in glacial acetic acid.

When chromium(VI) oxide is added to a solution of a primary or secondary alcohol in an inert solvent such as benzene, a yellow to yellow-orange color is produced. Within a short period of time the solution becomes turbid and the yellow color fades. Attempts to isolate these unstable chromates have been futile.

Westheimer (32) has discussed the participation of a chromate ester in the oxidation of isopropyl alcohol by chromic acid. His mechanism for the oxidation involves two steps: formation of a chromate half ester followed by decomposition of the chromate half ester by removal of the α-hydrogen atom of the propyl group to form acetone. The latter decomposition is considered to be the rate determining step. The lack of stability of the primary and secondary alcohols may be related to the ease of removal of their α-hydrogen atoms.

The chromate esters which have been prepared, isolated, and characterized are listed in Table IV according to the alcohols from which they are derived. Other chromate esters have been proposed, but they have not been isolated in pure form or characterized.

Zeiss and Matthews (36) claim that the chromate esters may be obtained in pure form by a freeze-drying technique which removes all volatiles except the chromate ester. They also report that the chromate esters may be stored indefinitely in the dark at -60°C.

TABLE IV

CHROMATE ESTERS OF VARIOUS TERTIARY ALCOHOLS

Alcohol	Properties of Chromate	Reference
triphenylcarbinol	m.p. 174°C (decomp.)	31
tert-butanol	liquid, decomp.	34, 36
2-methylfenchol	m.p. 109.5°C	33, 37
2-ethylfenchol	decomp. 140°C	33
2-methylborneol	decomp. 105°C	33, 35, 37
cedrol	decomp. 122°C	33, 35
1-octadecylcyclohexanol	m.p. 37-38°C (decomp.)	35
decahydro-8a-napthol	m.p. 74-76°C (sealed tube)	35
cis-terpene hydrate	decomp. 135°C	35
2,4-dimethyl-4-hexanol	liquid, decomp.	36
3-ethyl-3-pentanol	liquid, decomp.	36

Several studies have been made of the reactions of the chromate esters (35, 36, 37, 38, 39), particularly their hydrolysis and alcoholysis. In all cases, hydrolysis and alcoholysis yield the parent alcohol and a reduced chromium species which is claimed to be (H_2CrO_3). The hydrolysis of bis(*tert*-butyl)chromate and bis(triphenylmethyl)chromate has been carried out in water enriched in O^{18}(38). These studies reveal that the oxygen-chromium bond is broken on hydrolysis in the case of bis(tert-butyl)chromate, and that the carbon-oxygen bond is broken in bis(triphenylmethyl)chromate. The hydrolysis or methanolysis of bis(2,4-dimethyl-4-hexyl)chromate derived from the dextrorotary alcohol gave the dextrorotary alcohol with retention of configuration, which substantiates chromium-oxygen bond fission on hydrolysis or alcoholysis.

Toxicity of Hexavalent Chromium. The toxic action of chromium is confined to the hexavalent state (23). These compounds have an extremely irritating, corrosive, and, under some circumstances, toxic action on body tissue. The most common effects of chromium compounds on industrial workers are those which result from direct contact of the skin with chromates or chromium(VI) oxide. These skin reactions are of two different types: chrome ulcers and chrome dermatitis.

Chrome ulcers are very persistent without proper treatment. They are generally caused by contact only with the broken skin; however, even contact with the slightest abrasion of the skin may cause ulcers. Chrome dermatitis may result from contact of the skin with hexavalent chromium. This is easily avoided by proper washing after contact.

Perforation of the nasal septum is a common result of inhalation of chromate dust. The perforation is not disabling in any way, and it does not interfere with normal breathing, but inhalation may cause cancer of the respiratory tract. Many studies have shown that the death rate due to respiratory cancer is very high among chromate workers. Also, prolonged contact with chromate dusts may cause chronic irritation of the respiratory tract, but there is no evidence that chromate workers are susceptible to tuberculosis.

Oral ingestion of hexavalent chromium compounds may lead to intense irritation of the gastrointestinal tract resulting in violent epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhages. With large doses, circulatory collapse, unconsciousness, and death may follow rapidly. Other systemic effects from ingestion which have been reported in men or experimental animals include bronchi, serious cavities, liver damage, hyperglycemia, glycosuria, marked fall in blood pressure, leukocytosis, anemia, muscle cramps, loss of weight, staggering, convulsions, paralysis, and death.

The fatal dose by ingestion has been determined to be one gram for chromium(VI) oxide and six grams for potassium dichromate. Symptoms of intoxication have been reported from ingestion of 0.5 g of potassium dichromate. It is also believed that exposure to chromates may increase susceptibility to infectious diseases.

Normal caution is the best personal protection against chromium poisoning. Safety glasses, rubber gloves, and protective clothing should be used when handling chromates for extended periods. The person working with hexavalent chromium compounds should also shower promptly after work.

Chemistry of Organosilicon Compounds

The chemistry of the organosilicon compounds has been widely studied, largely because of the commercial value of the familiar silicones. The books by Rochow (40), Andrianov (41), and Gmelin's Handbuch der Anorganischen Chemie (42) are particularly good for their coverage of organosilicon chemistry. These references have been used extensively for the following discussion.

Organosilicon compounds are prepared by two general methods. The first is a direct method in which a reaction of silicon or silicon compounds and organic reagents at high temperatures gives the organosilicon compound (e.g., cyclohexane and silicochloroform to give cyclohexyltrichlorosilane). The second is the reaction of halo or alkoxy silanes with organometallic reagents (e.g., methylmagnesium iodide and ethylsilicate to give dimethyldiethoxysilane). The successive addition of organic groups to the silicon atom increases in difficulty with the number of groups bound to the silicon atom.

The organochlorosilanes form the most important group of organosilicon compounds since they are easily prepared and serve as intermediates in the preparation of other compounds. The disubstituted chlorosilanes are easily prepared by passing an organic chloride over silicon metal at 275-375°C in the presence of copper as a catalyst. The mono and trisubstituted chlorosilanes are prepared by the reaction of organometallic reagents with silicon tetrachloride. The organometallics of zinc, mercury, aluminum, sodium, lithium, and Grignard reagent are the common organometallic reagents used to prepare organosilicon compounds. The latter two reagents have been most widely used.

The organosubstituted ethoxysilanes are prepared directly by the reaction of organometallic reagents with ethyl silicate or by the reaction of ethyl alcohol with a chlorosilane. Similar reactions are used to prepare the other alkoxy silanes.

Organosilanols or diols are prepared by the hydrolysis of the chlorosilane or alkoxysilane. The hydrolysis of organotrichloro or triethoxysilanes leads only to resinous polymers.

The hydrolysis of the dichlorosilanes illustrates the differences in the chemistry of these compounds. When dimethyldichlorosilane is hydrolyzed, the product is octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, and other siloxanes. The preparation of dimethylsilanediol is only achieved by careful hydrolysis of dimethyldiethoxysilane (43), but the diol slowly condenses on standing to siloxanes. Diethylsilanediol can be prepared by careful hydrolysis of the dichlorosilane at 0^oC, and the direct hydrolysis of diphenyldichlorosilane gives only diphenylsilanediol.

Diphenylsilanediol is different from dimethylsilanediol in that it only undergoes condensation when heated above its melting point. It condenses in the presence of acids to hexaphenylcyclotrisiloxane, and in the presence of base to octaphenylcyclotetrasiloxane.

The hydrolysis of dimethyldichlorosilane is the basis of the preparation of the polysiloxanes. Polysiloxanes are particularly important because of unique properties. They are heat resistant, moisture resistant, have good dielectric properties, and have considerable compressibility under high pressure. They form the basis of rubbers of high thermal stability, resins for plastics and electrical insulation, and water repellent liquids with a low temperature dependence of viscosity.

The direct hydrolysis of dimethyldichlorosilane yields an oil which is composed of a mixture of siloxanes. Distillation of the oil under reduced pressure separates a distillate composed largely of octamethylcyclotetrasiloxane and lesser amounts of the cyclic pentamer, hexamer, and trimer. The residue is composed of higher cyclic siloxanes and high molecular weight linear siloxanes. This residue is treated with trimethylchlorosilane to produce methyl silicone oil. This treatment with trimethylchlorosilane is necessary to prevent further condensation of linear polymers.

Silicone rubber is produced by further polymerization of the original hydrolysis product of dimethyldichlorosilane. Polymerization is accomplished by means of strong acids or bases which are capable of opening the cyclic rings to produce cations or anions which lead to high polymers by addition polymerization. Molecular weights as high as several million have been reported for elastomeric dimethylpolysiloxane.

Silicone resins are produced by three different methods. The first is hydrolysis of dimethyldichlorosilane to form dimethylpolysiloxane and then oxidation of the product with air to attain the desired CH_3/Si ratio. The second method is based on the cohydrolysis of dimethyldichlorosilane and methyltrichlorosilane to produce the resin by co-condensation. Also, silicon tetrachloride may be methylated to the desired CH_3/Si ratio and the reaction mixture hydrolyzed to the resin.

The structure of polysiloxane fluids and elastomers is based on the linear disubstituted siloxy linkage $\left[(R)_2SiO\right]$. Fluids and elastomers differ only in molecular weight. Polysiloxane resins consist of a three-dimensional structure with cross-linking between chains of linear siloxanes. Cross-linking is achieved by introduction of the $(RSiO_{1.5})$ group.

The siloxane cyclic trimers, $(R_2SiO)_3$, have been shown to have a planar structure and may contain some bond strain (44), whereas the siloxane cyclic tetramers, $(R_2SiO)_4$, have a puckered ring conformation and are free of strain. The higher cyclic siloxanes undoubtedly also have a puckered ring or crown configuration.

Many other polysiloxanes with groups other than methyl are on the market today; those containing phenyl groups are more thermally stable than the aliphatic polysiloxanes. Phenyl-containing polysiloxanes, however, are not desirable since they set into brittle glasses.

The similarity between the structures of organosiloxanes and the inorganic silicates has been observed in x-ray and electron diffraction studies on the siloxanes (44). The silicon-oxygen distance in these compounds is 1.61-1.67 A, which is about the same as that found in inorganic silicates, and it is considerably less than 1.83 A, which is the sum of the covalent radii. This indicates that there is a high degree of ionic character in the siloxane bond. As a result of this ionic character, siloxane bonds are quite non-directional. Rochow (40) states, "The rigidity of silica and the silicates does not result from a rigidity of the bond angles of silicon and oxygen but from the high fields of force set up by all surrounding metal ions. Similarly, the silicon-oxygen tetrahedra of silica are uniform only because of the uniformity of the electric field pattern around them." There is also an apparent softness of these bonds and freedom of motion of the organosilicon unit. This is substantiated by the flexibility of silicone rubber and the compressibility of siloxane fluids.

The bond angles of the silicates and siloxanes in the solid state are also similar. The oxygen-silicon-oxygen bond angles in the siloxanes are close to the tetrahedral angle found in the silicates.

The silicon-oxygen-silicon angle in "unstrained" siloxanes is the same as that found in α-quartz (142°), which is greater than the tetrahedral angle. The carbon-silicon-carbon angle in the organosiloxanes is approximately tetrahedral, and the silicon-carbon bond distance is close to the sum of the covalent radii (1.90 A).

In the organosiloxane polymeric materials the thermal stability of the siloxane bond is considerably weaker than in the silicates, and an increase in the number of organic radicals attached to the silicon atom decreases stability further. The molecular configuration (cyclic or linear) also has an influence on thermal stability. This is illustrated by the cracking of linear dimethylsiloxanes at 400°C to form cyclic siloxanes. Cracking must involve breaking of the silicon-oxygen bond to form the more stable cyclic siloxane linkages. The chemical stability of the silicon-oxygen bond is very great and is ruptured only by heating with such reagents as concentrated hydrochloric acid, strong alkali, and fluorides.

Chemically and thermally, the weak link in the polysiloxanes is the carbon-silicon bond. The bond energy of this linkage is about the same as the carbon-carbon bond, but it is believed that introduction of a silicon-carbon bond in organic compounds increases their thermal stability. The basis of this belief is the higher thermal stabilities of the organosilicon compounds compared with similar organic compounds. The silicon-carbon bond is subject to cleavage by air oxidation at temperatures above 300°C. The chemical reactivity to various reagents depends to a large extent on the group attached to the silicon atom, but generally vigorous conditions are necessary for cleavage of the silicon-carbon bond.

Bonding Considerations in Organosilicon Compounds and Chromates

Silicon. The electronegativity difference between carbon and silicon is 0.85, which, according to Pauling (45), indicates 16% ionic character in the bond. This difference in electronegativity suggests that the electron density constituting the bond between the two atoms is slightly larger nearest the carbon atom. Nucleophilic attack on the silicon atom should then depend on the influence of substituents on the carbon and silicon atoms.

Rochow (40) has discussed the nucleophilic attack of silicon by the hydroxide ion. The intermediate of the chemical reaction is believed to be a pentacovalent species which decomposes by elimination of a negative group forming an Si-OH bond. The ease of nucleophilic substitution of the silicon-carbon bond may be reduced by placing positive substituents on the carbon (e.g., hydrogen atoms) and negative substituents (e.g., oxygen atoms) on the silicon. This is found to be true since methylsiloxanes require strong alkali and high temperatures (200°) to liberate methane, while trichloromethyl groups are removed from silicon by water at room temperature. Thus it is reasonable to conclude that inductive effects play a large role in substitution reactions of organosilicon compounds. The inductive effect of phenyl groups on silicon is withdrawal of electron density from the carbon attached to silicon, and the polarity of the bond is thereby enhanced.

Sommer and his coworkers (46, 47) have proposed a pentacovalent intermediate in the substitution reactions of asymmetric and bridgehead silicon atoms. The high reactivity of substituents on a bridgehead silicon atom, such as in 1-silabicyclo(2.2.2)octane in which siliconium ions are unlikely and attack from the rear is impossible, required the postulation of a pentacovalent reaction intermediate. This was also proposed for the substitution reactions of optically active silicon compounds which gave pure retention of configuration. In these studies they further postulated that the intermediate addition complex was bound by use of one of the 3d orbitals of silicon. The configuration of the complex was suggested to be trigonal bipyramidal and the bonding to be the hybrid dsp^3. Furthermore, the entering group and the group which is displaced need not occupy the apexes of the trigonal bipyramid. Instead of an angle near 180°, the entering group may form an angle near 90° with the group to be displaced and the central Si atom.

The concept of pentacovalent silicon was first introduced by Sidgwick (48) in 1927. At that time he compared the stability of the carbon and silicon tetrahalides to hydrolysis and ammonolysis, and suggested that in the case of the silicon tetrahalides the reactivity resulted from coordination of the water or ammonia molecules prior to reaction. Pauling (45) also suggested utilization of 3d orbitals to form ionic and double-bonded resonance structures which account for the abnormally short bond distances in some silicon compounds.

Stone and Seyferth (49) reviewed and interpreted the available literature concerning the use of d orbitals in silicon bonding. They point out that the coordination number of silicon is not always four; indeed, the fluorosilicate ion and siliconium acetylacetonate have coordination number six. The silicon tetrahalides also form addition compounds with trialkylamines with an apparent coordination number of five and a reported coordination number as high as eight. The bonding in the octahedral complexes is believed to be $3sp^3d^2$ hybridization.

In another example they cite the weak electron donor properties and planar structure of trisilylamine, $(H_3Si)_3N$, as an indication that the lone pair of electrons of the nitrogen are involved with the d orbitals of the silicon atom. On this basis they predicted that disiloxane, $(H_3Si)_2O$, should have a nearly linear structure; this was later observed by Lord, Robinson, and Schumb (50), and Curl and Pitzer (51) from infrared studies (Lord suggested 180° and Pitzer estimated 150°). Dipole moment data on dimethyldisiloxane by Sauer and Mead (52) predict a silicon-oxygen-silicon bond angle of 160°. Dipole moment data on many organosilicon compounds have been interpreted to indicate d orbital bonding.

The acid strength of the trialkyl or triaryl silanols (53) compared to the carbinols suggests a removal of electron density on oxygen by silicon, resulting in a weaker oxygen-hydrogen bond which produces acids titratable in basic solvents.

Finally, Craig, Maccoll, Nyholm, Orgel, and Sutton (54) discussed the question of d_π-p_π bonding in a number of compounds, including silicon compounds, in some detail. From an evaluation of overlap integrals they conclude that highly electronegative ligands (F, O, N) are needed to form complexes with regular elements involving sp^3d^2 hybridization, and that a strong π-bond may arise between an outer d orbital and a p orbital of an adjacent atom. In discussing the silicones in particular, they state that such bonding is possible between oxygen and silicon atoms and is indicated by the short silicon-oxygen bond distances, as compared to the bond distances expected from ionic radii. This would not affect the freedom of rotation about the bonds because there are five d orbitals available on each silicon atom which may form π-bonds with oxygen no matter what the orientation of one silicon-oxygen bond to any other in the chain.

Chromium. Little information is available on the nature of the bonding in hexavalent chromium compounds. Wolfsberg and Helmholz (55) have made semiempirical molecular orbital calculations on the chromate ion. Agreement with the observed spectrum of the chromate ion was only fair. The most significant result of their calculation was the prediction of strong bonding of the π-electrons of oxygen, which implies a double bond stronger than expected from valence bond theory. These results have been criticized by Ballhausen and Liehr (56) as being based on an over-simplified calculation. Using a different model and energy lever scheme, they have made calculations which agree quite well with experiment. Their conclusion was that the charge transfer spectrum of the chromate ion cannot be interpreted on the basis of σ-bonding electrons alone, but that the oxygen π-molecular orbitals must also be included. Since the model used assumes tetrahedral symmetry for the chromate ion, one must conclude that the extent of π-bonding between the oxygen and chromium atoms is uniform for each bond.

This is also substantiated by the force constants obtained from Raman data for the chromate ion in aqueous solution by Stammreich, Bassi, and Sala (57). Their model was based on the tetrahedral structure of the chromate ion with equal chromium-oxygen bonds, and they obtained a value of 5.48 mdyn/A for the stretching force constant of the chromium-oxygen bond. Their studies on the dichromate ion (58) based on a chromium-oxygen-chromium bridge model give two stretching force constants for the chromium-oxygen bond. These values were 3.27 and 6.07 mdyn/A. A comparison of the results of the two ions suggests that the chromate ion could be considered to be symmetrically bonded with double bond character in each bond, while the dichromate ion possesses non-equivalent chromium-oxygen bonds. The higher force constant for the dichromate ion compared to the chromate ion is expected since the double bond character is restricted to the outer chromium-oxygen bonds and the lower value is attributed to the chromium-oxygen single bond of the bridge.

The concept of double bonding in chromates may also account for the observed feeble paramagnetism of the chromates (27). That is, the the imperfect pairing suggested by Datar may be caused by contributions to π-bonds.

Helmholz, Brennan, and Wolfsberg (59) have extended semiempirical calculations from the chromate ion to the halochromate ion and chromyl chloride. The results of these calculations agree well with experiment. The conclusions from these calculations are particularly interesting. The first transition (555 mμ) in chromyl chloride is assigned to $3b_2 \longrightarrow 5a$, and the final excited orbital (5a) is strongly chromium-chlorine anti-bonding. The symmetry of this transition is B_2 and involves a transfer of charge from chlorine to chromium which therefore leads to the dissociation $CrO_2Cl_2 \longrightarrow CrO_2 + Cl_2$, as observed by Schwab and Prakash (14).

The coefficients of the atomic orbitals in the molecular orbitals of chromyl chloride permit a rough calculation of the relative importance of π - and σ -bonding in the molecule. The σ/π ratio for chlorine is 1.5, and for oxygen, 0.73, which indicates a decreased importance of π -bonding for chlorine relative to oxygen. The stretching force constants of chromyl chloride calculated by Stammreich, Kawai, and Tavares (60) also substantiate this latter conclusion. The values obtained were 2.56 mdyn/A for the chromium-chlorine bond, and 7.17 mdyn/A for the chromium-oxygen bond.

A comparison of the absorption frequencies of the symmetric chromium-oxygen stretching modes of the chromate ion, dichromate ion, and chromyl chloride (859, 904, and 987 cm^{-1}, respectively) shows that the extent of π -bonding increases. This is also observed in the stretching force constants which increase (5.48, 6.07, and 7.17 mdyn/A) for chromate ion, dichromate ion, and chromyl chloride.

Inorganic Polymerization Reactions

The concept of inorganic polymers--that is, high molecular weight compounds containing regular repeating units other than carbon--is relatively new, even though inorganic materials with a high state of aggregation have been known for some time. The importance of this subject is manifest in the increased activity in this field in the past few years.

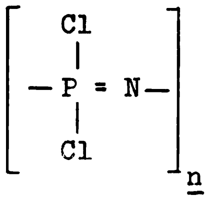
Inorganic reactions may lead to high molecular weight products by three means: condensation, addition, and coordination. Condensation reactions involve the elimination of simple molecules between the reactants to form the aggregate. Addition polymerization reactions transform low molecular weight monomeric units into higher molecular weight substances by self-reaction of the monomers. Condensation of a metal ion with a polydentate ligand to form higher aggregates, incorporation of metals into polymers by coordination, and polymerization of monomers containing coördinated metal ions are all classes as coordination polymerization reactions.

Sulfur is a familiar example of the many elements that exist in phases which can be classed as polymeric. When rhombic sulfur (S_8) is heated to 187°C, a viscous mass is produced which, on slow cooling, becomes a rubber-like, elastic material believed to be composed of linear chains of up to 40,000 sulfur atoms (61). Amorphous phases of selenium, tellurium, phosphorus, arsenic, antimony, and bismuth exist in states which may be classed as polymeric (62).

The silicate minerals, particularly the pyroxenes and amphiboles, are composed of linear silicate chains and can be considered to be inorganic polymers. Amphibole asbestos is a good example of this type of inorganic polymer.

Sulfur trioxide vapor may be condensed at a temperature less than 25°C in a dry receiver to a modification composed mostly of cyclic trimers (63). Introduction of a trace of moisture causes addition polymerization to an asbestos-like form which has a melting point of 31.5°C. This substance is composed of long chains of sulfur trioxide molecules.

Phosphonitrilic chloride is probably the best known of the synthetic inorganic polymers. A mixture of the cyclic trimer and tetramer of phosphonitrilic chloride is prepared by the action of phosphorus pentachloride on ammonium chloride. If the mixture is heated to 300°C for several hours, the melt becomes viscous, and finally a rubber-like mass is obtained. This "inorganic rubber" is composed of chains of up to 200 units with the following structure:



$$\left[-\underset{\underset{\textstyle Cl}{|}}{\overset{\overset{\textstyle Cl}{|}}{P}} = N- \right]_{\underline{n}}$$

It is thermally and hydrolytically unstable. A considerable effort is being made by many researchers (63) to modify the structure of phosphonitrilic chloride in an attempt to improve its properties.

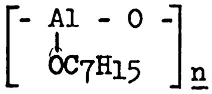
Aggregation of inorganic compounds by coordination to form polymeric materials has been known for some time. Familiar examples of these coordination polymers are the dimers of aluminum and ferric chlorides, the planar chains of palladium(II) chloride, the linear tetrahedral chains of silicon disulfide, and the highly aggregated hydrous oxides of many metals. Attempts have been made (63) to prepare linear polymers by coordination of bis(bidentate) ligands with tetracoordinate metal ions, and bis(tridentate) ligands with hexacoordinate metal ions. The materials obtained from such reactions have good thermal properties but are either amorphous powders or brittle glasses. Other attempts (64) include incorporation of metal ions into polymeric Schiff base ligands and polymerization of monomeric coordination compounds containing groups that undergo addition or condensation. These compounds also have good thermal properties but are brittle.

Recently Wagner (65) has reported the preparation of dimethylphosphinoborine polymers with a degree of polymerization as high as 183. These polymers have been prepared by the pyrolysis of dimethylphosphine borine in the presence of trialkylamine bases which act as blocking groups for the ends of the linear chains. In the absence of these blocking groups, only the cyclic trimer and tetramer of dimethylphosphinoborine are formed. The reaction for the preparation of these polymers is:

$$\underline{n}(CH_3)_2PHBH_3 + R_3N \longrightarrow [(CH_3)_2PBH_2]_{\underline{n}} \cdot NR_3 + \underline{n}H_2$$

These polymers show reasonable resistance to oxidation, hydrolysis, and heat.

The preparation of polyaluminoxanes (modified alumina polymers) has received considerable attention recently. Theobald (66) obtained a brittle resin by heating isopropoxydiheptanoxyaluminum. This resin was soluble in toluene and had a molecular weight of 5730. The structure is believed to be that of polyheptanoxyaluminoxane,



$$\left[\begin{array}{c} -\ Al\ -\ O\ - \\ | \\ OC_7H_{15} \end{array}\right]_{\underline{n}}$$

, but no structural proof is offered. Kugler (67) has prepared hard, brittle resins involving aluminum-oxygen linkages by the hydrolysis of an aluminum chelate in the presence of aluminum alcoholates. Andrianov and his coworkers (68) obtained poly(triethylsiloxy)aluminoxanes by passing moist air through tris(triethylsiloxy)aluminum at 165-170°C. This polymer is a transparent, colorless, glassy substance.

Certainly the most active field of inorganic polymer research is the preparation of polymetallosiloxanes. The intention of this research is to prepare high molecular weight heteropolymers with a metallosiloxane backbone. It is felt by many active in this field of research that alteration of the siloxane linkage to include metals in the backbone of the structure may produce polymers of high thermal stability (as the metal silicates) and good mechanical properties (as the polysiloxanes).

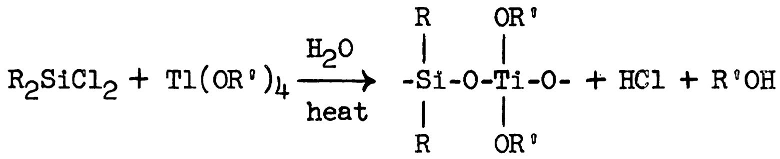
Recently Andrianov (69) has reviewed the preparation of the polymeric metallosiloxanes of aluminum, titanium, boron, tin, antimony, phosphorus, and lead. The polymers containing these elements have not had particularly desirable properties. In the case of aluminum, titanium, tin, and antimony, brittle solids with a high silicon-to-metal ratio were obtained. Boron and phosphorus gave viscous fluids with poor thermal properties.

More recently, Hornbaker and Conrad (70) have reported the preparation of polymeric metallosiloxanes of tin, lead, magnesium, and zinc. These polymers all have a very good silicon-to-metal ratio, but they decompose rather easily to form siloxanes and metal oxides. Very little structural or molecular weight data is available for these compounds.

Arsonosiloxanes have been prepared by Kary and Frisch (71). The products they have obtained range from transparent, rubbery materials to fine white powders. The authors suggest that these materials could be used for pest control products as well as for the products made from the conventional silicones.

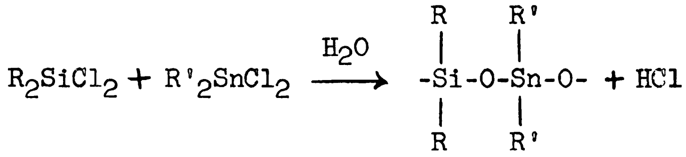
A wide variety of condensation reactions have been used to prepare the polymetallosiloxanes. Variation of the organic groups used to block valences and the metal-containing reactants has led to a large number of products (69). The groups most commonly attached to the metalloid compounds are methyl, ethyl, and phenyl. Alkoxy groups of the metals have been ethoxy, isopropoxy, and n-butoxy. The reactions used to produce the polymers may be classed in the following way:

1. Cohydrolysis of a chlorosilane and metalalkoxide (69).



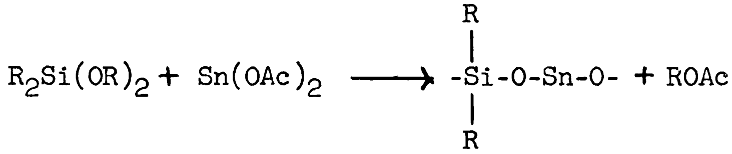
$$R_2SiCl_2 + Tl(OR')_4 \xrightarrow[\text{heat}]{H_2O} -\underset{R}{\overset{R}{Si}}-O-\underset{OR'}{\overset{OR'}{Ti}}-O- + HCl + R'OH$$

2. Cohydrolysis of a chlorosilane and metal chloride (69).



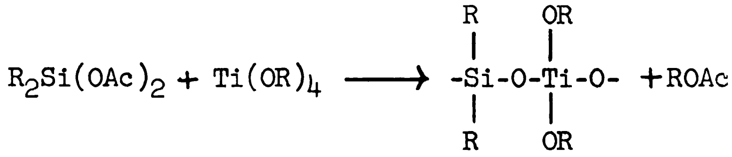
$$R_2SiCl_2 + R'_2SnCl_2 \xrightarrow{H_2O} -\underset{R}{\overset{R}{Si}}-O-\underset{R'}{\overset{R'}{Sn}}-O- + HCl$$

3. Transesterification (69).



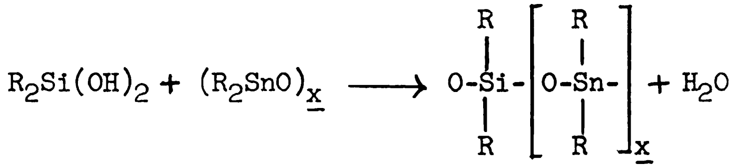
$$R_2Si(OR)_2 + Sn(OAc)_2 \longrightarrow -\underset{R}{\overset{R}{Si}}-O-Sn-O- + ROAc$$

or



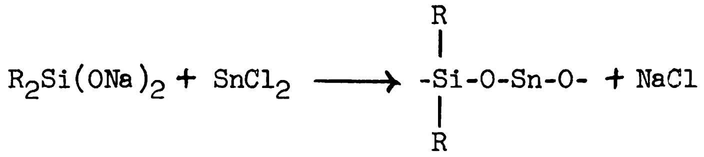
$$R_2Si(OAc)_2 + Ti(OR)_4 \longrightarrow -\underset{R}{\overset{R}{Si}}-O-\underset{OR}{\overset{OR}{Ti}}-O- + ROAc$$

4. Condensation of a silanediol with a metal oxide (72).



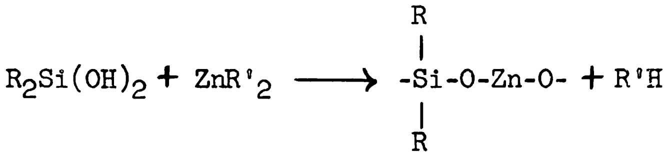
$$R_2Si(OH)_2 + (R_2SnO)_x \longrightarrow O-\underset{R}{\overset{R}{Si}}-\left[O-\underset{R}{\overset{R}{Sn}}-\right]_x + H_2O$$

5. Condensation of a disodium silanolate with a metal chloride (70).



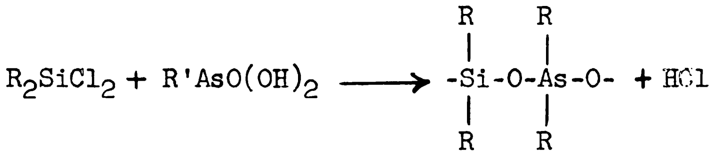
$$R_2Si(ONa)_2 + SnCl_2 \longrightarrow -\underset{R}{\overset{R}{Si}}-O-Sn-O- + NaCl$$

6. Reaction of silanediols with metal alkyls (70).



$$R_2Si(OH)_2 + ZnR'_2 \longrightarrow -\overset{R}{\underset{R}{Si}}-O-Zn-O- + R'H$$

7. Condensation of metallo acids with chlorosilanes (71).



$$R_2SiCl_2 + R'AsO(OH)_2 \longrightarrow -\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{As}}-O- + HCl$$

A large number of trialkyl or triarylsiloxy metal-containing compounds have been prepared. These compounds are tabulated in Table V. The condensation reactions used for the preparation of these compounds involve the following reaction combinations:

1. Metal and silanol.
2. Metal alkoxide and silanol.
3. Metal halide and silanol.
4. Metal halide and sodium silanolate.
5. Metal oxide and disiloxane.
6. Metal oxide and silanol.
7. Metal acid and silanol.
8. Silver salt and chlorosilane.
9. Metal acid and chlorosilane.
10. Metal acid and alkoxysilane.

Other trialkyl and triarylsiloxy compounds are known; these include the alkalimetal salts, sulfates (42), phosphates (42), perchlorates (93), and intermediate siloxy-titanium (94, 95) and siloxy-vanadium (83) compounds.

TABLE V

METAL SILOXY COMPOUNDS

Compound	Method of Preparation	Melting or Boiling Point in ^{o}C	Reference
$(Me_3SiO)_3B$	9, 10	b.p. 90	73, 74
$(Et_3SiO)_3B$	6	b.p. 152-4/3 mm	75
$(Et_3SiO)_3Al$	1	m.p. 150	69
$(Ph_3SiO)_3Al$ (?)	2	m.p. 75-80	76
$(Me_3SiO)_4Ti$	2, 3, 4	b.p. 60/0.1 mm	77, 78, 79
$(Me_2EtSiO)_4Ti$	2	b.p. 86/0.1 mm	79
$(MeEt_2SiO)_4Ti$	3	b.p. 120/0.1 mm	80
$(Et_3SiO)_4Ti$	3	m.p. 110	80
$(Me_2\underline{n}PrSiO)_4Ti$	2	b.p. 112/0.2 mm	79
$(Me_2\underline{i}PrSiO)_4Ti$	2	b.p. 115/0.2 mm	79
$(Me_2PhSiO)_4Ti$	3	b.p. 274-5/7 mm	81
$(MePh_2SiO)_4Ti$	3	b.p. 370-4/6 mm	81
$(Ph_3SiO)_4Ti$	4	m.p. 480 (decomp.)	80
$(Me_3SiO)_3VO$	4, 6	b.p. 118-20/18 mm	82, 83
$(Me_2EtSiO)_3VO$	4, 6	b.p. 124-6/7 mm	82
$(MeEt_2SiO)_3VO$	4, 6	b.p. 169-70/5 mm	82
$(Et_3SiO)_3VO$	4, 6	b.p. 198-201/13 mm	82
$(Et_2PhSiO)_3VO$	4, 6	b.p. 263-8/0.1 mm	82

Continued

TABLE V - Continued

Compound	Method of Preparation	Melting or Boiling Point in ^{o}C	Reference
$(Ph_3SiO)_3VO$	4,6	m.p. 228	82
$(Me_3Si)_2CrO_4$	5	b.p. 60/0.2 mm	84, 85
$(Ph_3Si)_2CrO_4$	6	m.p. 154-5	86
$(Ph_3SiO)_4Ge$	4	m.p. 472 (decomp.)	87
$(Et_3SiO)_4Sn$	4	b.p. 200-2/4 mm	88
$(Ph_3SiO)_2SnMe_2$	6	m.p. 165-6	72
$(Ph_3SiO)_4Sn$	4	m.p. 322 (decomp.)	88
$(Me_3SiO)_4Zr$	4	m.p. 152	89
$(Me_2EtSiO)_4Zr$	4	m.p. 105	89
$(MeEt_2SiO)_4Zr$	4	m.p. 30	89
$(Et_3SiO)_4Zr$	4	b.p. 103/0.5 mm	89
$(Me_2\underline{n}PrSiO)_4Zr$	4	m.p. 60	89
$(Me_2\underline{i}PrSiO)_4Zr$	4	b.p. 110/0.1 mm	89
$(Ph_3SiO)_4Zr$	4	m.p. 410 (decomp.)	87
$(Ph_3SiO)_4Hf$	4	m.p. 383 (decomp.)	87
$(Me_3SiO)_5Nb$	4	?	89
$(Me_2EtSiO)_5Nb$	4	?	89
$(Me_3SiO)_5Ta$	4	m.p. 80	89
$(Me_2EtSiO)_5Ta$	4	m.p. 135	89

Continued

TABLE V - Continued

Compound	Method of Preparation	Melting or Boiling Point in ^{o}C	Reference
$(MeEt_2SiO)_5Ta$	4	m.p. 180	89
$(Et_3SiO)_5Ta$	4	m.p. 210	89
$(Me_2\underline{n}PrSiO)_5Ta$	4	b.p. 170/0.1 mm	89
$(Me_2\underline{i}PrSiO)_5Ta$	4	m.p. 180	89
$(Me_3Si)ReO_4$	5, 8	m.p. 80	90
$(Me_3SiO)_2Pb$	6	?	91
$(Et_3SiO)_2Pb$ (?)	6	?	92

Symbols: Me = methyl, Et = ethyl, nPr = n-propyl, iPr = isopropyl, Ph = phenyl.

The melting point is given for materials which are solid at room temperature and the boiling point is given for liquids.

In general, the trialkylsiloxy compounds can be hydrolyzed to the silanol or disiloxane by water with varying difficulty (89). With the exception of bis(trimethylsilyl)chromate which explodes on heating, all the compounds have better than average thermal stability.

The two chromates in Table V are important because of later work. Schmidt and Schmidbaur (84) have prepared bis(trimethylsilyl)chromate, but full characterization of the compound is not reported. The patent of Granchelli and Walker (86) indicates the preparation of bis(triphenylsilyl)chromate based on analytical data. A more complete discussion of these compounds will be found in a later section.

EXPERIMENTAL

Preparation of Reactants

A large variety of organosilicon compounds are commercially available and have been utilized in this work. The major commercial sources are the Dow-Corning Corporation, Midland, Michigan, and Anderson Chemical Company, Weston, Michigan. A new organosilicon compound, cyclohexyldiphenylsilanol, has been prepared.

Synthesis of Cyclohexyldiphenylsilanol.

$$Ph_2SiCl_2 + Li(cyclohex) \longrightarrow (cyclohex)Ph_2SiCl \xrightarrow[H_2O]{KOH,\ EtOH} (cyclohex)Ph_2SiOH$$

Cyclohexyllithium was prepared by the method of Nebergall and Johnson (96). To this reagent 25.36 g (0.1 mole) of diphenyldichlorosilane in 100 ml of petroleum ether was added dropwise with constant stirring over one hour while the reaction mixture was cooled with an ice bath. After addition of the dichlorosilane, the reaction mixture was refluxed for five hours. Unreacted lithium was then removed by filtration, excess cyclohexyllithium was destroyed with hydrochloric acid, the petroleum ether layer was separated, and the solvent removed by evaporation. No attempt was made to isolate the chlorosilane. When the resulting yellow-brown oil was added to 200 ml of boiling alcoholic potassium hydroxide, a precipitate of potassium chloride formed. The silanol was precipitated by adding 300 ml of water to the alcoholic solution, and the crude product was separated by filtration. Recrystallization from benzene-alcohol gave an oily product from which the remainder of the oil was removed by a simple extraction method. A small portion of the product was placed in the bottom of a fluted filter paper supported by a short-stem funnel. The filter paper tip was immersed in about 1 mm of hexane, and the funnel was covered with a watch glass. Within three hours the oil was carried to the top of the filter paper. After recrystallization from hexane, the product had a melting point of 143°C. The yield of the cyclohexyldiphenylsilanol was 7.1 g (25% of theory). Its molecular weight was found to be 290 (theory, 282). Analysis of the compound gave 77.55% C (theory, 77.66%) and 7.94% H (theory, 7.85%).

Preparation of Tricyclohexylsilanol. The method of Nebergall and Johnson (96) was used to prepare tricyclohexylsilanol. Cyclohexyllithium was prepared by the reaction of cyclohexylchloride with lithium in petroleum ether. A solution of 17 g (0.1 mole) of silicon tetrachloride in 50 ml of petroleum ether was added to cyclohexyllithium at 0°C over a period of 1.5 hours. The mixture was allowed to stand at room temperature overnight and then was refluxed for an additional two hours. Excess lithium was separated by filtration, and excess cyclohexyllithium was destroyed with 6 N hydrochloric acid. The organic layer was separated and evaporated to an oil which was crystallized from glacial acetic acid. The white, sticky solid was added to 200 ml of boiling 5% alcoholic potassium hydroxide, and 300 ml of water was added to precipitate the silanol. The product was separated by filtration and recrystallized from a mixture of acetone and petroleum ether (yield, 5.8 g crude product; m.p. 173-5°C). Recrystallization from petroleum ether gave 4.6 g (16% of theory) of product melting at 176-8°C. Nebergall

and Johnson report 52% yield, while Eaborn (97) reports 13% yield using the same method of preparation.

Preparation of Dicyclohexylsilanediol. An attempt to prepare tricyclohexylsilanol by the method described above, except for the omission of refluxing, gave 6.2 g (27% yield) of dicyclohexylsilanediol, m.p. 164-5°C (reported, 164-5°C). Dicyclohexylsilanediol was also prepared by use of a four-to-one ratio of cyclohexyl chloride and silicon tetrachloride.

Preparation of p-Tolyldiphenylsilanol. Speck's method (98) of treating excess of the Grignard reagent of p-bromotoluene with diphenyldichlorosilane in ether solution was used to prepare this compound. The chlorosilane was separated, distilled, and then hydrolyzed by shaking its ether solution with water. The silanol (yield, 21%) was purified by sublimation and recrystallization from petroleum ether. The melting point of the silanol was 83-85°C (reported, 87-88°C).

Preparation of Tri(1-naphthyl)silanol. This compound was prepared by the reaction of naphthyllithium with silicon tetrachloride as described by Gilman and Brannen (99). The chlorosilane was separated and recrystallized with a Soxhlet extractor and ethyl alcohol as solvent. Hydrolysis was carried out by adding water to the chlorosilane in 5% alcoholic potassium hydroxide. The resulting silanol was recrystallized from ethyl alcohol to give a product melting at 197-199°C (reported, 208-209°C).

Preparation of Methyldiphenylsilanol. A mixture of methyldiphenylsilanol and s-dimethyltetraphenyldisiloxane was prepared by the hydrolysis of methyldiphenylchlorosilane in aqueous ammonia. The silanol was separated by distillation (b.p. 120-122°C at 1 mm).

Preparation of Hexaphenylcyclotrisiloxane and Octaphenylcyclotetrasiloxane. An attempt was made to prepare hexaphenylcyclotrisiloxane by heating diphenylsilanediol to 180°C as described by Kipping (100), but only an oil was obtained which apparently contained polysiloxanes.

The method of Burkhard (101) gave better results for the preparation of hexaphenylcyclotrisiloxane. Ten grams of diphenylsilanediol was dissolved in 200 ml of ethyl ether, and 5 ml of concentrated hydrochloric acid was added. The reaction mixture was allowed to reflux on a steam bath for three hours, and the ether was then removed. The resulting mass was taken up in benzene-ethanol and filtered; on cooling, two crops of crystals separated. The crude product was recrystallized from acetone to give 3.8 g of hexaphenylcyclotrisiloxane, m.p. 188-89°C (reported, 188-89° and 190°C). This compound was also prepared by the reaction of 1 mole of diphenyldichlorosilane and 2 moles of diphenylsilanediol in chloroform.

The method described by Burkhard (101) was used for the preparation of octaphenylcyclotetrasiloxane. Diphenylsilanediol was dissolved in boiling ethanol and a few drops of aqueous potassium hydroxide were added. Within 15 minutes crystals separated from the boiling mixture. After cooling, the product was removed by filtration and recrystallized from benzene-ethanol. The needles obtained had a melting point of 201-201.5°C (reported, 201-202°C).

Preparation of Hexaphenyltrisiloxane-1,5-diol. The method of Kipping and Robison (102) was used to prepare hexaphenyltrisiloxane-1,5-diol in very poor yield. Diphenyldichlorosilane was hydrolyzed in concentrated aqueous ammonia and the product was separated by recrystallization from a mixture of chloroform and petroleum ether.

Hornbaker and Conrad (70) have reported that the major product of the reaction of disodium diphenylsilanediolate with zinc chloride is hexaphenyltrisiloxane-1,5-diol. They also prepared hexaphenyltrisiloxane-1,5-diol from the reaction of diethylzinc with diphenylsilanediol.

Hexaphenyltrisiloxane-1,5-diol was prepared in this investigation by the reaction of twenty grams of diphenylsilanediol and twelve grams of fused zinc chloride in about 300 ml of acetone. The mixture was heated to reflux for three hours and the acetone was evaporated. The product was taken up in benzene, and after boiling and filtering the mixture, the solvent was removed from the filtrate and the oily residue was taken up in chloroform. Petroleum ether was added to the chloroform solution until it became turbid. The solution was separated from an oil by decantation and was allowed to crystallize overnight. The white crystalline product was separated by filtration, giving 13 g of crude product (m.p. 94-100°C). The product was recrystallized twice from chloroform and petroleum ether to give 5.2 g of product (m.p. 110-111°C; reported, 111°C).

Preparation of Chromyl Chloride. A mixture of chromium(VI) oxide and concentrated hydrochloric acid was dehydrated with concentrated sulfuric acid at 0°C to give chromyl chloride (3). The chromyl chloride layer of the reaction mixture was separated and purified by distillation (b.p. 115°C). The distillate was stored in a brown glass bottle fitted with a Teflon lined cap.

Preparation of Silylchromates

Preliminary to the study of polycondensation reactions, an investigation of the synthesis and properties of compounds in the general class $(R_3Si)_2CrO_4$ was undertaken. 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.

Schmidt and Schmidbaur (84) recently have 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 Walker (86) have patented a method for the preparation of 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.

The following general reaction was used for the preparation of the silylchromates: $2R_3SiOH + CrO_3 \xrightarrow[heat]{CH_2Cl_2} (R_3Si)_2CrO_4 + H_2O$ Reactions were carried out by adding 3 g of chromium(VI) oxide to a solution of about 6 g of the silanol in 150-200 ml of methylene chloride and heating the mixture to reflux (40°C) with stirring. The reactions were conducted in a 300 ml single-necked flask fitted with a reflux condenser. The reaction mixture was heated with a heating mantle and stirred by use of an external magnetic stirrer. In general, the reaction was quite rapid. At the end of three hours 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.

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 triphenylchlorosilane 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. Stirring the reaction mixture only seemed to shorten reaction time.

The second reaction was carried out in refluxing carbon tetrachloride with calcium oxide present to remove the hydrochloric acid formed by the reaction and to destroy the slight excess of chromyl chloride used. By the reaction

$$2Ph_3SiOH + CrO_2Cl_2 \longrightarrow (Ph_3Si)_2CrO_4 + 2HCl$$

the crude product was obtained in a 99% yield. Cohydrolysis of triphenylchlorosilane and chromyl chloride was used in an attempt to prepare the silylchromate. This reaction was carried out by rapidly mixing a carbon tetrachloride solution of triphenylchlorosilane and chromyl chloride with a two-fold excess of water. Only a small amount of the silylchromate was formed by this reaction; the major product was unreacted triphenylchlorosilane. The use of a base did not improve the yield of the silylchromate. Because of the success of other methods, cohydrolysis was not investigated further.

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. Several attempts were made to recrystallize bis(triphenylsilyl)chromate from diethyl ether, but the ether solution turned black after a short time. Analytical data are recorded in Table VI.

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

Bis(cyclohexyldiphenylsilyl)chromate. The preparation of bis(cyclohexyldiphenylsilyl)chromate was effected by the general method. After filtering off excess chromium(VI) oxide, the solvent was evaporated from the filtrate. The residue was treated with 10 ml of pentane to dissolve the silylchromate, and the less soluble silanol was filtered off. This extraction operation was repeated five times, and the filtrate was evaporated to give a red-orange solid. The crude product had a melting point of 81-83°C and a molecular weight of 614 (calculated for bis(cyclohexyldiphenylsilyl)chromate, 647). This product was again extracted with five portions of pentane and the filtered extract was

TABLE VI

ORGANOSILYL CHROMATES PREPARED

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-tolyldiphenyl-silyl)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(cyclohexyldiphenyl-silyl)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	

partially evaporated to crystallize out unreacted silanol. After evaporation of the solvent from the filtrate, the resulting orange solid was dried under vacuum at room temperature.

Material so purified had a melting point of 84-85°C. Solid bis(cyclohexyldiphenylsilyl)chromate does not appear to decompose at its melting point but is unstable at 100°C. The yield after purification was 2.7 g (47%). Analytical data are recorded in Table VI. The purity of the silylchromate 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 silylchromate 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.

Bis(tricyclohexylsilyl)chromate. This compound was also prepared by the general method described on page 43. It was recrystallized twice from methylene chloride and washed with petroleum ether. The red-orange product was dried *in vacuo* at room temperature and had a melting point of 125-6°C. It is unstable above its melting point and is unique in that it differs in color and in absorption spectrum (Figure 4, page 71) from the other compounds in this series.

Bis(trimethylsilyl)chromate. An explosion resulted when an attempt was made to follow Schmidt and Schmidbaur's procedure (84) for the preparation of bis(trimethylsilyl)chromate by refluxing hexamethyldisiloxane containing suspended chromium(VI) oxide. Therefore a solvent was used to avoid overheating. 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 of the distillation was stable when stored at -78°C in the dark, but at room temperature and in the absence of light it showed appreciable signs of decomposition within three hours.

This compound was also prepared by the reaction of the silanol with chromium(VI) oxide in methylene chloride. In this case, the rate of formation of the silylchromate is faster than when the disiloxane is used as a reactant.

The infrared (Appendix 2, Figure 14), visible, and ultraviolet (Figure 2, page 69) spectra were recorded for this compound in solution without isolation of the compound; this was accomplished by preparing the silylchromate from the silanol and excess chromium(VI) oxide in the appropriate spectroscopic solvent.

An attempt to determine the molecular weight of bis(trimethylsilyl)chromate in benzene failed because of reaction of the silylchromate with benzene.

Bis(methyldiphenylsilyl)chromate. Methyldiphenylsilanol was allowed to react with chromium(VI) oxide according to the general method (page 43). The resulting red liquid, possibly bis(methyldiphenylsilyl)-chromate, decomposed at 85°C at 0.3 mm Hg pressure when an attempt was made to distill it. Vacuum evaporation into a trap cooled with liquid air was unsuccessful. Because of its instability, this product was not investigated further.

Bis[tri(1-naphthyl)silyl]chromate. An attempt was made to prepare a chromate from tri(1-naphthyl)silanol. Brown noncrystalline materials were obtained. Crystallization from methylene chloride was attempted, but infrared spectra of the fractions failed to show a decrease in complexity. Attempts at chromatographic separation were likewise unsuccessful. A model of the compound suggests that steric hindrance might well prevent its formation.

Properties of Silylchromates. All of the silylchromates 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 silylchromates, while bis(trimethylsilyl)chromate decomposes most rapidly on exposure to light. All except the aliphatic silylchromates may be safely stored in the dark at room temperatures.

The aliphatic silylchromates and bis(cyclohexyldiphenylsilyl)-chromate are decomposed by concentrated nitric acid, and all are decomposed by a mixture of concentrated sulfuric and nitric acid. 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 silylchromates 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.

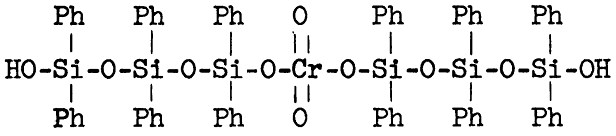
The silylchromates are very soluble in methylene chloride, carbon tetrachloride, chloroform, acetone, and ethanol. With the exception of bis(cyclohexyldiphenylsilyl)chromate and the aliphatic silylchromates, they are all only slightly soluble in cyclohexane and aliphatic hydrocarbons.

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.

The presence of electron donor groups in the silylchromates seems to lower stability. Thus bis(trimethylsilyl)chromate is explosive when heated, and bis(methyldiphenylsilyl)chromate and bis(p-tolyldiphenylsilyl)chromate decompose easily. Because of the higher stability of bis(triphenylsilyl)chromate, polymerization reactions have been studied using diphenylsilanediol.

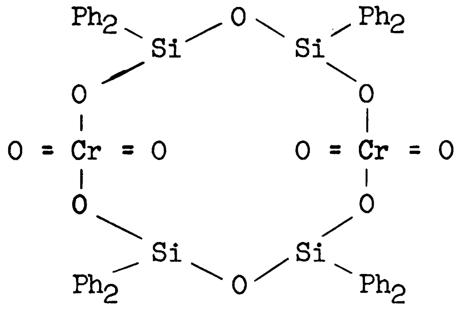
Reactions of Diphenylsilanediol and Its Condensation Products With Chromium(VI) Compounds

The reaction of diphenylsilanediol with chromium(VI) oxide or chromyl chloride in methylene chloride or carbon tetrachloride has been studied. Although polysilylchromates with repeating Cr-O-Si linkages have not been obtained owing to the tendency of diphenylsilanediol to undergo self-condensation, two interesting silylchromates have been prepared. Compound I is a dark orange amorphous substance containing six silicon atoms for every chromium atom; compound II is a yellow-orange crystalline solid having a silicon-to-chromium ratio of two-to-one. These compounds are:



$$HO-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}-O-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}-O-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}-O-\underset{O}{\overset{O}{\underset{||}{\overset{||}{Cr}}}}-O-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}-O-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}-O-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}-OH \qquad (I)$$

and



(II)

A study has been made of the reactions of chromyl chloride with hexaphenylcyclotrisiloxane and with octaphenylcyclotetrasiloxane to determine if addition of the chromyl group to cyclic siloxanes is possible. Addition occurred in low yield with the trimer, but the tetramer did not react.

The reaction of hexaphenyltrisiloxane-1,5-diol and chromyl chloride gives a small amount of compound I and largely hexaphenylcyclotrisiloxane. Tetraphenyldisiloxane-1,3-diol and chromium(VI) oxide gives compound II.

Reaction of Diphenylsilanediol and Chromyl Chloride. The reaction of chromyl chloride and diphenylsilanediol has been carried out under various conditions. The principal product of this reaction is compound I, with smaller amounts of compound II and hexaphenylcyclotrisiloxane. The variation of reaction time, method of addition, and solvent only varies the yield of the above products. Direct mixing of the reactants for thirty minutes, followed by isolation of products, was found to be the most convenient reaction method. The following is a typical reaction.

A slurry of 30 g of diphenylsilanediol and 200 ml of methylene chloride was added portion-wise to 12 ml of chromyl chloride in 100 ml of methylene chloride contained in a single-neck 500 ml flask. The flask was fitted with a condenser and heated to reflux for 30 minutes. During this period, the mixture was stirred by a magnetic stirrer. Excess chromyl chloride was destroyed by adding about 30 g of anhydrous sodium bicarbonate in small portions to the reaction mixture. The reaction mixture was then filtered through a fluted filter to remove the bicarbonate. The filtrate was reduced to about 50 ml, cooled, and then filtered to remove crystalline compound II. The filtrate was evaporated to near dryness and then treated with a mixture of methylene chloride and petroleum ether and filtered to remove compound II. This operation was repeated once more. The yield of compound II was 5.5 g (16% based on the diol). The filtrate was dried in vacuo at room temperature to give 17.5 g of crude compound I (58% based on the diol). The molecular weight of this product was 1090. This material was once more treated with methylene chloride and petroleum ether and filtered. The filtrate was dried in vacuo for two days. The resulting product had a molecular weight of 1330 and contained 12.97% silicon, 4.93% chromium, 65.80% carbon, and 4.80% hydrogen. The structure proposed for compound I corresponds to a molecular weight of 1307 and to the composition Si, 12.88%; Cr, 3.98%; C, 66.13%; and H, 4.78%. The high results for chromium and the molecular weight may be accounted for by a small amount of compound II which is not very soluble in benzene and which has a high chromium content.

The above reaction was varied by use of carbon tetrachloride as a solvent, addition of the diol by use of a Soxhlet extractor, longer reaction times, and use of benzene to destroy the excess chromyl chloride. The use of carbon tetrachloride as a solvent gave compound I in a slightly lower yield and enabled a better separation of compound II because of its lower solubility in carbon tetrachloride. The addition of the diol by use of a Soxhlet extractor required a longer reaction time, and the Soxhlet thimble was attacked by chromyl chloride which distills with the solvent. Longer reaction time and use of benzene to destroy the excess chromyl chloride resulted in a reduction of the yield of compound I to 18%, along with an increase in the amount of decomposition products.

Two other methods were used to purify compound I. Partition chromatography using columns of cellulose, sugar, and anhydrous sodium bicarbonate resulted in only partial removal of impurities. Absorption chromatography using columns of activated alumina and charcoal was unsuccessful because compound I decomposed on these columns. The best method for purifying compound I was a mixed solvent technique. The product was dissolved in a minimum amount of methylene chloride and reprecipitated by addition of hexane. The hexane mixture was boiled to remove methylene chloride and increase the solubility of the impurities, after which the solution was decanted from the separated oil. It was also possible to obtain compound I by cooling the hexane solution which was decanted from the oil. Treatment by this method reduced the yield of compound I considerably. This method, however, removes all of compound II and as high as 2 g of hexaphenylcyclotrisiloxane (based on 30 g of the diol).

The analytical data for compound I is given in Table VII. Repeated purification lowers the chromium content of the compound since compound II, with a higher chromium content, is removed.

Reaction of Diphenylsilanediol and Chromium(VI) Oxide. The reaction of diphenylsilanediol and chromium(VI) oxide has been carried out in methylene chloride, carbon tetrachloride, and glacial acetic acid. The principal product isolated was compound II, with lesser amounts of compound I except when glacial acetic acid was used as a solvent.

TABLE VII

ANALYTICAL DATA FOR COMPOUND I FROM THE REACTION OF DIPHENYLSILANEDIOL WITH CHROMYL CHLORIDE

Run	Solvent	% Si	% Cr	% C	% H	Molecular Weight
1	CCl_4	.....	....	.....	....	1029
	Repeated purification	.....	....	.....	....	1134
	Repeated purification	13.22	4.16	.....	....	1127
2	CCl_4	13.48	4.00	.....	....	1047
	Repeated purification	.....	....	.....	....	1303
	Repeated purification	13.63	3.89	.....	....	1284
3	CCl_4	12.47	7.12	.....	....	1281
	Repeated purification	.....	....	.....	....	1278
	Repeated purification	12.92	5.48	.....	....	1153
4	CCl_4	13.25	4.95	.....	....	1315
	Repeated purification	13.02	4.73	.....	....	....
5	CH_2Cl_2	13.54	3.82	.....	....	....
6	CH_2Cl_2	.....	....	.....	....	1090
	Repeated purification	12.97	4.93	.....	....	1330
7	CH_2Cl_2	13.10	4.35	65.80	4.80	1190
8	CH_2Cl_2	13.38	3.44	66.25	4.75	1110
9	CH_2Cl_2	13.29	4.20	65.94	4.68	1180
Calculated for compound I		12.88	3.98	66.13	4.78	1307

The reaction of the diol and chromium(VI) oxide in methylene chloride served as the best method for the preparation of compound II. A slurry of 30 g of diphenylsilanediol and 200 ml of methylene chloride was added in small portions to about 15 g of chromium(VI) oxide covered with 200 ml of methylene chloride. During the addition, the mixture was brought to reflux temperature by heating with a mantle; magnetic stirring was used. The reaction was allowed to continue for 30 minutes after the addition of the diol. The reaction mixture was filtered while hot to remove excess chromium(VI) oxide. Solvent was removed from the filtrate to give a total volume of about 50 ml. This was then cooled and filtered to remove a brown mass. The filtrate was further concentrated, cooled, and filtered twice more to remove the brown material. This brown mass was washed with two 25 ml portions of precooled methylene chloride to give 18.6 g (54% based on the diol) of a yellow-orange crystalline material, compound II. Compound II is easily recrystallized from methylene chloride to give a yellow-orange solid. The filtrate from which compound II was separated was evaporated to give 5.4 g of compound I (18% yield). Table VIII (page 58) gives the elemental analysis of compound II.

When carbon tetrachloride is used as a solvent, the yield of compound I is increased and that of compound II diminished. Compound II is not very soluble in carbon tetrachloride. The reaction of the diol and a solution of chromium(VI) oxide in glacial acetic acid gave a very small amount (3.3% yield) of compound II and a large amount of green reduction products (not characterized).

Characteristics of Compounds I and II. Numerous determinations of molecular weight and elemental analysis of compound I have been made and are reported in Table VII. 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 (page 50).

The infrared spectrum of this compound (Appendix 2, Figure 16) shows weak OH, strong Si-O-Si, and strong Cr=O absorptions. The presence of the OH group was determined only by the OH absorption. A strong OH absorption was obtained by using more concentrated solutions or pressing a sample between sodium chloride plates. Several attempts were made to prepare the acetyl and benzoyl derivatives of this compound by reaction with acetyl chloride and benzoyl chloride, but decomposition of compound I took place; the only product isolated and identified was hexaphenylcyclotrisiloxane. A solution of this compound in anhydrous benzene did not react with sodium metal.

Compound I is repellent to cold water and slowly attacked by hot water. It can be hydrolyzed completely by adding water to an acetone solution. In this case, the only product isolated was hexaphenylcyclotrisiloxane.

This compound is sticky when freshly prepared and is easily drawn into fibers. On standing, it hardens into a yellow-brown glassy substance. It is quite stable at room temperature in the absence of light. In the presence of light, it slowly decomposes to a black mass from which hexaphenylcyclotrisiloxane has been isolated. Even in the glassy state, the compound is easily melted with the heat of the hand. The differential thermal analysis of this compound (Figure 1) shows that it undergoes fusion from room temperature to 275°C, where it begins to decompose. The decomposition reaches a maximum at 460°C. The decomposition products appear to be chromium(III) oxide and silicon dioxide.

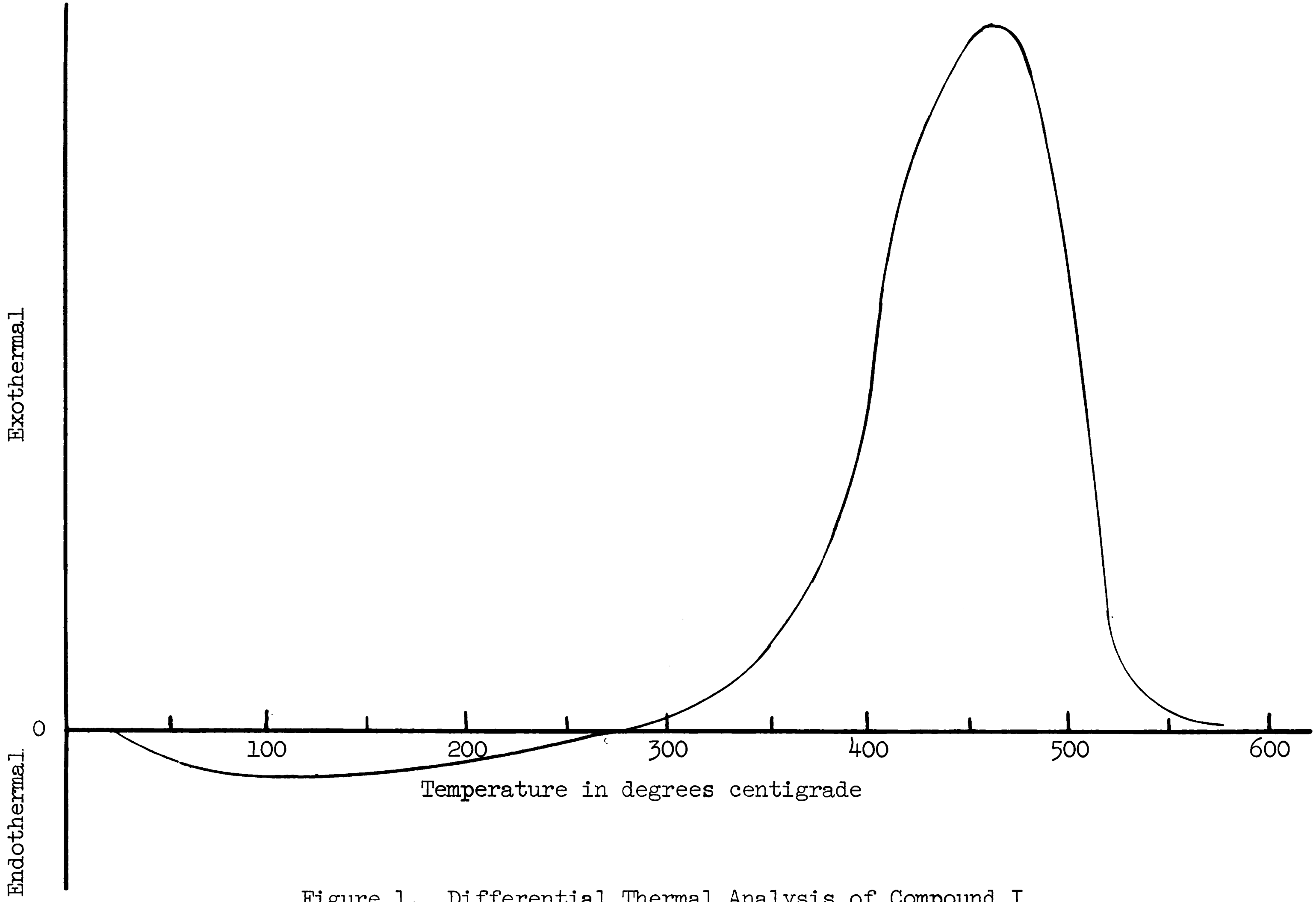


Figure 1. Differential Thermal Analysis of Compound I

The x-ray diffraction pattern of a fiber showed broad diffraction at 10.3 and 4.5 A, which indicates a very low order of crystallinity. The intrinsic viscosity in 3% benzene solution was determined to be 0.0192 dl/g.

Compound I is highly soluble in carbon disulfide, benzene, toluene, methylene chloride, carbon tetrachloride, and chloroform. It is only slightly soluble in aliphatic hydrocarbon solvents. I appears to be partially decomposed by acetone. The last traces of the soluble solvents are very difficult to remove from the compound. Drying *in vacuo* is facilitated by continually turning up new surfaces since diffusion of the solvent to the dried surface does not take place.

The analytical data for compound II is given in Table VIII.

TABLE VIII

ELEMENTAL ANALYSIS OF COMPOUND II

Element	% Calculated (Structure II)	% Found
Carbon	58.05	58.16, 58.14
Hydrogen	4.06	4.17, 4.29
Chromium	10.48	10.42, 10.47, 10.60, 10.40, 10.37, 10.49
Silicon	11.30	11.58, 11.59, 11.27, 11.36, 11.51, 11.53

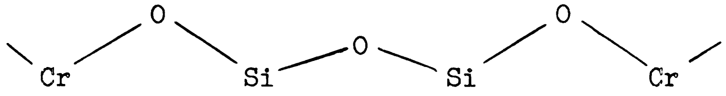
The molecular weight of compound II using diphenyl as a cryoscopic solvent (m.p. 71°C, K_f 8.46) was 1155, 1180, and 1170 ± 100 in separate determinations. The molecular weight in benzene was found to be 1030, 1030, and 1170 ± 100. The low accuracy of these determinations is due to low solubility of compound II in the cryoscopic solvents. The value 1170 may be in error since a slight turbidity of the solution was detected (this would give a high value). Higher values of the molecular weights were obtained, but in each case not all the solute had dissolved in the solvent. A search for more satisfactory solvents failed. The solute is either insoluble or reacts with the common solvents (12) used for molecular weight determinations.

The elemental analysis indicates a ratio of two silicon atoms for every chromium atom in this compound and is consistent with the basic unit, $\left[(Ph_2SiO)_2CrO_3\right]$. The molecular weight of this unit is 496.5, suggesting that two units are present in compound II.

Compound II may be hydrolyzed by adding water to its acetone solution. Tetraphenyldisiloxane-1,3-diol has been isolated from the hydrolysis products in 84% yield. This information indicates that the disiloxy group exists in compound II.

The infrared spectrum (Appendix 2, Figure 18) of this compound shows no OH absorption, medium Si-O-Si absorption characteristic of strain-free siloxanes, and Cr=O absorptions. These data are consistent with structure II (page 50).

The molecular weight of this compound is 993; its elemental composition is given in Table VIII. A rough model of this structure using bond angles and distances of strain-free cyclic siloxanes (44) indicates that the above structure is plausible and probably has a "crown" conformation:



This compound 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. The compound is sparingly soluble in cold methylene chloride, chloroform, carbon tetrachloride, carbon disulfide, and acetonitrile.

The infrared spectrum of this compound does not decrease in complexity on continued recrystallization from methylene chloride. The x-ray powder diffraction pattern is given in Appendix 3.

Compound II in anhydrous benzene does not liberate hydrogen when sodium metal is added. This compound is also repellent to water but can be hydrolyzed from homogeneous solution. Compound II does not react further with chromium(VI) oxide in methylene chloride, but does react with excess diphenylsilanediol to give a product with the characteristics of compound I.

Reaction of Cyclic Siloxanes with Chromyl Chloride. The addition of chromium(VI) compounds to cyclic siloxanes has been studied because of its relationship to the complex reaction of diphenylsilanediol with chromium(VI) compounds. It was found that diphenylsilanediol dissolves in methylene chloride in the presence of a trace of chromyl chloride to give hexaphenylcyclotrisiloxane and an oil with a degree of polymerization of 3.6. Diphenylsilanediol is only slightly soluble in methylene chloride even at reflux, while its condensation products are soluble in this solvent. This indicates that condensation of the diol takes place under the influence of chromyl chloride.

The reaction of hexaphenylcyclotrisiloxane with chromyl chloride and a small amount of water was carried out several times in methylene chloride solution in the manner described for diphenylsilanediol using a one-to-one ratio of siloxane and chromyl chloride. The length of the reaction was varied between 12 and 30 hours. The reaction mixture was filtered, evaporated, and treated with hexane to remove unreacted hexaphenylcyclotrisiloxane. The treatment of the filtrate with hexane was repeated several times, but complete removal of the siloxane is very difficult. The products isolated had molecular weights from 690 to 990. The molecular weight of hexaphenylcyclotrisiloxane is 598, and compound I is 1307. The yield of the product was less than 10%. In general, the yield of the product increased with increased reaction time and with the use of sodium hydroxide to supply water and destroy excess chromyl chloride. The purified product is similar in appearance and has the same x-ray diffraction pattern as compound I. The lower molecular weight is probably due to incomplete removal of the siloxane. Final removal of the siloxane probably could be effected by the above purification procedure, but the amount of chromium-containing product is decreased drastically.

Hexaphenylcyclotrisiloxane does not react with chromyl chloride in moist carbon tetrachloride; this may be due to the insolubility of the siloxane in carbon tetrachloride. It also does not react with chromyl chloride under anhydrous conditions.

Apparently addition takes place, but only to a very small extent; it is catalyzed by the presence of a base such as water or sodium hydroxide. A comparison of the ease of formation of compound I in the reaction of diphenylsilanediol with chromyl chloride and the difficulty of addition of chromyl chloride to hexaphenylcyclotrisiloxane leads to the conclusion that the latter reaction is not involved in the reaction of the diol with chromyl chloride.

The reaction of octaphenylcyclotetrasiloxane with chromyl chloride and water has also been attempted in the same manner as described for hexaphenylcyclotrisiloxane, but the tetrasiloxane was recovered largely unchanged. A very small amount (4.5%) of a brown product with an apparent molecular weight of 875 was obtained; the molecular weight of octaphenylcyclotetrasiloxane is 793. It is therefore concluded that the tetrasiloxane is not significantly attacked by chromyl chloride. This may be due to the high stability of this compound.

Reaction of Hexaphenyltrisiloxane-1,5-diol and Tetraphenyldisiloxane-1,3-diol with Chromium(VI) Compounds. The reaction of hexaphenyltrisiloxane-1,5-diol and chromium(VI) oxide was carried out in methylene chloride solution for three hours. The methylene chloride-hexane method was used to separate 65% of the starting material from a small amount of black amorphous material. Compound I was not formed.

A product with the characteristics of compound I was obtained from the reaction of 11 g of hexaphenyltrisiloxane-1,5-diol with excess chromyl chloride in methylene chloride. The reaction was carried out for three hours, after which the excess chromyl chloride was destroyed with sodium bicarbonate and the mixture was filtered. Three grams of the product was separated from three grams (yield, 28%) of hexaphenylcyclotrisiloxane by the methylene chloride-hexane method. The infrared spectrum of the product was similar to that of compound I but the molecular weight was determined to be 841, which is lower than the value of 1307 required of compound I.

The reaction of tetraphenyldisiloxane-1,3-diol and chromium(VI) oxide was carried out for one hour in methylene chloride solution. Compound II was recovered in 68% yield from the reaction mixture. No other products were isolated. The yield of compound II in this case is comparable to that obtained in the reaction of diphenylsilanediol with chromium(VI) oxide.

Reaction of Diphenyldialkoxysilanes with Chromyl Chloride

The reaction of chromyl chloride and dialkoxysilanes was undertaken to determine if condensation could take place through evolution of ethyl chloride. The results of the study of this reaction indicate that chromyl chloride attacks the alkoxy group to form an Étard complex which, when decomposed with water, gives largely polysiloxanes. The reaction of chromyl chloride and diphenyldiethoxysilane in methylene chloride serves as an example of the general reaction.

When 13 ml of chromyl chloride were added to a solution of 30 g of diphenyldiethoxysilane in 300 ml of methylene chloride, a reaction took place immediately. This reaction was almost violent, but it subsided to give a red-brown mixture. Water was added to decompose excess chromyl chloride, the methylene chloride layer was separated, and the solvent was removed to leave a viscous, brown oil. By dissolving the product in methylene chloride and reprecipitating it with hexane, two grams of hexaphenylcyclotrisiloxane was separated and 13 g of product remained. Its molecular weight was determined to be 707. Further treatment with methylene chloride and hexane removed less than one gram of hexaphenylcyclotrisiloxane from the product and raised its molecular weight to 718. Analysis gave 13.90% silicon and 0.70% chromium, which corresponds to one chromium atom for every thirty-seven silicon atoms. This ratio is not reasonable in a pure compound with a molecular weight of 718. The calculated silicon content for diphenylsiloxane, $(Ph_2SiO)_{\underline{n}}$, is 14.15%.

The observed silicon content and that calculated for diphenylsiloxane are close enough to conclude that the product is composed mostly of polysiloxanes. The infrared spectrum of this product shows strong Ph-Si, Si-O-Si, and Si-O absorptions as expected for polydiphenylsiloxane.

Several attempts were made to distill the reaction product. In all cases a yellow oil with a molecular weight of 653 was separated by distillation. Hexaphenylcyclotrisiloxane (molecular weight 598) was the major compound of the distillate. The glassy residues of the distillations contained small amounts of chromium and had molecular weights as high as 2000.

The reaction of chromyl chloride and diphenyldiethoxysilane was carried out in carbon tetrachloride and, with inverse addition of reactants, in methylene chloride. The same product was obtained except that the content of hexaphenylcyclotrisiloxane was higher.

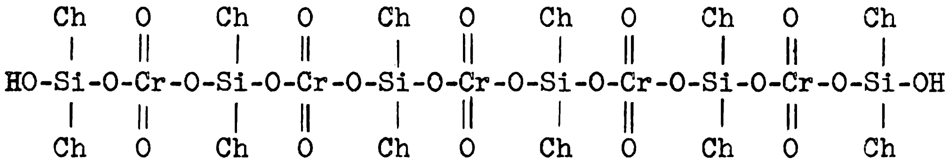
The reaction of chromyl chloride and diphenyldimethoxysilane under the same conditions as those for the diethoxysilane gave a very high yield of hexaphenylcyclotrisiloxane.

It can only be concluded that the reaction of chromyl chloride and diphenyldialkoxysilanes under the conditions described produces polysiloxanes. This reaction probably proceeds through the formation of an Étard complex between the chromyl chloride and the aliphatic groups of the alkoxide. The addition of water decomposes the Étard complex and cleaves the carbon-oxygen bond of the dialkoxysilane to produce polysiloxanes. Because of the acidic conditions, hexaphenylcyclotrisiloxane is the principal product.

The evidence for the formation of the Étard complex is the suspension of a brown solid (characteristic of Étard reactions) in the reaction mixture and the highly exothermic reaction when water is added to the reaction mixture.

Reaction of Dicyclohexylsilanediol with Chromium(VI) Oxide

The reaction of dicyclohexylsilanediol with chromium(VI) oxide was carried out in methylene chloride. Excess chromium(VI) oxide was added to a solution of 5.39 g of dicyclohexylsilanediol in 300 ml of methylene chloride and the reaction mixture was stirred at reflux temperature three hours even though the reaction appeared to be quite rapid. The mixture was then filtered to remove excess chromium(VI) oxide, and the solvent was removed from the filtrate to give a bright red, viscous oil. The oil was dissolved in pentane and filtered to remove unreacted dicyclohexylsilanediol. The pentane was partially evaporated from the filtrate and cooled. This was then filtered to remove very little of the diol. The pentane was removed from the filtrate and the product was dried *in vacuo* overnight. The resulting product (6.48 g) was a dark red, amorphous solid. The molecular weight of this product was 1690 ± 50. Analysis gave the following results: Si, 9.45%; Cr, 15.23%; C, 48.19%; H, 7.50%. The ratio of silicon to chromium is 1.15:1, and the ratio of carbon to silicon is 11.9:1. The following structure was found to fit these data (Ch = cyclohexyl):



$$\mathrm{HO-\underset{\underset{Ch}{|}}{\overset{\overset{Ch}{|}}{Si}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{Ch}{|}}{\overset{\overset{Ch}{|}}{Si}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{Ch}{|}}{\overset{\overset{Ch}{|}}{Si}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{Ch}{|}}{\overset{\overset{Ch}{|}}{Si}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{Ch}{|}}{\overset{\overset{Ch}{|}}{Si}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{Ch}{|}}{\overset{\overset{Ch}{|}}{Si}}-OH} \qquad \mathrm{(III)}$$

Structure *III* requires a molecular weight of 1780 and the following elemental composition: Si, 9.46%; Cr, 14.61%; C, 48.50%; H, 7.58%. The ratio of silicon to chromium is 1.20:1 and that of carbon to silicon is 12:1.

The yield of the above reaction based on structure *III* was 93%. Two previous runs of this reaction with less extensive purification have given a similar product in 100% yield. In one case, the crude product was isolated and analyzed without purification. The molecular weight was 1420, and the content of silicon and chromium was 9.26 and 13.37% respectively. The second reaction product was treated once with pentane and filtered to give a product with a molecular weight of 1700, a silicon content of 9.18%, and a chromium content of 15.60%.

The infrared spectrum (Appendix 2, Figure 20) of this compound shows weak OH absorption, strong Cr=O absorption, and a medium absorption

at 9.3μ, which may correspond to either Si-O-Si or cyclohexyl absorption. The possible presence of Si-O-Si absorption is not consistent with structure III. The possibility of the compound being a mixutre of siloxanes and chromates is precluded by the high molecular weight of the product and the unlikelihood of polydicyclohexylsiloxanes. The formation of an Si-O-Si linkage consistent with the 1.15 silicon-to-chromium ratio and the molecular weight is also unlikely.

Compound III decomposes on standing at room temperature in the dark to form a black, brittle, amorphous solid. The product shows considerable signs of decomposition within four days after preparation. Extraction with pentane and methylene chloride gives a product with a molecular weight of 1220 and the following composition: Si, 11.06%; Cr, 8.78%; C, 56.46%; and H, 9.08%. The ratio of silicon to chromium is 2.34:1, while the carbon-to-silicon ratio remains 11.9:1. The high silicon-to-chromium ratio is due to the presence of cyclohexylsilicon compound in the extracted product. The residue of the extraction is a black solid which is probably high in chromium content.

The formation of a mixture of products rather than a single compound is to be expected in a polycondensation reaction such as that which leads to compound III. Thus a mixture of larger and smaller chains than compound III may contribute to the number average molecular weight. Because of the low degree of polymerization involved, it is also possible that under the conditions of the reaction only compound III is formed; that is, bond breaking and bond making may be in equilibrium at the chain length corresponding to compound III.

Spectroscopic Data

Ultraviolet and Visible Spectra. The ultraviolet and visible absorption spectra (Figures 2, 3, 4) of the major products described previously were measured in methylene chloride solution with a Cary Model 11 Spectrophotometer. The compounds which contain phenylsubstituents all show similar absorption in this region; compounds with only cyclohexyl substituents on the silicon atom are similar in absorption particularly in the near ultraviolet region. The phenyl-containing silylchromates all show an absorption plateau in the 300-350 mμ region and phenyl absorptions in the 250-270 mμ region. Bis(tricyclohexylsilyl)chromate has a distinct maximum absorption at 407 mμ; compound III (page 66) has a less distinct maximum absorption at 400 mμ. Both show absorption in the ultraviolet which is probably due to chromate since cyclohexyl groups, unlike phenyl, do not absorb in this region. Bis(cyclohexyldiphenylsilyl)chromate has greater absorption in the visible region than the other phenyl-containing silylchromates, and bis(p-tolyldiphenylsilyl)chromate has the most intense absorptions of the silylchromates. Bis(trimethylsilyl)chromate is similar in absorption to the phenyl-containing silylchromates in the 320-450 mμ region but is distinctly different in the far ultraviolet. The extinction coefficients (Figure 2) for this compound are arbitrary.

Infrared Spectra. The infrared spectra of the compounds prepared in this investigation are compiled in Appendix 2. These spectra were recorded in carbon disulfide, carbon tetrachloride solutions, and in potassium bromide pellets where appropriate. The absorptions present

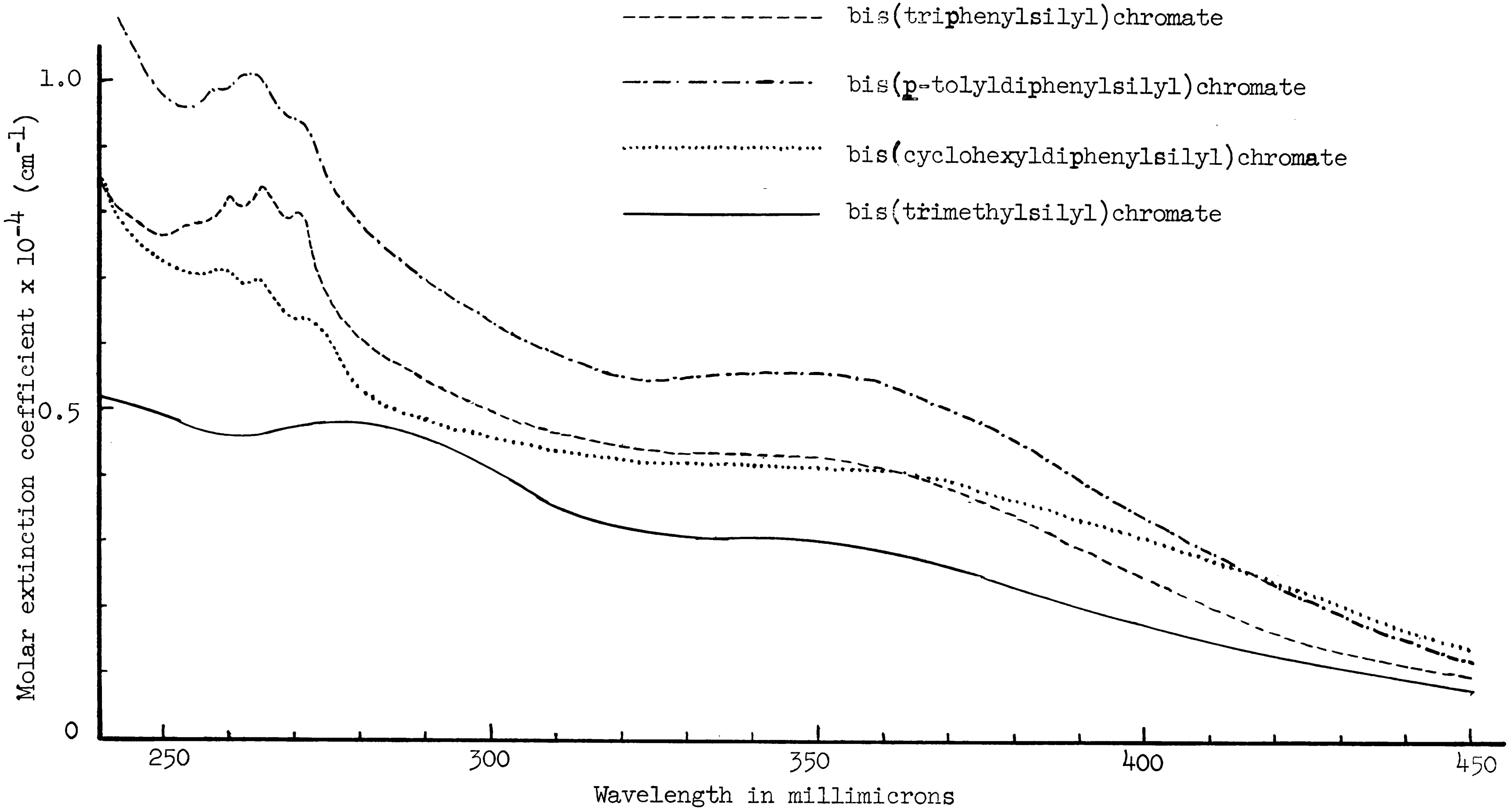


Figure 2. Ultraviolet and Visible Spectra of Bis(triphenylsilyl)chromate, Bis(p-tolyldiphenylsilyl)chromate, Bis(cyclohexyldiphenylsilyl)chromate, and Bis(trimethylsilyl)chromate

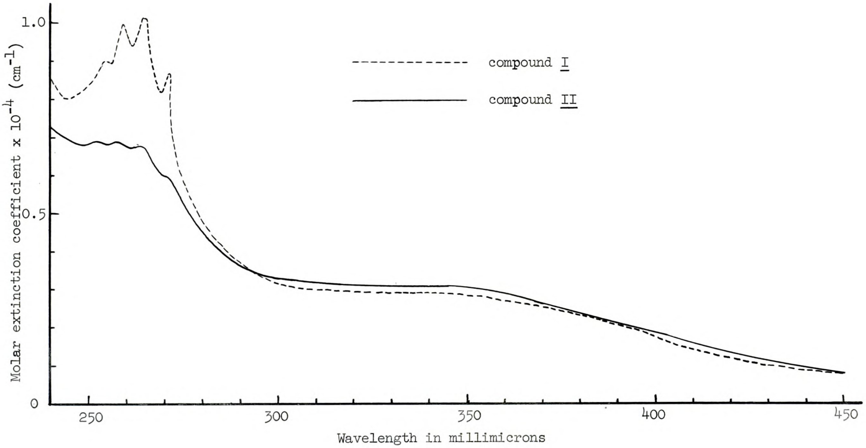


Figure 3. Ultraviolet and Visible Spectra of Compounds I and II

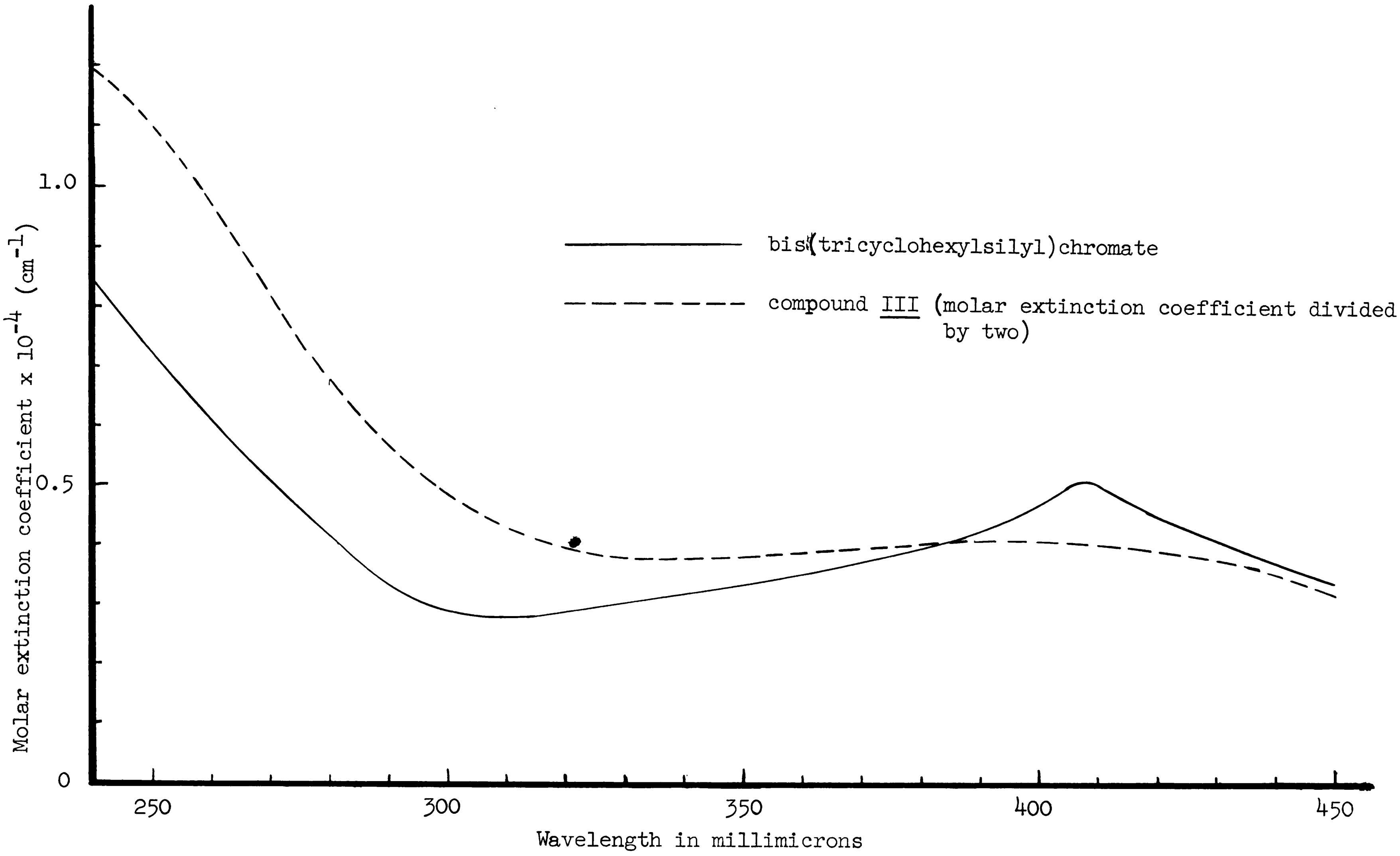


Figure 4. Ultraviolet and Visible Spectra of Bis(tricyclohexylsilyl)chromate and Compound III

in the silylchromates but not present in the corresponding silanol are tabulated in Table IX.

TABLE IX

INFRARED ABSORPTIONS OF SILYLCHROMATES IN CS_2 (μ)

Compound	Cr=O Asymmetric Stretch	Cr=O Symmetric Stretch	Unassigned	Unassigned	Si-O-Cr Stretch
$(Me_3Si)_2CrO_4$	10.14 (s)	10.29 (s)		10.7 (m)	12.1 (vs)
$(Ph_3Si)_2CrO_4$	10.14 (s)	10.26 (s)	10.4 (m)*	10.9 (m)*	11.4 (vs) broad
(*p*-$TolPh_2Si)_2CrO_4$	10.15 (s)	10.27 (s)	10.5 (m)*		11.5 (vs) broad
$(Ph_2ChSi)_2CrO_4$	10.13 (s)	10.26 (s)	10.4 (m)*		11.4 (vs)
$(Ch_3Si)_2CrO_4$	10.20 (s)	10.30 (s)			11.6 (vs)
Compound I	(masked)**	10.22 (m)			11.5 (s) broad
Compound II	10.10 (s)	10.25 (s)			11.0 (vs)
Compound III	10.15 (vs)	10.30 (vs)			11-12 (vs) broad

Intensities: (s) strong, (m) medium, (vs) very strong
* shoulder
** masked by Ph-Si

Absorptions at 10.1 and 10.3μ correspond to the asymmetric and symmetric stretching frequencies of Cr=O recently reported for chromyl chloride (103). There is evidence (104, 105, 106, 107) that the Si-O-M (M = metal) linkage absorbs in the 10-11.5μ region. Silylchromate absorptions in the 11.4-11.5μ region may tentatively be assigned to the Si-O-Cr linkage; however, Smith (108) assigns absorptions in this region

to the asymmetric stretching frequency of Si-O. This region is diagnostic for silanols, while no absorptions are present for cyclosiloxanes or alkali metal salts of the silanols.

Discussion. The ultraviolet absorption of bis(trimethylsilyl)-chromate, bis(tricyclohexylsilyl)chromate, and compound III is due to the chromate group since the other groups of these compounds do not absorb in this region and other chromium(VI) ions and compounds do absorb in this region.

The spectra of bis(tricyclohexylsilyl)chromate and compound III are similar in the visible region (maxima 407 and 400 mμ, respectively), but compound III exhibits a broad absorption similar to the phenyl-containing silylchromates and longer extinction coefficients. The absorption spectra of these compounds are markedly different from the other silylchromates except bis(cyclohexyldiphenylsilyl)chromate, which has a broader absorption in the visible and could be considered an admixture of the spectra of bis(triphenylsilyl)chromate and bis(tricyclohexylsilyl)chromate. The spectra of bis(2-methylfenchyl)chromate (39), which has a maxima at 393 and 287 mμ, and chromyl acetate (22) with maxima at 400 and 283 mμ, indicate a similarity in chromate absorption with the cyclohexyl-containing silylchromates in the visible region.

The phenyl-containing silylchromates and bis(trimethylsilyl)-chromate have similar absorption in the near ultraviolet. This absorption is due to the chromate group since this region is characteristic of the absorption of chromates, and the silanols do not absorb in this region. The broadening and shifting to lower wavelengths of the chromate absorption is suggestive of interaction of the chromate and silyl groups.

The phenyl absorptions of diphenylsilanediol and triphenylsilanol (Figure 5) are shifted to higher wavelengths, increased in intensity, and decreased in fine structure when compared to benzene (109). These effects are not as pronounced as in phenol or aniline, but do suggest that interaction of the phenyl groups and the silicon atom does take place. This interaction has been used by previous workers to explain the dipole moment, substitution reactions, and ionization constants of trimethylsilyl substituted phenyl, phenol, and aniline compounds (49). However, except for compound I, the phenyl-containing silylchromates show a decrease in fine structure beyond the parent silanol. This reduction in fine structure by replacing hydrogen with chromium(VI) suggests interaction of the metal with the phenyl group, for if they were perfectly insulated from one another, the fine structure reduction would not be observed. Once again this effect may not be too large since it is not accompanied by a shift of the absorption of the phenyl groups to higher wavelengths. The presence of chromate absorption in the phenyl region prohibits an intensity study. The exceptional phenyl fine structure of compound I is explained by its structure. It is not composed extensively of Cr-O-Si bonds as are the other phenyl-containing silylchromates, and it possesses fine structure similar to the diphenylsilanediol.

A comparison of the extinction coefficients of the silylchromates in the 300-350 mμ region gives no correlation among the compounds. No experiment was performed to determine if Beer's Law is obeyed by these compounds.

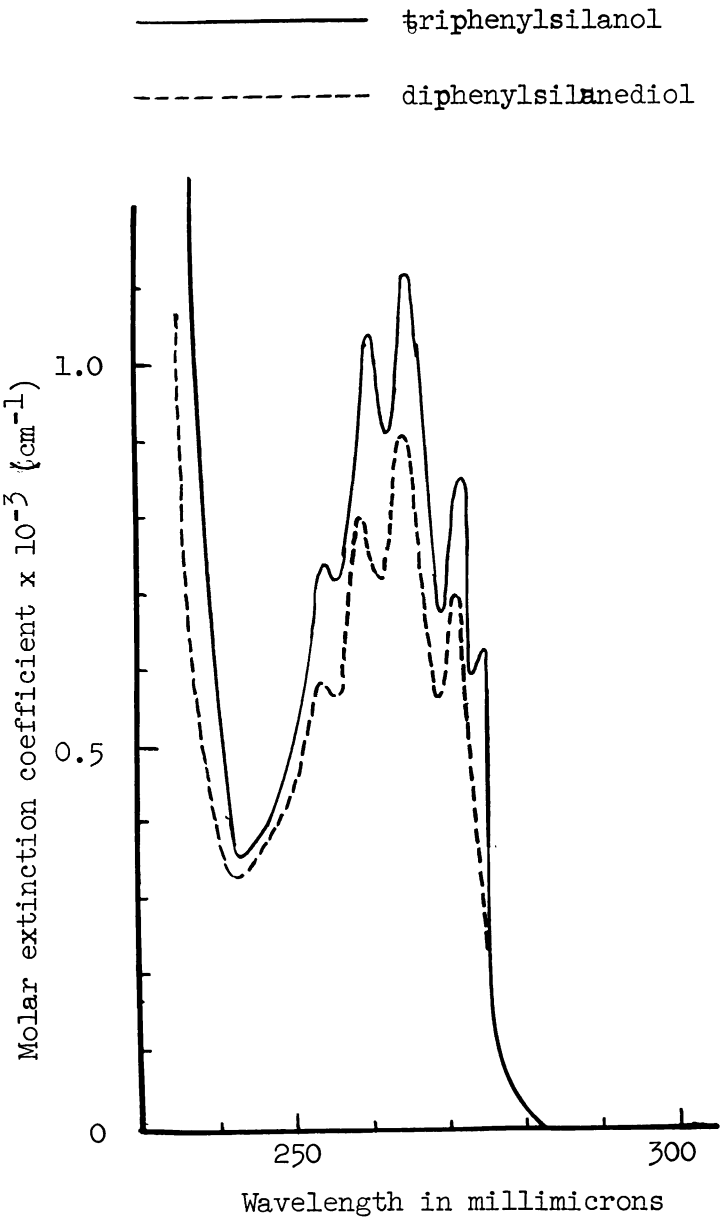


Figure 5. Ultraviolet Spectra of Triphenylsilanol and Diphenylsilanediol

Infrared spectroscopy has been useful in the determination of the structures of the compounds prepared in this work. The detection of OH group in compounds I and III and the absence of OH absorption in compound II was achieved by a study of these compounds in concentrated solutions. In each case, the difference between observed absorption of the compound and the blank of the sodium chloride cells confirmed or denied the presence of the OH group. The strong infrared absorption of the Si-O-Si linkage has also been used for confirmation of structure.

Analytical Methods

The determination of silicon and chromium in silylchromates is troublesome because complete decomposition of the compounds and total oxidation of chromium is difficult. The following methods were found to be satisfactory for the determination of silicon and chromium in silylchromates. Carbon and hydrogen analyses in this investigation were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

All silylchromates prepared except compound II are highly soluble in benzene; molecular weights were therefore determined cryoscopically in that solvent.

Chromium Analysis. The sample was weighed into an iron crucible (low in chromium) and mixed with sodium carbonate as a protective flux. The crucible was then heated for about two hours on a hot plate at high heat to decompose the silylchromate. After cooling the crucible, sodium peroxide was added and the covered crucible was heated with a Meker burner. If the preliminary decomposition was not done carefully, an instantaneous reaction sometimes blew off the cover. Fusion temperature was maintained for three to four minutes. The cooled sample was washed into a beaker and the solution boiled for one-half hour to remove any peroxide. The solution was acidified with sulfuric acid and chromate was titrated with a recently standardized ferrous sulfate solution. The end point of the titration was determined amperometrically using a rotating platinum anode and a calomel cathode at a potential difference of one volt (110). The detection of a diffusion current by a sensitive galvanometer in the circuit indicated the equivalence point. If an overtitration occurred, the equivalence point could be determined by extrapolation of the galvanometer readings to zero current. Titration to the diphenylamine sulfonate end point was found to be unsatisfactory because of its sensitivity to acid concentration, particularly phosphoric acid. A dead stop amperometric titration using similar platinum electrodes came to equilibrium too slowly to be used for rapid titrations.

Silicon Analysis. A method of silicon analysis based on the procedure of McHard, Servais, and Clark (111) was used in this investigation. The silylchromate sample was weighed into a platinum crucible and two mililiters of fuming sulfuric acid was added cautiously. Two mililiters of fuming nitric acid were added to the cooled mixture if needed to facilitate decomposition. The digestion and evolution of sulfur trioxide was carried out with a low Bunsen burner flame. The decomposition takes from one to two days. When the sulfur trioxide fumes ceased, the crucible was gradually heated to redness for about one-half hour and then heated at 800°C in a pre-heated muffle furnace for one hour. The

crucible was cooled in a desiccator and weighed. The weight of the residue was taken as chromium(III) oxide and silicon dioxide.

Two mililiters of 46% hydrofluoric acid and one mililiter of sulfuric acid were cautiously added and the hydrogen fluoride and sulfur trioxide fumes were removed with the low heat of a Bunsen burner. The crucible was ignited to redness for one-half hour after fumes of sulfur trioxide ceased, and then at 800°C for one hour. The weight loss of the cooled crucible represents silicon dioxide. The weight of the residue of chromium(III) oxide served as a check on the chromium analysis.

Molecular Weights. The molecular weights of all the compounds prepared in this investigation were determined by freezing point depression of benzene solutions. An apparatus based on temperature measurement with a thermistor was constructed for the measurement of the freezing point of these solutions.

A thermistor*, two 1000 ohm resistors (0.1%)**, and two resistance boxes in series were used to construct a Wheatstone bridge circuit. The current for the Wheatstone bridge was supplied by a 1.5 volt dry cell battery. Bridge balance was determined with a Scalamp Galvanometer***.

The thermistor was attached to a cap which could be screwed onto a two ounce, narrow-mouth, amber bottle containing the solution. The

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*Victory Engineering Corporation, Union, New Jersey.

**Shallcross Company, Collingdale, Pennsylvania.

***W. G. Pye, Ltd., Cambridge, England

bottle was fitted into a cylinder surrounded by ice, and the solution was stirred by a magnetic stirrer.

The thermistor was calibrated using the resistance values for the freezing points of conductivity water (0.000°C) and benzene which had been purified by recrystallization twice and distillation (5.493°C) (20). Intermediate temperature values were calculated from the exponential equation of resistance:

$$\frac{(T - T_o)B}{T_oT(2.71828)} = \log \frac{R}{R_o}$$

The constant B is characteristic of the thermistor and was calculated using the freezing points of water and benzene. The resistance of the thermistor, R, at temperature T (°K) was calculated using the resistance R_o and the temperature T_o for the freezing point of water. The calibration was extended to 5.750°C so that nitrobenzene could be used as a cryoscopic solvent (Table X).

The sample and benzene for the molecular weight determination were weighed directly into the sample bottle, the magnetic stirring bar and thermistor were inserted, and the bottle was placed into the ice bath. Resistance was measured at intervals as the solution cooled and froze. The cooling and freezing curves were then extrapolated to their intersection at the freezing point. The freezing point in ohms was then converted to degrees centigrade by interpolation. The difference between the freezing point of benzene (prior determination) and the solution gave the depression of the freezing point of the solution. The molecular weight was then calculated from the freezing point depression equation

$$\text{M.W.} = \frac{K_f \text{Wt.solute}(1000)}{\Delta T \text{ Wt.solvent}}$$

TABLE X

CALIBRATION OF THE THERMISTOR

Temperature in °C	Resistance in ohms
4.000	5559.1
4.100	5534.7
4.200	5510.6
4.300	5486.3
4.400	5462.3
4.500	5438.3
4.600	5414.4
4.700	5390.7
4.800	5367.1
4.900	5343.5
5.000	5320.2
5.050	5308.7
5.100	5297.0
5.150	5285.4
5.200	5274.0
5.250	5262.4
5.300	5250.9
5.350	5239.5
5.400	5228.0

Continued

TABLE X - Continued

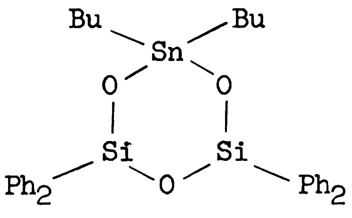
Temperature in ^{o}C	Resistance in ohms
5.450	5216.6
5.500	5205.3
5.550	5193.9
5.600	5182.5
5.650	5171.3
5.700	5160.0
5.750	5148.8

where M.W., Wt.solute, Wt.solvent, and ΔT are the molecular weight, weight of solute, weight of solvent, and freezing point depression respectively. K_f is the freezing point depression constant which is given as 5.069 (20). A check on the use of this constant was made using high purity p-tolylsulfonylmethylnitrosamide. The observed molecular weight was 231.2 (calculated, 231.3) using the above constant. The error in the determination is ± 0.4 ohms, which is equivalent to ± 0.002°C.

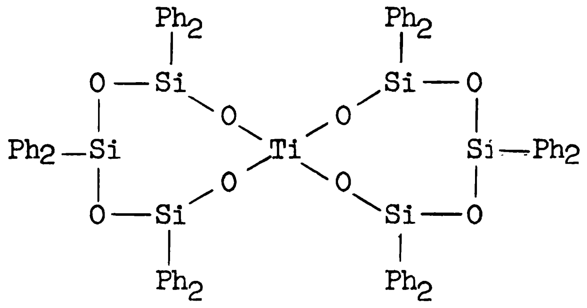
DISCUSSION

Prior to this investigation, two silylchromates have been reported in the literature. Bis(trimethylsilyl)chromate was prepared from hexamethyldisiloxane and chromium(VI) oxide and bis(triphenylsilyl)-chromate was reportedly prepared by the reaction of triphenylsilanol with chromium(VI) oxide (86). In this investigation bis(p-tolyldiphenylsilyl)chromate, bis(cyclohexyldiphenylsilyl)chromate, and bis(tricyclohexylsilyl)chromate have been prepared and characterized; bis(triphenylsilyl)chromate was prepared and characterized independently. In addition, further information was obtained on unstable bis(trimethylsilyl)chromate and bis(methyldiphenylsilyl)chromate, and the preparation of a new silanol, cyclohexylsilanol, was achieved.

Numerous investigators (69, 70, 71, 72) have reported the preparation of polysiloxy-metal compounds but none have been characterized. No known heteropolycompound with an A-B repeating unit of moderate molecular weight has previously been prepared. The preparation of compound III (page 66) is the first instance of the formation of such a heteropolymer. Cyclic siloxanes containing metals have been reported by Koenig (72) and by Zeitler and Brown (112). Koenig obtained the following compound from the reaction of dibutyltinoxide and diphenylsilanediol in dioxane:



Zeitler and Brown have reported the preparation of the following compound from the reaction of titanium tetrachloride and diphenylsilanediol:

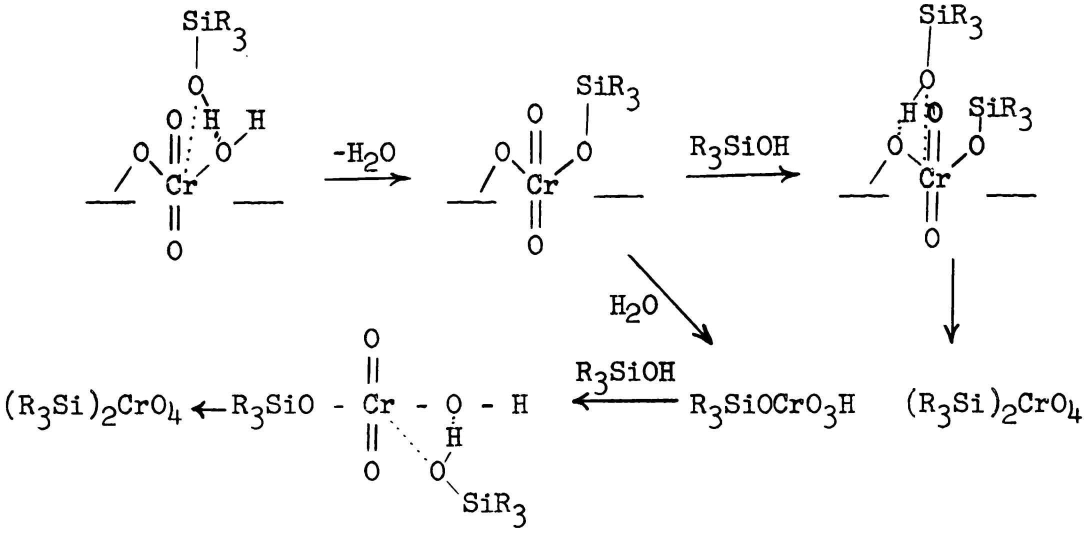


Compound II (page 50) is unique in that it is a large ring compound containing two metal atoms and is the first reported compound of this type containing chromium. Compound I (page 50) is also unique for chromium and is also the first characterized structure of this type. Compounds similar to compound I may have been obtained in previous works but they have not been isolated or well characterized.

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. The products of these reactions were in general easily isolated and purified. Characterization of the products was based upon analytical and spectrophotometric data.

Since chromium(VI) oxide is insoluble in the solvent, the initial step of the reaction for the formation of the silylchromate is probably absorption of the silanol on the surface of chromium(VI) oxide. Surface reactions sites probably are defects which contain chemisorbed water--that is, sites containing chromic acid. The absorption complex may be attacked by the silanol to give the silylchromate or by water to form the half chromate ester. The half chromate ester ($R_3SiOCrO_3H$) may be freed from the surface by the solvent and react immediately with a second silanol molecule to form the silylchromate:

REACTION SCHEME A



The proposed formation of a half ester is based on a similar proposal in the oxidation of alcohols by chromic acid (32), and retention of oxygen by the silicon atom is based on studies involving organochromate esters (36, 38) and the silicon-oxygen bond strength. Chromic acid or hydrated chromium(VI) oxide is justified by the observed enhancement of the reaction when slightly moist chromium(VI) oxide is used as a reactant. The homogeneous reaction of triphenylsilanol and chromyl chloride probably proceeds by a similar two-step mechanism in solution with elimination of hydrogen chloride.

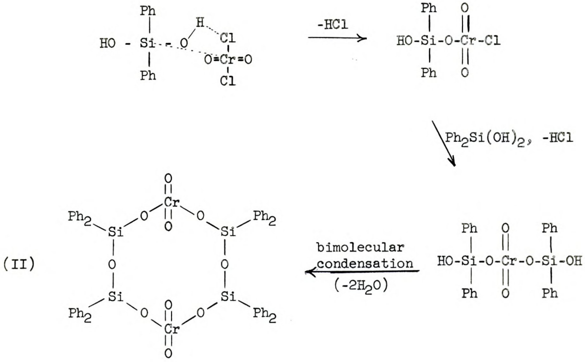
The rapid reaction of diphenylsilanediol with either chromium(VI) oxide or chromyl chloride is surprising. Formation of a mixture of compounds I and II in each case was accomplished within thirty minutes, whereas longer reaction times (10-30 hours) reduced the yields of products and increased the yield of decomposition products. No decomposition products were obtained from the thirty-minute reaction.

Failure to obtain an A-B silylchromate with alternate chromium-oxygen-silicon-oxygen bonds from the reaction of diphenylsilanediol and chromium(VI) oxide or 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.

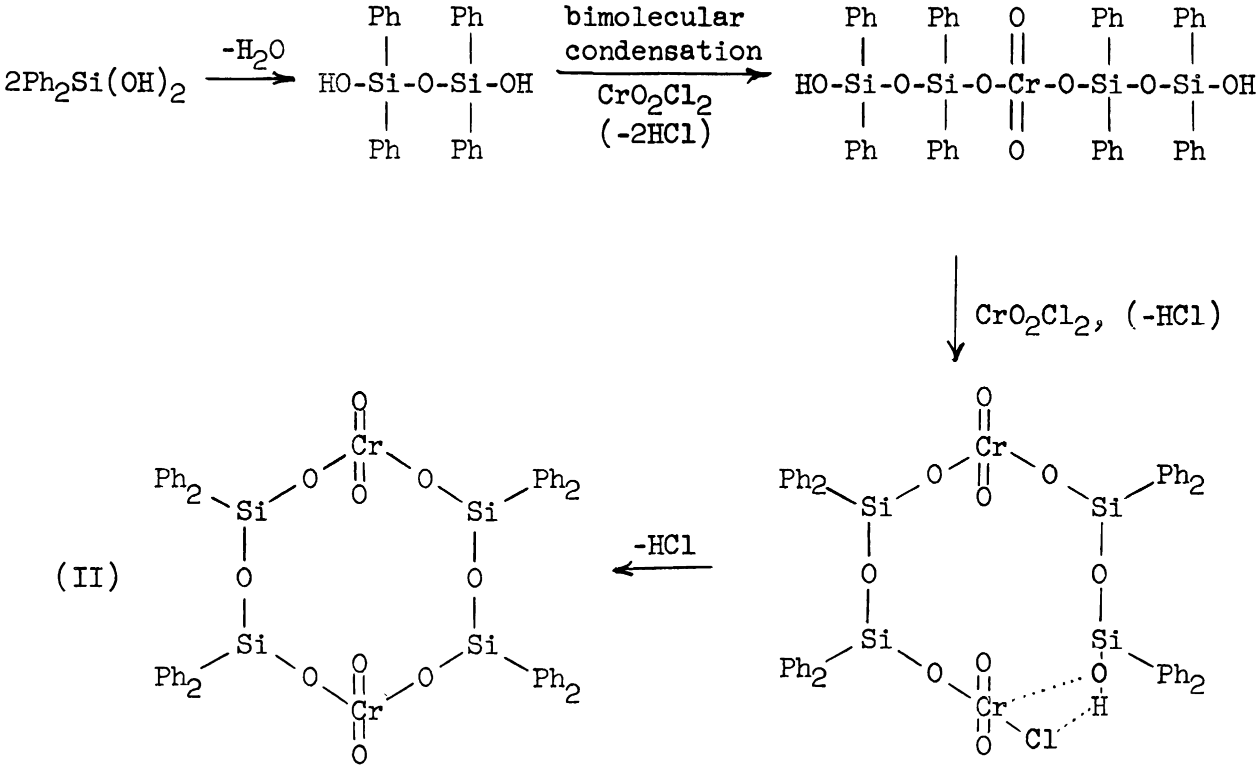
A possible mechanism for the formation of compound II from the reaction of diphenylsilanediol with chromyl chloride in methylene chloride is a reaction of the diol with chromyl chloride by elimination of hydrogen chloride to form $Ph_2(OH)SiOCr(O_2)Cl$. This intermediate may react with a second molecule of the diol to form $Ph_2(OH)SiOCr(O_2)OSi(OH)Ph_2$, 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:

REACTION SCHEME B



REACTION SCHEME C

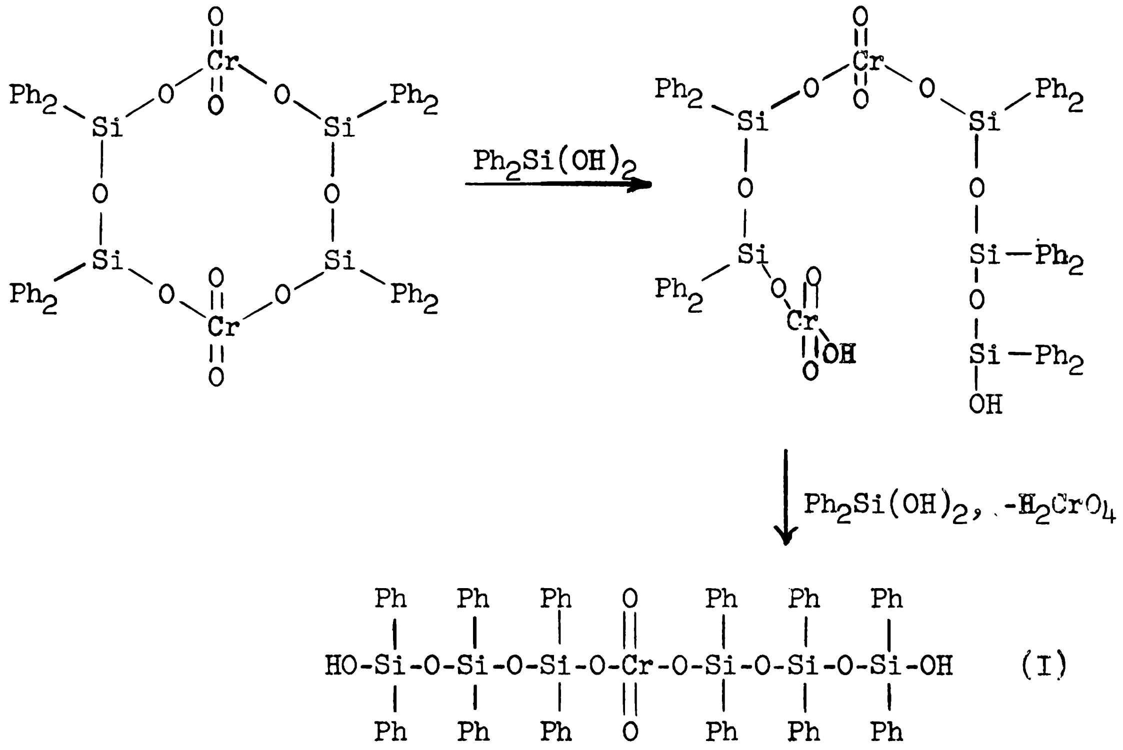


Compound I may be formed from the reaction of 2 molecules of diphenylsilanediol with compound II (Reaction Scheme D), hexaphenylcyclotrisiloxane with chromyl chloride, or hexaphenyltrisiloxane-1,5-diol with chromyl chloride (Reaction Scheme E). Only the first and last reactions seem plausible.

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

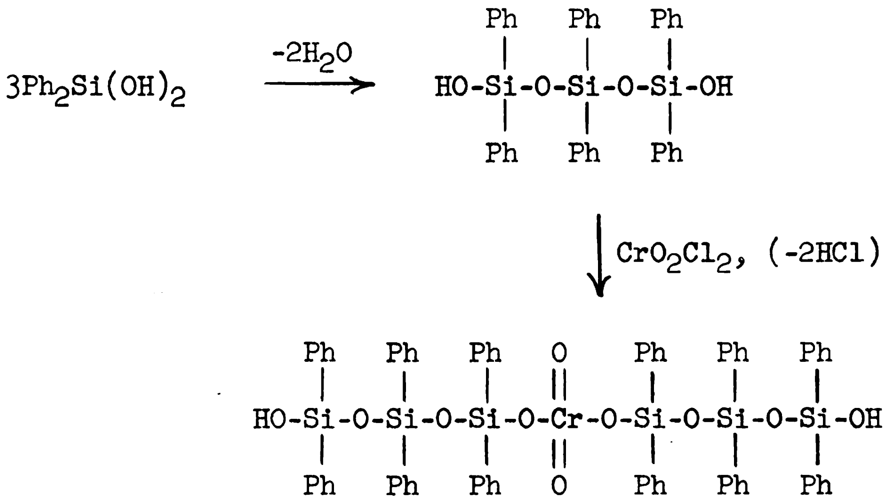
REACTION SCHEME D

(II)



(I)

REACTION SCHEME E



$$3Ph_2Si(OH)_2 \xrightarrow{-2H_2O} HO\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}OH$$

$$\xrightarrow{CrO_2Cl_2,\ (-2HCl)} HO\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{O}{\overset{O}{Cr}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{Si}}\text{-}OH$$

(I)

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 formation of compound III from the reaction of dicyclohexylsilanediol and chromium(VI) oxide can only be envisaged as resulting from consecutive chain-building reactions such as are suggested by Scheme A. The termination of the reaction of structure III could be due to an equilibrium of bond making and breaking which prevents the formation of longer chains. It is also possible that a cyclic intermediate is formed and that this terminates the reaction. Compound III might then be formed by the reaction of the cyclic structure with the diol in a manner similar to Scheme D. It is also possible that compound III is largely a mixture of compounds with an A-B structure but with silicon-to-chromium ratios of 5:4, 6:5, and 7:6 which are formed in a reaction similar to that of Scheme A.

Self-condensation of dicyclohexylsilanediol takes place only under conditions which are probably not attained in the heterogeneous reaction of the diol with 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-tolyldiphenylsilyl)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. Compound III decomposes on standing, and no thermal investigation was made on the freshly prepared oil. The high stability of compound I may be due to the presence of the linear chains of siloxy groups in the molecule; linear polysiloxanes containing phenyl groups are stable to 400-500°C (40). Incorporation of chromium(VI) into the siloxane moiety apparently reduces its stability. Compound II, like compound I, possesses siloxy groups in its structure; however, its lower stability may be due to thermal cracking of the cyclic structure. Even though their structures are different, a comparison of the stabilities of compounds I, II, and III suggests that the lower the silicon-to-chromium ratio, the lower the stability of the product. This further implies that a high temperature stable heteropolymer containing repeating oxygen-chromium(VI)-oxygen-silicon linkages cannot be prepared under the conditions discussed in this work.

The spectra of the silylchromates (Figures 2, 3, 4) suggest that the nature of the bonding in these compounds is complex. The phenyl-containing silylchromates as well as bis(trimethylsilyl)chromate have a similar absorption spectrum in the near ultraviolet. The chromate ion

has a sharp absorption at 379 mμ while bis(2-methylfenchyl)chromate and chromyl acetate absorb at 393-400 mμ. The near ultraviolet absorption in the silylchromates is unquestionably due to the chromate group. The broadening and shifting of this absorption to lower wavelengths may be due to interaction of the chromate group with the substituents of the silicon atom. The failure to obtain any correlation of the extinction coefficients for this absorption and the reduction of the fine structure of the phenyl absorptions in the ultraviolet further substantiate this hypothesis. The similar near ultraviolet absorption of bis(trimethylsilyl)chromate and the phenyl-containing silylchromates indicates a similar effect is operative.

The silicon and oxygen atoms of silanols are known to interact to form a partial double bond involving a vacant d orbital on the silicon atom and a filled p orbital on the oxygen. This bond lowers the electron density on the oxygen atom forming $R\text{-}Si^{-}{=}O^{+}$. In phenyl-containing silicon compounds there is also evidence that the π-electrons of the benzene ring may partially overlap with the vacant d orbitals of silicon. Thus in the phenyl-containing silanols the oxygen atom is partially in conjugation with the phenyl group. The removal of charge from the oxygen atom and the conjugative effect should tend to stabilize the chromium-oxygen bond since the chromium atom is highly electrophilic. A similar stabilization in the case of the methyl group could be brought about by hyperconjugation of the protons of the methyl group. These effects may only be operative to stabilize the excited states brought on by the absorption of near ultraviolet radiation rather than

stabilization of the ground state. The definite inductive effect of the trimethylsilyl group (49) should increase the electron density on the oxygen atom and this in turn should facilitate charge transfer to the electrophilic chromium atom. Bond fission thereby becomes more likely. Thus bis(trimethylsilyl)chromate should have lower thermal stability as observed.

The exceptional near ultraviolet spectrum of the cyclohexylsilylchromates may be due to two separate effects. The cyclohexyl group is unable to undergo the complex interactions possible with the methyl and phenyl groups and therefore would not stabilize the excited state as proposed. Steric hindrance is always a consideration of cyclohexyl compounds, since it is a bulky group. This effect may be particularly operative in the tricyclohexylsilyl group since tricyclohexylsilane fails to react even with methyllithium (96) under forceful conditions. Thus if operative in bis(tricyclohexylsilyl)chromate, steric hindrance should destabilize the ground state and bring about absorption at higher wavelengths. This is partially substantiated by the broad absorption spectrum of compound <u>III</u> in which steric hindrance is less likely.

The infrared spectra of the silylchromates (Table IX or Appendix 2) all show absorptions at 10.1 and 10.3μ. These absorptions are identical to those assigned to asymmetric and symmetric stretching frequencies of the chromium-oxygen double bond in chromyl chloride (60, 103). A comparison with the higher wavelength infrared absorptions of the chromate and dichromate ions (60), where pure double bonds are not involved, suggests that in the silylchromates as in chromyl chloride the absorptions are due to the presence of a chromium-oxygen double bond.

Tentatively the infrared absorptions of the silylchromates in the 11.5μ region have been assigned to the chromium-oxygen-silicon linkage, and the shift of this absorption to 12.1μ in bis(trimethylsilyl)chromate might be taken as corroborating evidence for the existence of hyperconjugation effects. This same absorption occurs at 11.0μ in compound II which may represent Cr-O-Si in strain-free cyclic systems.

All of the silylchromates prepared in this work are sensitive to light. Photochemical decomposition did not seriously hamper this investigation, since it is slow enough to allow the compounds to be exposed to light for short periods. An example of this is the decomposition of compound II in light. The bright yellow-orange crystals of this compound fade to a brown color within two-three hours of exposure to room light; on prolonged exposure only an unidentified black, amorphous solid remains.

The photochemical decomposition of the silylchromates may be analogous to that of chromyl chloride (14, 59), since the internal symmetry about the central chromium atom is the same in each case. This decomposition would involve absorption of radiation in the near ultraviolet which gives rise to charge transfer to the central chromium atom and leads to the dissociation:

$$(R_3Si)_2CrO_4 \xrightarrow{h\nu} (R_3Si)_2O + CrO_2 + \tfrac{1}{2}O_2$$

Since the products have not been isolated, this can only be considered as a possible mode of decomposition.

The toxicity of all known hexavalent chromium compounds (page 16) 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. This investigator has had contact between the skin and these compounds with no adverse effects; however, in each case of contact the area was thoroughly cleansed.

SUMMARY AND CONCLUSIONS

Condensation of silanols and silanediols with chromium(VI) oxide and chromyl chloride proceeded easily to give several interesting products. Triorganosilanols react with chromium(VI) oxide to give bis(triorganosilyl)chromates in good yields, while the reaction of diorganosilanediols with chromium(VI) oxide or chromyl chloride gave more complex products. The products obtained were the first reported A-B heteropolymer containing silicon and chromium, the first cyclic siloxane containing chromium, and a linear siloxy-chromium compound. The compounds were easily prepared and characterized, but isolation of the product in a pure state varies since final removal of impurities was difficult in some cases.

The reactions of triorganosilanols with chromium(VI) oxide gave a series of interesting compounds which were easily isolated, purified, and characterized. The stability and spectra of these compounds were related to the organic substituents of the silicon atom.

Reaction of either chromium(VI) oxide or chromyl chloride with diphenylsilanediol in chlorinated methane solvents gave a mixture of two siloxy-chromium compounds. Compound I, a linear siloxy chromate, was the most difficult to obtain in a pure state because of contamination by compound II, a cyclic siloxy chromate, and by condensed siloxanes. These compounds contain the siloxane (Si-O-Si) linkage due to the tendency of diphenylsilanediol to undergo condensation under the reaction conditions. Studies of the reactions of the condensation products of diphenylsilanediol with chromyl chloride or chromium(VI) oxide enabled the postulation of reaction schemes for the production of compounds I and II.

Self-condensation of dicyclohexylsilanediol is unlikely when the diol undergoes reaction with chromium(VI) oxide in methylene chloride solution. The product of this reaction, compound III, was assigned a structure containing regular A-B repeating units of chromium-oxygen-silicon-oxygen on the basis of analytical data. This product decomposed on standing to a black, amorphous solid.

Attempts to prepare silylchromates by addition of chromyl chloride to cyclic siloxanes was unsuccessful. Also, the condensation of dialkoxysilanes with chromyl chloride was unsuccessful due to the probable reaction of chromyl chloride with the aliphatic groups.

All of the silylchromates prepared in this investigation slowly decompose in the presence of light. The thermal stability of these compounds is dependent on the substituents of the silicon atom and the structure of the compound. In general the phenyl-containing compounds were the most stable, while the least stable silylchromates were those containing aliphatic groups. Also, it was found that the larger the number of siloxy groups in the compound, the greater the stability.

Spectral studies of the silylchromates reveal that interactions of the silicon substituents and the chromate group are operative. The observed shifts of chromate absorption to lower wavelengths may be due to stabilization of the excited state rather than the ground state. The anomalous spectrum of the cyclohexyl-containing silylchromates was

tentatively explained on the basis of steric hindrance or inability of interaction. Further studies of related compounds are necessary to interpret fully the nature of the proposed interactions.

Infrared spectroscopy was important as a means of product identification. All the groups present in the silylchromates participate in absorptions in the infrared. The absorptions of the OH, Si-O-Si, and tentatively assigned Cr-O-Si linkages were particularly important for structural assignments.

The original intention, to prepare high temperature stable polymers containing chromium and silicon, was not achieved. A comparison of the stabilities of compounds I, II, and III in which the silicon-to-chromium ratio varies from 3:1 to 1.2:1 indicates that an increased chromium(VI) content in the siloxane moiety lowers its thermal stability; this comparison neglects structural differences which also may effect the stability of the compound. The thermal decomposition may be due to fission of the chromium-oxygen bond as in the thermal decomposition of chromium(VI) oxide. The stability trends and proposed interactions may be particularly important in view of their relation to siloxy compounds of other transition metals.

RECOMMENDATIONS FOR FUTURE WORK

1. Compound II has been obtained as prismatic needles of almost a centimeter in length when slowly crystallized from methylene chloride solutions. Single crystal x-ray diffraction studies should be carried out to determine its structure in the solid state.

2. Kinetic studies on the formation and decomposition of the silylchromates prepared in this work might give considerable information on the stability of chromium-oxygen-silicon linkage. The formation of the bis(triorganisilyl)chromates could easily be followed by spectrophotometric techniques, as could their photochemical decomposition. The direct hydrolysis of bis(trimethylsilyl)chromate with water enriched in O^{18} would enable a determination of the relative stability of the bonds in this compound. Homogeneous hydrolysis of the other silylchromates in acetone-water solutions could also be studied using O^{18}.

3. The reaction of cyclic compound II with diphenylsilanediol has only been studied qualitatively. From these observations compound I apparently is easily produced in good yield. The reaction of the diol and compound II should be studied more thoroughly and the products characterized. This reaction should give compound I in a higher purity since the diol is easily separated from compound I. The reaction might also be carried out using other diols or trisubstituted silanols to give a whole series of derivatives which would have varying properties.

4. The further polymerization of compounds I, II, and III should be studied. The terminal OH groups of compounds I and III should undergo further condensation with chromyl chloride or chromium(VI) oxide to give higher molecular weight products. The cyclic structure of compound II suggests that it may undergo addition polymerization in the presence of a catalyst such as Lewis acids or alkali.

5. The failure to produce an A-B heteropolymer from the reaction of chromyl chloride and diphenylsilanediol may be due to the reaction conditions. Perhaps at lower temperatures (-40°C) condensation of the diol and chromyl chloride may give the A-B heteropolymers. This same reaction might also be tried in a solvent like acetic anhydride in which both the diol and chromyl chloride are soluble.

6. Resolution of the nature of the interactions predicted from the spectral studies of the silylchromates might be accomplished by studies of silylchromates containing allyl, vinyl, and isopropyl groups. The π-electrons of the vinyl group reportedly interact with silicon in vinylsilanes, but the π-electrons of the allyl group do not interact with silicon. The isopropyl group has about the same inductive effect as a cyclohexyl group but is less subject to steric hindrance.

APPENDIX 1

REACTIONS OF CHROMYL CHLORIDE

At the beginning of this investigation a search was made for potential co-monomers for reaction with chromyl chloride to give polymeric materials. This search was unsuccessful; however, some of the information should be reported. Chromyl chloride reacts with the following compounds in methylene chloride to give hygroscopic, brown addition compounds which dissolve in water to give green solutions:

succinic acid
terephthalic acid
ethylene glycol
dimethyltindichloride
dibutyltindiacetate
glycol di-mercaptoacetate

The chromyl chloride addition products of these materials may probably be considered to be Étard complexes.

Ethylenediamine reacts with chromyl chloride in methylene chloride to give a red-brown solid which dissolves in water to form a dark red solution and may be a complex of chromium(III). Silico-oxalic acid gives silicon dioxide when it reacts with chromyl chloride. Sulfur reacts with chromyl chloride in carbon disulfide to give a brown precipitate which decomposes on addition of water to give sulfur and a green solution.

The reaction of the Étard complex of benzene and chromyl chloride with ethylene glycol gave a hard, green solid which is soluble in water.

The cohydrolysis of dimethyldichlorosilane and chromyl chloride in refluxing methylene chloride gave orange needles when pyridine was used as a base. In the presence of other bases and lower temperatures only brown addition compounds were obtained. The orange needles slowly decomposed into a brown solid; they may be the methyl analog of compound <u>II</u>. Cohydrolysis of dimethoxydichlorosilane and chromyl chloride gave only brown solids which were easily hydrolyzed to silicon dioxide.

Addition of chromyl chloride to a glacial acetic acid solution of potassium chromate gave potassium chlorochromate as bright orange platelets. The hydrolysis of very dilute carbon tetrachloride solutions of chromyl chloride at different temperatures indicates that the hydrolysis is slow and the rate decreases with decreasing temperature.

APPENDIX 2

INFRARED SPECTRA

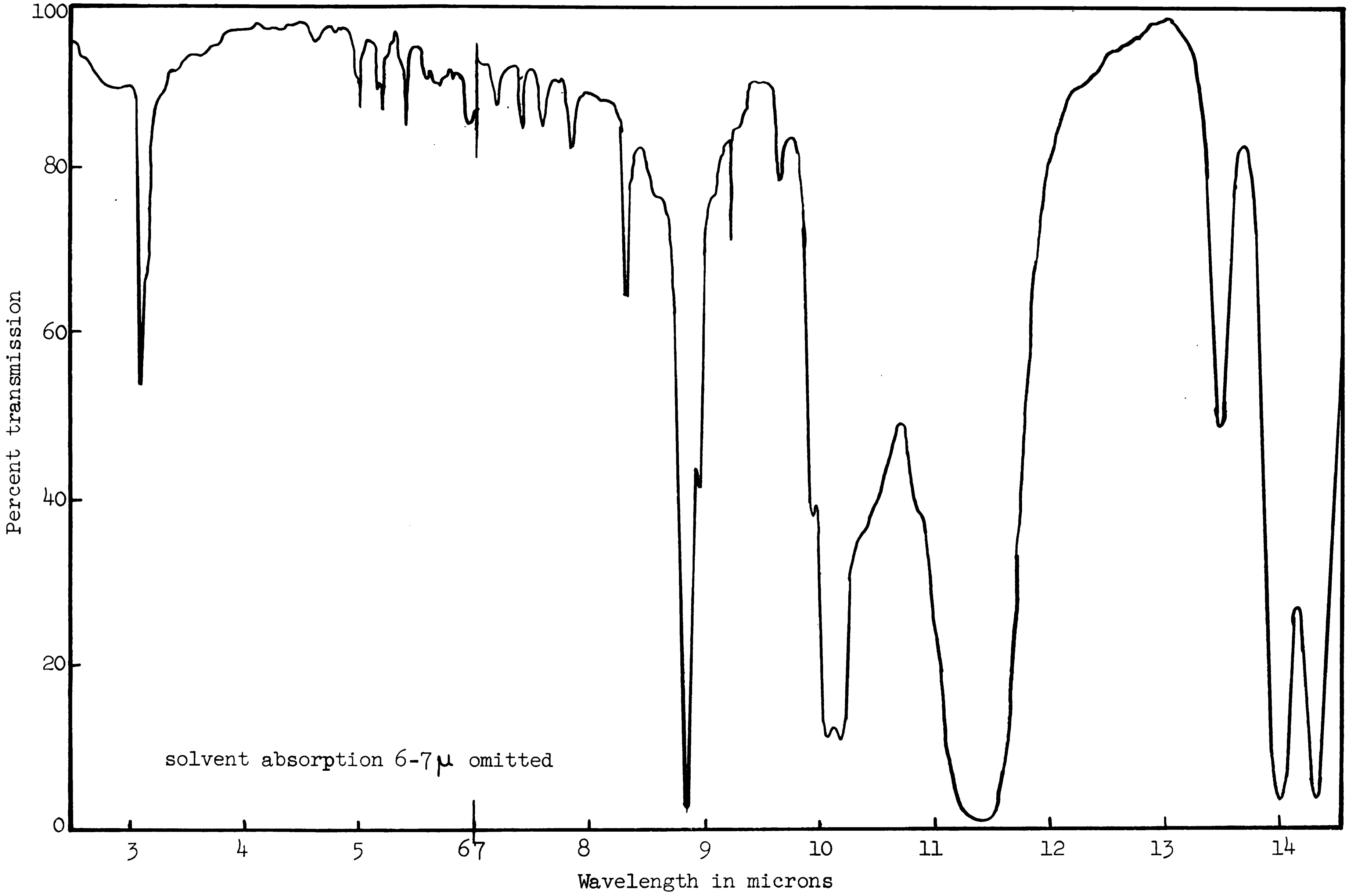


Figure 6. Infrared Spectrum of Bis(triphenylsilyl)chromate in Carbon Disulfide

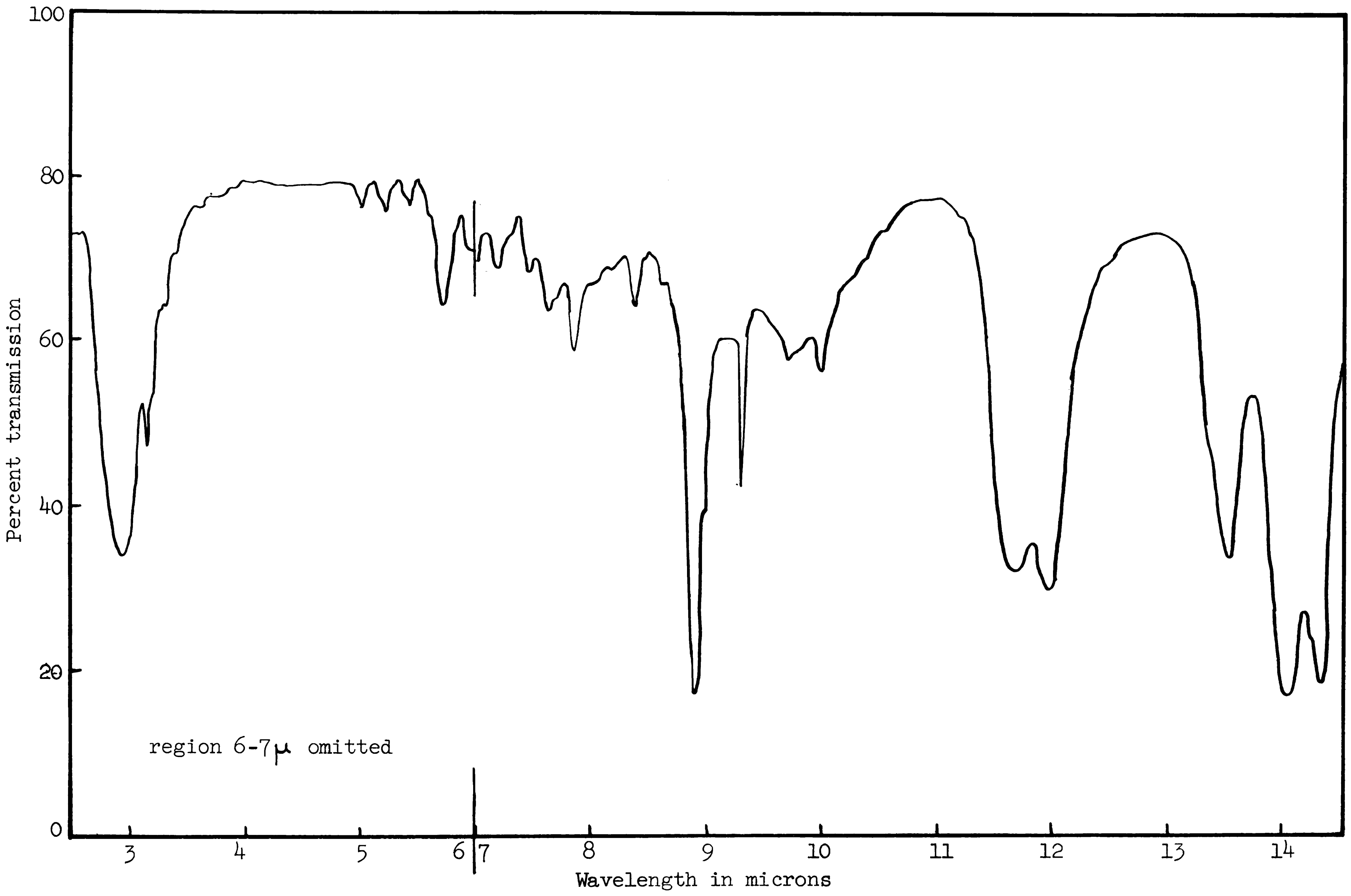


Figure 7. Infrared Spectrum of Triphenylsilanol in Potassium Bromide Disc

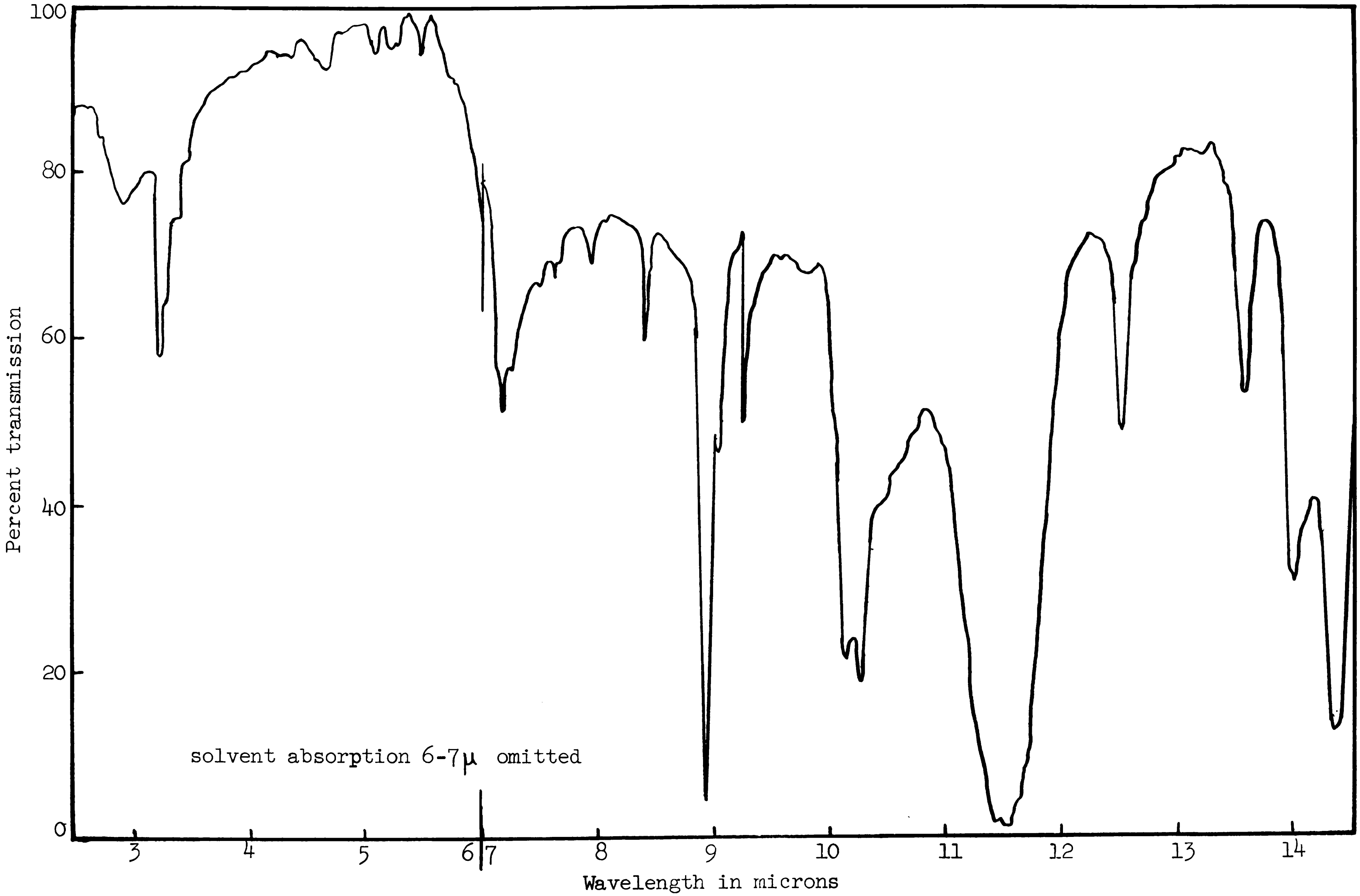


Figure 8. Infrared Spectrum of Bis(p-tolyldiphenylsilyl)chromate in Carbon Disulfide

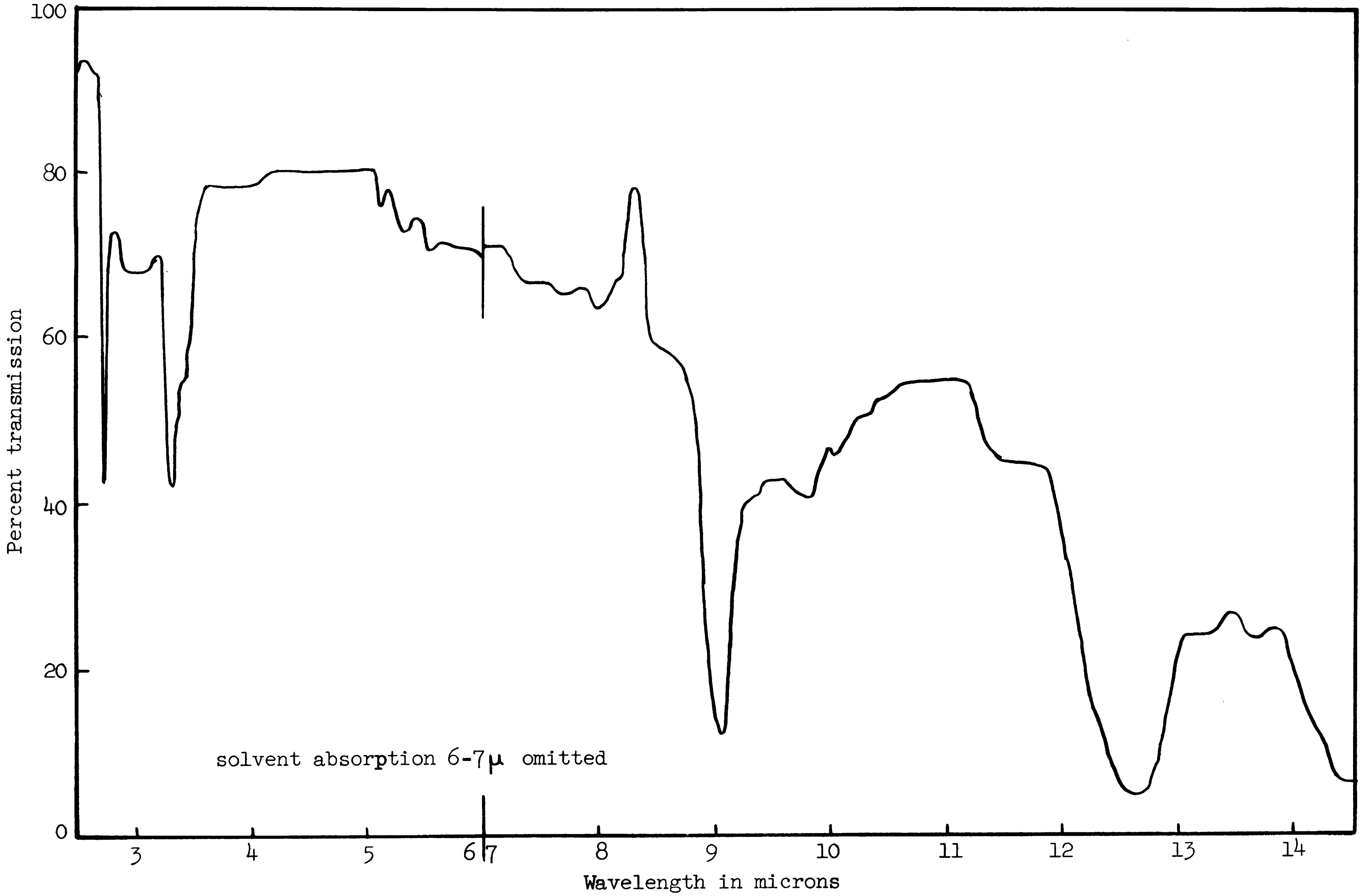


Figure 9. Infrared Spectrum of **p**-Tolyldiphenylsilanol in Carbon Disulfide

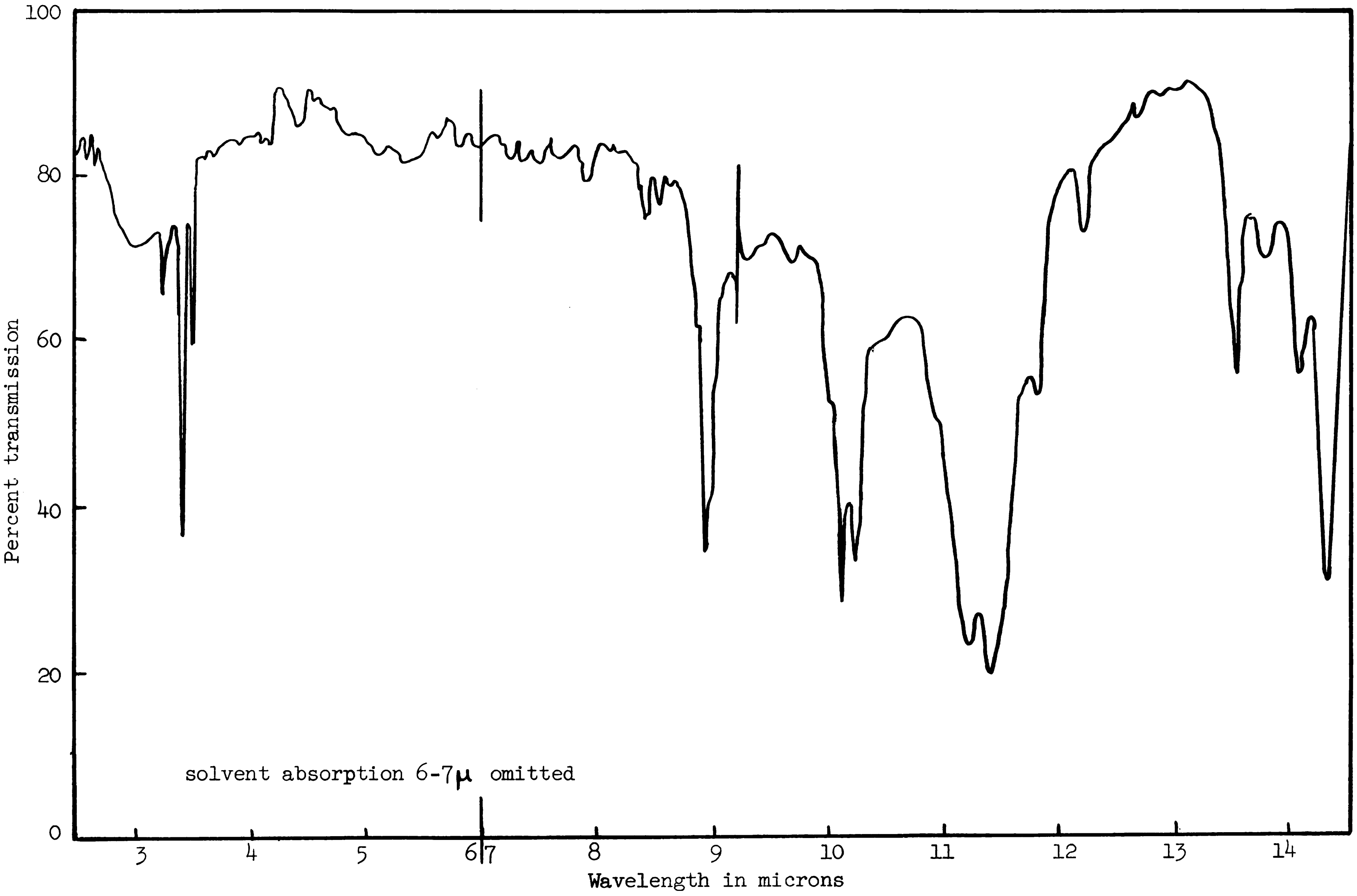


Figure 10. Infrared Spectrum of Bis(cyclohexyldiphenylsilyl)chromate in Carbon Disulfide

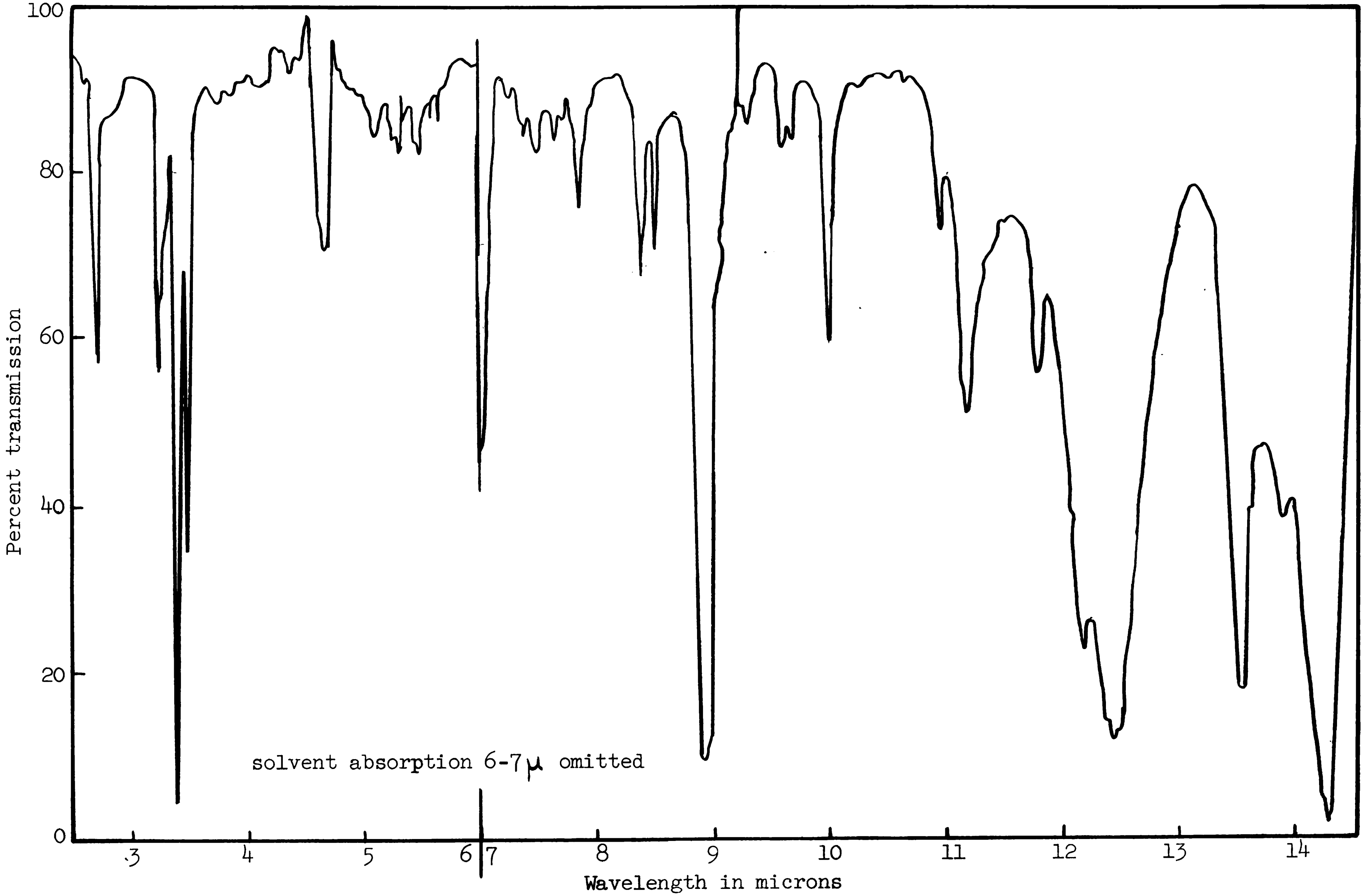


Figure 11. Infrared Spectrum of Cyclohexyldiphenylsilanol in Carbon Disulfide

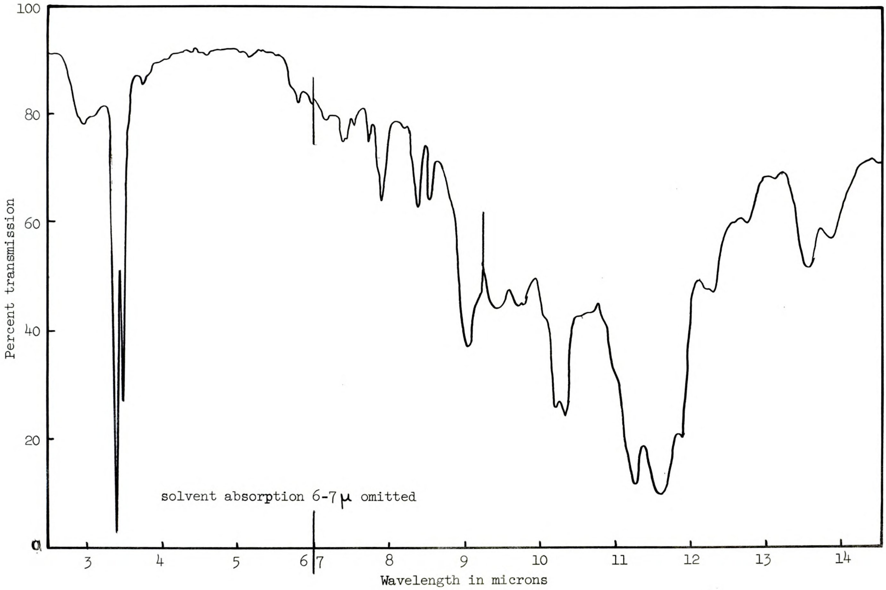


Figure 12. Infrared Spectrum of Bis(tricyclohexylsilyl)chromate in carbon disulfide

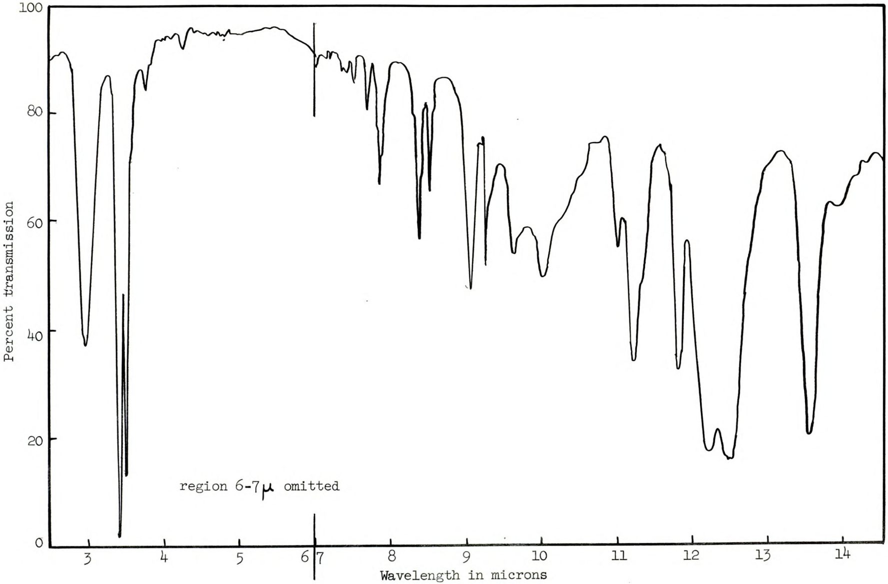


Figure 13. Infrared Spectrum of Tricyclohexylsilanol in Potassium Bromide Disc

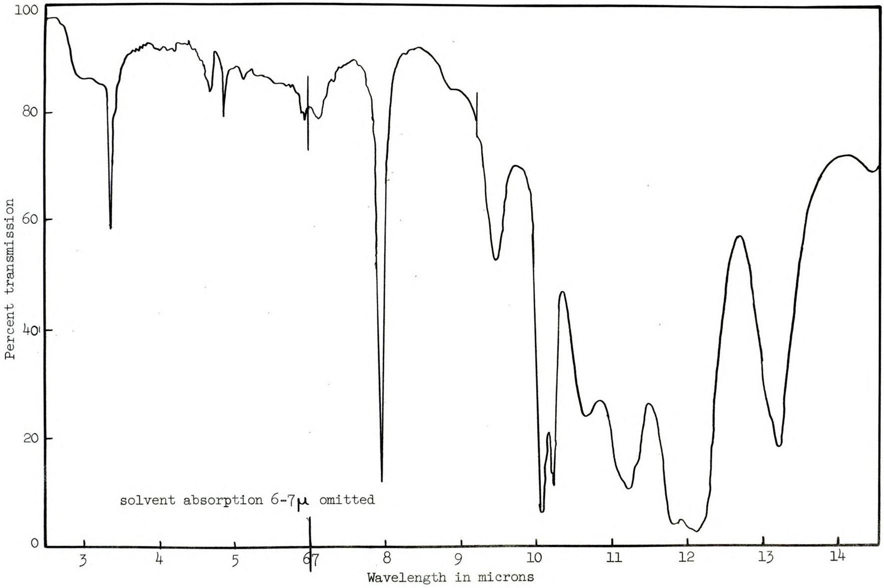


Figure 14. Infrared Spectrum of Bis(trimethylsilyl)chromate in Carbon Disulfide

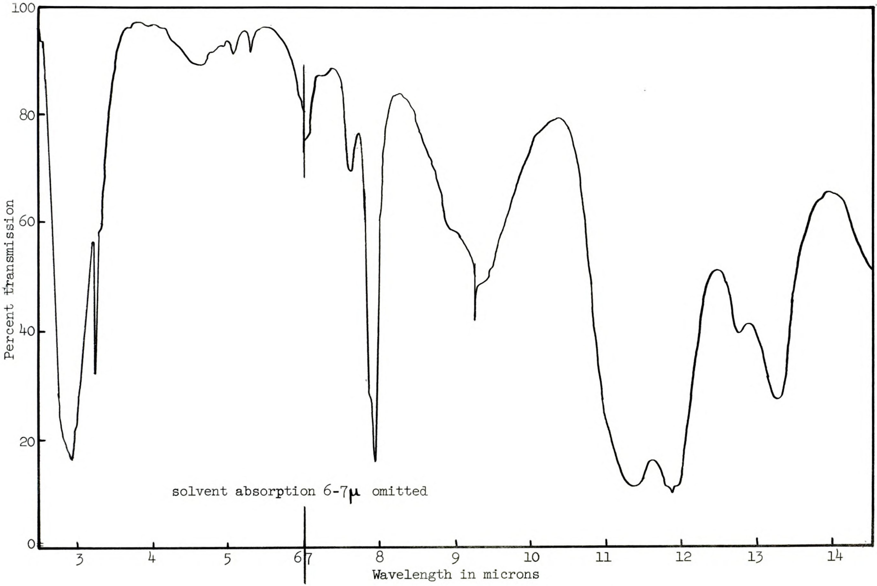


Figure 15. Infrared Spectrum of Trimethylsilanol in Carbon Disulfide

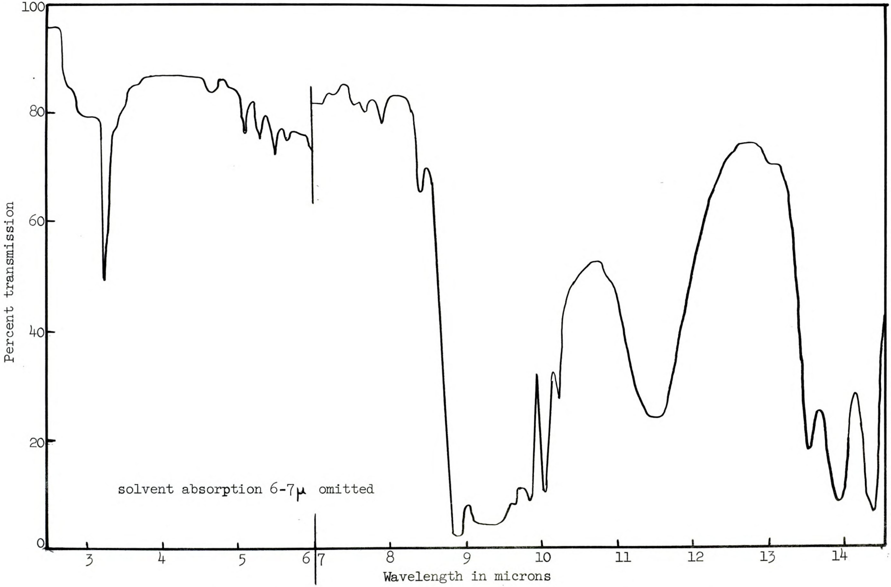


Figure 16. Infrared Spectrum of Compound I (page 50) in Carbon Disulfide

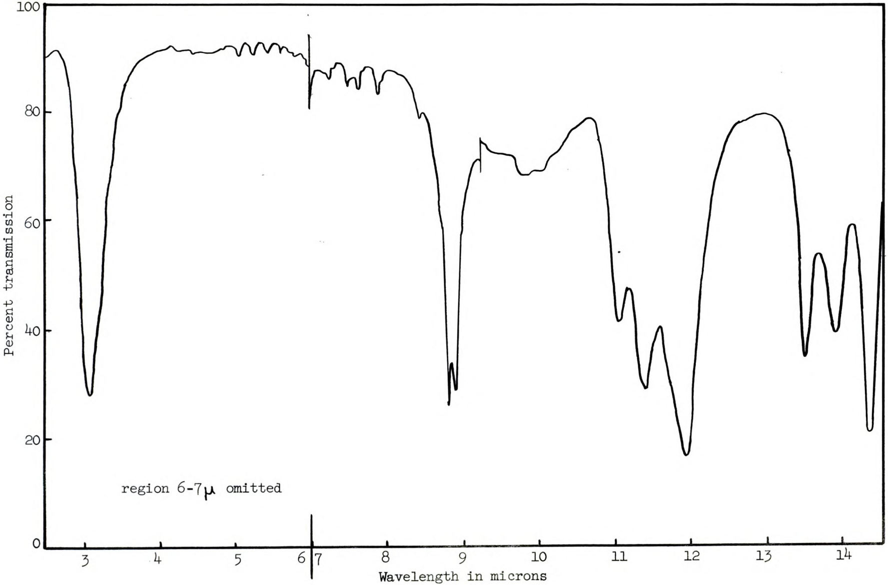


Figure 17. Infrared Spectrum of Diphenylsilanediol in Potassium Bromide Disc

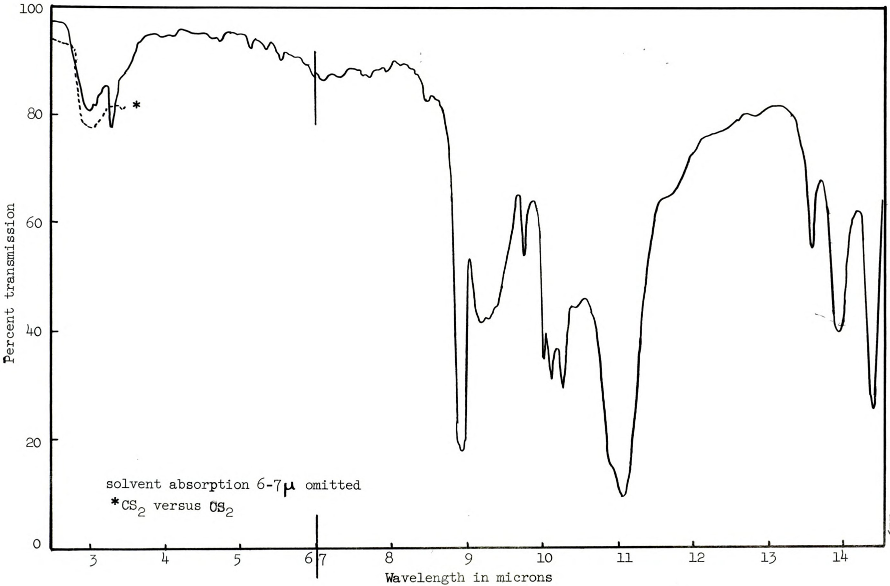


Figure 18. Infrared Spectrum of Compound II (page 50) in Carbon Disulfide

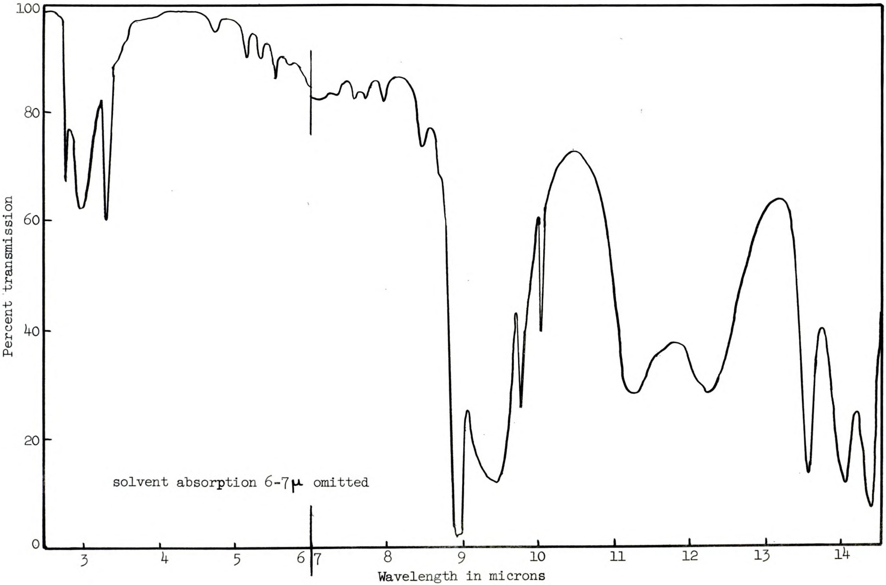


Figure 19. Infrared Spectrum of Tetraphenyldisiloxane-1,3-diol in Carbon Disulfide

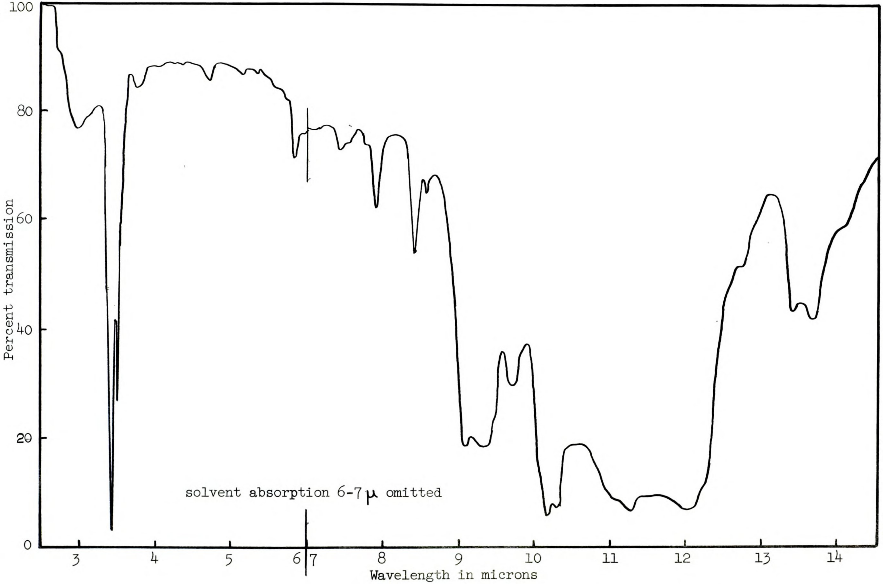


Figure 20. Infrared Spectrum of Compound <u>III</u> (page 66) in Carbon Disulfide

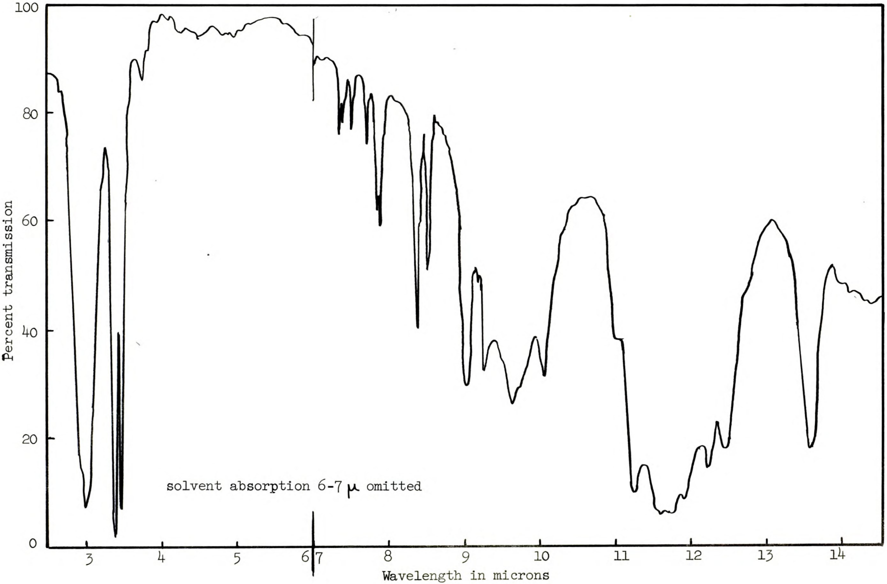


Figure 21. Infrared Spectrum of Dicyclohexylsilanediol in Carbon Disulfide

APPENDIX 3

X-RAY POWDER DIFFRACTION DATA

TABLE XI

INTERATOMIC SPACINGS FOR BIS(TRIPHENYLSILYL)CHROMATE

Line	Θ (degrees)	d_{hkl} (A)	Relative Intensity
	Chromium K Radiation (λ = 2.2909 A)		
1	5.58	11.79	5
2	7.51	8.77	8
3	8.58	7.68	1
4	9.15	7.20	5
5	9.64	6.84	1
6	10.29	6.42	1
7	11.23	5.88	2
8	12.09	5.48	2
9	13.76	4.82	3
10	14.11	4.70	1
11	15.04	4.42	10
12	16.10	4.13	3
	Copper K Radiation (λ = 1.5418 A)		
13	10.95	4.06	1
14	11.38	3.91	1
15	11.69	3.81	1
16	12.84	3.47	1
17	13.20	3.38	0.5
18	13.51	3.30	1
19	14.34	3.11	1
20	14.80	3.02	1
21	15.46	2.90	1
22	16.05	2.79	1
23	18.54	2.47	1

TABLE XII

INTERATOMIC SPACINGS FOR BIS(P-TOLYLDIPHENYLSILYL)CHROMATE

Line	Θ (degrees)	d_{hkl} (A)	Relative Intensity
Chromium K Radiation (λ = 2.2909 A)			
1	5.59	11.75	4
2	7.00	9.39	5
3	7.54	8.73	5
4	8.14	8.09	7
5	8.59	7.67	5
6	9.86	6.68	10
7	11.15	5.92	3
8	12.18	5.43	3
9	12.86	5.15	5
10	13.58	4.88	1
11	14.10	4.70	1
12	14.71	4.51	9
13	15.04	4.41	10
14	15.31	4.34	1
15	15.79	4.21	1
16	16.30	4.08	2
17	17.05	3.91	1
18	17.45	3.82	2
19	19.24	3.48	1
20	19.83	3.38	1
21	20.30	3.33	1
22	21.23	3.16	1
23	21.60	3.11	1
24	22.23	3.03	1
25	23.29	2.90	1
26	24.13	2.81	1
27	24.96	2.72	1
28	25.75	2.64	1
29	26.23	2.60	1
30	26.64	2.55	1
31	28.20	2.42	1

TABLE XIII

INTERATOMIC SPACINGS FOR BIS(TRICYCLOHEXYLSILYL)CHROMATE

Line	Θ (degrees)	d_{hkl} (A)	Relative Intensity
	Chromium K Radiation (λ = 2.2909 A)		
1	5.29	12.41	4
2	7.08	9.30	4
3	8.08	8.16	4
4	9.00	7.33	6
5	9.39	7.03	2
6	9.95	6.64	1
7	10.60	6.24	1
8	12.33	5.37	2
9	13.34	4.97	1
10	13.74	4.83	10
11	14.34	4.63	10
12	15.19	4.38	1
13	15.51	4.28	1
14	16.36	4.07	2
15	18.43	3.62	1
16	19.00	3.52	1
17	19.61	3.41	1
18	20.21	3.33	1
19	21.00	3.20	1
20	21.66	3.10	1
21	22.35	3.01	1
22	22.93	2.94	1
23	23.66	2.85	1
	Copper K Radiation (λ = 1.5418 A)		
24	16.66	2.69	1
25	17.99	2.50	1
26	18.15	2.48	1
27	18.64	2.41	1
28	22.46	2.02	1
29	26.83	1.71	1

TABLE XIV

INTERATOMIC SPACINGS FOR COMPOUND II

Line	Θ (degrees)	d_{hkl} (A)	Relative Intensity
Chromium K Radiation ($\lambda = 2.2909$ A)			
1	5.65	11.62	7
2	6.78	9.70	7
3	7.44	8.84	10
4	8.85	7.44	2
5	9.63	6.84	1
6	10.46	6.31	1
7	11.36	5.81	1
8	12.43	5.32	1
9	13.68	4.84	10
10	15.06	4.41	10
11	15.66	4.24	8
12	15.96	4.17	3
13	16.38	4.07	1
14	17.08	3.90	2
15	17.79	3.75	1
16	18.20	3.67	2
17	19.70	3.40	1
18	20.25	3.31	1
19	20.70	3.24	1
20	21.25	3.16	1
21	21.54	3.12	1
22	21.99	3.06	1
23	23.14	2.92	1
24	23.84	2.83	1
25	26.54	2.56	1
26	27.51	2.48	1
27	30.79	2.24	1
28	31.58	2.18	1
29	32.34	2.14	1

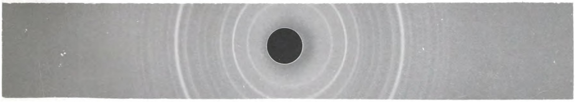


Figure 22. X-ray Diffraction Pattern of Bis(triphenylsilyl)chromate, Chromium K_α Radiation

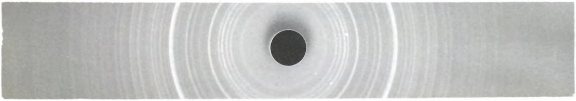


Figure 23. X-ray Diffraction Pattern of Bis(p-tolyldiphenylsilyl)chromate, Chromium K_α Radiation

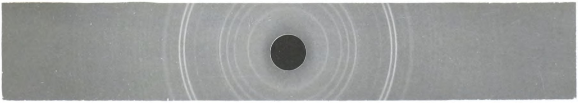


Figure 24. X-ray Diffraction pattern of Bis(tricyclohexylsilyl)chromate, Chromium K_α Radiation

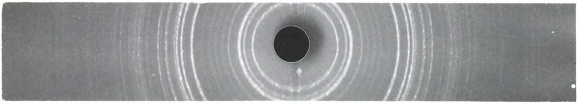


Figure 26. X-ray Diffraction Pattern of Compound II, Chromium Kα Radiation

Figure 25. X-ray Diffraction Pattern of Compound I, Chromium Kα Radiation

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