

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 $\nu_{\text{a}}\text{SiOSi}$

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

Acknowledgment. The authors are indebted to Miss D. V. McClung for the infrared spectra, and to Messrs. H. W. Middleton, J. Magnusen, and E. M. Hadsell for the analyses.

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-cyclo-tetrasiloxanetetrol (phenyl- $\text{T}_4(\text{OH})_4$), the epimeric tetracyclo[7.7.1.1^{3,13}-1^{5,11}]octasiloxanediols (α , β , and γ phenyl- $\text{T}_3(\text{OH})_2$), 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, non-equilibrative) 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, phenylsilicic 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.

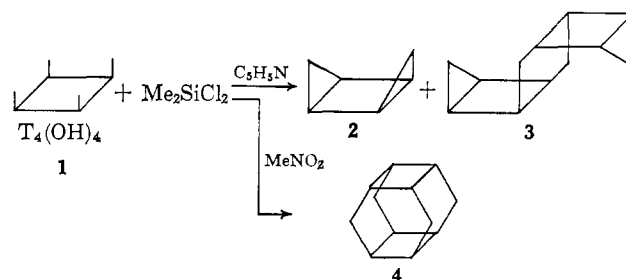
The recent findings that equilibrated polyphenylsiloxanes possess orderly structures,⁷⁻⁹ and that

the nonequibrative 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 $\text{T}_4(\text{OH})_4$,⁵ **1**.

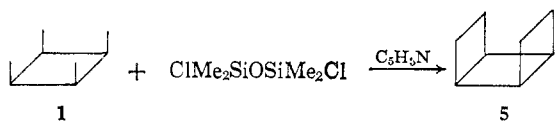
For identification, the tetrol was treated with dimethyldichlorosilane and pyridine in ether. This gave small amounts of a 1:2 condensation product, formulated as the *cis-syn-cis*-tricyclo[7.3.1.1^{3,7}]hexasiloxane (**2**) and a 2:4 product, formulated as the *cis-syn-cis*-



- (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_mX_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_mX_n is $(\text{RSi})_m\text{O}_{(3m-n)/2}\text{X}_n$, 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.

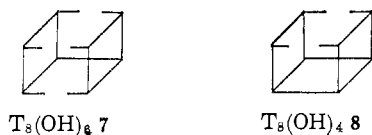
- (7) J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kiser, and K. W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194 (1960).
- (8) J. F. Brown, Jr., *J. Polymer Sci.*, **1C**, 83 (1963).
- (9) J. F. Brown, Jr., L. H. Vogt, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1120 (1964).
- (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).

anti-cis-syn-cis-pentacyclo[15.7.1.1^{5,13}.17.11.1^{19,23}]dodecasiloxane (3). Treatment with dimethyldichlorosilane alone in warm nitromethane gave a different 2:4 adduct, formulated as the pentacyclo[13.9.1.1^{3,13}.17.21.1^{9,19}]dodecasiloxane (4), also in poor yield.¹³ Reaction with 1,3-dichlorotetramethyldisiloxane gave a fair yield of the *cis-syn-cis*-tricyclo[9.5.1.1^{3,9}]octasiloxane (5). The weakness of the lowest frequency



infrared band, which must result from the ν_a SiOSi chain vibrational mode characterized by a $\pi/4$ phase difference,¹⁴ clearly indicated the *syn* configuration about the central ring. The implied conclusion that the tetrol **1** must have had an all-*cis* configuration was supported by observations of its surface activity; at an air-water interface the limiting film area was 125 Å.² per molecule, indicating a disposition of polar groups which would allow the tetramer molecules to lie flat upon the surface.

The crystalline *cis-cis-cis*-T₄(OH)₄ deposited by the original hydrolysate mixture was accompanied by progressively increasing amounts of an amorphous resin (6) which generally resembled the "phenylsiliconic acids" previously described.¹⁻³ Such resins had somewhat lower silanol contents than the T₄(OH)₄, and about twice the molecular weight. A spectrally indistinguishable resin could also be made by briefly heating the T₄(OH)₄ in toluene. The infrared spectra showed that virtually all of the silanol groups in these resins were intramolecularly hydrogen bonded, an observation which derives particular significance from the fact that silanol groups on adjacent siloxane residues do not form hydrogen bonds with each other.¹⁵ The siloxane skeletal vibrational spectrum of resin 6 showed a low-frequency absorption resembling that in oxybis(heptamethylcyclotetrasiloxane)¹⁶ and another resembling that of the *cis-syn-cis*-tricyclooctasiloxane (5). It was tentatively concluded that the resin consisted of the all-*cis* hexol T₆(OH)₆ (7) and the all-*endo* tetrol, T₄(OH)₄ (8), probably contaminated with non-crystalline monocyclics, T_x(OH)_x. The only known



crystalline species corresponding to the T₆(OH)₆ stage of polycondensation are the T₆(OH)₂(OEt)₂'s, formulated as tricyclo[9.5.1.1^{3,9}]octasiloxanes of unknown steric configuration, reported by Sprung and Guenther.⁴ We obtained samples of these from Dr.

(13) 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.

(14) J. F. Brown, Jr., Division of Polymer Chemistry Preprints, Vol. 2, No. 2, American Chemical Society, Washington, D. C., 1961, p. 112.

(15) G. I. Harris, *J. Chem. Soc.*, 5978 (1963); we have also observed lack of intramolecular silanol-silanol bonding in hexamethylcyclotetrasiloxane-*cis*-2,4-diol.

(16) N. N. Sokolov, *Zh. Obshch. Khim.*, 29, 248 (1959).

Sprung and observed that the ν_a SiOSi skeletal patterns agreed very closely with that in **5**, and that intramolecular OH-OH or OH-OEt bonding did occur, supporting the idea that these were indeed *endo*-substituted *cis-syn-cis*-tricyclo[9.5.1.1^{3,9}]octasiloxanes having structure **8**.

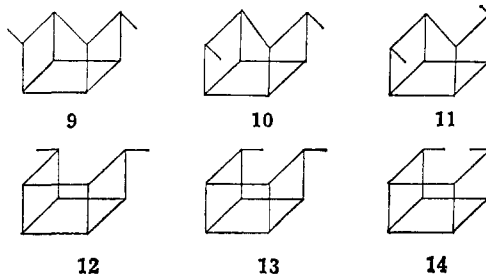
2. *Polycondensation in Aqueous Acetone. Later Products.* When a dilute solution of phenyltrichlorosilane in acetone was mixed with half its volume of water and the hydrolysate was allowed to stand for 4 months at room temperature, products quite different from those obtained in the analogous cyclohexyl-T system resulted. Only a little crystalline solid (mainly T₈) precipitated. The remainder of the condensate was partitioned by fractional precipitation from aqueous acetone and from cyclohexane, and by crystallization from nonpolar solvents. Infrared examination of the various fractions obtained showed that the condensate consisted of three groups of species, designated A, B, and C.

The group A species (about 75% of the total) were the most soluble in aqueous acetone, moderately soluble in cyclohexane, and showed ν_a SiOSi bands near 1082 (ms) and 1118 (s) cm.⁻¹. This group consisted largely or solely of three crystallizable phenyl-T₈(OH)₂'s, designated as the α , β , and γ isomers in order of increasing solubility in CS₂.

Group B (about 15% of the total) was designated as those species which showed one main ν_a SiOSi band near 1120 cm.⁻¹. Part of this group consisted of the crystalline polysiloxanes originally present in the crude product. These included phenyl-T₈ (formed in 4% over-all yield), a little T₈(OH)₂, designated the δ isomer, and probably a second T₈(OH)₂, designated the ϵ (?) isomer. The remainder of the group B species appeared in the resin fractions which were the most soluble in cyclohexane. From these one crystalline compound, a phenyl-T₉OH, was isolated; the remainder appeared to consist of cage-like Γ_{10} (OH)₂, T₁₁(OH), and/or T₁₂(OH)₂ species.

The group C species (about 10% of the total) were the least soluble in either aqueous acetone or cyclohexane, and showed a medium ν_a SiOSi near 1050, in addition to a main peak near 1125 cm.⁻¹.

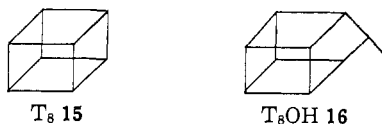
The infrared spectra showed that the α , β , and γ isomers of phenyl-T₈(OH)₂ possessed one siloxane skeleton, while the δ and ϵ (?) isomers possessed another. Neither group showed the low-frequency ν_a SiOSi bands characteristic of cyclotrisiloxane structures, nor the intensity enhancements and splittings in the 998 and 1029 cm.⁻¹ C₆H₅Si group modes characteristic of phenyl substitution on a small siloxane ring.¹⁷



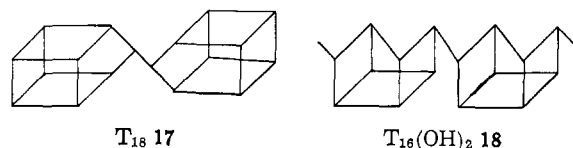
(17) C. W. Young, P. C. Servais, C. C. Currie, and M. J. Hunter, *J. Am. Chem. Soc.*, 70, 3758 (1948); note also the data on 2 and 3 reported below.

There are only two possible tetracyclooctasiloxane arrangements which do not contain cyclotrisiloxane rings, namely, the tetracyclo[7.7.1.1^{3,13}.1^{5,11}]octasiloxane skeleton, **9–11**, and the tetracyclo[9.5.1.1^{3,9}.1^{5,15}]octasiloxane skeleton, **12–14**. Each of these is capable of yielding three stereoisomeric T₈-diols, namely, the *exo-exo* (**9**, **12**), *exo-endo* (**10**, **13**), and *endo-endo* (**11**, **14**) forms. The facts that none of the isomers obtained showed evidence of intramolecular OH–OH bonding, and that only the ϵ (?) isomer showed definite evidence of OH–C₆H₅ bonding, suggested that the missing isomer was **14** and that the ϵ (?) form was **13**. This in turn would require the δ isomer to be **12** and the α , β , and γ isomers to be **9–11**. This conclusion was strongly supported by the appearance of the ν_a SiOSi spectra: isomers α – γ showed the double-peak spectrum characteristic of strainless semicage-like tri- and tetracyclic siloxanes, whereas δ – ϵ showed spectra much more similar to the single, unresolved band of a strainless cage.⁹ Within the α – γ series, the trend of the small variations in band intensities and frequencies, as well as the trend in solubility, indicated a structural progression in the sequence α , β , γ . Assuming that the *exo* positioning of the silanols would lead to decreased solubility in nonpolar solvents, this suggested a tentative structural assignment of **9** for α , **10** for β , and **11** for γ . The assignment of the less symmetrical structure **10** to β was supported by its low melting point (181 vs. 272 and 247° for α and γ).

The phenyl-T₈ isolated was the known^{4,9} form, for which the cube-like pentacyclic structure **15** is well established. The phenyl-T₈(OH) was a new compound, but its ν_a SiOSi spectrum showed it to contain the same strainless pentacyclic structure, **16**, previously found in the methyl-T₈(OR) series.¹⁸



The group C species appeared to have molecular weights two to three times those of the species in groups A and B. No crystalline compounds were isolated from this group in the phenyl-T series, but one was obtained (and also synthesized from T₉OH) in the corresponding methyl-T series, namely, the oxybis-pentacyclic T₁₈, **17**. This showed a spectrum rather similar to that observed in group C, and suggested that group C consisted simply of the expected intermolecular condensation products of the group A and B silanols, e.g., structures **17** and **18**.



3. *Polycondensations in Other Solvents.* Earlier preparations of phenyl-T condensates,^{1–3} as well as commercial practice in silicone resin manufacture, have generally used less polar solvent systems and higher concentrations than those employed above, resulting in much faster polymerizations. Brief ex-

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

Table I. Approximate Molecular Distributions in Phenyltrichlorosilane Hydrolysates

Solvent	Concn. ratio ^a	Temp., °C.	% in D.P. range		
			8–12 ^b	16–30 ^c	>30 ^d
Aq. acetone	4	25	90	10	..
Ether	53	35	50	50	..
Toluene	67	23	10	60	30
Toluene	116	50	8	37	55

^a Grams of PhSiCl₃ per 100 ml. of solvent. ^b Groups A and B species. ^c Groups C and C' species. ^d Group D species.

amination of several such polycondensates gave the results shown in Table I.

The use of less polar solvents (and higher concentrations) changed the polymer composition in three main respects. First, the content of T₈–T₁₂ silanols (group A and B species) dropped sharply. Second, their condensation products, the group C species, also disappeared; the T₂₀-range species formed instead a different spectrally distinct group, group C'. Third, higher molecular weight species, designated group D, were also formed.

Group C' consisted of resinous species which were insoluble in 2:1 acetone–water, but extractable by cold cyclohexane, and which showed a ν_a SiOSi pattern consisting mainly of a strong, broad band centered near 1120 cm.⁻¹ with a 1060-cm.⁻¹ shoulder. They appeared to have a reasonably narrow size distribution centered near T₂₂, and to carry 3–4 silanol groups per molecule. The spectral pattern indicated that the (approximately) decacyclic siloxane skeleton must be quite compact, but the SiOSi and OSiO angular requirements are known to preclude sphere-like cage structures except in the T₈–T₁₂ range.^{9,18} Presumably, compact 2- or 3-lobed polycyclic blocks are formed by fusing together two or three cage-like groupings of 8–12 T units each. The group C' spectra were, in fact, fairly similar to those of the lowest molecular weight (T₂₂–T₂₄) equilibrated phenylsilsequioxane “prepolymer” fractions, which must consist of two T₈–T₁₂ cages fused together.^{8,9} In both cases, the lowest frequency ν_a SiOSi appears as an indistinct shoulder near 1060 cm.⁻¹ rather than as the sharp band near 1050 cm.⁻¹ observed in oxybispolycyclics such as **17** or **18**.

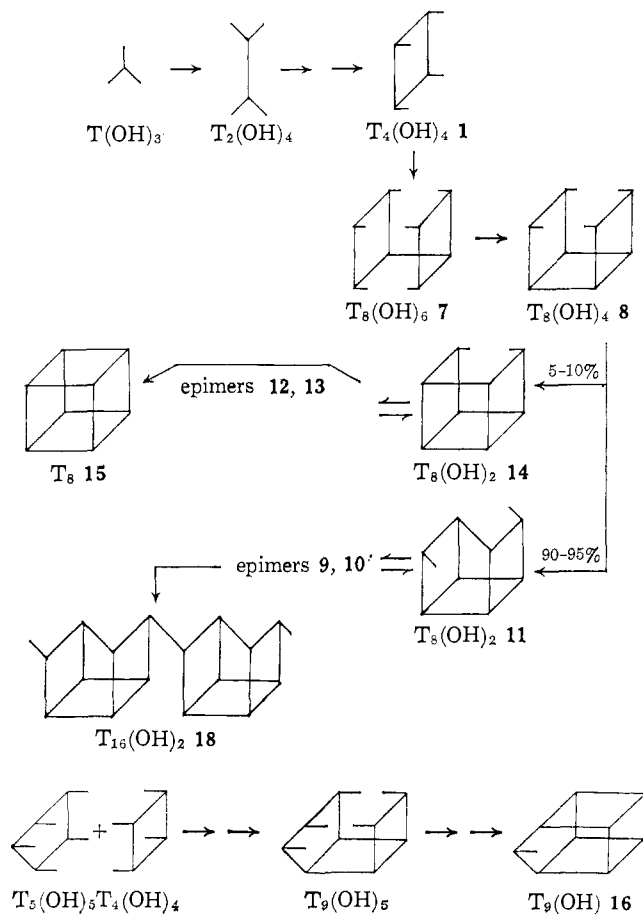
The group D species (insoluble cold cyclohexane, broad ν_a SiOSi absorption near 1050 cm.⁻¹ in addition to the group C' pattern) appeared to be simple polycondensates having two, three, or more group C' polycyclic blocks linked together.

Discussion

The simplest rationalization of the above results is that the predominant (70–90% of the total) pathway followed during the polycondensation of phenylsilanetriol in cold, dilute, aqueous acetone is shown below.

One of the minor reaction pathways probably results from the formation of T₅(OH)₅ in the initial cyclization, rather than T₄(OH)₄. Its subsequent conversion by a similar pathway would lead to the T₉OH. Another possible side reaction may involve the trimerization of the T₄(OH)₄ (e.g., through T₄(OH)₄–T₈(OH)₄ interaction), leading eventually to T₁₂ diols.

At first glance, it might appear surprising that so much of the polycondensation follows a single pathway. Polymer theory has long viewed such polycondensations



as series of random events, leading to complex, polydisperse mixtures of molecular species.^{2,6} On the other hand, it is probably unfortunate that the statistical theory of polycondensate structure was ever applied to the homopolymers of small polyfunctional monomers in the first place. The principle of equal reactivity of all functional groups, upon which the theory is based, is of dubious validity in such a system. Functional groups variously attached to branchable chains and cyclized structures (unlike those attached to the ends of straight chains) are grossly nonequivalent structurally, and hence can be of very different reactivity. Moreover, much of the condensation must proceed *via* intramolecular (cyclizative) rather than intermolecular reactions, and hence will be guided by the specific cyclization tendencies of the ring systems rather than the statistics of acyclic combination.

As regards the phenylsilanetriol condensation itself, we can identify two specific sources of silanol reactivity differences, and hence pathway selectivity. One is steric hindrance: as the condensation proceeds and the polyphenylsiloxane molecules grow, the remaining silanol groups will be increasingly screened by the bulky phenyls, and therefore progressively less reactive. As a result, growth of straight (rather than branched) chains will be favored in the early stages of reaction, and cyclization (rather than further chain growth) will occur whenever possible. This will favor tetramer ring formation: in the phenyl-T silicones (unlike the cyclohexyl-T's)¹⁰ trimer rings are not stable in aqueous acids, so that the cyclotetrasiloxane ring is the smallest which can be formed irreversibly. The preferential reactivity of the smallest species present will also keep

the molecular size distribution narrow, and hence favor an otherwise improbable monomer to dimer to tetramer to octamer to hexadecamer reaction sequence.

A second source of selectivity is probably the strong, multiple hydrogen bonding which can occur when two cyclic polysilanol are brought together, as in the dimer of cyclohexyl- $T_7(OH)_3$ ¹⁰ or in the intramolecularly bonded forms of **7** and **8**. Siloxane bond formation between rings thus positioned would lead to *syn* (rather than the thermodynamically preferred⁹ *anti*) ring fusion.

The formation of the group C' species in nonpolar solvents may have a similar origin. Phenylsilanetriol and its immediate condensation products, $T_2(OH)_4$ and $T_4(OH)_4$, all have surfactant-like structures, with highly polar silanol groups at one end of the molecule and nonpolar phenyls at the other. A concentrated solution of such species in a nonpolar solvent should form micelles having the silanol groups on the inside and united by hydrogen bonding, and the phenyls projecting outwards. If siloxane formation proceeded within the micelle, replacing the SiOH-(OH)Si linkages with SiOSi groups, a compact polycyclic would result which preserved the original size of the micelle, and probably as much of its original spherical form as could be retained strainlessly.

When phenyltrichlorosilane hydrolysates or cohydrolysates are heated, preferably in the presence of amine carboxylate salts which catalyze silanol condensation but not siloxane rearrangement,¹⁹ further condensation occurs to give "cured" silicone resins. These high polymers have usually been viewed as randomly connected three-dimensional network structures. From the present work it would appear more likely that their structures actually resemble irregularly branched strings of beads, in which the "beads" are the polycyclic blocks (group A, B, or C' species) formed in the initial polycondensation. Such "bead string" polymers would be, in fact, no more than higher molecular weight versions of the group C and D species already present in the condensates. The "bead string" structures, incidentally, are obtainable in the phenyl-T polymer system only as kinetically determined forms. The thermodynamically stable form is the *cis* syndiotactic double chain, or "ladder" structure, in which cyclotetrasiloxane rings are fused *cis-anti-cis*.⁷⁻⁹

Experimental Section

Polycondensation to 1 and 6. In a typical procedure, phenyltrichlorosilane (82.3 g.), dissolved in cold acetone (140 ml.) was added in a thin stream to an ice-water slurry (3100 g.) with vigorous stirring. The mixture produced was initially clear, but soon became turbid. After standing for 2 days at 0°, a mixture of crystalline and resinous solids precipitated. Filtration gave 48.0 g. (*ca.* 90%) of air-dried solid. This was stirred with 100 ml. of carbon disulfide, cooled to 0°, filtered, and washed with more carbon disulfide to give 27.8 g. (52%) crude tetrol **1**, m.p. 166–174° dec. Vacuum evaporation of the solvent gave the resin **6** as a brittle froth. Variations of the procedure using 1–3 g. of chlorosilane per 100 ml. of solution and 4–10% (by volume) acetone in the condensation medium gave

(19) R. L. Merker, M. J. Scott, and G. C. Haberland, *J. Polymer Sci.*, **2A**, 31 (1964).

similar results. However, only a little tetrol precipitated when the acetone was omitted, or when the polycondensation was carried out at room temperature. It was repeatedly noted that the first portion of the precipitate (e.g., that formed after 1 day of standing) appeared highly crystalline and contained only 20–25% CS₂-soluble material; the resin content increased steadily as the condensation progressed.

Phenyl-T₄(OH)₄ 1, cis-cis-cis-2,4,6,8-Tetraphenylcyclotetrasiloxane tetrol. The crude tetrol was purified by repeated precipitations from cold solutions; it was too unstable for recrystallization from warm solutions to be effective. The form obtained by slowly adding a dilute solution in acetone to ten volumes of a 4:1 water-acetone mixture at 0° consisted of stout needles, m.p. 198–202° dec., which showed prominent X-ray reflections at 16 (s), 11.5 (s), 7.4 (m), 6.5 (m), 4.5 (s, broad), 4.3 (m), and 3.86 (s) Å. The form obtained by shaking a solution in benzene-acetone with water to extract the acetone melted at 186–192° and showed X-ray reflections at 15 (s), 11.2 (s), 7.4 (w), 6.9 (m), 5.6 (s), and 4.95 (s) Å. Both forms showed identical infrared spectra in solution. The "melting" (decomposition) points varied markedly with the particle size and the rate of heating, and were not regarded as meaningful characteristics of either identity or purity; one specimen of crude tetrol was observed to melt at 195–200°, and one thrice recrystallized specimen at 173–178°.

The tetrol was insoluble in cold CS₂, CCl₄, or benzene, slightly soluble in CS₂ containing small amounts of acetone or resin **6**, and readily soluble in methanol or acetone. A 2-mg./ml. solution could be prepared in boiling benzene; on cooling to room temperature this set up to a gel (hydrogen-bonded network?) which persisted for 24 hr. before crystallization occurred and the tetrol reprecipitated. When 4.5 g. of the tetrol was boiled with 300 ml. of toluene, solution occurred within a few minutes. After cooling, only 1.4 g. reprecipitated; the remainder had formed a soluble amorphous resin indistinguishable from resin **6** in its 2–15-μ spectrum. The tetrol itself showed ν₄SiOSi (in 9:1 CS₂-acetone or in *t*-butyl alcohol) as a single strong band at 1102 cm.⁻¹.

Anal. Calcd. for C₂₄H₂₄O₈Si₄: C, 52.2; H, 4.4; mol. wt., 552. Found: C, 51.9; H, 4.5; mol. wt. (ebullioscopic in acetone), 538 ± 5%.

Siloxane 3, cis-syn-cis-anti-cis-syn-cis-3,3,9,9,15,15,23,23-Octamethyloctaphenylpentacyclo[15.7.1.1^{5,13}.1^{7,11}.1^{19,23}]dodecasiloxane. To a solution of the tetrol **1** (1.38 g., 0.0025 mole) in dry ether (60 ml.) was added dimethyldichlorosilane (0.61 ml., 0.005 mole) and then pyridine (0.81 ml., 0.010 mole). The hydrochloride formed was filtered off, and the solution was washed with water and evaporated to a sirup. Crystallization from 3 ml. of cold ethanol gave 0.058 g. (3.5%) of **3**, small rhombs, m.p. 267–270° from benzene-ethanol. The 950–1150-cm.⁻¹ spectrum showed sharp bands at 996 (ms), 1002 (m), 1025 (ms), 1031 (ms), 1069 (vs), ~1110 (wsh), 1122 (ms), and 1134 (s) cm.⁻¹. The last of these appeared to be a normal C₆H₅Si band; the 998- and 1029-cm.⁻¹ C₆H₅ group bands had undergone the intensification and displacement, however, characteristic¹⁷ of phenyl substitution on a cyclotrisiloxane ring. The remaining bands were all inter-

preted as the ν_aSiOSi skeletal vibrations of a non-cage-like, cyclotrisiloxane-containing ring system. The relative intensities of the 696- and 1261-cm.⁻¹ bands indicated that C₆H₅SiO_{3/2} and (CH₃)₂SiO groups were present in 2.0 molar ratio.

The p.m.r. spectrum (as 2–6% solutions in CDCl₃ at 40 ± 3° using a Varian A-60 spectrometer; chemical shifts measured relative to internal cyclohexane, taking 1.43 p.p.m. as its chemical shift relative to tetramethylsilane) showed CH₃Si proton signals at τ 9.76 (2.03), 9.71 (1.00), and 9.58 (0.93) and complex aromatic absorption in the τ 2.2–2.9 region. Within the limits of resolution of the spectrometer (<0.5 c.p.s.) all of the CH₃Si signals were singlets. Since the bond angular relationships in siloxanes preclude *trans* fusions between cyclotrisiloxane and/or cyclotetrasiloxane rings, the observation of three distinct methyl environments, containing respectively two, two, and four CH₃ groups, was taken to show that the fusions across the central cyclohexasiloxane ring must be *anti*.

Anal. Calcd. for C₃₆H₆₄O₁₆Si₁₂: C, 50.6; H, 4.9; mol. wt., 1338. Found: C, 51.2; H, 5.2; mol. wt. (Mechrolab osmometer, benzene), 1315 ± 10%.

Siloxane 2, cis-syn-cis-5,5,11,11-Tetramethyltetraphenyltricyclo[7.3.1.1^{3,7}]hexasiloxane. The mother liquors remaining after the removal of **3** were evaporated to dryness and dissolved in a little cyclohexane. After 10 days, a few milligrams of a second crystalline product, m.p. 228–229°, separated. Its 9–10-μ spectrum showed 997 (m), 1026 (vs), 1031 (sh), 1050 (s), and 1067 (m) cm.⁻¹; again intensification of the C₆H₅ modes normally appearing at 998 and 1029 cm.⁻¹ was evident. A reference spectrum of the *cis-anti-cis*-octamethyl analog of **2** showed ν₄SiOSi at 1024 (s), 1054 (s), and 1078 (m) cm.⁻¹. The relative intensities of the 696- and 1261-cm.⁻¹ bands in **2** indicated that C₆H₅-SiO_{3/2} and (CH₃)₂SiO groups were present in 2.0 molar ratio.

The major product of the tetrol-Me₂SiCl₂ condensation was a low molecular weight, cyclotrisiloxane-rich condensation polymer rather than the simple polycyclics **2** and **3**.

Siloxane 4, 5,5,11,11,17,17,23,23-Tetramethyloctaphenylpentacyclo[13.9.1^{3,13}.1^{7,21}.1^{9,19}]dodecasiloxane. The tetrol **1** (1.38 g.) and dimethyldichlorosilane (0.61 ml.) were warmed together in 50 ml. of dry nitromethane to 80–90° for 0.5 hr. After cooling, the condensate was precipitated by dilution with water. Recrystallization from benzene-ethanol gave a few milligrams of blade-like rods, m.p. about 420–428° with partial sublimation. The infrared spectrum showed C₆H₅-SiO_{3/2} and (CH₃)₂SiO groups to be present in molar ratio 2.0 ± 0.1, no silanol groups, and the cage-like polysiloxane skeleton already suggested by the high melting point: ν_aSiOSi a very strong and somewhat broad peak at 1106 cm.⁻¹ with a possible shoulder under the 1134-cm.⁻¹ C₆H₅Si band.

Siloxane 5, cis-syn-cis-Octamethyl-1,3,9,11-tetraphenyltricyclo[9.5.1.1^{3,9}]octasiloxane. Use of the procedure for preparing **3**, except with 1,3-dichlorotetramethyldisiloxane instead of Me₂SiCl₂, gave 0.54 g. (26%) of crystals which melted sharply at 124° and then resolidified and remelted sharply at 129°. The in-

frared spectrum showed $C_6H_8SiO_{3/2}$ and $(CH_3)_2SiO$ groups to be present in 1:1 molar ratio.

Anal. Calcd. for $C_{32}H_{44}O_{10}Si_3$: C, 47.8; H, 5.5; mol. wt., 812. Found: C, 47.4; H, 5.4; mol. wt. (Mechrolab osmometer, benzene), $817 \pm 5\%$.

The p.m.r. spectrum (taken as above, but in CCl_4) showed sharp CH_3Si proton signals at τ 9.89 (0.98) and 9.69 (1.00), and complex aromatic absorption in the τ 2.4–2.9 region. The observation of two methyl environments, each containing 4 CH_3 groups, was interpreted as demonstrating the presence of a *cis*-fused tricyclo[9.5.1.1^{3,9}]octasiloxane ring system (rather than, e.g., a [7.7.1.1^{3,11}] pattern).

The ν_aSiOSi spectrum of the *cis-syn-cis*-phenylmethyl- T_4D_4 siloxane **5** was compared with that of the *cis-anti-cis*-methyl- T_4D_4 analog (prepared from *cis-trans-cis*-methyl- $T_4(OH)_4$ by the procedure used for **5**) and also with those of the crystalline phenyl- $T_8(OH)_2(OEt)_2$ species reported by Sprung and Guenther⁴ (Table II). As regards the latter, the spectra of fractions m.p. 45–47, 50–52, and 55–57° were indistinguishable and are reported as a single compound; that of a fraction m.p. 73–76° appeared just different enough to have represented a different positional isomer.

Table II

Compd.	ν_aSiOSi , cm^{-1}
PhMe- T_4D_4 (siloxane 5)	1062 (m), 1093 (sh), 1105 (vs)
Ph- $T_8(OH)_2(OEt)_2$ m.p. 55–57°	~1068 (m), ~1095 (sh), 1116 (vs)
Ph- $T_8(OH)_2(OEt)_2$ m.p. 73–76°	~1069 (m), ~1096 (sh), 1118 (vs)
Me- T_4D_4 m.p. 147–147.5°	1060 (s), 1085 (w), 1115 (ms)

Making allowance for the slight shift resulting from replacing Me groups by OR groups (inductive effect), and for the difficulty of identifying the exact positions of ν_aSiOSi bands which come near the $SiOEt$ bands, the spectra of **5** and the $T_8(OH)_2(OEt)_2$ species were sufficiently nearly superimposable to indicate the presence of a common tricyclic skeleton. The *cis-anti-cis*-octasiloxane showed bands in about the same positions but with a markedly different intensity distribution. Its ν_aSiOSi intensity pattern resembled that of decamethyltetrasiloxane,²⁰ which presumably has an extended chain conformation, while the other spectra resembled that of a 1-azacyclotetrasiloxane,²¹ where the $SiOSiOSiOSi$ system must adopt a U-shaped conformation. In the former case, the lowest frequency ν_aSiOSi , which corresponds to the mode having the lowest allowed chain vibrational phase difference ($\pi/4$),¹⁴ would be expected¹⁴ to be strongly infrared active, while in the latter it should be relatively weak.

Resin 6. Subject to the usual uncertainties of analyzing thermally unstable, amorphous resins which cannot be completely dried, the gross composition of resin **6** agreed reasonably well with a phenyl- $T_8(OH)_2$ formulation.

Anal. Calcd. for $C_{48}H_{46}O_{15}Si_3$: C, 53.0; H, 4.3; mol. wt., 1086. Found: C, 52.4; H, 4.4; mol. wt. (ebullioscopic in acetone), $1010 \pm 10\%$.

However, when a 25% solution of the resin in CS_2 was cooled to 0°, a lower layer containing 15% of the

(20) N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).

(21) J. G. Murray and R. K. Griffith, *J. Org. Chem.*, **29**, 1215 (1964).

total separated. This had a molecular weight of 783, vs. 1050 for the remainder, indicating the presence of a little lower molecular weight material (probably $T_4(OH)_4$ or $T_5(OH)_5$ monocyclics).

In order to detect $Si(OH)_2$ groups, the resin was treated with 1,3-dichlorotetramethyldisiloxane as in the preparation of **5**. The resulting condensate showed no absorption in the 1020- cm^{-1} region, indicating the absence of cyclotrisiloxane rings, and hence also of $-OSiPh(OH)_2$ end groups in resin **6**.

The 3- μ region spectrum showed a broad, symmetrical, and very strong ($E_{1\%}^{1\text{cm}}$ 5.5 in CS_2) band at 3390, with weak shoulders near 3570, 3620, and 3680 cm^{-1} ; this was unaltered upon dilution to 0.05% in CCl_4 except for a sharpening of the weak shoulders. The relative intensities of bonded and free νOH bands, as well as the magnitude of the shift,¹⁰ indicated that the silanol groups were almost completely hydrogen bonded to each other in sizable clusters.

The ν_aSiOSi pattern showed one strong, rather broad band at 1109 cm^{-1} with a long slope on the low-frequency side suggesting poorly resolved, weak, broad shoulders near 1060 and 1045 cm^{-1} . It was presumed that the first of these might arise from a tricyclo-octasiloxane such as **8**, whereas the latter might arise from an oxybis-cyclotetrasiloxane such as **7**. Oxybis-(heptamethylcyclotetrasiloxane)¹⁶ was observed to show ν_aSiOSi at 1045 (m) and 1084 (s) cm^{-1} in CS_2 .

Later Polycondensation Products. Phenyltrichlorosilane (40 g.) dissolved in 700 ml. of acetone was added to 250 ml. of water, and the solution was left standing at room temperature. After 6 days, precipitation of fine crystals commenced; after 24 days, separation of a lower liquid layer. After 4 months, the product was found to contain 1.5 g. of acetone-insoluble crystalline solid, about 11 g. of resin in the lower layer, and 12.7 g. of resin in the upper (main) layer. The phase separation evidently resulted from incomplete solubility of a major constituent in 70% acetone; the condensate resin was completely soluble in 80% acetone, completely insoluble in 50% acetone, and the 70% acetone-soluble and insoluble fractions were very similar spectrally.

Cold, dilute solutions of the resin in CS_2 slowly deposited α -Ph- $T_8(OH)_2$ on standing; more concentrated ones the β isomer as well. The remaining resin was separated into three fractions on the basis of its solubility in succession portions of 2:1 acetone-water, and then each of these was separated into three fractions on the basis of solubility in cold or hot cyclohexane. On standing in cold cyclohexane, one of the three "group A" rich (most soluble in aqueous acetone) fractions deposited more α - + β - $T_8(OH)_2$, and all of the "group B" rich (most soluble in cyclohexane) fractions deposited T_9OH . About 60% of the estimated "group A" content was isolated as α - and β - $T_8(OH)_2$, in about 1:2 ratio; the γ isomer did not crystallize from the crudes. The relative proportions of the group A, B, and C products were estimated from the relative absorption intensities at 1120, 1080, and 1050, using the β - $T_8(OH)_2$ intensity ratios as a reference for group A, the T_9OH intensities for group B, and those of the least soluble, highest molecular weight fraction obtained for group C.

α -Phenyl- $T_8(OH)_2$, *exo-exo*-Octaphenyltetracyclo[7.7.1.1^{3,13}.1^{5,11}]octasiloxane-7,15-diol (**9**). This was

separated from the β isomer by repeated crystallization from benzene-cyclohexane, m.p. 270–272° dec. The spectrum in CS₂ showed unbonded silanol ν OH at 3675 ($E_{1\text{cm}}^{1\%}$ 2.6), and $\nu_{\text{a}}\text{SiOSi}$ at 1083 (ms) and 1117 (s) cm.⁻¹.

Anal. Calcd. for C₄₈H₄₂O₁₃Si₈: C, 54.9; H, 4.0; OH, 3.24; mol. wt., 1050. Found: C, 54.7; H, 3.9; OH (Zerewitnoff), 3.32; mol. wt. (Mechrolab osmometer, acetone), 1070 ± 10%.

In another preparation, 2.51 g. of once-recrystallized tetrol **1** was dissolved in 70 ml. of acetone, 26 ml. of water, and 4.5 ml. of concentrated hydrochloric acid. After 5 months at room temperature, 50 ml. of water was added to complete the precipitation, the condensate was separated and dried, taken up in acetone, filtered to remove the T₈ + δ -T₈(OH)₂ (0.141 g.), evaporated again, taken up in 50 ml. of hot cyclohexane, and cooled to 8° to precipitate everything but the group B species (0.29 g.), and the precipitate was taken up in 3 ml. of CS₂. On standing for 2 weeks, only the α -T₈(OH)₂, 0.71 g. (30%), crystallized out. The group B fraction subsequently gave 0.034 g. of T₉OH (1.4%), suggesting that the T₄(OH)₄ used contained at least 0.7% T₅(OH)₅.

β -Phenyl-T₈(OH)₂, *exo-endo-Octaphenyltetracyclo[7.7.1.1^{3,13}.1^{5,11}]octasiloxane-7,15-diol (10)*. In our fractional crystallizations, this was separated from the α and γ isomers by crystallization from concentrated solutions in benzene, m.p. 177–181° dec. The spectrum in CS₂ showed unbonded silanol ν OH at 3675 ($E_{1\text{cm}}^{1\%}$ 2.6), and $\nu_{\text{a}}\text{SiOSi}$ at 1082 (ms) and 1118 (s) cm.⁻¹.

Anal. Calcd. for C₄₈H₄₂O₁₃Si₈: C, 54.9; H, 4.0; OH, 3.24; mol. wt., 1050. Found: C, 55.1; H, 4.2; OH (Zerewitnoff) 3.4; mol. wt. (Mechrolab osmometer, chloroform), 1100 ± 10%.

γ -Phenyl-T₈(OH)₂, *endo-endo-Octaphenyltetracyclo[7.7.1.1^{3,13}.1^{5,11}]octasiloxane-7,15-diol (11)*. This did not crystallize from CS₂ or cyclohexane solutions of the original polycondensate, but a little was occluded by the mixed α + β isomer precipitate, and was recovered on further fractionation. This involved alternating crystallizations from benzene-cyclohexane, which gave mainly the α isomer, and from concentrated solutions in benzene, which gave mainly the β isomer. The final CS₂-soluble residue gave the γ isomer, differentiated from the others by its X-ray pattern as well as by its solubility. It was recrystallized from benzene-cyclohexane, m.p. 242–247° dec. The spectrum in CS₂ showed ν OH at 3675 ($E_{1\text{cm}}^{1\%}$ 2.65) and $\nu_{\text{a}}\text{SiOSi}$ at 1082 (ms) and 1119 (s) cm.⁻¹.

Anal. Calcd. for C₄₈H₄₂O₁₃Si₈: C, 54.9; H, 4.0; OH, 3.24. Found: C, 55.0; H, 4.2; OH (from ϵ 3675), 3.3.

In the α , β , γ isomer series the progressions in the $\nu_{\text{a}}\text{SiOSi}$ band positions, and in the intensities relative to the 1135 cm.⁻¹ C₆H₅Si peak, were as shown in Table III.

δ -Phenyl-T₈(OH)₂, *exo-exo-Octaphenyltetracyclo[9.5.1.1^{3,9}.1^{5,15}]octasiloxane-7,13-diol (12)*. The 1.5-g. crystalline fraction of the condensate was dissolved in 30 ml. of hot *o*-dichlorobenzene and cooled, whereupon the phenyl-T₈ (**15**), identified by its X-ray pattern⁹ and infusibility below 400°, precipitated; 1.0 g., 4.1% over-all yield. The *o*-dichlorobenzene-soluble frac-

Table III

Isomer	ν_{max}	$A(1082)/A(1135)$	$A(1118)/A(1135)$
α	1083, 1117	0.51	0.55
β	1082, 1118	0.53	0.59
γ	1082, 1119	0.58	0.64

tion was dried, taken up in a little hot toluene, and cooled to 0°. After 3 days, 0.19 g. of solid, m.p. \approx 355°, deposited. Suspecting the presence of phenyl-T₁₂, this was redissolved in hot toluene, an equal volume of tetrahydrofuran was added, and then a seed crystal of the very insoluble T₁₂-THF clathrate⁹; no precipitate formed. Recrystallization from toluene was then resumed, giving the δ isomer of phenyl-T₈(OH)₂, m.p. \approx 360° dec. on rapid heating. The spectrum (in CH₂Cl₂ because of insolubility in CS₂) showed unbonded silanol ν OH at 3660 ($E_{1\text{cm}}^{1\%}$ ca. 2.5) and $\nu_{\text{a}}\text{SiOSi}$ at 1075 (wsh) and 1113 (vs) cm.⁻¹.

Anal. Calcd. for C₄₈H₄₂O₁₃Si₈: C, 54.9; H, 4.0; OH, 3.24. Found: C, 54.4; H, 4.5; OH (from ϵ 3660), ca. 3.2.

ϵ -Phenyl-T₈(OH)₂(?), *exo-endo-Octaphenyltetracyclo[9.5.1.1^{3,9}.1^{5,15}]octasiloxane-7,13-diol (13)*(?). The mother liquors remaining after the recrystallization of the δ isomer from toluene deposited a few milligrams of a different crystalline solid from toluene-cyclohexane. On rapid heating, this melted momentarily near 300° and then resolidified. Its spectrum in CH₂Cl₂ showed ν OH mainly at the position expected for silanol hydrogen bonded to phenyl (3640 cm.⁻¹, $E_{1\text{cm}}^{1\%}$ 1.5) with a shoulder near 3680 cm.⁻¹ indicating unbonded silanol, and a weak peak near 3400 suggesting a silanol-silanol bonded contaminant such as **14**. The siloxane region showed $\nu_{\text{a}}\text{SiOSi}$ at \approx 1080 (wsh) and 1118 (vs) cm.⁻¹.

Phenyl-T₉OH, *Nonaphenylpentacyclo[9.7.1.1^{3,9}.1^{7,13}]nonasiloxan-15-ol (16)*. Three fractions of group B (cyclohexane soluble) resin concentrates aggregating 0.94 g. were allowed to stand in cyclohexane solution (ca. 100 ml./g.) for 2 months, whereupon 0.31 g. of T₉OH precipitated, suggesting an initial concentration in the polycondensate of about 4%. Recrystallization from benzene-cyclohexane gave a product, m.p. 246–249° dec., which, unlike the T₈(OH)₂'s, remained fluid rather than resolidifying when held above its melting point. The spectrum (in CS₂) showed unbonded silanol ν OH at 3675 ($E_{1\text{cm}}^{1\%}$ 1.3) and $\nu_{\text{a}}\text{SiOSi}$ at \approx 1100 (wsh) and 1125 (vs) cm.⁻¹.

Anal. Calcd. for C₅₄H₄₆O₁₄Si₉: C, 55.4; H, 3.9; OH, 1.45; mol. wt., 1170. Found: C, 55.0; H, 4.1; OH (from ϵ 3675), 1.5; mol. wt. (Mechrolab osmometer, benzene), 1090 ± 10%.

Noncrystalline Group B Constituents. About 8% of the condensate prepared from either PhSiCl₃ or phenyl-T₄(OH)₄ in aqueous acetone consisted of group B species (cyclohexane soluble) other than T₉OH. The specimens recovered from the various cyclohexane-soluble fractions after crystallizing the T₉OH were waxy solids showing very similar spectra in CS₂: unbonded silanol ν OH at 3675 cm.⁻¹ ($E_{1\text{cm}}^{1\%}$ \sim 1.8), $\nu_{\text{a}}\text{SiOSi}$ resembling that of ϵ -T₈(OH)₂: a single unsymmetrical peak suggesting an unresolved weak

shoulder near 1095 cm^{-1} on the edge of a very strong 1120- cm^{-1} band.

The formation of these species *via* the $\text{T}_4(\text{OH})_4$ condensation, as well as the apparent OH content ($\sim 2.3\%$ from ϵ 3675), suggested their formulation as T_{12} -diols; however, the detection of small amounts of T_{10} , T_{11}OH , and T_{12} in the condensates of methylsilanetriol prepared under the same conditions suggested that $\text{T}_{10}(\text{OH})_2$ and $\text{T}_{11}(\text{OH})$, as well as $\text{T}_{12}(\text{OH})_2$, isomers might be present.

Group C Resin Constituents. The fraction of the resin which was the least soluble in either aqueous acetone or cyclohexane had a molecular weight of $2540 \pm 10\%$ (Mecrolab osmometer, acetone) showed unbonded silanol νOH at 3675 ($E_{1\text{cm}}^{1\%}$ 1.3), a shoulder suggesting phenyl-bonded silanol at 3630, and $\nu_a\text{SiOSi}$ at 1046 (m), ~ 1085 (msh), 1125 (s), and ~ 1150 (sh) cm^{-1} . Some of the slightly more soluble fractions showed similar spectra with the lowest frequency $\nu_a\text{SiOSi}$ variously shifted up to 1052 cm^{-1} . The frequency of the in-phase siloxane chain vibration is known to be chain length dependent in linear siloxane oligomers,^{14,19} and similar variations in band position are normally observed during fractionation of homologous series of polysiloxanes. The group C materials thus probably consisted of both $\text{T}_6(\text{OH})_2$ dimers (mol. wt., 2082, $\nu_a\text{SiOSi}$ ca. 1052 cm^{-1}) and trimers (mol. wt., 3114, $\nu_a\text{SiOSi}$ ca. 1044 cm^{-1}). The methyl- T_9OH dimer, 17, showed $\nu_a\text{SiOSi}$ at 1050 (m), 1075 (w), and 1125 (s) cm^{-1} .

Other Polycondensates. An old sample of ether hydrolysate resin which had been prepared from 423 g. of phenyltrichlorosilane, 800 ml. of ether, and 216 ml. of H_2O , followed by washing and drying at 110° , was roughly fractionated by twice precipitating a 5-g./300-ml. solution in acetone with 150 ml. of water. It was found that about 10% consisted of polyols (soluble in 50% acetone, bonded νOH below 3400 cm^{-1}), 40% was single cage species (soluble in 67% acetone, insoluble in 50%; νOH and $\nu_a\text{SiOSi}$ patterns very similar to those in the group A + B mixtures prepared in aqueous acetone), and that 50% consisted of higher molecular weight species (insoluble in two 450-ml. portions of 67% acetone). The latter did not closely resemble the group C condensates; $\nu_a\text{SiOSi}$ occurred mainly at 1060 (msh), 1095 (wsh), 1115 (s), and ~ 1150 (sh) cm^{-1} , with only a weak shoulder at the 1045- cm^{-1} group C position. There was also a weak, sharp cyclotrisiloxane ring peak at 1016 cm^{-1} , as is typical for polyol resins which have been thermally condensed.

An old sample of toluene hydrolysate resin which had been prepared by prolonged agitation of a 50% (by weight) solution of phenyltrichlorosilane in toluene with four-thirds its weight of water at 50° , followed by washing and drying by distillation, was fractionated by precipitation from 2:1 acetone-water as before,

followed by three extractions with cyclohexane at increasing temperatures. It was found that about 8% consisted of single cage species (soluble in 67% acetone; $\nu_a\text{SiOSi}$ resembling a group B resin fraction; but νOH showed bonded silanol at 3380 as well as unbonded silanol at 3675 cm^{-1} , both $E_{1\text{cm}}^{1\%}$ about 1.1). About 37% consisted of species designated "group C" (soluble in two 200-ml. portion per 5 g. of cold cyclohexane; $\nu_a\text{SiOSi}$ 1060 (msh), 1095 (wsh), 1120 (s), ~ 1150 (sh) cm^{-1} ; νOH of silanol-bonded silanol at 3320 cm^{-1} , $E_{1\text{cm}}^{1\%}$ 1.5 g., with weak shoulder of phenyl-bonded silanol at 3630; mol. wt., $2760 \pm 10\%$ in acetone, $3530 \pm 10\%$ in benzene). The spectrum, which generally resembled that of the higher molecular weight species formed in ether, or those of condensates prepared by refluxing resin 6 in 1,2-dichloroethane, indicated a fairly compact polycyclic siloxane; the analytical data suggested the mean composition of a $\text{T}_{21}(\text{OH})_3$ or $\text{T}_{22}(\text{OH})_4$ decacyclic. The remaining 55% of the condensate consisted of "group D" species which were increasingly difficultly soluble in hot cyclohexane. The least soluble fraction (30% of the total condensate) had a molecular weight of $8070 \pm 10\%$ in acetone, a silanol content and distribution still fairly similar to that in the group C' fractions (suggesting $\text{T}_{62}(\text{OH})_{10}$ as an average composition), and a $\nu_a\text{SiOSi}$ resembling that in C' but with an additional broad shoulder in the 1050- cm^{-1} region, suggesting a distribution of chain lengths in a randomly connected "bead chain" structure.

Another sample of condensate was prepared by adding a solution of 200 g. of phenyltrichlorosilane in 300 ml. of toluene to 500 ml. of water held at $20\text{--}25^\circ$ over 0.5 hr., then stirring for 1 additional hr., decanting the acid layer, washing with water, and removing the toluene in vacuum at $20\text{--}25^\circ$. The molecular distribution in this was examined by gel permeation chromatography in methylene chloride, the retention volumes being calibrated as to molecular weight using phenyl- T_8 , T_{12} , and ladder "prepolymer" fractions^{8,9} as standards. The chromatogram showed a single main peak at 4000 mol. wt., with a medium shoulder corresponding to a ca. 7000 mol. wt. component and a weak shoulder at 1000. The infrared spectrum suggested a 2:1 mixture of group C' and D species. Presumably, in methylene chloride as in benzene, some association of the group C species occurred, resulting in apparent molecular weights about 1.5 times those observed in acetone. (It was observed that resin 6, mol. wt. 1000 in acetone, had an apparent molecular weight of 3000 in methylene chloride on the g.p.c. column.)

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