Problems of synthesis of tetrahedral organosilsesquioxanes. Hydrolytic condensation of hexafunctional branched organotetrasiloxanes

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The hydrolytic condensation of methyltris(methyldichlorosiloxy)silane (**1b**), methyl- (**1a**), and vinyltris(methyldiethoxysiloxy)silanes (**1c**) in dilute homogeneous solutions was studied. It was found by X-ray diffraction and ^{1}H NMR methods that, irrespective of reaction conditions, only octaorganooctasilsesquioxanes (**T$_8$**), namely, octamethyloctasilsesquioxane and 1,4-divinylhexamethyloctasilsesquioxane, were obtained instead of the expected tetraorganotetrasilsesquioxanes (**T$_4$**). These data suggest that the condensation processes involved in the hydrolysis of **1a—c** are predominantly intermolecular, and the molecules of the starting oligomers do not undergo rearrangements. Probably, the formation of **T$_4$**, whose molecules are built of four strained six-membered organosiloxane cycles, is less favorable thermodynamically than the formation of their homologs (**T$_8$**) built of eight-membered organosiloxane cycles.

Key words: polyorganosilsesquioxane polyhedra, hydrolytic condensation of functional organosiloxanes, X-ray diffraction study, hydrosilylation.

Polyhedral organosiloxanes are one of the structural forms of oligoorganosilsesquioxanes. To date, a number of individual polymers of general formula $(RSiO_{1.5})_n$, where R is an organic radical or a functional group and $n = 6, 8, 12, 14, 16$ (Fig. 1), have been obtained.[1—12]

Such oligomers have been first identified in low yields among the products of hydrolytic condensation of trifunctional organosilanes. The maximum yields were generally found in the case of organosilsesquioxanes possessing cubic structure (**T$_8$**). Furthermore, it was found that molecules of the other isolated oligomer-homologs are mainly built of eight-membered organosilsesquioxane cyclic moieties. Similar data were also obtained in a study of the structure of polymeric organosilsesquioxanes, irrespective of the conditions of their synthesis.[13]

An alternative process, thermocatalytic depolymerization of polymeric organosilsesquioxanes at 250—400 °C in the presence of sodium or potassium hydroxides, gave only **T$_8$**-type oligomers.[3]

In both cases, the formation of tetrahedral organosilsesquioxanes (**T$_4$**), which are the first members of the corresponding homologic series, was not observed. This fact was explained by the extremely high strain of

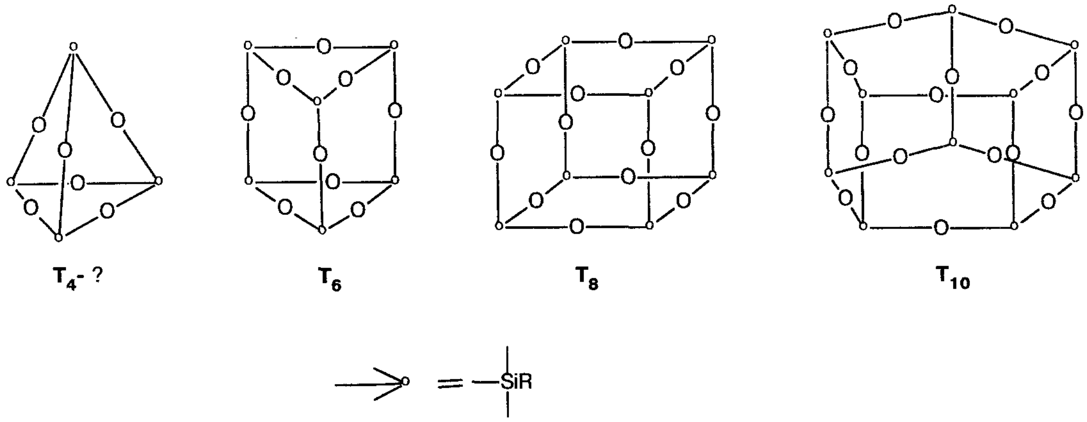


Fig. 1. Schematic presentation of the molecules of the first members of the homologic series of organosilsesquioxane polyhedra.

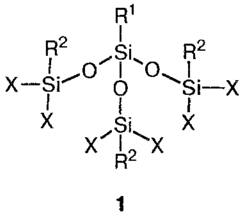
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1332—1339, July, 1995.

1066-5285/95/4407-1286$12.50

the molecules of **T_4** oligomers built of four condensed six-membered cyclic organosiloxane moieties. It was assumed on this basis that compounds with **T_4** structure are thermodynamically unstable.[3] However, it is clear that the data available are insufficient for drawing decisive conclusions about the possibility of the existence of **T_4** compounds. In fact, the above methods for synthesizing polyhedral organosilsesquioxanes have low selectivity of action on the structure of the final products. For this reason, these methods result in spontaneous appearance of the most thermodynamically favorable structures based on the eight-membered organosiloxane cycle. Probably, the unsuccessful attempts to synthesize tetrahedral organosilsesquioxanes are due not only to their high strain, although this is an important factor, but also to unsuitability of traditional methods for obtaining oligomers of this structure. It is therefore possible that the use of more effective methods for synthesizing organosiloxanes would make it possible to solve this problem.

The **T_4** oligomers are also interesting from some non-theoretical aspects. There is every reason to assume that tetrahedral organosilsesquioxanes should possess an unusual combination of properties. In this respect, they are undoubtedly interesting from the practical viewpoint.

In context of the above considerations, the determination of the possibility to obtain tetrahedral organosilsesquioxanes and the conditions of their prolonged existence is rather an interesting and urgent problem. The use of new starting reagents, whose molecular structures would be most favorable for the formation of **T_4** oligomers, is likely to be one of the possible ways for solving this problem. In the present work we tried to use for this purpose hexafunctional branched organotetrasiloxanes synthesized by us previously:[14,15]



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1a: $R^1 = R^2 = Me, X = OEt$
1b: $R^1 = R^2 = Me, X = Cl$
1c: $R^1 = CH{=}CH_2, R^2 = Me, X = OEt$

The formation of **T_4** compounds can be expected during hydrolytic condensation of oligomers **1**. In order to increase the probability of intramolecular condensation, the hydrolysis was carried out in dilute homogeneous solutions.

Results and Discussion

First, we studied the hydrolytic condensation of oligomers **1a,b**, whose molecules contain small methyl radicals at each of the four silicon atoms. During the hydrolytic condensation of oligomer **1a** in a dilute (3 %) dioxane solution in the presence of a catalytic amount of hydrochloric acid at 85 °C, formation of a compact finely crystalline precipitate was observed over a period of ~11 h with an overall yield of 23 %. The resulting compound was insoluble in organic solvents and did not melt on heating up to 500 °C in a sealed capillary. On the other hand, it sublimed quantitatively *in vacuo* (1 Torr) at 180—190 °C or under atmospheric pressure at 340—350 °C giving clearly edged colorless crystals. The residue formed after separation of the crystals and removal of the dioxane was a polymeric product (m.p. 150—160 °C), which contained one unassociated hydroxyl group per 20 silicon atoms (^1H NMR data).

It was found by X-ray diffraction and mass spectrometric methods that the compound isolated was the next oligomer homolog, octamethyloctasilsesquioxane (**T_8-Me**), rather than **T_4**.

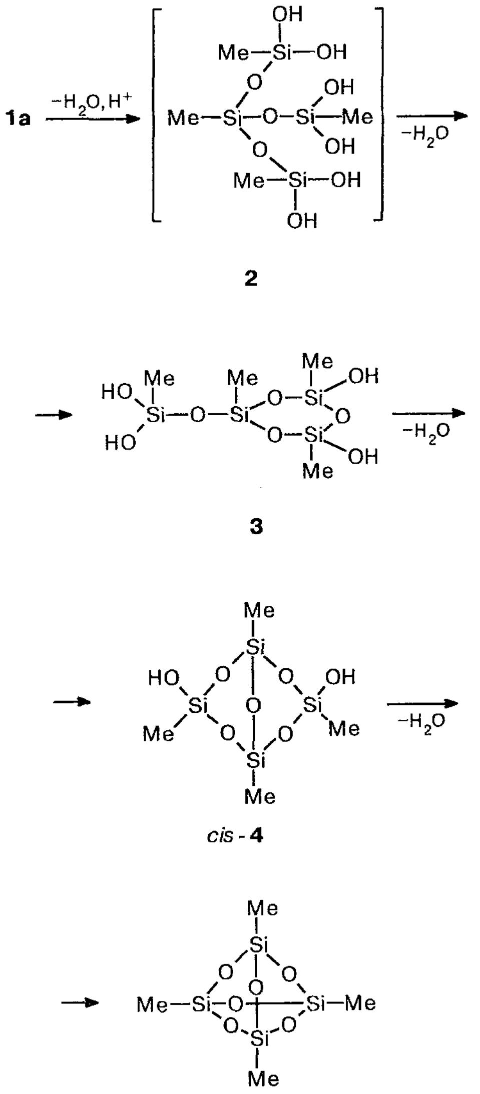
Formally, the result obtained is inconsistent with the conditions of hydrolytic condensation. The conditions specified above favor condensation processes occurring by an intramolecular mechanism (Scheme 1). The molecules of the resulting primary oligomeric products **3** and **4** should incorporate six-membered methylsiloxane moieties.

Naturally, such moieties should also be incorporated in molecules of higher-molecular oligomers formed by intramolecular condensation of the primary products. Hence, it was reasonable to expect the formation of structural isomer **6** rather than **T_8-Me**, whose molecules are built exclusively of eight-membered cycles. The molecule of oligomer **6** could be formed by intermolecular condensation of two bicyclic molecules of the *cis* isomer **4**.

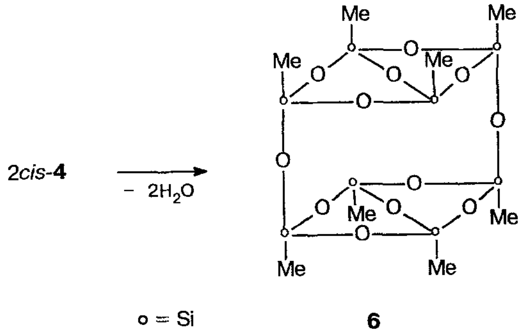
Taking the above data into account, the following hypothesis was put forward first: oligomers **5** and **6** formed during hydrolytic condensation undergo thermal rearrangement into **T_8-Me** during sublimation due to their high internal strain. On the other hand, the IR spectra of the products before and after sublimation turned out to be absolutely identical. Moreover, hydrolytic condensation of oligomer **1a** under mild conditions (at room temperature in an ether—ethanol medium in the presence of AcOH or traces of HCl) also results in **T_8-Me** in 20—23 % yields. Unlike the previous case, the **T_8-Me** is precipitated from the reaction mixture as sufficiently large crystals suitable for an X-ray diffraction study without preliminary sublimation. Similar results were obtained in a study of the hydrolytic condensation of oligomer **1b**.

Thus, the formation of **T_8-Me** occurs just during hydrolytic condensation. It follows from the data pre-

Scheme 1



Scheme 2

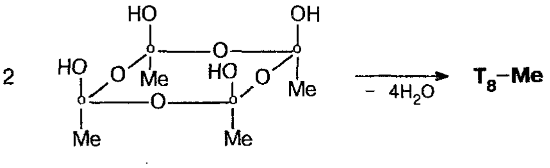


o = Si 6

sented that Scheme 1 proposed previously does not reflect the actual processes occurring in the reaction system. At least two versions satisfactorily describing these results are possible.

1. Rearrangement processes occur in the system during hydrolysis. They result in oligomers, whose molecules are built of the most stable eight-membered tetramethylsiloxane moieties. According to this version, **T_8-Me** molecules can result from condensation of two molecules of *cis*-1,1,1,1-tetramethyl-1,1,1,1-tetrahydroxycyclotetrasiloxane (**7**).

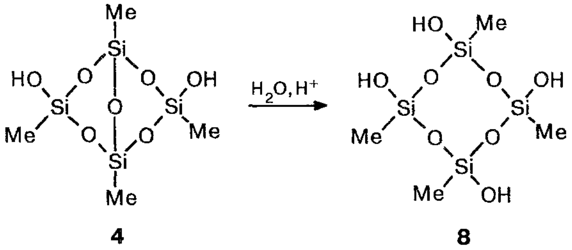
Scheme 3



7 o = Si

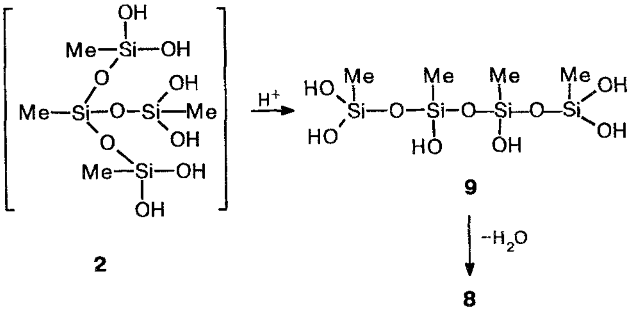
The formation of a mixture of stereoisomers of tetrole **7** is, for example, possible through decomposition of oligomer **4** (Scheme 4) with water in an acidic medium.

Scheme 4



The same result can be achieved by the sequence of chemical transformations presented in Scheme 5.

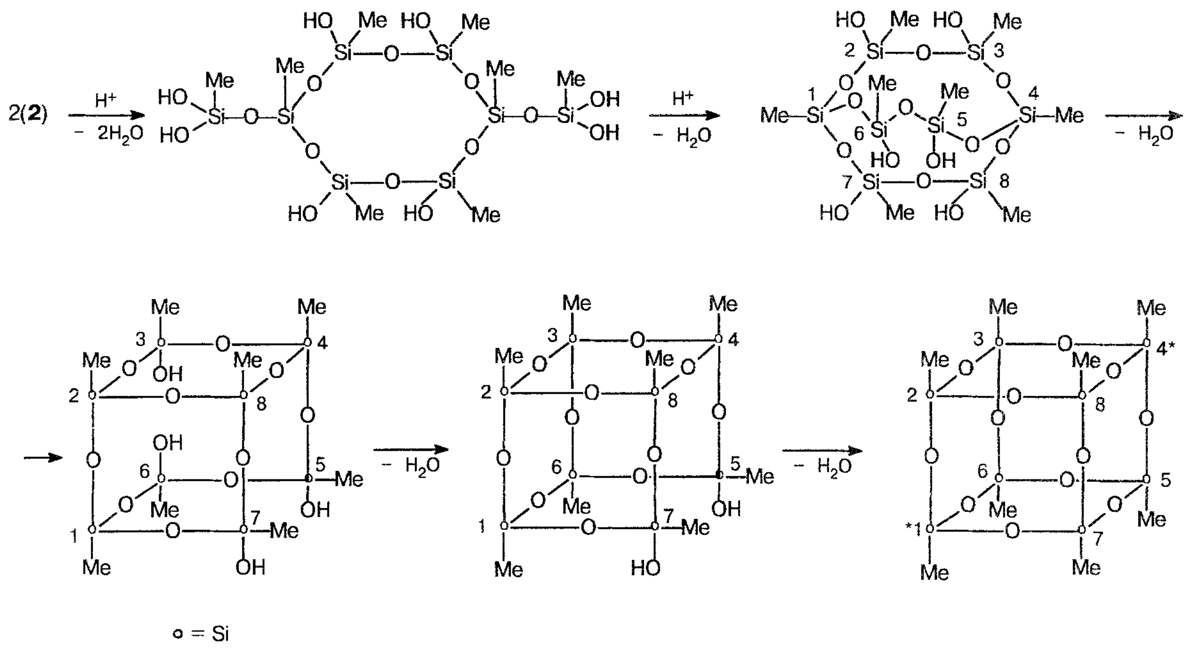
Scheme 5



Rearrangement of branched hexol **2** into its linear isomer **9** is quite probable, if one takes the data reported in Ref. 16 into account.

2. **T_8-Me** can be formed directly by intermolecular condensation of the primary product of hexol **2** hy-

Scheme 6



drolysis without its initial isomerization. It should be taken into consideration that the formation of strained six-membered methylsiloxane cycles, unlike that of eight-membered cycles, is much less thermodynamically favorable.[17] The scheme of intermolecular assembling of **T$_8$-Me** molecules during hydrolytic condensation can be represented as follows (Scheme 6).

In this case, the pathway for the formation of **T$_8$-Me** molecules is not so obvious as when they are formed from the corresponding *cis*-tetrole (Scheme 3). For clarity of the scheme, the silicon atoms in the molecules of intermediates are numbered.

Although, formally, both pathways describe the formation of the same compound, **T$_8$-Me**, in the reaction systems, they differ considerably, not only in the type of the processes occurring, but also in the final stereochemical result. In fact, if the second pathway is operative, the branching silicon atoms 1* and 4* (Scheme 6) in the molecules of the starting oligomers **1a** should be located at one of spatial diagonals of the cube in a molecule of **T$_8$-Me**. In the opposite case (pathway 1), they are expected to be statistically distributed over the cube vertices.

Based on the above data, it was impossible to prefer any of the variants. This originates from the fact that the organic surrounding of all four silicon atoms is the same (methyl radicals) in molecules of the starting oligomers, and hence they become indistinguishable in a **T$_8$-Me** molecule. Taking this fact into account, we synthesized hexafunctional tetrasiloxane **1c**, whose molecules contain vinyl radicals at branching silicon atoms and methyl radicals at silicon atoms in the side chains. We chose the vinyl radical as the probe due to the following considerations: the volumes of vinyl and methyl radicals are similar, and hence their steric effects on a particular reaction should also be similar. This allows us to hope that the hydrolytic condensation of oligomers **1a** and **1c** occurs in a similar way. On the other hand, we can try to reveal the position of the vinyl radical in the final **T$_8$-Me** by an X-ray diffraction study. In addition, various derivatives of the final polyhedra can be synthesized on the basis of reactive vinyl groups.

Hydrolytic condensation of oligomer **1c** was carried out for five days in a dilute ethereal—ethanolic solution in the presence of a catalytic amount of hydrochloric acid.

The X-ray diffraction data obtained for the resulting crystalline product (yield 20 %) suggest unambiguously that it has a **T$_8$** molecular skeleton (Fig. 2). However, we could not reveal the position of vinyl groups in the skeleton, despite the low temperature (−80 °C) of the X-ray diffraction experiment (see Experimental). The unsuccessful result originates from three objective reasons: 1) similarity of the volumes of vinyl and methyl groups favoring orientational disordering of molecules in the crystal*; 2) almost complete absence of intramolecular interactions hindering the rotation of the vinyl group, which favors orientational (and, certainly, conformational) disordering of the structure; 3) high symmetry of both the molecules themselves and their packing.

Thus, the X-ray diffraction data do not rule out the presence of any of the three possible isomers of divinylhexamethyloctasilsesquioxane (Fig. 3), which can be discriminated by NMR spectroscopy. However, it was impossible to record directly the NMR spectra of this

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* Thus, such a similarity, which is an important beneficial factor in the synthetic part of this work, can also have an adverse effect.

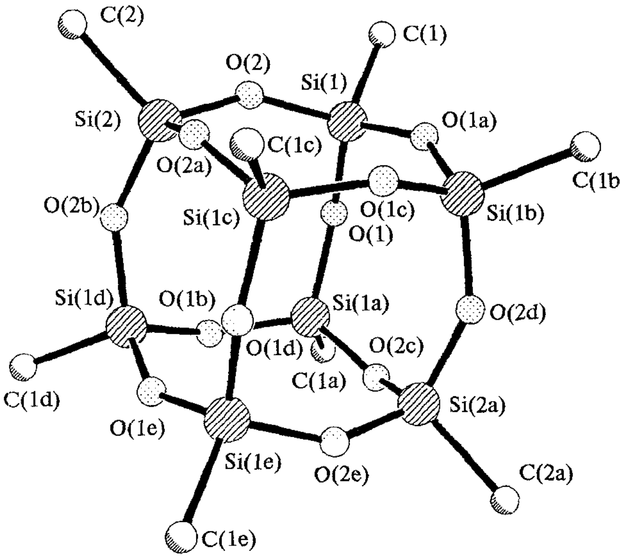
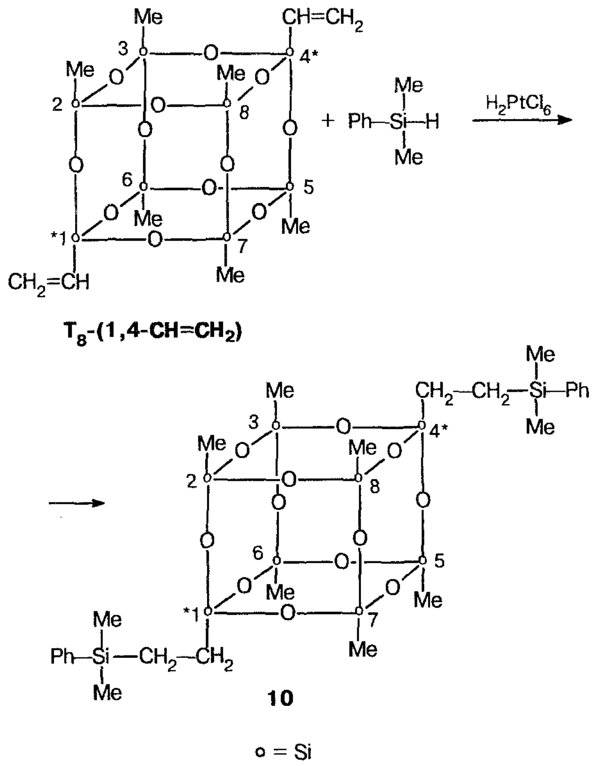


Fig. 2. General view of the molecule T_8-**(1,4-CH=CH$_2$)** according to X-ray diffraction data. The terminal CH_2 of vinyl substituents were not revealed.

Scheme 7



compound, since it is almost insoluble in any of the known organic solvents. Therefore, we decided to synthesize its soluble derivative by addition to the vinyl groups using dimethylphenylsilane as the reagent (Scheme 7).

The hydrosilylation reaction was carried out with a twofold excess of dimethylphenylsilane in toluene at 110 °C in the presence of a catalytic amount of H_2PtCl_6. 1,4-Bis-[2-(dimethylphenylsilyl)ethyl]hexamethyloctasilsesquioxane (**10**) was obtained in 63 % yield. The ^{1}H NMR spectrum of this compound contains a singlet of equivalent protons of methyl radicals at silicon atoms in the silsesquioxane fragment (δ_1 0.117), a singlet of protons of methyl radicals at silicon atoms in the side chains (δ_2 0.229), two multiplets in the regions δ_3 0.520 and 0.697, and a multiplet of protons of phenyl radicals at δ_4 7.3. The spectrum does not contain signals typical of the $\equiv$Si—CH(CH$_3$)—Si$\equiv$ moiety, which suggests that the hydrosilylation occurs exclusively as α-addition. The ratio of integral intensities of proton signals agrees with the values calculated theoretically. These data confirm that the divinylhexamethyloctasilsesquioxane obtained by hydrolytic condensation is an almost pure T_8-**(1,4-CH=CH$_2$)** isomer (Fig. 3).

Thus, the data obtained support version 2 as the one most correctly describing the proccesses in the systems studied. An additional piece of useful information is that the siloxane cage of the starting oligomers **1** is not liable to structural rearrangements under the conditions chosen for hydrolytic condensation.

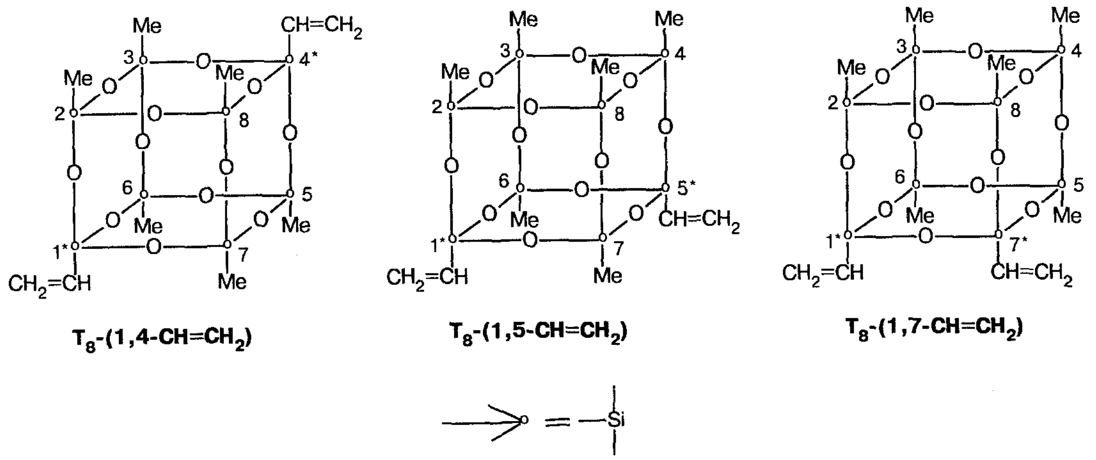


Fig. 3. Isomers of divinylhexamethyloctasilsesquioxane.

We also could not detect the formation of tetramethyltetrasilsesquioxane (**T_4-Me**) in a study of hydrolytic condensation of oligomer **1b** in a dilute ethereal solution in the presence of pyridine as an acceptor of HCl evolved. The reaction was carried out by slow dropwise addition of an ethereal solution of water and pyridine to an 1 % ethereal solution of compound **1b** at room temperature. In this case, hydrolytic condensation occurred as heterofunctional condensation, which usually occurs readily:

$$\equiv Si-Cl + H_2O \xrightarrow{Py} \equiv Si-OH + Py \cdot HCl$$

$$\equiv Si-OH + Cl-Si\equiv \xrightarrow{Py} \equiv Si-O-Si\equiv + Py \cdot HCl$$

Unfortunately, **T_4-Me** was not formed even under such favorable conditions. Furthermore, we did not detect any individual polycyclic methylsilsesquioxanes among the reaction products. The final product was a liquid oligomer, which transformed into a cross-linked polymer on storage.

At present, the data obtained are insufficient for drawing general conclusions on the principal possibility of synthesizing organosilsesquioxanes with tetrahedral molecules. However, it can be stated definitely that the formation of such compounds with low-volume organic radicals at silicon atoms by hydrolytic condensation is unlikely. In fact, even hydrolytic condensation of organosiloxanes so suitable for forming **T_4** as compounds **1a—c** occurs almost intermolecularly and results in high molecular mass oligomers. On the other hand, the synthetic potential of type **1** compounds has not been exhausted. Good results can be expected if bulky organic substituents are introduced at the silicon atoms in the side chains of the starting oligomers **1**. Such a procedure should decrease the fraction of intermolecular reactions during hydrolysis and facilitate the formation of six-membered cyclosiloxane fragments due to intramolecular condensation.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200 spectrometer in CCl_4, IR spectra were recorded on a Bruker IFS-110 spectrophotometer, and mass spectra were obtained on an MKh instrument. GLC analyses of the starting compounds were carried out on LKhM-8MD and PAKhV-08 chromatographs, column lengths 1 and 2 m, diameters 2 and 4 mm, using catharometer detectors, helium as the carrier gas (volume rate 30 mL min^{-1}), and Chromaton N-AW-HMDS (5 % SE-30) as the fixed phase. The starting oligomers, methyl- (**1a**) and vinyltris(methyldiethoxysiloxy)silane (**1c**), were obtained by the reaction of sodiumoxymethyldiethoxysilane with methyl- and vinyltrichlorosilanes, respectively.[14] Methyltris(methyldichlorosiloxy)silane (**1b**) was obtained by the reaction of compound **1a** with thionyl chloride.[15]

X-Ray diffraction study of 1,4-divinylhexamethyloctasilsesquioxane. The X-ray diffraction experiment was carried out at −80 °C on a Syntex $P2_1$ diffractometer (λMo$K\alpha$, graphite monochromator, $\theta/2\theta$-scanning, $2\theta_{max}$ = 48°, 920 measured reflections). Crystal structure data: $a = b = c = 8.600(9)$ Å, $\alpha = \beta = \gamma = 94.51(9)°$, $V = 630(3)$ Å^3, $d_{calc} = 1.48$ g cm^{-3}, $Z = 1$ ($C_{10}H_{24}O_{12}Si_8$), space group $R3$ (molecule in a special position on axis 3). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for hydrogen atoms, which were localized by difference synthesis. Attempts to determine the positions of terminal atoms of vinyl groups by Fourier synthesis gave a series of electron density peaks, which were lower than the peaks of "ordered" carbon atoms (those in methyl groups or the α-atoms of vinyl groups). However, refinement of the specified positions of terminal C atoms at any population (0.2—1.0) resulted in shortening of the C=C distances to ~1.0 Å. Fixing the distances made the refinement procedure unsteady, while the thermal parameters of disordered atoms became unrealistic. Obviously, strong disordering of vinyl groups combined with orientational disordering of the whole molecule (four possible orientations for the 1,4-$CH=CH_2$ isomer) make it impossible to localize the positions of terminal $=CH_2$ groups on the background of the methyl groups, whose population is three times as high. The orientational disordering of the structure is indicated by the thermal parameters of the **T_8** cage atoms, which are *ca.* twice as high as the usual values for low-temperature experiments. The packing of molecules is rather loose: the forbidden intermolecular contacts (C...C ≤ 3.5 Å) of methyl and vinyl groups are absent for almost every position and orientation of the latter localized by Fourier synthesis.

As a result, structure refinement was carried out only for ordered atoms. The final divergence factors were $R = 0.048$, $R_w = 0.048$ for 464 reflections with $I > 2\sigma(I)$. All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS[19] programs. The coordinates and thermal parameters of atoms are presented in Table 1, and the bond lengths and bond angles are given in Table 2.

Hydrolytic condensation of methyltris(methyldiethoxysiloxy)silane (1a). 1.1. A solution of oligomer **1a** (10 g, $2.02 \cdot 10^{-2}$ mol) in 1,4-dioxane (320 mL) was added dropwise with stirring at 85 °C over a period of 3 h to a mixture of water (18 mL, 1 mol), 0.1 *N* HCl (0.1 mL), and 1,4-dioxane (50 mL). The reaction mixture was stirred for 4 h at 85 °C and cooled to ~20 °C. After 14 h passed, the resulting precipitate of **T_8-Me** was filtered off, washed with ether on a filter (3 × 25 mL), and dried *in vacuo* (1 Torr) at 50 °C. Sublimation at 200 °C (1 Torr) gave 1.26 g (23%) of **T_8-Me**. Found

Table 1. Coordinates (×10^4; for H atoms, ×10^3) and thermal parameters (Å^2×10^3) of atoms in the crystal structure of **T_8-(1,4-$CH=CH_2$)**

Atom	x	y	z	U_{iso}
Si(1)	4272(2)	6391(2)	2368(2)	56(1)
Si(2)[a]	3033(2)	3033(2)	3033(2)	61(1)
O(1)	6129(4)	6256(5)	2597(5)	68(2)
O(2)	3387(5)	4644(5)	2246(5)	68(2)
C(1)	3769(13)	7320(12)	588(12)	82(3)
C(2)[a]	1706(9)	1706(9)	1706(9)	96(2)
H(11)	436(10)	800(12)	43(11)	100(30)
H(12)	273(9)	781(11)	26(9)	130(30)
H(13)	425(11)	672(10)	−25(10)	150(40)
H(2)	165(6)	153(6)	57(4)	110(20)

[a] Population of position is 1/3.

Table 2. Bond lengths (Å) and bond angles (deg) in **T_8-(1,4-CH=CH$_2$)** molecule

Bond	*d*	Angle	ω
Si(1)—O(1)	1.608(4)	O(1)—Si(1)—O(2)	108.6(2)
Si(1)—O(2)	1.621(4)	O(1)—Si(1)—C(1)	110.3(4)
Si(1)—C(1)	1.820(9)	O(2)—Si(1)—C(1)	109.4(3)
Si(1)—O(1a)	1.616(4)	O(1)—Si(1)—O(1a)	108.9(2)
Si(2)—O(2)	1.607(4)	O(2)—Si(1)—O(1a)	109.3(2)
Si(2)—C(2)	1.81(1)	C(1)—Si(1)—O(1a)	110.2(4)
		O(2)—Si(2)—C(2)	109.5(2)
		O(2)—Si(2)—O(2a)	109.4(2)
		Si(1)—O(1)—Si(1a)	149.6(3)
		Si(1)—O(2)—Si(2)	148.8(3)

(%): C, 18.01; H, 4.43; Si, 41.52. $C_8H_{24}O_{12}Si_8$. Calculated (%): C, 17.89; H, 4.50; Si, 41.84. The mother liquor was concentrated *in vacuo*, toluene (40 mL) was added to the residue, and the mixture was washed with water. The toluene solution was concentrated to give 3.8 g of glassy polymethylsilsesquioxane (m.p. 150—160 °C). According to ^{1}H NMR spectroscopic data, the product contained one non-associated hydroxy group per 20 silicon atoms.

1.2. A solution of oligomer **1a** (2 g) in ether (45 mL) and ethanol (10 mL) was mixed at ~20 °C with water (1.5 mL, $8.3 \cdot 10^{-2}$ mol) in ethanol (10 mL) acidified by 0.1 *N* HCl. After one day, well-formed crystals of **T_8-Me** began to precipitate from the homogeneous mixture. After four days, the mother liquor was poured off from the crystals, which were then washed with ethanol and dried at 50 °C (1 Torr) to give 0.22 g (20 %) of **T_8-Me** overall.

1.3. A solution of oligomer **1a** (2 g) in ether (45 mL) and ethanol (10 mL) was mixed at ~20 °C with water (1 mL, $5.5 \cdot 10^{-2}$ mol) and AcOH (0.5 mL, $8.7 \cdot 10^{-3}$ mol) in ethanol (10 mL). After 14 days, 0.11 g (10 %) of **T_8-Me** formed.

Hydrolytic condensation of vinyltris(methyldiethoxysiloxy)silane (1c). The reaction of compound **1c** (5.0 g, 10^{-2} mol) according to procedure 1.2 gave 0.59 g (21 %) of 1,4-divinylhexamethyloctasilsesquioxane: **T_8-(1,4-CH=CH$_2$)**. Found (%): C, 21.23; H, 4.30; Si, 40.20. $C_{10}H_{24}O_{12}Si_8$. Calculated (%): C, 21.41; H, 4.31; Si, 40.05.

Hydrolytic condensation of methyltris(methyldichlorosiloxy)silane (1b). 1. A solution of compound **1b** (2.57 g, $6 \cdot 10^{-3}$ mol) in acetone (40 mL) was mixed at 20 °C with a solution of water (0.64 mL, $3.5 \cdot 10^{-2}$ mol) in acetone (15 mL). The crystals of **T_8-Me** precipitated after 15 h were separated, washed with acetone, and dried at 50 °C (1 Torr) to give 0.32 g (20 %) of **T_8-Me**.

2. A solution of water (0.96 mL, $5.3 \cdot 10^{-2}$ mol) and pyridine (8.46 g, $1.1 \cdot 10^{-1}$ mol) in ether (400 mL) was added dropwise with stirring at ~20 °C over a period of 7 h to a solution of compound **1b** (7.71 g, $1.8 \cdot 10^{-2}$ mol) in dry ether (900 mL). The reaction mixture was stirred for an additional 3 h with refluxing. The resulting precipitate of Py • HCl was filtered off, washed three times with ether on a filter, wetted with acetone, and dissolved in water. No products insoluble in water were found. The filtrate was concentrated to give 3.94 g of a liquid oligomeric compound, which transforms into a three-dimensional polymer on storage.

Hydrosilylation of T_8-(1,4-CH=CH$_2$) with phenyldimethylsilane. A solution of H_2PtCl_6 ($2.23 \cdot 10^{-4}$ g) in toluene (0.19 mL) was added in a stream of argon to a suspension of **T_8-(1,4-CH=CH$_2$)** (1.50 g, $2.675 \cdot 10^{-3}$ mol) and dimethylphenylsilane (1.45 g, $1.06 \cdot 10^{-2}$ mol) in dry toluene (1.5 mL), and the mixture was heated. After 1 h at 110 °C, the reaction mixture became completely homogeneous. The toluene and excess dimethylphenylsilane were removed at 90 °C (1 Torr). Crystallization from toluene gave 1.4 g (63 %) of the hydrosilylation product, 1,4-bis-[2-(dimethylphenylsilyl)ethyl]-hexamethyloctasilsesquioxane (**10**). Found (%): C, 37.83; H, 5.90; Si, 33.32. $C_{26}H_{48}O_{12}Si_{10}$. Calculated (%): C, 37.47; H, 5.76; Si, 33.72.

References

1. M. M. Sprung and F. O. Günter, *J. Am. Chem. Soc.*, 1955, **77**, 3990.
2. M. M. Sprung and F. O. Günter, *J. Am. Chem. Soc.*, 1955, **77**, 3996.
3. A. J. Barry, W. H. Daudt, J. J. Domicone, and J. W. Gilkey, *J. Am. Chem. Soc.*, 1955, **77**, 4248.
4. K. A. Andrianov, and V. A. Odinets, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1959, 460 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1959 (Engl. Transl.)].
5. J. F. Brown, J. L. Vogt, and P. I. Prescott, *J. Am. Chem. Soc.*, 1964, **86**, 1120.
6. K. A. Andrianov, N. M. Petrovnina, T. V. Vasil'eva, V. E. Shklover, and B. I. D'yachenko, *Zh. Obshch. Khim.*, 1978, **48**, 2692 [*J. Gen. Chem. USSR*, 1978 (Engl. Transl.)].
7. C. L. Frye and W. T. Collins, *J. Am. Chem. Soc.*, 1970, **92**, 5586.
8. L. M. Chananasvili, Y. S. Chernishev, R. Sh. Theshelasvili, Ts. Vardosanidze, and V. I. Savushkina, *6-th International Symposium of Organosilicon Chemistry*, Budapest, 1981, Abstracts, p. 31.
9. P. A. Agaskar, V. W. Dag, and W. G. Klemperer, *J. Am. Chem. Soc.*, 1987, **109**, 5554.
10. P. A. Agaskar, *Synth. React. Inorg. Met. Org. Chem.*, 1990, **20**, 483.
11. V. V. Kireev, T. V. Vasil'eva, I. P. Stakhanov, V. A. Ignatov, A. S. Kuprin, L. A. Prikhod'ko, and N. M. Petrovnina, *Dokl. Akad. Nauk SSSR*, 1986, **290**, 859 [*Dokl. Chem.*, 1986, **290** (Engl. Transl.)].
12. V. V. Vasil'eva, V. V. Kireev, V. M. Chukova, A. I. Chernov, S. L. Derevyanko, *Vysokomolek. Soedinen.*, 1988, **30A**, 487 [*Polym. Sci. USSR*, 1988, **30A** (Engl. Transl.)].
13. K. A. Andrianov, V. N. Spektor, B. A. Kamaritskii, V. D. Nedorosol, and P. V. Ivanov, *Zh. Prikl. Khim.*, 1976, **49**, 2295 [*J. Appl. Chem. USSR*, 1976, **49** (Engl. Transl.)].
14. E. A. Rebrov, A. M. Muzafarov, and A. A. Zhdanov, *Dokl. Akad. Nauk SSSR*, 1988, **302**, 346 [*Dokl. Chem.*, 1988, **302** (Engl. Transl.)].
15. E. A. Rebrov, A. M. Muzafarov, V. S. Papkov, and A. A. Zhdanov, *Dokl. Akad. Nauk SSSR*, 1989, **309**, 376 [*Dokl. Chem.*, 1989, **309** (Engl. Transl.)].
16. E. A. Rebrov, A. M. Muzafarov, and V. D. Myakushev, *International School-Seminar for Young Scientists*, Alma-Ata, 1990, Abstracts, p. 189.
17. J. Tamas, A. Gömöry, I. Besenyei, V. N. Khabashesku, Z. A. Kerzina, N. D. Kagramanov, and I. O. Bragilevsky, *J. Organometal. Chem.*, 1990, **387**, 147.
18. K. A. Andrianov, *Metody Elementoorganicheskoi Khimii. Kremnii* [*Methods of Organometallic Chemistry. Silicon*], Nauka, Moscow, 1968, 400 (in Russian).
19. W. Robinson and G. M. Sheldrick, *SHELX. In Crystallographic Computing Techniques and New Technologies*, Oxford, Oxford Univ. Press, 1988, 366.

Received November 2, 1994;
in revised form December 20, 1994