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Crystalline Organosilsesquioxanes[*]

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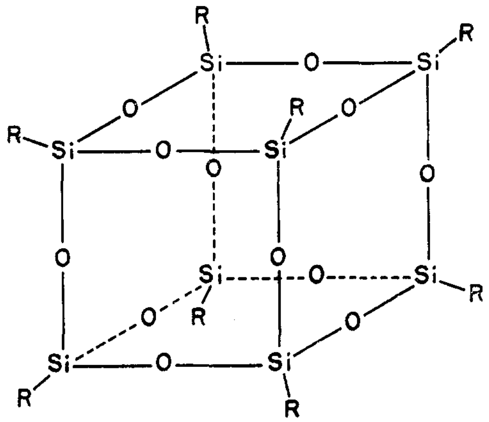
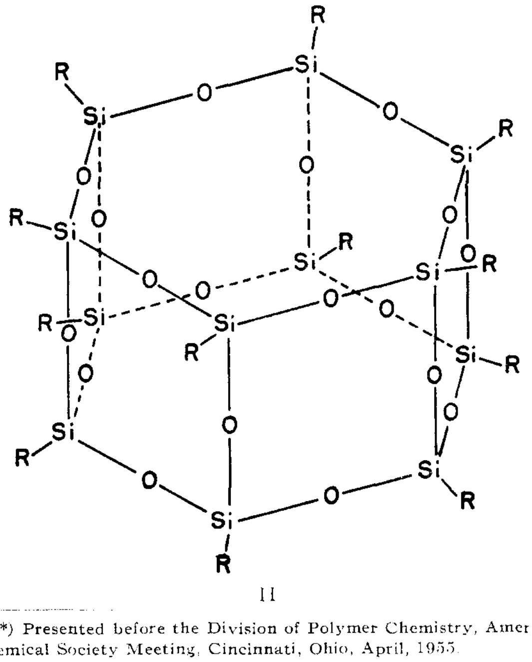
Low-polymer organosilsesquioxanes $(RSiO_{3/2})_n$ were prepared by alkali-catalyzed siloxane rearrangement of organotrichlorosilane hydrolyzates. Crystalline cubic octamers (I) of methyl-, ethyl-, *n*-propyl-, *n*-butyl- and cyclohexyl-silsesquioxanes were isolated. A hexagonal prismatic dodecamer (II) and several unidentified species of crystalline methylsilsesquioxanes were also obtained. A phenylsilsesquioxane, which is probably a triangular prismatic hexamer, was prepared from an alkaline solution.

Siloxanes having only $HSiO_{3/2}$ units, and their derivatives, are termed silsesquioxanes. A sublimed methylsilsesquioxane, of low solubility and undetermined molecular weight, was reported by Scott.[1] It was formed in small amounts with other polycyclic methylsiloxanes by thermal depolymerization of a cohydrolyzate of methyltrichlorosilane and dimethyldichlorosilane. Soluble ethyl, *n*-propyl and *n*-butyl-silsesquioxanes also were prepared.[2] The crystalline phase of each of these products was identified as the octamer (I). However, the molecular weight and analytical data, on which this identification was based, were not given. This paper presents a more detailed description of the alkylsilsesquioxane octamers and other low-polymer organosilsesquioxanes.



I



II

The most probable of the simple three-dimensional structures are prisms having cyclotetrasiloxane faces and cyclic siloxane bases of various sizes, as exemplified by the cubic octasilsesquioxanes (I) and the hexagonal prismatic dodecasilsesquioxanes (II). Pyramidal tetrasilsesquioxanes $(RSiO_{1.5})_4$, with structures akin to that of hexamethylenetetramine, also are conceivable; but their formation seems unlikely because of strain considerations. Consequently, the various low-polymer silsesquioxanes may be generally expected to have an even number of units above 4. These compounds may be considered prototypes of the more complex, irregular, highly crosslinked polymers which constitute silicone resins having predominantly $RSiO_{3/2}$ units. Indeed, small amounts occasionally volatilize from such resins above 200°.

Hydrolysis of organotrichlorosilanes is a vigorous reaction in which there is rapid replacement of the Si–Cl by Si–OH and concurrent condensations to give cross-linked resins or gels. When this reaction is conducted in a solvent, such as diethyl ether, gelation may be avoided. Dilution limits the degree of polymerization by favoring increased cyclization and less complete hydroxyl condensation. After the hydrolyzates are washed free of acid, they may be concentrated to viscous liquids or soluble solids, depending upon the character of the organic groups and the extent of condensation. Thus, with methyl or phenyl groups, the unheated products are hard, glassy resins, whereas with ethyl and higher alkyl groups they are generally highly viscous oils. To obtain soluble resins from methyltrichlorosilane, it is important to employ high dilution, remove the acid quickly and concentrate at low temperature.[3] The hydrolyzates have from 0.2 to 1.0 hydroxyl group per silicon and consist mainly of branched and cyclic polysiloxanols. Occasionally, small amounts of silsesquioxanes crystallize from them.

Heating the solvent-free hydrolysis products causes them to set to infusible resins or gels. At 200–250°, small amounts of low polymers are volatilized. The methyl octamer I was isolated in about 1% yield by this means.

When the hydrolysis products were heated above 400° at low pressure, thermal depolymerization occurred and low-polymer alkylsilsesquioxanes dis-

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(*) Presented before the Division of Polymer Chemistry, American Chemical Society Meeting, Cincinnati, Ohio, April, 1955.

(1) D. W. Scott, THIS JOURNAL, **68**, 356 (1946).

(2) A. J. Barry and J. W. Gilkey, U. S. Patent 2,465,188 (1949).

(3) W. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 358 (1946).

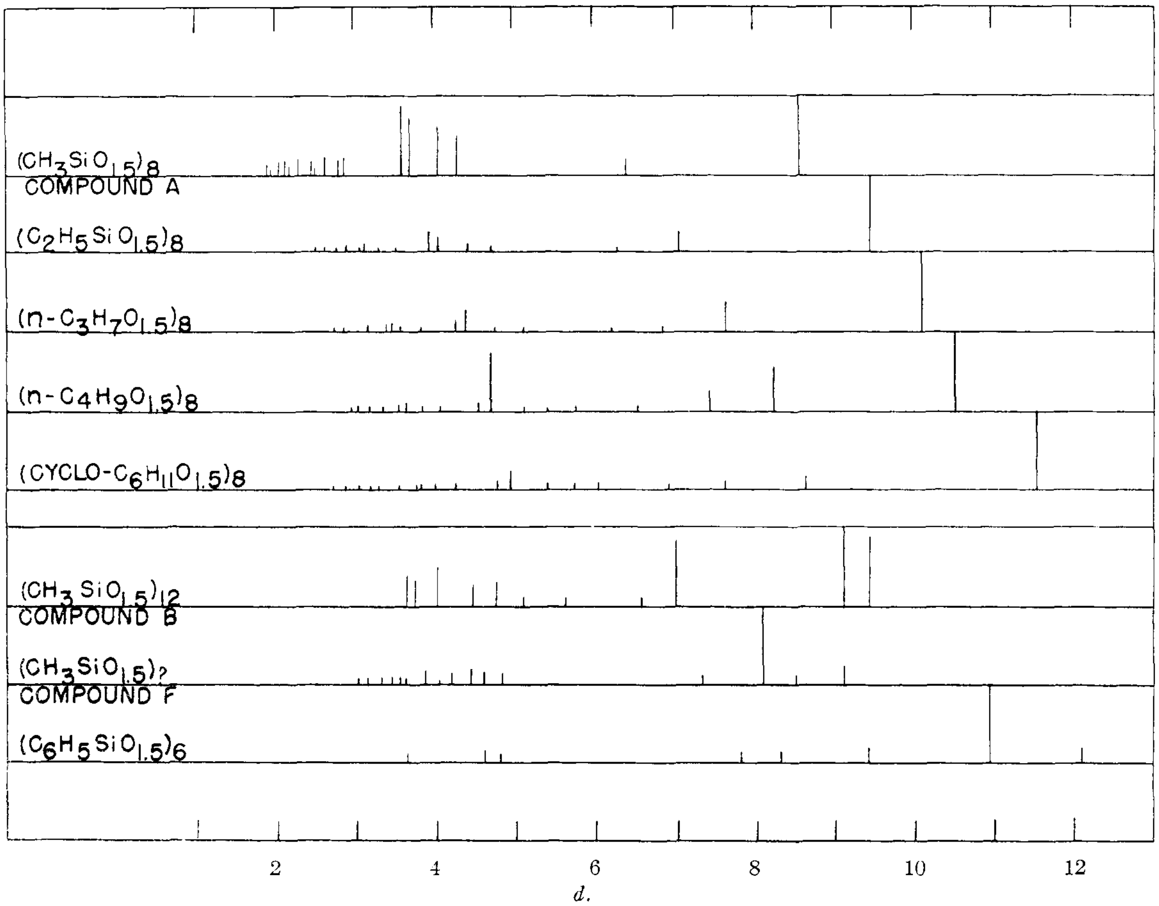

Fig. 1.—Plot of X-ray powder pattern data. The heights of the lines for the various *d* values are proportional to the relative intensities (I/I_0).

tilled. However, this uncatalyzed depolymerization afforded low yields of distillate and was attended with considerable pyrolysis. Apparently the silsesquioxanes formed less readily than the cyclic[3,4] and polycyclic[1] siloxanes.

Alkali-catalyzed siloxane cracking proceeds more efficiently and at lower temperatures than the thermal process in the preparation of cyclic dialkylsiloxanes.[4] In the work here reported, this catalytic method was found to be eminently suited to the preparation of low-polymer silsesquioxanes.

The preferred method of preparation consisted of heating a soluble hydrolysis product of the alkyltrichlorosilane in contact with powdered sodium or potassium hydroxide (1–10 mole %) at 250 to 400° under reduced pressure. The alkali formed polysiloxanol salts which catalyzed both siloxanol condensation and siloxane rearrangement. High conversion to the low-polymers was usually possible, because they were formed continuously in a dynamic equilibrium and were simultaneously removed by distillation. In general, the heated mixtures remained fluid and underwent vigorous boiling and foaming when the low-polymers split out near 300°.

The distilled ethyl, propyl and butyl products were semi-solids, of which nearly half crystallized from solvents. These crystals resembled pseudocubic rhombs and melted at 282°, 220° and 195°, respectively. They were isomorphous, as indicated in Fig. 1, and were identified by cryoscopic molecular weights as octamers (I). The molecular weight and hexahedral structure were ascertained for the ethyl compound by a single-crystal X-ray analysis. Somewhat higher molecular weight values, indicating about 11 $RSiO_{3/2}$ units, were obtained for the crude hydroxyl-free distillates.

The cyclohexyl product was a crystalline sublimate which was poorly soluble and did not melt below 400°. A recrystallized sample was identified as the octamer I by ebulliometric molecular weight and X-ray diffraction analysis. It was isomorphous with the other octamers.

A preparation starting with 2-methylpentyltrichlorosilane afforded an oil mixture which failed to crystallize.

Preparation of the methylsilsesquioxane low polymers was less smooth than for its homologs. The hydrolyzates were hard solids in which the alkali catalyst was dispersed less readily. However, when potassium hydroxide was added to solutions of the hydrolyzate, insoluble powders containing well-dispersed potassium salts were obtained. They were precipitated either by immediate concentration or upon standing. Prolonged heating of these powders at 250–400° afforded 50–64% of crystalline and

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(4) (a) M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, THIS JOURNAL, **68**, 667 (1946); (b) J. F. Hyde, U. S. Patents 2,438,478 (1948); 2,455,999 (1948).

oily low polymers. Predominantly crystalline material was obtained when the temperature did not exceed 300°.

The crystalline phase of the methyl products was sublimable and had very low solubility. It was apparently similar to Scott's $(CH_3SiO_{3/2})_{2n}$ product.[1] Our crystalline material was a mixture of species in solid solution. It was partly resolved by fractional extraction and crystallization. The principal constituent (A) had the lowest solubility. Crystallographic and X-ray diffraction data showed it was isomorphous with and structurally similar to the other crystalline alkylsilsesquioxanes. Its structure therefore was established as that of the octamer I. Crystallization of the mother liquors afforded a second methylsilsesquioxane (B), in amount about one-fourth that of the octamer. Molecular weight determinations indicated a dodecamer, for which structure II is proposed. At least four additional crystalline species were found in small amounts in the mother liquors.

An attempt to prepare phenylsilsesquioxanes by the thermal alkali-catalyzed process failed. No low polymers distilled below 400°, and extensive decomposition was encountered at higher temperatures.

An alternate method of preparation of crystalline organosilsesquioxanes consisted of alkali-treating the trichlorosilane hydrolyzates in dilute solutions. Thus, the methyl octamer formed as nearly cubic crystals, in 15% yield, from 1% solutions in alcohol or benzene.[5]

A crystalline phenylsilsesquioxane was prepared in 85% yield by the catalytic action of potassium hydroxide on a dilute phenyltrichlorosilane hydrolyzate solution at room temperature. It was poorly soluble in organic solvents, did not melt below 400°, and was not isomorphous with the crystalline alkylsilsesquioxanes. An ebulliometric molecular weight determination indicated 6.5 $C_6H_5SiO_{3/2}$ units per molecule. Since an even number of units is required theoretically, the silsesquioxane must be a hexamer. It probably has a skeletal structure with the silicon atoms at the vertices of a triangular prism.

The similarity of X-ray diffraction data for the powdered crystalline alkylsilsesquioxane octamers is illustrated in Fig. 1 by the plot of the d-values and relative intensities (I/I_0). Considerably different crystal structures are indicated by the plots for the two other methyl (B and F) and phenyl compounds.

Infrared absorption spectra of the crystalline silsesquioxanes show no absorption for hydroxyl or other functional groups. Like those for quartz and silicone resins containing silsesquioxane units, they show a common strong Si–O band at about 9.0 μ; this wave length is somewhat shorter than that for linear, branched and cyclic siloxanes.[6]

Experimental Part

***n*-Propylsilsesquioxanes.**—To 1000 g. of *n*-propyltrichlorosilane in 2 l. of diethyl ether, 500 g. of water was added slowly, with external cooling to maintain a temperature of 25°. The ether solution was washed, concentrated over a steam-bath, and then heated at 21 mm. pressure to give 514 g. of a viscous oil. A mixture of 345 g. of the hydrolyzate oil and 7.7 g. of powdered sodium hydroxide was heated at 0.10–0.15 mm. by a metal bath at 300–380°. There was considerable foaming and vigorous boiling due to the splitting out of volatile polymers, which distilled at 200–270° and partly crystallized to a stiff paste on cooling. A small residue was dark, glass-like and spongy. Collection of 9.8 g. of water in a cold trap indicated the hydrolyzate oil had an OH/Si ratio of 0.28.

The semi-crystalline paste gave a mol. wt. value of 1033 (f.p. with cyclohexane), indicating an average of about 11 $C_3H_7SiO_{3/2}$ units per mol. Infrared analysis indicated nil OH. With low proportions of potassium isopropoxide or lead naphthenate at 200°, this material underwent catalytic polymerization and thermoset to a hard clear resin.

Nearly half of the distillate paste crystallized from acetone or hexamethyldisiloxane as **octa-*n*-propyloctasilsesquioxane**, m.p. 219–220°. The crystals were pseudo rhombs having a nearly cubic configuration. The melting point remained unchanged upon standing over five years at room temperature. At 150°, however, the melting point was depressed to 205–211° in 24 hours, and in 16 days the crystals were transformed to hard lumps which did not melt at 230°. This polymerization behavior at 150° was attributed to oxidation of the propyl groups. The X-ray powder data showed the crystals were isomorphous (see Fig. 1) with those for the other alkylsilsesquioxane octamers.

Anal. Calcd. for $(C_3H_7SiO^{3/2})_8$: Si, 29.4; mol. wt., 761.2. Found: OH, nil (infrared); Si, 29.1, mol. wt., 810, 773 (cyclohexane), 728 (benzene). X-Ray data: $d(I/I_0)$ = 10.1 (1.00); 7.6(0.42); 6.8(0.13); 6.2(0.01); 5.1(0.03); 4.72(0.08); 4.36(0.33); 4.20(0.17); 3.77(0.02); 3.53(0.04); 3.39(0.04); 3.30(0.04); 3.09(0.03); 2.81(0.01); 2.69(0.01).

In another preparation 87 g. of the propyl hydrolyzate, which had gelled upon standing several days, was submitted to a destructive distillation in the absence of a catalyst. The gel depolymerized to a viscous oil during 20 hours at 400°. Only water condensed in the receiver. The pressure then was reduced to 1–2 mm., where there was vigorous boiling and distillation began. After ten hours at 400–500°, the pot liquid had solidified and 39 g. of an oil had distilled at 200–280° (1–2 mm.). Analysis of this distillate was in fair agreement with that for a propylsilsesquioxane mixture.

Anal. Calcd. for $(C_3H_7SiO_{3/2})_n$: C, 37.9; Si, 29.4. Found: C, 38.9; Si, 30.6.

***n*-Butylsilsesquioxanes.**—Hydrolysis of *n*-butyltrichlorosilane to a viscous liquid product and depolymerization with caustic (3% by weight of hydrolyzate) were carried out as before. The water eliminated amounted to 3.0% of the hydrolyzate, indicating a ratio of 0.37 OH/Si. The low-polymers (89% yield) distilled at 220–320° (0.5–1.1 mm.) as a semi-crystalline paste; a mol. wt. value of 1155 indicated 10.6 $C_4H_9SiO_{3/2}$ units per mol. When some of the paste was heated with 0.3 mole % of potassium isopropoxide for six hours at 200°, it polymerized to a high-viscosity oil. The crystalline portion was isolated by recrystallization from acetone. The nearly cubic crystals, m.p. 190–195°, were identified as **octa-*n*-butyloctasilsesquioxane** by analysis and their isomorphism with the other alkylsilsesquioxane octamers.

Anal. Calcd. for $(C_4H_9SiO_{3/2})_8$: Si, 25.72; mol. wt., 873. Found: Si, 25.7, 25.4; mol. wt., 953 (cyclohexane), 830 (benzene). X-Ray powder data: $d(I/I_0)$ = 10.5 (1.00); 8.2(0.58); 7.4(0.25); 6.52(0.05); 5.75(0.04); 5.4(0.03); 5.1(0.08); 4.67(0.75); 4.50(0.21); 4.02(0.03); 3.78(0.04); 3.62(0.10); 3.52(0.10); 3.31(0.10); 3.14 (0.02); 2.98(0.03); 2.88(0.03).

Ethylsilsesquioxanes.—When ethyltrichlorosilane was hydrolyzed in ether, it gave on concentration a very viscous oil. This material was mixed with 6% by weight of sodium hydroxide and then heated in a bath at 405–450° until 35% of it had distilled at 190–220° (1–7 mm.). The distillate was a stiff paste. Crystallization from acetone or hexamethyldisiloxane afforded **octaethyloctasilsesquioxane** as pseudo-cubes, m.p. 280–282°.

Anal. Calcd. for $(C_2H_5SiO_{3/2})_8$: Si, 34.64; mol. wt., 649.2. Found: Si, 34.6, 34.5; mol. wt., 566 (benzene).

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(5) This method was employed, with higher concentrations of methyl- and phenyltrichlorosilane cohydrolyzates, to prepare soluble thermoplastic resins; J. F. Hyde and W. H. Daudt, U. S. Patents 2,482,276 (1949); 2,610,169 (1952).

(6) N. Wright and M. J. Hunter, THIS JOURNAL, **69**, 803 (1947); C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

The molecular weight and structure (I) of this compound were determined by X-ray analysis of a single crystal, grown after a month from evaporation of a solution in hexamethyldisiloxane. The X-ray data and a measured density of 1.3079 g./ml., established a rhombohedral and singly primative unit cell, with $a = 9.50 \pm 0.04$ Å. and $\alpha = 95.9 \pm 0.5°$, and fixed the value of 8 $C_2H_5SiO_{3/2}$ units per molecule. Powder diffraction data on the crushed crystals showed isomorphous reflections (see Fig. 1) with the other four alkylsilsesquioxane octamers, thereby confirming the degree of polymerization of 8 for the series.

$d(I/I_0)$ = 94.(1.00); 7.0(0.30); 6.25(0.06); 4.67(0.10); 4.38(0.16); 3.99(0.20); 3.88(0.30); 3.48 (0.04); 3.27 (0.03); 3.10(0.08); 3.04(0.06); 2.83(0.06); 2.73(0.01); 2.59(0.02); 2.47(0.02).

The lines did not match either the isometric or tetragonal systems. Microscopic examination showed that the crystals were anisotropic, probably triclinic, and had an extinction angle of about 41°; the interfacial angles averaged 83° and 97°.

In one instance, some of the pseudo-cubic octamer crystals (n_D 1.465) separated directly from 80 g. of a washed and concentrated hydrolysis product (found 3.2% OH) of ethyltrichlorosilane. The crystals (2% of hydrolyzate) were freed from the very viscous oil product by extraction with methanol.

Anal. Found: Si, 35.3; OH, nil.

Cyclohexylsilsesquioxanes.—Hydrolysis of cyclohexyltrichlorosilane in ether gave, on concentration, an amorphous solid. The melt was heated with 3% of its weight of sodium hydroxide by a metal bath at 340–440° until 36% of it had sublimed. The crystalline sublimate was poorly soluble in benzene or cyclohexane at room temperature.

Anal. Calcd. for $(C_6H_{11}SiO_{3/2})_n$: Si, 20.78. Found: Si, 20.8, 21.1.

Large, nearly cubic, crystals of **octacyclohexyloctasilsesquioxane** deposited from hot toluene. They did not melt below 400°, had a density of 1.174 g./ml., and were isomorphous with those of the other alkylsilsesquioxane octamers. Erratic results were obtained in attempted determinations of its molecular weight by cryoscopic means. However, values near that calculated were found by an ebulliometric method.[7]

Anal. Calcd. for $(C_6H_{11}SiO_{3/2})_8$: Si, 20.78; mol. wt., 1082. Found: Si, 20.6, 20.3; mol. wt., 968, 1124 (methylene chloride).

An X-ray pattern obtained for a sample of crushed crystals gave prominent *d*-values only at 11.5, 8.6, 7.6, 4.96, 3.80 and 3.50 Å. A second pattern, for a sample prepared by resublimation at about 400° (1 mm.) and fine grinding, gave the same lines plus a larger number of less intense reflections. These corresponded closely with the other alkyl octamers, as shown in Fig. 1. The data were indexed on a rhombohedral cell with lattice constants a_{rh} = 11.6 Å., α = 95°. (The lattice constants of the hexagonal cell were a = 17.1 Å., c = 18.15 Å., c/a = 1.06.) Using these values and the density, the number of $C_6H_{11}SiO_{3/2}$ units per unit cell was calculated to be 8.06.

X-Ray Data for Resublimed Sample

d	I/I_0	hkl	d	I/I_0	hkl
11.5	100	011	4.00	0.8	311
8.6	10	110	3.80	1.3	303
7.7	3.8	102	3.74	1.8	132
6.9	1.3	201	3.51	1.8	105, 124
6.05	0.8	003	3.33	0.5	231
5.75	0.5	022	3.20	.8	140, 322
5.40	1.8	121	3.03	.8	314, 215
4.95	19	300, 113	2.86	.8	404
4.77	1.0	122	2.71	.5	234, 135
4.30	0.5	220			

2-Methylpentylsilsesquioxanes.—Hydrolysis of (2-methylpentyl)-trichlorosilane[8] to a viscous liquid and depolymerization of the latter were carried out as before. The water collected amounted to 4.1% of the hydrolyzate (indicating 0.65 OH/Si). The low-polymers distilled at 290–325° (2–2.5 mm.) in 87% yield. This product was an oil having a viscosity of 820 cs. at 20° and nil hydroxyl content (infrared). An average of about 15 $C_6H_{13}SiO_{1.5}$ units per mol was indicated by a cryoscopic molecular weight determination (found: 2024). The mixture failed to give a crystalline compound.

Methylsilsesquioxanes.—Hydrolysis of 356 g. (2.00 moles) of methyltriethoxysilane was effected in a solution containing 11.4 g. (0.20 mole) of potassium hydroxide, 280 ml. of water and 3.5 l. of methanol. An amorphous powder (product 1), which precipitated overnight and coagulated in two more days, was collected on a filter. It was rinsed with methanol and dried at 160°; yield 125.5 g. The filtrate (no. 2) contained 70% of the alkali. A 61.3-g. portion of the alkaline powder (no. 1) was heated under vacuum (1 mm.) in a 500-ml. Claisen flask to which a wide side arm and receiver were sealed. A small amount of solid (no. 3) readily sublimed from the mixture at 200°. At 300–325°, crystalline material (no. 3) formed at a decreasing rate during 68 hours. It was carried over to the receiver by occasional warming of the upper part of the flask and the side arm. A final 39 hours at 400° formed only a trace of additional sublimate and left 19.4 g. of charred residue. In an attached cold trap was found 2.5 g. of a mixture of water and a liquid, b.p. 197–200°, which is probably 1,3-dimethyltetraethoxydisiloxane.[9]

The entire sublimed product (no. 3) amounted to 34 g. (55% of no. 1) and consisted of a microcrystalline paste. It was digested with 75 ml. of hot acetone to extract oily and soluble material (no. 4). The remaining solids (no. 5) amounted to 14.4 g. (42% of sublimate no. 3) and gave an X-ray powder pattern characteristic of the octamers. However, microscopic examination revealed that material other than octamer was present in solid solution. Therefore, 12.75 g. of the solids (no. 5) was placed in a thimble of a Soxhlet apparatus and leached 5 days with acetone to extract a portion (no. 6) containing the more soluble constituents. The remainder was dissolved by another 5 days extraction with chlorobenzene. From the refluxing chlorobenzene there was deposited a 7.6-g. first crop of uniformly small platelets having a square outline. These were collected on a filter and the filtrate was concentrated to give 0.3 g. of a second crop of similar crystals. The first crop platelets were observed under the microscope to be of a single crystalline phase, indicating the presence of but one compound (A). The second crop crystals were essentially the same, except that their cores had a slightly lower refractive index; this indicated the same compound (A) with a trace of an impurity in solid solution.

The pure crystals were rhombohedra, equidimensional in two directions. However, they were actually biaxial (probably triclinic), and possessed a 30–40° extinction angle. They had very low birefringence (γ = 1.483, $\gamma - \alpha$ = 0.003), making their crystal systems uncertain. Under a stereomicroscope they appeared as very thin plates oriented on their well developed basal pinacoids. As a result of this orientation, even after fine grinding, several of the X-ray reflections were highly intensified (especially for d = 8.50 and d = 4.13). For an X-ray diffraction pattern of a randomly oriented powder, a microcrystalline sample was obtained by a rapid vacuum resublimation at about 200°.

$d(I/I_0)$ = 8.50 (1.00); 6.35(0.20); 4.22(0.48); 39.5 (0.62); 3.62(0.75); 3.52(0.88); 2.80(0.28); 2.77(0.23); 2.58(0.25); 2.46(0.08); 2.39(0.20); 2.24(0.23); 2.15(0.12); 2.14(0.15); 2.00(0.17); 1.89(0.08); 1.82(0.1).

The crystals sublimed without melting when heated above 150° at atmospheric pressure. On rapid heating a sublimation point at 365° was reached. The molecular weight of this compound (A) was not obtained because of its extremely poor solubility in organic solvents, including toluene, chlorobenzene, pyridine, dimethylformamide, octamethylcyclotetrasiloxane and camphor. However, the above X-ray data showed that the crystals were isomorphous with those of the other alkyl derivatives. Because of this structural similarity and its analogous preparation, the compound was assigned the cubic octamer structure for **octamethyloctasilsesquioxane**.

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(7) R. E. Kitson, A. N. Oemler and John Mitchell, *Anal. Chem.*, **21**, 404 (1949).

(8) A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, THIS JOURNAL, **69**, 2916 (1947).

(9) H. J. Fletcher and M. J. Hunter, *ibid.*, **71**, 2922 (1949).

Anal. Calcd. for $(CH_3SiO_{3/2})_8$: Si, 41.82. Found: Si, 41.9, 41.8.

The second acetone extract (no. 6, from Soxhlet apparatus) was filtered while it was still hot to remove an additional 1.4 g. of platelets of the octamer compound (A). Together with the above 7.9-g. crops from chlorobenzene, the yield of this compound totaled 9.3 g. (73% of solids no. 5, or 17% over-all from no. 1). Upon concentration and cooling of the filtrate, 2.05 g. (16% of solids no. 5) of a second methylsilsesquioxane compound (B) crystallized in three crops as elongated prisms, m.p. 321–323°. With further concentration of the mother liquor, replacement of the acetone with ethanol, and cooling, there was obtained 0.11 g. of mica-like flakes of another compound (F), m.p. 133–135°.

The first acetone extract (no. 4) also was concentrated; it deposited 1.04 g. (3.1% of crude sublimate, no. 3) of a solid mixture, leaving 16.7 g. (49% of no. 3) of an oil mixture (found: Si, 40.0). Recrystallization of this solid mixture gave five separate types of crystals in successive 0.1- to 0.15-g. crops. The first and the last of these types were found by microscopic examination to consist of the above methylsilsesquioxane compounds B and F, respectively. The intermediate fractions comprised other compounds C, D and E which, after recrystallization, melted at about 255, 257 and 270°, respectively. The latter compounds were not further characterized, except that they were determined to be crystallographically distinct.

Cryoscopic molecular weight determinations on compound B indicate an average value of 11.6 $CH_3SiO_{3/2}$ units per molecule. Since the number must be an even integer, the compound is apparently **dodecamethyldodecasilsesquioxane**, for which the structure II is proposed.

Anal. Calcd. for $(CH_3SiO_{3/2})_{12}$: Si, 41.82; mol. wt., 805.1. Found: Si, 41.8, 41.6; mol. wt., 753 (cyclohexane), 785, 787 (camphor).

This compound was slightly soluble in many organic solvents. It recrystallized from acetone as elongated prisms and, at the same time, as short prisms with prominent basal pinacoids. These crystals showed perfect cleavage in two directions, frequent twinning, and an extinction angle of about 20°. They were biaxial (probably monoclinic), positive, and had moderate birefringence (γ 1.470, α 1.460). A sample was vacuum-sublimed to afford a non-oriented and microcrystalline powder, which gave the following X-ray diffraction data.

$d(I/I_0)$ = 9.4(9.6); 9.1(1.00); 7.00(0.89); 6.55(0.16); 5.60(0.15); 5.10(0.18); 4.70(0.38); 4.40(0.36); 3.96 (0.51); 3.70(0.37); 3.66(0.42).

The dissimilarity of the dodecamer with the other compounds is indicated in Fig. 1. The same powder pattern was obtained after a 20-hour heating at 200°, followed by vacuum resublimation. When patterns were taken on powdered samples of larger crystals, certain *d*-values were intensified by preferential orientation. Furthermore, those patterns revealed surprising and marked changes in the relative intensities for different samples and also for repeat runs of the same sample.

The lowest-melting (135°) compound F was free of hydroxyl and ethoxy groups, according to infrared analysis. It was the most soluble of the crystalline methylsilsesquioxanes isolated. It crystallized from ethanol as large thin flakes, with a bluish-gray interference color. These crystals were biaxial and had low birefringence (γ 1.460, α 1.458), a wavy extinction and strong dispersion. This material did not change on long standing. Recrystallization from acetone–ethanol gave flat plates, m.p. 135–137°, which were powdered to give the following X-ray diffraction data (see Fig. 1).

$d(I/I_0)$ = 9.1(0.27), 8.5(0.10), 8.1(1.00); 7.3 (0.13); 4.78(0.20); 4.60(0.07); 4.39(0.17); 4.18(0.17); 4.02 (0.10); 3.80(0.17); 3.62(0.07); 3.51(0.10); 3.40(0.03); 3.29(0.03); 3.13(0.03); 2.99(0.07).

Additional nearly cubic crystals of the octamer $(CH_3SiO_{1.5})_8$ (compound A) deposited slowly from the above alcoholic filtrate (no. 2). A slightly alkaline mixture (7.4 g.) of crystals with some amorphous solids was collected after 35 days. The octamer was extracted with chlorobenzene in a Soxhlet apparatus, freed from amorphous material by sublimation at 200–220° (750 mm.), and was then recrystallized as rhombic platelets from chlorobenzene; yield 4.23 g. (3.1% yield from $CH_3Si(OC_2H_5)_3$). On longer standing, more of these crystals continued to form.

Anal. Found: Si, 41.4, 41.7.

The octasilsesquioxane (A) was produced also by an alkali treatment of methyltrichlorosilane hydrolyzates in dilute alcohol or benzene solutions under reflux.[5] The $CH_3SiO_{3/2}$ concentration was only 1% by weight and potassium hydroxide was added in small amounts to provide siloxanol salts and a K/Si ratio of 1:100. When benzene was used, the small amount of water produced was removed by distillation. After 2 or 3 days refluxing, crystals of the octamer were obtained in 15 to 20% yields. The filtrate afforded additional small amounts of solid upon concentration and sublimation below 200°. The residue then afforded larger amounts of solid above 300°, by the above described thermal process.

In other small-scale siloxane-cracking experiments, in which potassium hydroxide was added to hydrolyzates in molar concentrations of 1 or 10%, the yields of sublimed low-polymers ranged from 50 to 64%. When runs were made in which powdered potassium hydroxide was merely mixed with the hydrolyzate solids in a mortar, lower yields (up to 16%) were obtained. In one run using 2% by weight of sodium hydroxide, there was obtained a 24% conversion to crystalline and oily low-polymers, from which both the octamer (A) and dodecamer (B) were obtained. However, in the absence of a catalyst, no sublimable methylsilsesquioxanes were produced upon heating hydrolysis products below 400°, except for trace amounts of crystalline low-polymers which came over initially at 200°.

Crystals of the methyl octamer also have deposited in small amounts from hydrolyzate solutions employed in the preparation of some silicone resins.

Phenylsilsesquioxanes.—Hydrolysis of phenyltrichlorosilane in dilute ether solutions, followed by immediate washing and concentration, afforded brittle soluble solids, comprising polysiloxanols with 0.5 to 1.0 OH/Si ratios. When such a product was heated with 3 to 5% by weight of sodium hydroxide to 440° (2–3 mm.) by the procedure employed with the alkyl compounds, there was distilled only 6% of a mixture of water and benzene. Continued heating of the resin melt to 520° gave further decomposition, with formation of additional benzene and a small amount of an uncharacterized oil.

A 21-g. sample of phenyltrichlorosilane was hydrolyzed in 200 ml. of diethyl ether and washed neutral with water. Addition of 0.06 g. of potassium hydroxide in 150 ml. of 96% ethanol and 750 ml. of benzene gave a clear solution having a 1.4% $C_6H_5SiO_{3/2}$ concentration. Some small crystals having a square outline deposited overnight and accumulated in clusters on long standing. After three weeks there was filtered 7.7 g. (60%) of crystals (rods with diameters up to 150 μ) showing weak birefringence (γ 1.580) and a first-order gray polarization color. An additional 3.2 g. (25%) of crystals of the same type, with diameters up to 400 μ, was formed during the next ten months. The crystals did not melt when heated to 400° and decomposed at higher temperatures. They were but sparingly soluble in methylene chloride and in refluxing toluene or chlorobenzene. The molecular weight of 836, determined ebulliometrically[7] in methylene chloride, indicated the compound to be **hexaphenylhexasilsesquioxane.** An X-ray powder diffraction pattern was dissimilar to those for the alkyl compounds, as shown in Fig. 1. The presumed prismatic skeletal structure could not be corroborated, due to difficulty of growing crystals suitable for a single crystal X-ray analysis.

Anal. Calcd. for $(C_6H_5SiO_{3/2})_6$: C, 55.79; Si, 21.73; mol. wt., 775.1. Found: C, 55.8; Si, 21.5; OH, nil; mol. wt., 839, 832. X-Ray powder data: $d(I/I_0)$ = 12.1 (0.20); 10.9(1.00); 9.4(0.17); 8.3(0.11); 7.8(0.11); 4.82 (0.11); 4.63(0.13); 3.58(0.12).

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