

Siloxy Methylene Oxide Compounds*

H. H. ENDER, *Silicones Division, Union Carbide Corporation,
Tonawanda, New York*

INTRODUCTION

Siloxymethylene oxide compounds or "silyl formals" are interesting as easily polymerizing monomers and as reactive formaldehyde donors which allow the introduction of both the siloxane function and methylene oxide or methylol groups into organic molecules with active hydrogen.

Polymerization can take place in two directions: first, through the functionality of the —Si—O— bond tending to form long —Si—O—Si— chains and, second, through the ability of formaldehyde to form polymethylene oxide chains.

Henglein and Schmulder¹ published in 1954 a method of obtaining silicon ester acetals by reaction of methylene glycol diacetate with dimethyldiethoxysilane in the presence of sodium ethoxide; on the other hand, they obtained polymers by the reaction of dimethyldichlorosilane with methylene glycol in the presence of pyridine. Their attempt to make trimethylchlorosilane react with methylene glycol was not successful.

In 1956, Henglein and Niebergall² reported the synthesis of mono- and poly(silylchlorals) from trimethylchlorosilane, triethylchlorosilane, dimethyldichlorosilane, and diethyldichlorosilane.

In 1957, Henglein et al. obtained a German patent³ for "Polyalkylsilylacetals" that describes the transesterification reaction of dimethyldiethoxysilane with methylene glycol diacetate.

In no case has a reaction been described between a tri- or tetrafunctional chlorosilane as, e.g., methyltrichlorosilane or silicon tetrachloride and formaldehyde or a formaldehyde donor.

DISCUSSION

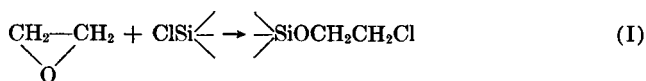
A large number of potential formaldehyde donors and their reactions with alkyl and aryl chlorosilanes were studied. Among others, the following

compounds were found to form $\text{>Si—OCH}_2\text{O—}$ groups: hexamethyl-

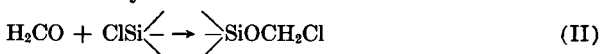
enetetramine, dimethylolacetone, paraformaldehyde dispersed in pyridine or in another HCl acceptor, aqueous formaldehyde and pyridine, and dialkoxymethanes, e.g., methylal and hemiformals (solutions of formaldehyde in alcohols).

*Presented in part before the Division of Polymer Chemistry at the 140th meeting of the American Chemical Society, Chicago, Ill., September, 1961.

The reaction between a chlorosilane and formaldehyde can be assumed to take place in a manner similar to that between a chlorosilane and an epoxy compound.^{4,5} Generally, formaldehyde undergoes many reactions which are typical of the oxirane ring. Thus, we can expect schematically that formaldehyde will add to a chlorosilane in such a manner that oxygen will bond to silicon and chlorine to carbon:



Ethylene oxide



Formaldehyde

The $\begin{array}{l} \diagleft \\ \diagright \end{array} \text{SiOCH}_2\text{Cl}$ group hydrolyzes easily to $\begin{array}{l} \diagleft \\ \diagright \end{array} \text{SiOCH}_2\text{OH}$ and HCl when water is present. In the absence of water, the chlorine-containing intermediate can be isolated and purified by distillation.

The reaction between a chlorosilane and formaldehyde or its derivatives can be carried out in the absence of an acceptor for HCl and water or in the presence of an acceptor, for instance, pyridine.

In the first case, even formaldehyde acts as an HCl acceptor, forming dichlorodimethyl ether:

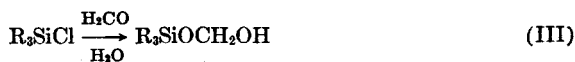


An intermediate in this reaction is the unstable chloromethanol ClCH_2OH . The chlorosilane is simultaneously transformed into a chloromethoxy compound which hydrolyzes with ice to a silyl formal, as shown in formula (II).

Reactions in Presence of a Basic HCl Acceptor

In the presence of pyridine, an equivalent amount of water, and an excess of formaldehyde (for instance, in methanol solution), the following reactions were observed.

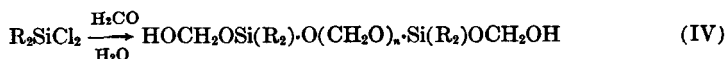
A. Monofunctionals



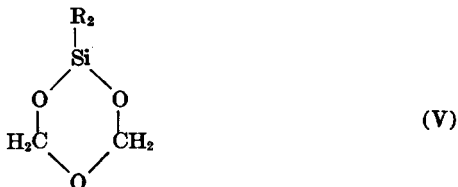
and



B. Bifunctionals



or



Silatrioxane derivative

EXPERIMENTAL

Materials and Apparatus

Chlorosilanes were redistilled with a simple fractionation column (2-3 plates) at normal pressure.

Pyridine, reagent grade, was dried with Linde Molecular Sieve type 4A.

Isopropyl ether was dried with calcium chloride and redistilled.

Dialkoxymethane. Commercial dimethoxy methane or methylal was used, dried with calcium chloride or Molecular Sieve, and redistilled (CaCl₂ eliminates water and methanol).

Hemiformal. The commercial product of the Celanese Corporation of America, Methylformcel, was used containing 55% formaldehyde, 33% methanol and 12% water; this is a mixture of monomeric and polymeric formaldehyde hemiacetals of methanol: HO(CH₂O)_nCH₃ where *n* is an integer. Since pure HOCH₂OCH₃ contains 48.8% formaldehyde and 51.6% methanol or, with 12% water, 42.6% formaldehyde and 45.5% methanol, the content of 55% formaldehyde in Methylformcel can be explained by the assumption that at least 30% of the formaldehyde is present in a polymeric state.

The apparatus was a three-necked 1000 ml. flask equipped with a stirrer, a dropping funnel, and a thermometer. The flask may be cooled or heated.

Reactions in Presence of a Basic HCl Acceptor

This method gives good yields with chlorosilanes of all functionalities. The reactions are carried out preferably in such a weight ratio that 1.5-2 moles of formaldehyde are used for each silicon-bonded chlorine atom.

The chlorosilane was applied in pyridine solution, with 1 mole pyridine for each chlorine and an additional excess of 10%. Only silicon tetrachloride cannot be used in pyridine solution because it forms a solid complex compound with pyridine.

A. Monofunctionals

A flask equipped with stirrer, thermometer, and dropping funnel was charged with 4 moles = 220 g. of Methylformcel; the dropping funnel, with a solution 2 moles = 217 g. of trimethylchlorosilane in 2 moles = 160 g. of pyridine.

The pyridine solution was added dropwise, the temperature maintained at -10-0°C. When all had been added the reaction mixture was allowed to come to room temperature and was then diluted with 500 g. of isopropyl ether. The ether solution was decanted as well as possible from pyridinium hydrochloride. The precipitate was dissolved in water and shaken re-

peatedly with isopropyl ether. The ether solutions were united, washed repeatedly with water, dried with anhydrous Na_2SO_4 and, finally, with CaCl_2 . The dry ether solution was filtered the next day and distilled *in vacuo* to eliminate the solvent. Some of the product is volatile *in vacuo* at 30°C . and condenses together with isopropyl ether in the trap cooled with dry ice. It can be recovered by redistillation at atmospheric pressure. Yield: 187 g. of a low-viscosity oil of the probable composition $(\text{CH}_3)_3\text{Si}\cdot\text{O}\cdot(\text{CH}_2\text{O})_2\cdot\text{CH}_2\text{OH}$.

ANAL. Calcd.: C 40.0%, H 8.9%, Si 15.5%, mol. wt. 180. Found: C 39.9%, H 8.2%, Si 15.6%, mol. wt. 220.

The infrared spectrum is characterized by an intense structure due to Me_3Si , a weak OH bond, the CH_2 structure indicated by intense bands at $\sim 1460\text{ cm.}^{-1}$, and an intense band at 1110 cm.^{-1} assigned to the $\text{Si}-\text{O}-\text{C}$ structure.

This substance can be distilled *in vacuo* but it undergoes condensation. Products like $(\text{CH}_3)_3\text{Si}\cdot\text{O}\cdot(\text{CH}_2\text{O})_n\text{Si}(\text{CH}_3)_3$ with n equal to 6 and 7 could be isolated from the distillate.

B. Bifunctionals

Dimethyldichlorosilane and methylvinylchlorosilane gave the formals in a smooth reaction with methylhemiformal in the presence of pyridine. For instance, 6 moles of Methylformcel and 2 moles of $\text{CH}_3(\text{C}_2\text{H}_3)\text{SiCl}_2$ + 4 moles pyridine afforded in the usual preparation a colorless low-viscosity oil of the structure $\text{HO}\cdot\text{CH}_2\text{OSi}(\text{C}_3\text{H}_6)\cdot\text{O}\cdot\text{CH}_2\text{OSi}(\text{C}_3\text{H}_6)\text{OCH}_2-\text{OH}$ ($\text{C}_3\text{H}_6 = \text{CH}_3 + \text{CH}:\text{CH}_2$) in 80% yield.

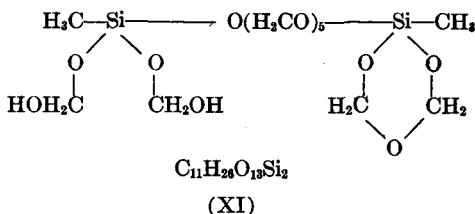
ANAL. Calcd.: C 38.7%, H 7.1%, Si 18.1%, mol. wt. 310. Found: C 38.9%, H 6.3%, Si 18.9%, mol. wt. 325.

C. Trifunctionals

Methylsilylformal. One mole = 149.5 g. of MeSiCl_3 is mixed with 3 moles + 10% excess = 264 g. of pyridine. This mixture was added slowly to a cooled solution of 6 moles = 330 g. of Methylformcel in 300 g. of isopropyl ether at a temperature maintained at $-10-0^\circ\text{C}$. The precipitated pyridinium hydrochloride was separated by filtration and washed with isopropyl ether. The ether solutions were washed with water to eliminate excess pyridine, pyridinium hydrochloride, and methanol. The solution was dried with CaCl_2 , and isopropyl ether was then removed by vacuum distillation at about 30°C . A water-clear liquid of low viscosity was obtained: sp. gr. at 25°C ., 1.135 g./ cm.^3 ; refractive index at 25°C ., 1.4137; viscosity at 25°C ., 7 cpoise.

At low temperatures it becomes increasingly viscous and sets at about -79°C . to a glasslike resin without showing a real melting point. Typical

analyses of pilot-plant preparations agree with the following structure:



The $-\text{CH}_2\text{OH}$ groups can also be methylated to $-\text{CH}_2\text{OCH}_3$, or a second silatritoxane ring can form by loss of water.

ANAL. Calcd. for $\text{C}_{11}\text{H}_{26}\text{O}_{13}\text{Si}_2$: C 31.3%, H 6.1%, Si 13.3%, mol. wt. 422. Found: C 31.6%, H 6.4%, Si 13.4%, mol. wt. 403.

Analogous results were obtained for phenylsilylformal and vinylsilylformal.

Methyldisilatritoxane Tetramer. Methyldisilatritoxane tetramer (X) was prepared in three different ways. In two cases acceptors for HCl were used: in one case, hexamethylenetetramine; in the other, pyridine. In the third case (see Formation of Formals, below) no basic HCl acceptor was applied.

Hexamethylene tetramine method. 1.6 moles (slight excess = 225 g. of hexamethylenetetramine was dissolved in 1000 g. of chloroform, and a solution of 0.5 mole of methyltrichlorosilane = 75 g. in 250 g. of chloroform was added dropwise with stirring, the temperature maintained at 20–25°C. A dense white precipitate appeared immediately upon addition of the MeSiCl_3 solution. When the addition was terminated, the mixture was heated to reflux for 30 min. and cooled to room temperature. Then 1.5 moles of water = 27 g. was added dropwise, the temperature maintained at 20–25°C.; then a larger amount of water was added to dissolve excess hexamethylenetetramine and its hydrochloride. The solution stayed neutral throughout the whole process. It was then washed repeatedly with water and dried with anhydrous Na_2SO_4 . When chloroform is distilled off, a viscous oil remains in a yield of 47.5% of theory.

The infrared spectrum shows free and bonded OH groups, and SiCH_3 , SiOCOSi , SiOSi , and strong CH_2 structures. The compound has, therefore, $\text{Si}-\text{O}-\text{Si}$ and SiOCH_2OSi units. See Table I for analysis.

Pyridine method. With aqueous formaldehyde: 0.4 moles = 36 g. of a 37% aqueous formaldehyde solution (10% excess) was mixed with 36 g. of pyridine. To this mixture, another mixture of 0.1 mole = 15 g. of MeSiCl_3 and 0.3 moles = 24 g. of pyridine was added dropwise, the temperature kept at 20–25°C. The product was then diluted with toluene and washed with water. An oil similar to that yielded in the hexamethylenetetramine procedure was obtained. The infrared spectrum is also very

similar. An excess of formaldehyde seems to improve the yield. See Table I for analysis.

D. Tetrafunctionals

Since silicon tetrachloride forms a solid addition compound with pyridine, the usual technique for the preparation of silyl formals described under Monofunctionals (above) had to be modified as follows:

A three-necked two-liter flask with dropping funnel, stirrer, and thermometer was charged with 6 moles = 327 g. of Methylformcel, 4 moles + 10% = 350 g. of pyridine, and 300 g. of isopropyl ether, and the mixture was cooled to -20°C . The dropping funnel was charged with 1 mole = 170 g. of SiCl_4 dissolved in 300 g. of dry isopropyl ether. The SiCl_4 solution was added to the solution in the flask so slowly that the temperature in the kettle never rose above 0°C . A voluminous precipitate of pyridinium hydrochloride formed. The excess pyridine produced a soft pasty precipitate which separated easily from the isopropyl ether solution. The precipitate was separated by decantation and washed repeatedly in the flask with portions of 100 g. of dry isopropyl ether until the ether did not extract any more oily substance.

The gathered ether extracts were shaken with calcium chloride to eliminate excess pyridine and methanol, and then filtered through a dry filter in a dry box. The clear solution was then evaporated *in vacuo* at about 30 and, finally, at 60°C . and 2 mm. Hg pressure. Yield: 171 g., or 63% of theory for a low-viscosity oil; refractive index at 25°C ., 1.4148; sp. gr. at 25°C ., 1.178 g./cc. This does not distill but loses formaldehyde *in vacuo* at about 120°C .

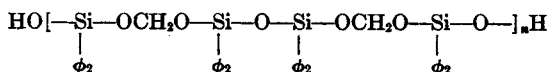
The analysis is in agreement with structure (VIII) $\text{C}_{10}\text{H}_{24}\text{O}_{10}\text{Si}$:

ANAL. Calcd.: C 36.1%, H 7.2%, Si 8.5%, H_2CO 54%, mol. wt. 332. Found: C 36.2%, H 7.4%, Si 8.6%, H_2CO 53%, mol. wt. 347.

Formation of Silyl Formals in Acid Solution

A. Difunctional

The reaction between diphenyldichlorosilane and formaldehyde was effected as follows. A 25 g. amount of diphenyldichlorosilane was mixed with 6 g. of paraformaldehyde and 3.6 g. of water added dropwise under cooling and stirring, temperature maintained at about 20°C . The reaction mixture was then heated up to 110°C . to eliminate HCl. It was then diluted with isopropyl ether, neutralized with sodium bicarbonate, and filtered, and the solvent was evaporated. A colorless viscous oil was obtained in 60% yield. The infrared spectrum shows the typical $-\text{CH}_2\text{O}-$ absorptions. The analysis was in agreement with the structure:



The part between the brackets is $\text{C}_{60}\text{H}_{46}\text{O}_7\text{Si}_4$.

ANAL. Calcd.: C 69.0%, H 5.2%, Si 12.8%. FOUND: C 68.6% and 69.2%, H 4.8% and 4.6%, OH 1.05%, Si 12.6%.

The found OH value would require n to be about 4.

B. Trifunctional

It was observed that dimethoxymethane does not react spontaneously with methyltrichlorosilane but that in the presence of small amounts of aluminum powder and copper powder an exothermic reaction starts. The activity of these metals could be increased by traces of HgCl_2 dissolved in ether. Good results were obtained with theoretical amounts of dimethoxymethane or methylal, or with a large excess—e.g., 6 moles of methylal for one mole CH_3SiCl_3 .

For instance, 30 g. of MeSiCl_3 (0.2 mole) and 110 g. of dimethoxymethane (1.45 moles) were refluxed in the presence of 1 g. of aluminum powder and 0.5 copper powder for 2 hrs. The temperature of the liquid rose from 42 (boiling point of dimethoxymethane) to 60°C. The mixture was allowed to cool to room temperature, then 35 g. of diisopropyl ether was added and the reaction mixture poured onto crushed ice, lowering the temperature to about -10°C. (addition of water rather than ice caused an undue increase in temperature, leading to decomposition). Washing the solution free of acid with water and drying and evaporating the solvent *in vacuo* yielded a viscous oil which gives the same IR spectrum as do the hexamethylenetetramine method and the pyridine method (above). These operations in the presence of water should be carried out within 2 to 3 hrs., to avoid undue hydrolysis.

Table I gives the analytical data. The structure (X) ($\text{C}_{12}\text{H}_{24}\text{O}_{17}\text{Si}_8$) is assumed for the three products prepared with hexamethylenetetramine (Hexa), prepared in the presence of pyridine (Py), and prepared with dimethoxymethane (Dimeth).

TABLE I
Calculated for Formula (X), $\text{C}_{12}\text{H}_{24}\text{O}_{17}\text{Si}_8$

Calcd., %	Found, %		
	Hexa	Py	Dimeth
C 21.4	21.6	21.4	22.1
H 5.1	5.9	7.3	5.8
Si 33.3	33.8	31.8	34.7
OH 5.05	4.5	—	4.8

It has to be taken into account that the products were not purified since they can be neither distilled nor crystallized and, in each case, mixtures of polymers were obtained.

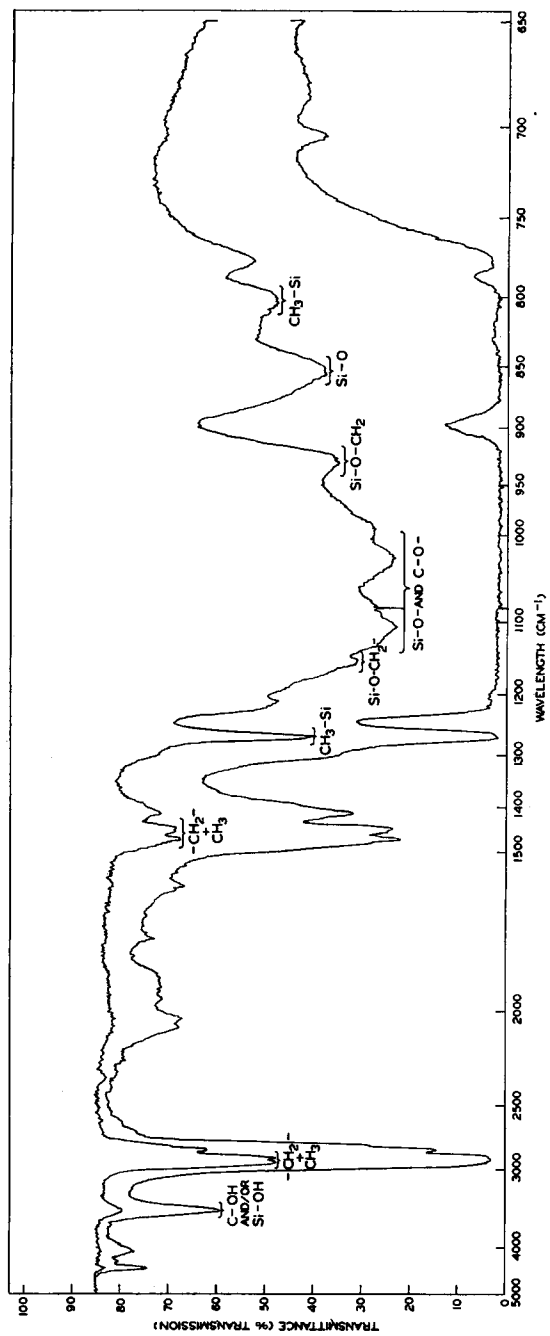
Properties

All the silyl formals obtained thus far are oils which become very viscous at low temperature and set at about -79°C . to a glass. They do not exhibit a definite melting point.

The polymer disilatrioxane derivative (X), ratio $\text{Si}/\text{H}_2\text{CO} = 2$, is a viscous oil at room temperature with a tendency to solidify in pure state within a few weeks. In solution at about 30–40% solids content it is stable at room temperature. It is soluble in most organic solvents, especially in diisopropyl ether-toluene mixtures. This solution is an excellent film former. Coatings on glass or metal cure at 125°C . in an hour to a hard brittle glasslike film which is insoluble in all solvents, is water-repellent, and prevents corrosion. Applied in extremely thin films of 5–8% solids-containing solutions, coatings that are elastic, heat-resistant and corrosion-inhibiting are obtained on various metals, especially on steel, copper, and aluminum.

The silyl formals with a ratio $\text{Si}/\text{H}_2\text{CO} = 1$ of all functionalities are oils of low viscosity and relatively high refractive index and specific gravity. They are soluble in all solvents with the exception of aliphatic hydrocarbons, and are themselves solvents for a great number of organic compounds, which facilitates the reactions with many of them, e.g., with phenols, amines, acids, aldehydes, ketones, alcohols, epoxides, isocyanates, fatty oils, and amides. They react also easily at room temperature with such proteins as skin or leather, tanning them and making them water-repellent simultaneously.

Upon heating, silyl formals lose formaldehyde which can react immediately with a phenol, urea, melamine, etc., derivative without precipitating the silicon-containing part of the silatrioxane molecule. This fragment is then built into the polymer which forms by the usual formaldehyde condensation process. In this way, oil-soluble and tung-oil-reactive phenol formaldehyde resins can be synthesized with a content of about 10% silicon metal. There is, thus, a large variety of possibilities for introducing silicon into organic molecules by using silyl formals as intermediates, which show the functions of polyfunctional silanols, e.g., $-\text{Si}(\text{OH})_3$, but are quite stable at room temperature and become reactive at temperatures from 120°C . upwards. When an acceptor for formaldehyde is present it will react; otherwise, formaldehyde will escape as a gas and the usual silanol condensation reactions can take place. There are also reactions that take place at room temperature, especially with amines, hydrazines, hydroxylamine, amides, proteins (for example, the tanning of skin and leather).



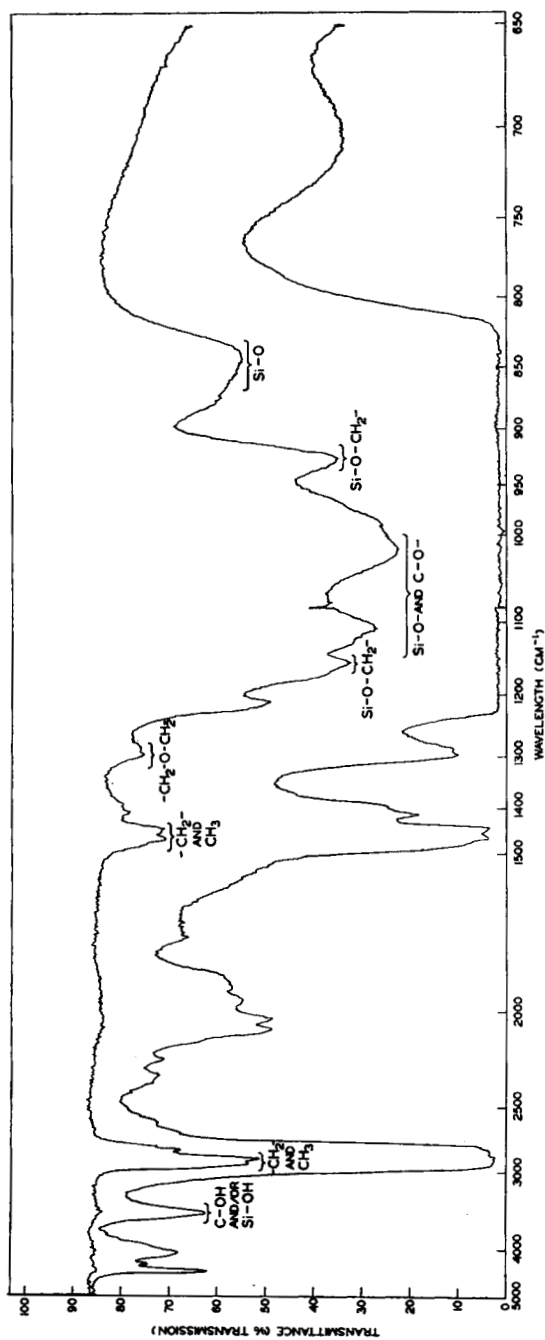


Fig. 1. Typical infrared absorption spectra for the trifunctional and tetrafunctional silyl formal; (a) trifunctional methylsilatroxane, (b) tetrafunctional formyl.

Whereas siloxanes do not react with LiAlH_4 , methyl silyl formal ignites, probably by formation of methylsilane (CH_3SiH_3).

Silyl tetraformal (VIII) differs from the above-mentioned formals by its solubility in water which, however, leads to hydrolysis within a few minutes of addition of water and which is also responsible for its sensitivity to moist air.

Silyl tetraformal is also a very effective crosslinker in many systems, e.g., in silicone gum stocks, epoxy resins, polyamines, etc. Its crosslinking ability is increased by metallic catalysts, e.g., tin octoate.

Figure 1 shows typical infrared absorption spectra for the trifunctional and tetrafunctional silyl formal.

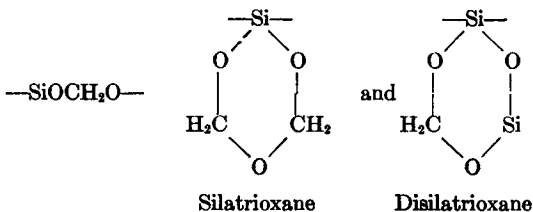
The author wishes to thank the management of the Silicones Division of the Union Carbide Corporation for the opportunity to carry through and publish this work. Thanks are also due Messrs. R. R. Sawyer, D. M. Ruttenbur, and J. J. Behen for the infrared spectroscopy, and Mr. R. G. Pankhurst and G. W. Heylman, all of the Linde Company, Union Carbide Corporation, for all other analytical work.

References

1. Henglein, F. A., and P. Schmulder, *Makromol. Chem.*, **13**, 53 (1954).
2. Henglein, F. A., and H. Niebergall, *Chem. Ztg.*, **80**, 611 (1956).
3. Henglein, F. A., P. Schmulder, and H. Niebergall, German Pat. 1,008,732 (1957); (through *Chem. Abstr.*, **53**, 21666a (1959) "Polyalkylsilyl acetals").
4. Patnode, W., and R. O. Sauer, U. S. Pats. 2,381,137; 2,381,138; 2,381,139 (1945).
5. Eaborn, C., *Organosilicon Compounds*, Butterworth, London, 1960, pp. 299-300.

Synopsis

Silicon containing chain and ring formals of the structures



were synthesized from the reaction of a chlorosilane with formaldehyde or a formaldehyde donor in acid solution or in the presence of an HCl acceptor. Mono-, di-, tri-, and tetrafunctional "silyl formals" were obtained; they are oily products of various degrees of polymerization and of relatively high refractive index and specific gravity. Silyl formals are stable at room temperature. They are useful intermediates in cases in which a siloxy group should be introduced into an organic molecule by reaction with an organic OH group or active hydrogen. Tri- and tetrafunctional silyl formals are effective crosslinkers in various systems.

Résumé

On a synthétisé des chaînes contenant des silicones et des cycles formals (v. le résumé en Anglais) en faisant réagir une chlorosilane avec le formaldéhyde ou un donneur de

formaldéhyde en solution acide ou en présence d'un accepteur d'acide chlorhydrique. On a obtenu des "formals silyliques" mono-, di-, tri-, et tétrafonctionnels. Ce sont des produits huileux à degrés de polymérisation variables, à indices de réfraction et à poids spécifiques relativement élevés. Les formals silyliques sont stables à ordinaire température. Ils sont d'intérêts intermédiaires dans les cas où un groupe silonyle devrait être introduit dans une molécule organique par réaction avec un groupe OH organique ou un hydrogène actif. Les formals silyliques tri- et tétrafonctionnels sont des agents de pontage actifs dans divers systèmes.

Zusammenfassung

Siliciumhaltige Ketten- und Ringformale (siehe englische Zusammenfassung) wurden durch Reaktion eines Chlorsilanes mit Formaldehyd oder einem Formaldehyddonor in saurer Lösung oder in Gegenwart eines HCl-Akzeptors synthetisiert. Mono-, di-, tri-, und tetrafunktionelle "Silylformale" wurden erhalten; sie bilden ölige Produkte mit verschiedenem Polymerisationsgrad, mit verhältnismässig hohem Brechungsindex und spezifischem Gewicht. Silylformale sind bei Raumtemperatur stabil. Sie sind zur Einführung einer Siloxygruppe in organische Moleküle durch Reaktion mit einer organischen OH-Gruppe oder aktivem Wasserstoff brauchbar. Tri- und tetrafunktionelle Silylformale bilden wirksame Vernetzer in verschiedenen Systemen.

Received March 19, 1962