The Polycondensation of Cyclohexylsilanetriol

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Cyclohexylsilanetriol, formed in dilute aqueous acetone solution by the hydrolysis of cyclohexyltrichlorosilane, condenses to give an easily isolated dimer, a trimer, and a tetramer. Further condensation gives a resinous mixture which very slowly converts to two crystalline species: hexacyclohexyltetracyclo[5.5.1.1³,¹¹.1⁵,⁹]hexasiloxane ("cyclohexyl-T_6") and, predominantly, heptacyclohexyltricyclo[7.3.3.1⁵,¹¹]heptasiloxane-endo-endo-endo-3,7,14-triol ("cyclohexyl-$T_7(OH)_3$"). The latter forms a very strongly hydrogen-bonded dimer. The formation of such a product in good yield indicates that the polycondensation of silanetriols can proceed in a fairly selective manner.

During a survey of the polymerization behavior of various trifunctional silicone systems, we observed that certain hydrolysates of cyclohexyltrichlorosilane in aqueous acetone deposited crystalline products in sizable yields. Since polymerizations of trifunctional silicones usually give resins, long believed to consist of very complex mixtures of polycondensates,[1,2] further investigation was undertaken.

Results

When a solution of cyclohexyltrichlorosilane in acetone was added to a large excess of water, immediate exothermic reaction occurred, 3 equiv. of HCl was produced, and a clear, homogeneous solution resulted. Since all of the cyclohexylsilicone condensation products are water insoluble, it was evident that only monomer could be present initially, *i.e.*, that the hydrolysis of cyclohexyltrichlorosilane to cyclohexylsilanetriol occurs very much more rapidly than the polycondensation of the latter to polysiloxanes.

After a few minutes at room temperature, deposition of a microcrystalline precipitate commenced and continued for 1 or 2 days. Filtration after 4 days gave the dimer, cyclohexyl-$T_2(OH)_4$,[3] in 84% yield.[4]

When the solvent mixture contained higher proportions of acetone, phase separation did not occur until the condensation had proceeded considerably further. Thus, 3–4% solutions of the chlorosilane in 60–80% acetone remained homogeneous for several days, and then slowly deposited a lower liquid layer containing part of the condensate. Crystalline products precipitated very slowly: 3% ($^1/_2T_6$, $^1/_2T_7(OH)_3$) after 1 month and 21% ($^1/_3T_6$, $^2/_3T_7(OH)_3$) after 4 months. Refluxing such an hydrolysate solution caused a little

T_6 to form rapidly, and then precipitation ceased. However, when the mixture was then allowed to stand at room temperature precipitation of a 10:1 T_7-$(OH)_3$–T_6 mixture proceeded steadily, and was apparently still continuing after 19 months, when the experiment was terminated (65% total yield). No trace of the very insoluble and easily recognized pentacyclic, cyclohexyl-T_8, could be detected in the products. This was unexpected, since methyl- and phenyltrichlorosilanes both gave T_8's under the conditions employed, a variety of alkyl and aryltrichlorosilanes have given T_8's in good yields under slightly more vigorous conditions,[5] and cyclohexyl-T itself was found to give T_8 easily in alkaline systems, which allow complete structural reorganization to occur.[6] It was also noted that adding a trace of HF (which presumably also produces at least partial siloxane equilibration) to an hydrolysate solution prevented the formation of *any* insoluble crystalline species.

The noncrystalline portions of the polycondensates were examined briefly. After 1 month at room temperature the lower layer (0.25 total) had the average composition $T_7(OH)_3$ while the upper averaged T_5-$(OH)_3$. The infrared spectra, however, showed the same sharp, $\nu_a SiOSi$ bands, characteristic of strained and/or polycyclic siloxanes, in both layers. It appeared likely that tricyclics and tetracyclics in the Si_6–Si_8 range which were barely soluble in 80% acetone were important constituents of the mixture, while the remainder consisted of more soluble, less highly condensed linear and monocyclic species in the Si_3–Si_5 range. The resin from the upper layer did, in fact, deposit small amounts of two such species upon standing in cyclohexane: one was a cyclotetrasiloxane, $T_4(OH)_4$, the other possibly the linear trisiloxane, $T_3(OH)_5$.

The resin remaining after refluxing followed by standing for 19 months was a monodisperse (by gel permeation chromatography) polycondensate showing the same $\nu_a SiOSi$ pattern as was observed after 1 month at 25°. Apparently, the pool of precursors from which the crystalline species were being drawn was little altered after removing 65% as T_6 and T_7-$(OH)_3$.

Attempts to identify the precursor(s) spectroscopically by reference to the extensive catalog of polycyclic siloxane $\nu_a SiOSi$ patterns which has accumulated in this laboratory were partially frustrated by the numerous weak bands arising from cyclohexyl group vibrations which also appeared in the 950–1150-cm.⁻¹ region. Nevertheless, three general conclusions were possible.

First, the mixture consisted solely of compact polycyclic siloxanes. The 1040–1050-cm.⁻¹ absorption

(1) J. A. Meads and F. S. Kipping, *J. Chem. Soc.*, 107, 459 (1915).

(2) M. M. Sprung, *Advan. Polymer Sci.*, 2, 442 (1961).

(3) According to the conventional silicone nomenclature, T denotes a trifunctional unit of siloxane structure, *i.e.*, a monoalkylsiloxy unit. For convenience, we shall indicate the empirical composition of our polycondensate by formulas of the type $T_m X_n$, where *m* represents the number of T units in the molecule and X_n the number and kind of uncondensed functional groups. The empirical formula corresponding to $T_m X_n$ is $(RSi)_m O_{(3m-n/2)} X_n$, and the number of rings in the molecule is $(m - n + 2)/2$.

(4) J. F. Brown, Jr., U. S. Patent 2,992,263 (July 11, 1961).

(5) K. Olsson, *Arkiv Kemi*, 13, 367 (1958); K. Olsson and C. Grönwall, *ibid.*, 17, 529 (1961).

(6) J. F. Brown, Jr., L. H. Vogt, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, 86, 1120 (1964).
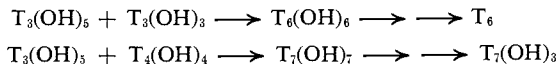
characteristic of ladder-type polymers, oxybipoly-cyclics, and other extended-chain species was conspicuously absent. Second, large strainless cage species such as T_9OH, T_{10}, or T_{12} were at most minor constituents. These all show intense absorption near 1125 cm.$^{-1}$,[6,7] while the resin showed little absorption above 1110 cm.$^{-1}$. (However, neither the spectrum nor the gel permeation chromatogram could exclude the possibility that strainless tricyclics and tetracyclics, such as epimers of the $T_7(OH)_3$ isolated or $T_8(OH)_2$'s analogous to those found in phenyl-T condensates,[8] might have been present in modest amounts. Such species usually show bands near 1080 and 1110 cm.$^{-1}$, where absorption was observed.) Third, the major (and possibly even the sole) constituents of the compact polycyclic siloxane mixture were unsymmetrical structures containing internal cyclotrisiloxane rings. Such species show highly characteristic $\nu_a SiOSi$ bands near 990 and 1065 cm.$^{-1}$, in addition to others in the 1080–1115-cm.$^{-1}$ range. These bands were conspicuous in the resin spectra, while 1020-cm.$^{-1}$ region bands, characteristic of isolated or terminal cyclotrisiloxane rings, were lacking.[9]

Polysiloxane skeletal arrangements which would be generally consistent with the observed resin spectra are 1, 2, and 3.[10] The silanol content of the condensate

T$_6$(OH)$_2$ T$_7$(OH)$_3$ T$_7$OH
1   2   3

at the 19-month stage corresponded to about two OH groups per seven T-units; *i.e.*, if $T_7(OH)_3$'s and T_7OH's were indeed the major constituents they were about equally abundant.

The crystalline cyclohexyl-T_6 isolated showed $\nu_a SiOSi$ bands very similar to those of the known methyl-T_6 and ethyl-T_6, and thoroughly consistent with the structure 4 previously assigned.[11]

T$_6$
4

The crystalline $T_7(OH)_3$, which was the predominant ultimate product of the reaction, was identified as the *endo-endo-endo*-tricyclo[7.3.3.1^{5,11}]heptasiloxanetriol (5) by its easy conversion to the known, cube-like octa-

(7) L. H. Vogt, Jr., and J. F. Brown, Jr., *Inorg. Chem.*, 2, 189 (1963).

(8) J. F. Brown, Jr., *J. Am. Chem. Soc.*, 87, 4317 (1965).

(9) Strong, sharp, low-frequency $\nu_a SiOSi$ bands would also be expected for the highly strained, adamantane-like, T_4 skeleton. It is reported by E. Wiberg and W. Simmler, *Z. anorg. allgem. Chem.* 282, 330 (1955), that the hydrolysis of isopropyl- and *t*-butyltrichlorosilanes with stoichiometric amounts of water in cold, dilute, ethereal solutions gives the corresponding branched alkyl T_4's. Despite repeated search, we have as yet been unable to detect any T_4's in hydrolysates of methyl, phenyl, or cyclohexyltrichlorosilanes prepared with excess water.

(10) Our structural diagrams are drawn so as to indicate the manner in which the siloxane units (rather than the individual atoms) are interconnected. The polysiloxane skeleton may be derived from such a diagram by locating a silicon atom at each vertex and an oxygen in the middle of each connecting line.

(11) M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, 77, 3990 3996 (1955).

silsesquioxane, cyclohexyl-T_8, (6),[12] upon treatment with cyclohexyltrichlorosilane and pyridine, or to heptacyclohexyl (hydrogen) T_8 upon treatment with silicochloroform and pyridine.

T$_7$(OH)$_3$ T$_8$
5   6

The most remarkable characteristic of the $T_7(OH)_3$ 5 was its tendency to form a stable (K_{diss} 3.7 $\times$ 10^{-3} mole/l. in benzene at 25°) dimer in which all of the hydroxylic hydrogens were hydrogen bonded. As a result the compound was insoluble in weakly basic polar solvents, such as acetone, which normally dissolve siloxanols readily. The infrared spectrum in CCl_4 showed no free OH even in 0.05% solution, but instead a strong, broad band at 3230 cm.$^{-1}$. This represents a 460-cm.$^{-1}$ shift from the position of free siloxanol OH groups in this solvent (about twice the shift observed in ordinary hydrogen-bonded dimers of these groups) and corresponds, in fact, to the band position usually observed in crystalline silanols, where infinite OH$\cdots$OH$\cdots$OH$\cdots$OH chains can be formed. Previously, it had been noted that large hydrogen-bonded rings of phenolic OH groups can show the same spectral shifts as long chains.[13] Accordingly, we suggest that the dimer has the two $T_7(OH)_3$ groups so positioned that a puckered ring of six hydrogen-bonded silanol groups can be formed, as in 7.

7

Discussion

Had the cyclohexylsilanetriol polymerization proceeded as an acyclic polycondensation of a difunctional monomer (or of a trifunctional monomer in which the third function reacts very slowly) we should have expected a polydisperse product containing species of different molecular size in a "most probable" distribution. Had it proceeded as a simple acyclic polycondensation of a trifunctional monomer, we should have expected a still broader size distribution, leading to gelation. The fact that only species in the Si_6–Si_8 range were produced indicates that cyclization and polycyclization must have occurred at an early stage in the polycondensation, and that the polycyclic Si_6–Si_8 silanols formed must have been essentially inert toward further intermolecular condensation under the reaction conditions.

A reasonable mechanistic interpretation is that the polycondensation started out normally, giving linear polymers, but that these cyclized as soon as the chains were long enough to form stable rings. Judging from

$$T(OH)_3 \longrightarrow T_2(OH)_4 + T_3(OH)_5 + T_4(OH)_6$$

$$\downarrow\uparrow \qquad \qquad \downarrow$$

$$T_3(OH)_3 \qquad T_4(OH)_4$$

(12) A. J. Barry, W. H. Daudt, J. J. Domicone, and J. W. Gilkey, *ibid.*, 77, 4248 (1955).

(13) T. Cairns and G. Eglinton, *Nature*, 196, 535 (1962).

the initial condensation rate, the above steps were probably mostly completed in 1 or 2 weeks in our system. Intermolecular condensation of these Si_3 and Si_4 species would then produce the precursors for the Si_6, Si_7, and possibly Si_8 polycyclics ultimately formed. The immediate precursor of the T_6 was prob-

$$T_3(OH)_5 + T_3(OH)_3 \longrightarrow T_6(OH)_6 \longrightarrow \longrightarrow T_6$$
$$T_3(OH)_5 + T_4(OH)_4 \longrightarrow T_7(OH)_7 \longrightarrow \longrightarrow T_7(OH)_3$$

ably the *endo,endo* epimer of diol **1**, which would be expected to close rather slowly because of the considerable strain in the tetracyclic system. The pre-

1   4
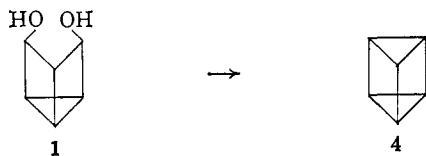
cursor of the $T_7(OH)_3$ was probably the tetracyclic **3**, which is strongly implicated by the $\nu_a SiOSi$ pattern and low silanol content of the precursor mixture. This T_7OH, in turn, must have resulted from some structural isomer of the $T_7(OH)_3$. A reasonable possibility is **2**, which could be easily formed by condensation of the $T_3(OH)_5$ and $T_4(OH)_4$ intermediates.
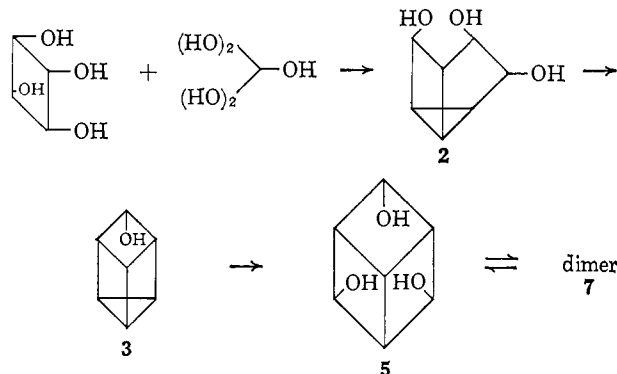
Whatever the detailed mechanism, the formation of a single heptameric product in good yield indicates a considerable degree of nonrandomness, or selectivity, in the polymerization, since its formation requires the condensation of 18 silanol groups in a specific pattern. Interestingly enough, the pathway selected is quite different from that followed by phenylsilanetriol under the same conditions (which leads mainly to $T_8(OH)_2$'s[8]) and also from those which would lead to thermodynamically stable[6,7,14] silsesquioxanes such as T_8, T_{10}, T_{12}, or ladder polymer.

Experimental Section

Equilibrative Polycondensation. Paralleling a phenylsilsesquioxane equilibration procedure,[6] a mixture of cyclohexyltriethoxysilane (61 g., 0.25 mole), water (14 g., 0.78 mole), tetraethylammonium hydroxide (0.0088 mole), and methyl isobutyl ketone (250 ml.) was refluxed. The mixture became homogeneous in 2 hr., but crystallization commenced shortly thereafter. After 8 hr. of refluxing and 6 days at room temperature, filtration gave 25.2 g. (75%) of the previously reported[12] cyclohexyl-T_8, octacyclohexylpentacyclo[9.5.1^{3,9}.1^{5,17}.1^{7,13}]octasiloxane, pseudo-cubic

rhombohedra from benzene, sublimes $>400°$, $\nu_a SiOS$ 1116 cm.$^{-1}$ (in CS_2).

Anal. Calcd. for $C_{48}H_{88}O_{12}Si_8$: C, 53.3; H, 8.2; mol. wt., 1080. Found: C, 53.1; H, 8.3; mol. wt. (ebullioscopic in benzene), 1100.

Cyclohexyl-$T_2(OH)_4$. Cyclohexyltrichlorosilane (26 g.) was dissolved in 100 ml. of acetone and the solution was added to 1200 ml. of cold water. After 4 days at room temperature, filtration gave 15.3 g. (84%) of 1,3-dicyclohexyldisiloxanetetrol (cyclohexyl-$T_2(OH)_4$), m.p. 205–215° dec. after recrystallization from ethanol-benzene, $\nu_a SiOSi$ (in *t*-butyl alcohol) *ca.* 1093 cm.$^{-1}$ (broad).

Anal. Calcd. for $C_{12}H_{26}O_5Si_2$: C, 47.0; H, 8.5. Found: C, 47.1; H, 8.7.

Condensations in Aqueous Acetone. (1) Cyclohexyltrichlorosilane (50 g.) was dissolved in 1000 ml. of acetone, water (250 ml.) was added, and the mixture was allowed to stand for 4 months. The crystalline precipitate was filtered off, rinsed with acetone, and dried to give 7.15 g. (23%) of a 2:1 $T_7(OH)_3$–T_6 mixture. (2) The chlorosilane (3.5 g.) was dissolved in 80 ml. of acetone, and 20 ml. water was added (exotherm). Deposition of crystals commenced after 3–4 days (separation of a lower sirupy layer after 5 days). After 4 weeks, filtration gave 0.063 g. (3%) of a 1:1 $T_7(OH)_3$–T_6 mixture. Addition of the upper layer to 800 ml. of water precipitated resin 2A, 1.41 g. Addition of the lower layer to 200 ml. of water gave resin 2B, 0.54 g. (3) The chlorosilane (12.3 g.) was dissolved in 240 ml. of acetone, added to 80 ml. of ice water, then refluxed with occasional seeding with $T_7(OH)_3$ for 3 days, cooled, and filtered, giving 0.627 g. (8.2%) of pure (infrared) T_6. Refluxing for 1 additional day gave no further precipitate. Upon standing, several crops of mixed crystals, each about 10:1 $T_7(OH)_3$–T_6, precipitated: after 1 month, 0.631 g.; 3 months, 0.783 g.; 19 months, 3.027 g.; total, 5.068 g., 65%, comprised of 52% $T_7(OH)_3$ and 13% T_6. Addition of water to the final solution precipitated about 2.9 g. of resin 3.

The various $T_7(OH)_3/T_6$ ratios were estimated from the $\nu_a SiOSi$ region infrared spectra, which are mainly nonoverlapping, and, in the case of the final product from reaction 3, also gravimetrically after dissolving the $T_7(OH)_3$ in cold pyridine. Evidence for T_8 was sought first in the X-ray diffraction patterns of the $T_7(OH)_3$–T_6 mixtures, and then in the infrared spectrum of the T_6 left after removing the $T_7(OH)_3$ with pyridine. The T_8 content found was $0 \pm 2\%$ that of the T_6.

Characterization of the Resinous Products. Analysis of resin 2A indicated C, 51.3; H, 8.3; mol. wt. (ebullioscopic in acetone), 703 ($\pm 5\%$), corresponding to average molecular composition $T_5(OH)_3$. Analysis of resin 2B indicated C, 51.6; H, 8.3; mol. wt., 977 ($\pm 5\%$), corresponding to average composition T_7-$(OH)_3$. Gel permeation chromatography[15] of resin 3 in tetrachloroethane using a Waters Associates gel permeation chromatograph with 10^6, 10^4, and 10^3 Å. columns revealed a single peak having the same position and width as that produced by cyclohexyl-T_8. This indicated an essentially monodisperse condensate containing species having the same ($\pm 10\%$) ef-

(14) J. F. Brown, Jr., *J. Polymer Sci.*, 1C, 83 (1963).

(15) J. C. Moore, *ibid.*, 2A, 835 (1964).

fective mean molar volumes as T_8; the columns used could not have resolved T_6- and T_8-silanols admixed with T_7's but could have easily detected a more highly polydisperse system.

The infrared spectra (in CS_2) of all the resin specimens were remarkable for showing a series of sharp ν_aSiOSi skeletal bands, rather than the broad, featureless ν_aSiOSi absorption usually seen in unfractionated silicone resins. In the 950–1150-cm.$^{-1}$ region, bands were seen near 985 (sh), 999 (m)*, 1027 (m)*, 1038 (m)*, 1062 (s), 1079 (s), 1094 (s), 1110 (s) (*, partly), and ca. 1125 (sh)(?); those marked with an asterisk (*), however, could be adequately accounted for as silylcyclohexane group vibrations. The closest available reference spectra were those of methylsilicones, which normally show ν_aSiOSi bands at about 6-cm.$^{-1}$ higher frequencies than the cyclohexyl analogs because of the inductive effect. The endo isomer of methyl-T_7OH, structure 3, showed ν_aSiOSi at 990 (mw), 1068 (ms), 1086 (ms), and 1112 (s) cm.$^{-1}$. The methyl-T_4D_2 of structure 1, in which the inductive shift of replacing cyclohexyls by methyls would be more or less compensated by the opposite shift resulting from methyl for hydroxyl replacement, showed ν_aSiOSi at 986 (wsh), 997 (m), 1060 (s), 1089 (ms), and 1108 (msh) cm.$^{-1}$. The resins also showed the absorption bands of free silanol groups at 3680 cm.$^{-1}$ and of hydrogen-bonded silanols near 3350 cm.$^{-1}$. The extinctions, $E_{1\,cm}^{1\%}$, in the regions of the major νOH and ν_aSiOSi bands were as shown in Table I. The extinction coefficient of a cyclohexyl-T(OH) group is about 7 in either ν(OH) band; thus, the sum of the 3680 and 3350 extinctions corresponds fairly closely to the number of silanols per 7 T-units. The similarity of the ν_aSiOSi absorptions in resin 3 to those in resin 2, despite the presence of one more ring (two less silanols) on the average, probably results from the fact that rigid polycyclics such as 1 and 3 have sharp ν_aSiOSi bands which come in the same general regions as the broader bands of, e.g., bicyclics, and hence will dominate the spectra of mixtures.

Table I. Extinctions $(E_{1\,cm}^{1\%})$ at Various Frequencies

	3680	3350	1110	1094	1078	1065
Resin 2A	1.9	2.6	27	25	23	22
Resin 2B	1.7	1.2	27	26	25	24
Av. 2A + 2B	1.9	2.2	27	25	23	22
Resin 3	1.4	0.5	27	24	23	21

Cyclohexyl-$T_4(OH)_4$. Part (1.23 g.) of resin 2A was dissolved in cyclohexane and allowed to stand. Three successive crops of crystals, totaling 0.075 g., were collected over a 7-month period. The X-ray patterns failed to detect $T_2(OH)_4$ in any of these, but each could be separated into two constituents upon recrystallization from acetone. The major constituent formed long, silky needles, m.p. 187–193° dec. Its ν_aSiOSi spectrum (in t-butyl alcohol) showed a single band near 1100 cm.$^{-1}$, very similar in position and shape to those observed in the methyl- and phenyl-cyclotetrasiloxanetetrols.[8] Accordingly, it was formulated as a 2,4,6,8-tetracyclohexylcyclotetrasiloxanetetrol of unknown steric configuration.

Anal. Calcd. for $C_{24}H_{48}O_8Si_4$: C, 50.0; H, 8.4. Found: C, 49.5; H, 8.4.

Cyclohexyl-$T_3(OH)_5$ (?). The mother liquors from the $T_4(OH)_4$ recrystallization yielded 0.010 g. of fine granular crystals from benzene–acetone, m.p. 216–220° dec. Repeated concordant analyses indicated a composition best corresponding to an acyclic trimer, e.g., 1,3,5-tricyclohexyltrisiloxanepentol.

Anal. Calcd. for $C_{18}H_{38}O_7Si_3$: C, 47.8; H, 8.5. Found: C, 48.1; H, 7.9.

Cyclohexyl-T_6. The tetracyclic 4, hexacyclohexyl-tetracyclo[5.5.1.1^{3,11}.1^{5,9}]hexasiloxane, was separated from the $T_7(OH)_3$ either by fractional crystallization from acetone, in which it was the more soluble component, or by extraction of the triol with cold pyridine. Vacuum sublimation gave a product, m.p. 265–267°, which showed ν_aSiOSi (in CS_2) at 1051 (s) and 1078 (m) cm.$^{-1}$. In methyl-T_6^{11} and ethyl-T_6^{11} the band positions were 1057 (s), 1085 (m), and 1052 (s), 1079 (m) cm.$^{-1}$, respectively.

Anal. Calcd. for $C_{36}H_{66}O_9Si_6$: C, 53.3; H, 8.1; mol. wt., 810. Found: C, 53.6; H, 8.2; mol. wt. (cryoscopic in benzene), 810 (±5%).

Cyclohexyl-$T_7(OH)_3$. The triol 5, heptacyclohexyltricyclo[7.3.3.1^{5,11}]heptasiloxane-endo-endo-endo-3,7,14-triol, was separated from the T_6 by fractional crystallization or extraction with pyridine and recrystallized from benzene–acetone to give rhombs, m.p. ca. 267° dec. on rapid heating. The monomeric form, observed in pyridine–CS_2 solution, showed ν_aSiOSi near 1112 (s) and 1082 (sh) cm.$^{-1}$, but with the exact positions of the band maxima obscured by the C_6H_{11}Si modes. In the dimeric form (in CS_2) the absorptions shifted about 10 cm.$^{-1}$ to higher frequencies, giving a pattern superficially resembling that of a silsesquioxane cage,[6,7] but with a somewhat broadened band, and with the exact maximum and contours still obscured by the C_6H_{11}Si bands. The decamethyl analog (methyl-T_4D_3) of structure 5, reported as "compound D" by Scott,[16] showed ν_aSiOSi at 1079 (m) and 1110 (s) cm.$^{-1}$. The 3-μ region showed only a single peak at 3230 cm.$^{-1}$ in either CS_2 or CCl_4.

Anal. Calcd. for $C_{42}H_{80}O_{12}Si_7$: C, 51.6; H, 8.3; OH, 5.2; mol. wt., 977. Found: C, 51.5; H, 8.3; OH (Zerewitnoff), 5.3; mol. wt. (benzene solutions, Mechrolab osmometer, 25°), 1384 at 4.15, 1312 at 4.13, 1249 at 3.25, and 1237 at 2.37 mg./ml. The latter data were consistent with a molecular weight of 977 at zero concentration and a dissociation constant of 3.7×10^{-3} mole/l.

Conversion to Octacyclohexyl-T_8. The triol 5, 0.100 g., was dissolved in 1.0 ml. of warm nitrobenzene and 0.020 ml. of cyclohexyltrichlorosilane was added. No reaction occurred until pyridine (0.024 ml.) was added, whereupon an immediate precipitation of T_8 ensued. The recrystallized product, 0.047 g. (43%), was unequivocally identified as cyclohexyl-T_8 by its sublimability, ν_aSiOSi pattern, and X-ray diffraction pattern.[12]

Conversion to Heptacyclohexyl-T_8. The triol 5, 0.10 g., in 1.0 ml. of dry benzene was treated with

(16) D. W. Scott, J. Am. Chem. Soc., 68, 356 (1946).

pyridine (0.04 ml.) and silicochloroform (0.02 ml.). Precipitation of hydrochloride occurred immediately. The benzene-soluble portion of the product was vacuum distilled and then crystallized from benzene–acetone, whereupon an unidentified by-product (0.005 g.) separated as needles. After 1 month in methanol–benzene the desired pentacyclic separated, m.p. 280° dec. in air. The infrared spectrum showed SiH bands at 2250, 884, and 876 cm.$^{-1}$, and ν_aSiOSi

as a single, strong band near 1117 cm.$^{-1}$ (in CS$_2$), both as expected for heptacyclohexylpentacyclo[9.5.1.1^{3,9}.-1^{5,15}.1^{7,13}]octasiloxane.

Anal. Calcd. for C$_{42}$H$_{78}$O$_{12}$Si$_8$: C, 50.4; H, 7.9. Found: C, 50.5; H, 8.1.

The Polycondensation of Phenylsilanetriol

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Phenylsilanetriol, formed by the hydrolysis of phenyltrichlorosilane, undergoes polycondensation in a fairly selective manner. In aqueous acetone, the major pathway leads through the cis-cis-cis-cyclotetrasiloxanetetrol (phenyl-T$_4$(OH)$_4$), the epimeric tetracyclo[7.7.1.1^{3,13}- .1^{5,11}]octasiloxanediols (α, β, and γ phenyl-T$_8$(OH)$_2$), and thence to intermolecular condensation polymers of these. Minor side reactions give other 8- to 12-unit cage-like polycyclics. In less polar solvents, the size of the polycyclic blocks formed increases from 8–12 to 20–30 siloxane units, possibly because of micellization among the lower siloxanols prior to condensation. In any case, the structure of the high polymer formed upon complete condensation would appear to resemble a string of beads (the beads being the polycyclic blocks) rather than the regular double chain (ladder) obtained upon equilibration or the irregular, randomly connected network previously assumed.

The aqueous acid-catalyzed (presumably, nonequilibrative) polycondensation of phenylsilanetriol (or of species which can yield it upon hydrolysis) gives resinous products which have been variously known over the years as silicobenzoic acid, phenylsiliconic acid, polyphenylsiloxane, or phenyl-T resin.[1-5] The structural nature of these substances has been the subject of varied speculation,[1-4] but the long-standing view[2,6] that the polycondensation of trifunctional monomers must inevitably lead to extremely complex mixtures has discouraged serious investigation.

The recent findings that equilibrated polyphenylsilsesquioxanes possess orderly structures,[7-9] and that

the nonequilibrative polycondensation of cyclohexylsilanetriol proceeds in a fairly selective manner,[10] suggested, however, that a closer examination of the phenylsilanetriol polycondensation might be worthwhile.

Results

1. Polycondensation in Aqueous Acetone. Early Products. When a solution of phenyltrichlorosilane in acetone was added to a large excess of cold water, complete hydrolysis (exotherm; formation of 3 equiv. of acid) occurred instantly, and a clear solution resulted. Under the conditions employed both the initial hydrolysis product, phenylsilanetriol,[11] and the first condensation product, 1,3-diphenyldisiloxanetetrol,[12] were sufficiently water soluble to remain in solution. The first insoluble condensation product, isolated in yields up to about 50%, was a rather unstable crystalline solid, identified as the cyclic tetramer tetrol, or T$_4$(OH)$_4$,[5] **1**.

For identification, the tetrol was treated with dimethyldichlorosilane and pyridine in ether. This gave small amounts of a 1:2 condensation product, formulated as the *cis-syn-cis*-tricyclo[7.3.1.1^{3,7}]hexasiloxane (**2**) and a 2:4 product, formulated as the *cis-syn-cis-*
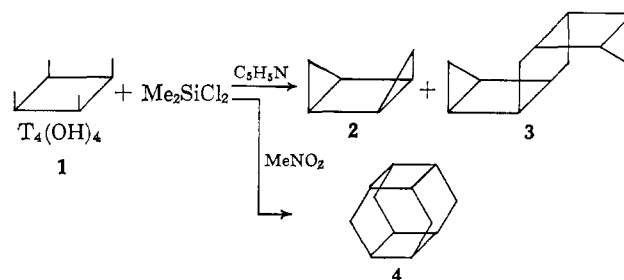
(1) A. Ladenburg, *Ber.*, **6**, 379 (1873); *Ann.*, **173**, 143 (1874).
(2) J. A. Meads and F. S. Kipping, *J. Chem. Soc.*, **107**, 459 (1915).
(3) K. A. Andrianov and A. A. Zhdanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1033 (1954).
(4) M. M. Sprung and F. O. Guenther, *J. Polymer Sci.*, **28**, 17 (1958).
(5) According to the conventional silicone nomenclature, T denotes a trifunctional unit of siloxane structure, *i.e.*, a monoalkylsiloxy unit. For convenience, we shall indicate the empirical composition of our polycondensates by formulas of the type T$_m$X$_n$, where m represents the number of T units in the molecule and X$_n$ the number and kind of uncondensed functional groups. The empirical formula corresponding to T$_m$X$_n$ is (RSi)$_m$O$_{(3m-n)/2}$X$_n$, and the number of rings in the molecule is $(m - n + 2)/2$.
(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter IX.

(7) J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kiser, and K. W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194 (1960).
(8) J. F. Brown, Jr., *J. Polymer Sci.*, **1C**, 83 (1963).
(9) J. F. Brown, Jr., L. H. Vogt, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1120 (1964).
(10) J. F. Brown, Jr., and L. H. Vogt, Jr., *ibid.*, **87**, 4313 (1965).
(11) L. J. Tyler, *ibid.*, **77**, 770 (1955).
(12) J. F. Brown, Jr., and G. M. J. Slusarczuk, *J. Org. Chem.*, **29**, 2809 (1964).