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Preparation and Characterization of the Lower Equilibrated Phenylsilsesquioxanes

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The alkali-equilibrated mixtures of polycyclic phenylsilsesquioxanes, formerly known as "silicobenzoic anhydride" or "phenylsiliconic anhydride," were among the first organosilicon compositions to be discovered, but their constitution has remained obscure. The present study was undertaken to illuminate this by preparing several such mixtures, determining their compositions, and characterizing the constituent phenylsilsesquioxanes as to spectra, structure, and kinetics of interconversion. The mixtures prepared by equilibration in aprotic solvents were found to contain octaphenylpentacyclo[9.5.1.1^{3,9}.1^{5,17}.1^{7,13}]octasiloxane ("phenyl-T₈," m.p. 500°), decaphenylhexacyclo[9.9.1.1^{3,9}.1^{5,17}.1^{7,13}.1^{13,19}]decasiloxane ("phenyl-T₁₀," m.p. 418°), dodecaphenylheptacyclo[13.9.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{11,23}]dodecasiloxane ("phenyl-T₁₂," m.p. 385°), a little noncrystalline material in the T₉-T₁₂ range, and a homologous series of predominantly linear polycyclics containing at least 22-24 silicone units ("phenyl-T ladder prepolymer"). Those prepared by equilibration in the presence of water and alcohol contained hydroxylated and alkoxyated species in addition to these. Equilibrations in cold solutions were usually displaced by precipitation of one of the constituents; depending upon the choice of solvent, either phenyl-T₈, phenyl-T₁₂, or a mixture of linear polycyclics containing up to 300 phenyl-T units could be obtained alone and in good yield. Spectroscopic studies on the various preparations indicated that only two basic types of structural arrangements are important in equilibrated phenylsilsesquioxanes: in one, cyclo-tetrasiloxane rings are fused *cis-syn-cis* at adjacent silicons so as to produce cage-like arrangements of 8-12 silsesquioxane units; in the other, they are fused *cis-anti-cis* to produce linear polycyclics resembling segments of the *cis*-syndiotactic double-chain polymer. The interconversions of the cage-like double-ring species (*i.e.*, T₈-T₁₂) and the double-chain linear structures are formally analogous to the interconversions of monocyclic rings and linear polymers, but were found to be complex mechanistically. Presumably the necessity for inverting stereochemical configuration at 4-6 silicon atoms precludes a simple mechanism.

It has been known since the 1870's that the treatment of phenylsilanetriol condensation products with alkali will produce soluble, relatively low molecular weight materials having the empirical composition (C₆H₅SiO_{1.5})_x.¹ Such compositions were first prepared during attempts to synthesize silicon analogs of the carboxylic acids, and have been variously known over the years as silicobenzoic anhydride, phenylsiliconic anhydride, phenylsilsesquioxane, or phenyl-T resin.² Their constitution, however, has remained largely unknown.

The first individual phenylsilsesquioxane was obtained as a crystalline precipitate when a mixture of phenyltrichlorosilane hydrolysate, KOH, ethanol, ether, and benzene was allowed to stand.³ This was originally reported to be the tetracyclic hexamer, phenyl-T₆,³ but was later shown to be the pentacyclic octamer, phenyl-T₈.⁴ Meanwhile, Sprung and Guenther⁵ found that a mixture of phenyltriethoxysilane, water, tetraethylammonium hydroxide, and methyl isobutyl ketone slowly deposited a higher polymer, (C₆H₅SiO_{1.5})_n, *n* > 40, upon standing, and that this in turn slowly rearranged in benzene solution to give phenyl-T₈. It has also been reported that the base-catalyzed equilibration of phenylsilsesquioxane in bulk at high temperatures produces very high molecular weight soluble double-chain polymers^{6,7} rather than the lower molecular weight polycyclic species that are obtained in more dilute systems.

The present investigation was undertaken in order to learn more about the species present in alkali-equilibrated phenyl-T solutions, and the processes by which they are formed and interconverted.

(1) A. Ladenburg, *Ber.*, **6**, 379 (1873); A. Ladenburg, *Ann.*, **173**, 143 (1874); J. A. Meads and F. S. Kipping, *J. Chem. Soc.*, **105**, 679 (1914); J. F. Hyde and W. H. Daudt, U. S. Patent 2,482,276 (Sept. 20, 1949).

(2) In the conventional silicone nomenclature, "T" denotes a trifunctional unit of siloxane structure, *e.g.*, a monoalkylsilicon group linked through oxygens to three other groups.

(3) A. J. Barry, W. H. Daudt, J. J. Doniccone, and J. W. Gilkey, *J. Am. Chem. Soc.*, **77**, 4248 (1955).

(4) K. Larsson, *Arkiv. Kemi.*, **16**, 209 (1960); K. Larsson and C. Grünwall, *ibid.*, **17**, 529 (1961).

(5) M. M. Sprung and F. O. Guenther, *J. Polymer Sci.*, **28**, 17 (1958).

(6) 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).

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

Results

When solutions of phenylsilsesquioxanes that had been equilibrated by refluxing with 0.1% KOH in toluene or diglyme were fractionated, it was found that two groups of molecular species were present. The first group consisted of molecules that contained 8 to 12 phenyl-T units and that showed only one ν_{a} -SiOSi band (at 1121-1129 cm.⁻¹) in the infrared. The second group of molecules contained at least 22-24 phenyl-T units, and showed two ν_{a} -SiOSi bands, centered at 1135-1150 and 1045-1060 cm.⁻¹, respectively. This latter group appeared to comprise a homologous series of molecules having the "most probable" molecular weight distribution expected for a family of linear polymers; it has previously been termed "phenyl-T ladder prepolymer" because of its convenience as a starting material for preparing the double-chain high polymers.⁶ No species containing 13-22 phenyl-T units could be isolated, nor could any species containing cyclotrisiloxane rings (*e.g.*, phenyl-T₆) be detected spectroscopically, nor did any fraction of the mixture show the ν_{a} -SiOSi bands in the 1070-1120 cm.⁻¹ range that are usually prominent in the spectra of non-equilibrated phenylsilsesquioxanes.

The compositions of the equilibrated phenylsilsesquioxane mixtures are given in Table I. This table shows that higher temperatures and higher dilutions both favored increased proportions of the T₈-T₁₂ species in the product, and also a shorter chain length in the prepolymer. It is noteworthy that phenyl-T₈ was only a minor constituent of the equilibrated mixtures. Evidently, its reported³⁻⁵ ease of formation results not from any great stability of the pentacyclo-octasiloxane structure, but instead from its very low solubility.

When alkaline solutions of phenyltriethoxysilane or phenyltrichlorosilane hydrolysis products were allowed to stand at room temperature, precipitation of some solid phase, often more or less solvated, invariably occurred sooner or later. When the solvent used was benzene, nitrobenzene, benzyl alcohol, pyridine, or ethylene glycol dimethyl ether, the precipitate was phenyl-T₈. With tetrahydrofuran, it was phenyl-T₁₂. With acetonitrile or diethylene glycol dimethyl ether (diglyme), it was an insoluble polymeric gel. With acetone or methyl isobutyl ketone, it was the soluble, moderately high (M_w 25-60 × 10³) polymer first ob-

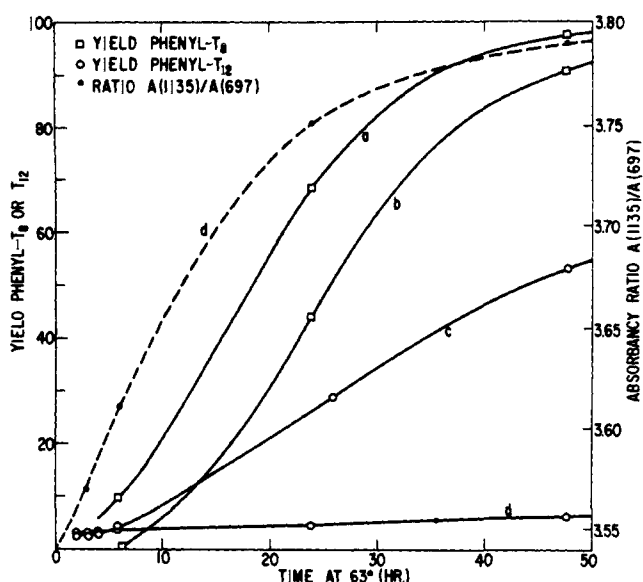


Fig. 1.—Rearrangement of phenyl-T ladder prepolymer to phenyl-T₈ or phenyl-T₁₂ in solutions containing phenyl-T, water, ethanol, and KOH in the molar ratios 1:3.1:10.0:0.078: a, phenyl-T, 0.60 M in benzene, product T₈; b, phenyl-T, 0.90 M in benzene, product T₈; c, phenyl-T, 0.90 M in tetrahydrofuran, product T₁₂; d, phenyl-T, 0.60 M in tetrahydrofuran, product T₁₂; dotted line shows A(1135)/A(697), indicating relative amount of cage-like structure in soluble fraction.

served⁵ by Sprung and Guenther. The conversions of phenyltriethoxysilane or the phenyl-T hydrolysis products to phenyl-T₈ or -T₁₂ generally behaved like equilibrations being continually displaced by phase separation, and could be made to give good yields of these products by refluxing sufficiently concentrated solutions until precipitation was complete. Similar treatment of alkaline solutions of the hydrolysis products of methyltriethoxysilane and cyclohexyltriethoxysilane in acetone or methyl isobutyl ketone has been found to give methyl-T₈ and cyclohexyl-T₈, respectively, also in high yields.

TABLE I
COMPOSITION OF EQUILIBRATED PHENYLSILSESQUOXANE SOLUTIONS

Phenylsilsesquioxane concn., %	36	48	5
Solvent	Toluene	Diglyme	Diglyme
Temperature, °C.	110	160	160
Constituent, wt. % of total (C ₆ H ₅ SiO _{1.5}) _x			
Phenyl-T ₈ , m.p. 500°	>0.1 ^a	0.2	2.2
Phenyl-T ₁₀ , m.p. 418°	2.5	1.9	6.0
Phenyl-T ₁₂ , m.p. 385°	2.2	2.1	3.6
Noncryst. T ₉ -T ₁₂	1.5	2.9 ^b	32.5 ^b
Prepolymer	94	93	44
Prepolymer degree of polymn. \bar{P}_n	85	61	31

^a Equilibrated solution supersaturated with respect to phenyl-T₈, which was being precipitated slowly. ^b These fractions included silanol-containing species, presumably derived from alcoholic impurities or decomposition products in the diglyme (diethylene glycol dimethyl ether).

The kinetics of phenyl-T₈ or -T₁₂ formation by the rearrangement of other phenylsilsesquioxanes in benzene or tetrahydrofuran solutions containing alkali, alcohol, and water was complex. The conversions to the crystalline products generally followed sigmoidal curves, with induction periods of 10–20 hr. during which the precipitation rates were low (Fig. 1). However, in some of the reactions in tetrahydrofuran there

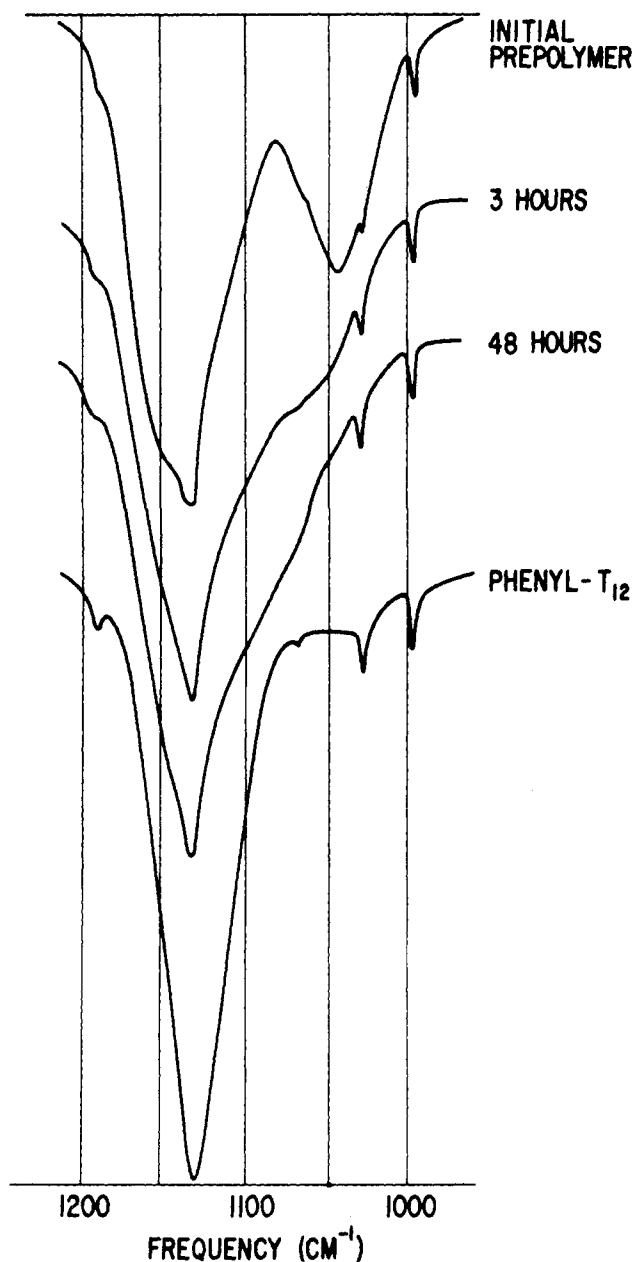


Fig. 2.—Infrared spectra of phenylsilsesquioxanes during rearrangement of prepolymer to phenyl-T₁₂ under conditions of run d on Fig. 1. Successive curves show the initial prepolymer, the soluble fraction after 3-hr. reaction, the soluble fraction after 48-hr. reaction, and the insoluble product, phenyl-T₁₂.

was also an initial rapid formation of 2–5% phenyl-T₁₂; this occurred particularly when the phenylsilsesquioxane being rearranged was T₁₆, the noncrystalline T₉-T₁₂ mixture, or a low molecular weight prepolymer fraction. Infrared observations of the material in solution during a rearrangement of prepolymer to T₁₂ (Fig. 2) showed that cleavage of the polymer chains (as indicated by the disappearance of the original 1045 cm.⁻¹ $\nu_{\text{Si-O-Si}}$ in-phase chain vibration) occurred very rapidly. Also, the equilibrium concentration of cage-like structure (indicated by the dotted line of Fig. 1) was largely attained before the maximal rate of T₁₂ precipitation was observed. The conclusion drawn was that the T₈ and T₁₂ were not being formed from the higher polymers by anything resembling a simple, one-step reaction. Other low molecular weight intermediates were involved, and it was entirely possible that total reorganization of the siloxane structure was occurring.

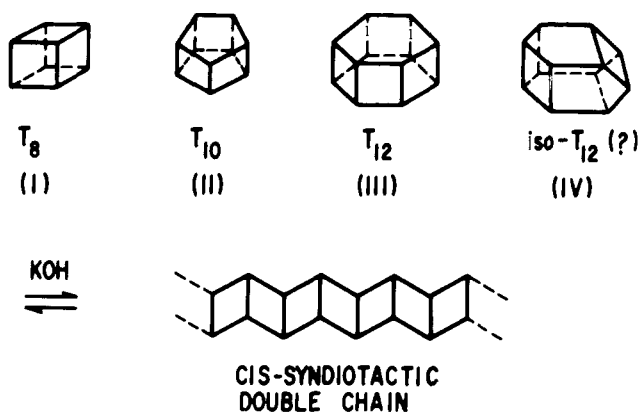


Fig. 3.—The double ring-double chain equilibrium in the phenylsilsesquioxanes. In the drawings, the vertices represent the locations of the C_6H_5Si groups, the lines the positions of the oxygens connecting them.

It has been proposed previously^{4,5} that the very insoluble phenyl- T_8 isomer under discussion here has the cube-like, pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane structure indicated as form I in Fig. 3. Our observations have continued to support this assignment. The two reasonable alternative pentacyclooctasiloxane structures both contain cyclotrisiloxane rings, which would be expected to produce low-frequency ν_aSiOSi vibrations and marked perturbations of the 998 and 1029 cm^{-1} phenyl ring modes.⁸ Neither of these was observed. The observed ν_aSiOSi came at 1121 cm^{-1} in CS_2 solution, very close to the 1122 cm^{-1} observed in methyl- T_8 ,⁹ for which the cube-like structure has been established by complete X-ray analysis.¹⁰ In addition, we found one crystalline form of the material to have a simple rhombohedral unit cell that could scarcely accommodate any molecule not cube-like in shape.

In the case of phenyl- T_{10} , the infrared spectrum again indicated an absence of cyclotrisiloxane rings or other strained structures. Since the only possible hexacyclodecasiloxane arrangement that lacks such small rings is the pentagonal prism-like hexacyclo[9.9.1.1^{3,9}.1^{5,17}.1^{7,15}.1^{13,19}]decasiloxane (form II), this was assigned. Again, the observed ν_aSiOSi (*ca.* 1128 cm^{-1}) was very similar to that (1127 cm^{-1}) found for methyl- T_{10} .⁹

For phenyl- T_{12} , however, the spectral evidence for the lack of small rings did not uniquely define a structure, since there are two heptacyclododecasiloxane arrangements (III and IV) that contain only cyclotetrasiloxane or larger rings. Evidence in favor of the heptacyclo[13.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{17,23}]dodecasiloxane structure (III) was found in the ultraviolet spectrum, which showed lower 1L_b benzenoid transition intensities than did those of the other phenyl-T cage species.¹¹ This is believed¹¹ to indicate a smaller mean angle between the Ph-Si axes than in phenyl- T_{10} or in the presumed isomer of phenyl- T_{12} present in the noncrystalline fraction. In addition, the ν_aSiOSi position (*ca.* 1129 cm^{-1}) suggested a close structural analogy to the methyl- T_{12} , m.p. 270° (ν_aSiOSi , 1128 cm^{-1}), for which the hexagonal prism-like structure (III) was indicated by the absence of splitting in the proton magnetic resonance signal.⁹

Phenyl- T_{12} was normally obtained from solution as solvated crystals which contained one or two molecules of solvent for each molecule of T_{12} . These solvates were all found to have the same basic crystal lattice,

(8) C. W. Young, P. C. Servais, C. C. Currie, and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

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

(10) K. Larsson, *Arkiv Kemi*, **16**, 203 (1960).

(11) J. F. Brown, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, in press.

and hence appeared to represent a family of clathrate-type inclusion compounds. The tetrahydrofuran adduct, phenyl- $T_{12} \cdot 2THF$, was of particularly low solubility (0.06 g./100 ml. of THF at 28°), thus allowing the preparation of phenyl- T_{12} by precipitation from equilibrating solutions in tetrahydrofuran.

The observation that there was very little variation in the ν_aSiOSi frequencies among the methyl and phenyl T_8 's, T_{10} 's, and T_{12} 's and that there was no splitting in the T_{10} and T_{12} bands at first caused concern, since pronounced variations in ν_aSiOSi with ring size are observed in the monocyclic siloxanes,¹² as is also splitting of the band,¹² and one would expect two different modes of infrared-active vibration in a prism-like T_{10} or T_{12} siloxane skeleton. However, calculations of the ν_aSiOSi frequencies showed that in rings of 4, 5, 6, or 7 siloxane units having coplanar silicon atoms, the expected effect of increased ring size in lowering the doubly degenerate ring frequency is almost exactly balanced by the effects of the increased SiSiSi angles in raising the frequency. In addition, it was estimated that the two infrared-active modes in prismatic structures of the T_{10} , T_{12} , or T_{14} types should always be within 10 cm^{-1} of each other, and hence unresolvable. (Individual ν_aSiOSi modes in unstrained structures normally have half-intensity band widths of about 40 cm^{-1} .) Evidently, the observation of a single ν_aSiOSi band, lying in the 1120–1130 cm^{-1} range, may be taken as good evidence for the presence of a strainless cage structure composed of 8–14 silsesquioxane units, but is of less help in distinguishing one type of silsesquioxane cage from another.

The fractions designated "noncrystalline T_9 - T_{12} " in Table I all showed a single ν_aSiOSi , centered near 1127 cm^{-1} , thus showing that they consisted of cage-like silsesquioxanes. Those obtained by equilibration in diglyme contained about one silanol group for each ten silicons, and were presumed to contain $T_9(OH)$ and $T_{11}(OH)$ species analogous to the $T_9(OEt)$ and $T_{11}(OEt)$ species obtained when methylsilsesquioxanes were equilibrated in the presence of ethanol.⁹ The specimen isolated from the products of equilibration in toluene was much lower in hydroxyl content, and showed an ultraviolet spectrum intermediate between those of phenyl- T_{10} and phenyl- T_{12} .¹¹ It was considered possible that this contained the other strainless heptacyclododecasilane isomer (structure IV); however, such a species was not isolated in a pure form.

The various fractions of "phenyl-T ladder prepolymer" all showed infrared and ultraviolet spectra resembling mixtures of cage-like silsesquioxanes and double-chain polymer. It has been reported⁷ that the molecules of prepolymer consist of short segments of the double-chain (linear polycyclic) structure, terminated by cage-like arrangements of 10–12 T units, thus giving dumbbell-shaped molecules. More extensive evidence in support of this conclusion will be presented elsewhere.

The polymers that slowly precipitated from alkaline solutions in acetone or methyl isobutyl ketone as in the Sprung-Guenther procedure⁵ were not of this type, however. They were composed of 150–300 phenyl-T units and 3–4 hydroxyl or ethoxy groups per molecule, and showed infrared spectra that, except for the very weak silanol group vibrations, were exactly the same as those of the double-chain high polymers. Accordingly, they would appear to represent 75–150 unit segments of "ladder" structure (*i.e.*, polycyclics with 75–150 linearly fused cyclotetrasiloxane rings) terminated mostly by hydroxyl and ethoxyl groups.

(12) N. Wright and M. J. Hunter, *ibid.*, **69**, 803 (1947); R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

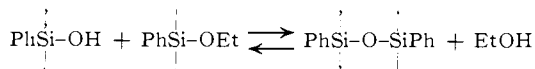
The phenylsilsesquioxanes remaining in the cold, alkaline, alcoholic, acetone solutions during the precipitation of these polymers contained about one ethoxyl and two hydroxyl groups for each 14 phenyl-T units, and showed $\nu_{\text{a}}\text{SiOSi}$ bands (centered near 1135 cm^{-1} , vs; 1057 cm^{-1} , m) resembling those in a prepolymer fraction of \bar{P}_n about 30. Presumably, this mixture contained a continuous family of linear polycyclic species that was being steadily displaced by precipitation of the highest molecular weight, acetone-insoluble, members. The phenylsilsesquioxanes remaining in the hot, alkaline, alcoholic tetrahydrofuran solutions during the precipitation of phenyl- T_{12} , however, were more predominantly cage-like. Their infrared spectrum (third curve on Fig. 2) suggests that of a T_9 - T_{12} cage mixture contaminated with other small (3-6 ring) polysiloxanols.¹³

Discussion

Although there is an almost infinite number of ways in which trifunctional siloxane units might conceivably combine with each other to form polycyclics, the present results show that only a few such arrangements are actually present in equilibrated phenylsilsesquioxanes. These structural arrangements are of two types. In the first type, cyclotetrasiloxane rings are united by *cis-syn-cis*-fusion at adjacent silicons so as to produce the cage-like arrangements of 8-12 siloxane units that are found in phenyl- T_8 , phenyl- T_{10} , phenyl- T_{12} , and probably also in the prepolymer chain-end structures. In the second type, cyclotetrasiloxane rings are united by *cis-anti-cis*-fusion at adjacent silicons so as to produce the linear polycyclic structures found in the prepolymers, in the precipitated linear polycyclics of the Sprung-Guenther type, and in the *cis*-syndiotactic double-chain high polymers. The preference for these two structural arrangements probably results from the facts that they allow the OSiO and SiOSi bond angles to assume their preferred values of 109.5 and 150-155°,⁹ respectively, and that they can accommodate the bulky phenyl groups without steric compression.

The crystalline phenyl- T_8 , - T_{10} , and - T_{12} cage species described here appear to correspond to the previously reported⁹ methyl- T_8 , - T_{10} , and - T_{12} species both in structure and in relative stability. However, the higher equilibrated polymethylsilsesquioxanes are probably not entirely analogous to the linear polycyclic phenylsilsesquioxanes, since they show 10-20 cm^{-1} lower $\nu_{\text{a}}\text{SiOSi}$ frequencies and marked tendencies toward gelation.

The phenylsilsesquioxane mixtures prepared by equilibration in solutions containing alcohols or water appear to be generally similar to those prepared in aprotic solvents, but in addition contain small proportions of silanol and alkoxy silane groups. Evidently, the equilibria for siloxane bond formation, *e.g.*



do not lie completely to the right. The silanol and alkoxy silane groups incorporated into the product seem to appear largely in the difficultly crystallizable $\text{T}_9(\text{OR})$ and $\text{T}_{11}(\text{OR})$ cage species, and as end groups on the linear polycyclics.

The mechanistic complexity of the cage-ladder interconversions is at first glance surprising, since these double ring-double chain interconversions are formally analogous to the well-known, mechanistically simple,

ring-chain interconversions observed in single-chain structures (Fig. 3). The reason for this complexity is presumably that the conversions of the *cis-syn-cis*-fused cage-like molecules to the *cis-anti-cis*-fused linear species requires inversions of configuration at half the silicons involved, and that considerable structural reshuffling is required in order to accomplish this.

Experimental

The crystalline phenylsilsesquioxanes were routinely characterized by their X-ray powder patterns; the soluble polymers by their 2-15 μ infrared spectra as 1-2% solutions in carbon disulfide using a Beckman IR 7 grating spectrophotometer. Such spectra, being mostly produced by C_6H_5 group vibrations, were essentially invariant except for (a) the characteristics bands¹⁴ of silanol and alkoxy silane groups, if any; (b) a variable shoulder near 729 cm^{-1} arising from splitting of the $\approx 740 \text{ cm}^{-1}$ $\text{C}_6\text{H}_5\text{Si}$ group mode; and (c) the very strong, broad bands in the 1040-1160 cm^{-1} region arising from coupled $\nu_{\text{a}}\text{SiOSi}$ vibrations (Fig. 2). These last are known to be very sensitive to variations in siloxane structure,⁸ and were of particular help in characterizing the various polysiloxane skeletons encountered.

Equilibrations in Aprotic Systems.—Equilibrations in refluxing toluene were all carried out for limited times, since the solutions were slightly supersaturated with respect to phenyl- T_8 , and precipitated it steadily. In a typical procedure, phenyltrichlorosilane (3 kg.) diluted with an equal volume of toluene was run into water (12 kg.) with stirring. After separation of the aqueous acid layer, the toluene solution of condensate was distilled to remove residual water and acid, along with 1300 g. of toluene. Next, potassium hydroxide pellets (1.41 g.) were added, and refluxing and trapping of the evolved water continued until dehydration was complete and the infrared spectrum no longer showed any silanol bands (9 hr.). The resulting mixture of sirup and precipitated phenyl- T_8 was cooled and filtered to remove the T_8 (245 g., unwashed wt.); the filtrate (3155 g., 50.3% phenylsilsesquioxanes) deposited no further crystals after standing for several weeks. Dry, unfractionated prepolymer $[\eta]$ 0.12 dl./g. (in benzene at 25°), \bar{M}_n 14,000, could be isolated by precipitation into methanol or ligroin. Similar preparations at a phenylsilsesquioxane concentration of 36% in toluene were carried out longer (16 hr.), but the amount of T_8 formed was lower (6-8%), as was also the intrinsic viscosity of the unfractionated prepolymer (0.085 dl./g.).

The use of refluxing diglyme (b.p. 160°, phenyl- T_8 solubility 0.52 g./100 ml.) circumvented the precipitation problem. Samples (10-20 g.) of dried but not decatalyzed prepolymers prepared in toluene were dissolved in freshly redistilled diglyme and the solutions refluxed 4 days under nitrogen. When a prepolymer specimen containing 6% suspended phenyl- T_8 was used, the solutions were homogeneous after refluxing for 1 day.

The attainment of equilibrium in these systems was demonstrated by the invariance of the product spectra, and by the constancy of the equilibrium constants⁷ calculated from runs made at different concentrations.

Fractionation of Prepolymers.—The toluene or diglyme solutions of equilibrated phenylsilsesquioxanes were neutralized with HCl, seeded with phenyl- T_8 crystals, and allowed to stand for several days while the bulk of the T_8 crystallized out. The soluble silsesquioxanes were then recovered from solution, dissolved in three times their weight of acetone, and allowed to stand overnight, whereupon much of the phenyl- T_{12} and any prepolymer above $[\eta]$ ca. 0.14 precipitated. These were filtered off and separated by extracting the prepolymer with tetrahydrofuran. The acetone solutions were then diluted to give polymer concentrations of about 10% and fractionated in the conventional way by adding successive increments of methanol at the boiling point, allowing the mixture to cool and stand until phase separation was complete, removing the solution, and reprecipitating the polymer from acetone into methanol. The prepolymer fractions thus recovered ranged in molecular weight (ebullioscopic in benzene) from 14,000 down to 3,000, and had \bar{M}_w/\bar{M}_n ratios near 1.4. (Fractionation of a 1% solution in acetone was attempted, but was found to require extremely long times for the phase separations.) All of the methanolic filtrates, as well as the final solution of materials soluble in 90% methanol, were retained and evaporated to recover the lower silsesquioxanes. A toluene solution of these deposited a little additional T_8 and T_{12} , which were separated from each other by extracting the T_{12} with a little boiling toluene. The final separation of the cage-like species (mol. wt. <1500, one $\nu_{\text{a}}\text{SiOSi}$ near 1127 cm^{-1}) from the lowest prepolymer fraction (mol. wt. >2900, $\nu_{\text{a}}\text{SiOSi}$'s near 1135 and 1062 cm^{-1}) was accomplished by repeated precipitation from toluene solution into nine volumes of methanol. The material soluble in 1:9 toluene-methanol was dissolved in an equal weight of toluene and allowed to stand several days while the T_{10} crys-

(13) These are indicated by the extra absorption shoulders in the 1070-1100 cm^{-1} region, which occur where the major bands of the strainless, non-cage-like tricycloheptasiloxanes, tri- and tetracyclooctasiloxanes, tri- and tetracyclononasiloxanes, etc., are normally observed.

(14) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

tallized out, leaving behind the noncrystalline T_9 - T_{12} cage compounds.

Survey of Solvent Effects.—Mixtures of phenyltriethoxysilane (12.0 g., 0.05 mole), water (2.7 g., 0.15 mole), tetraethylammonium hydroxide (0.0015 mole), and solvent (50 ml.) were allowed to stand at room temperature with occasional examination of the precipitates. The products, the relative rates of precipitation, and the yields after standing for 6 months were: acetone, slow formation ladder-like polymer, 54%; benzene, rapid precipitation of T_8 , >88%; benzyl alcohol, very slow, T_8 , 4%; methyl isobutyl ketone, slow precipitation of ladder-like polymer, 42%; tetrahydrofuran, 60-day induction period in first run, then rapid precipitation of T_{12} , 69%. Another series, identical except for the use of benzyltrimethylammonium hydroxide as the base, gave these results: acetonitrile, rapid precipitation of gelled ladder-like polymer, 82.5%; diethyl ether, rapid precipitation of soluble low mol. wt. ladder-like polymer, 84.5%; diethylene glycol dimethyl ether (diglyme), very slow, gelled ladder-like polymer, 4.2%; ethylene glycol dimethyl ether, slow, T_8 , 11.6%; ethylene diamine, unidentified crystals not containing C_6H_5 groups, 2.4% by weight; nitrobenzene, slow, T_8 , 43%; pyridine, slow, T_8 , 38%; tetrahydrofuran, rapid precipitation of T_{12} , 68%. Repetition of the reported procedure³ for "hexaphenylsilsequioxane" (KOH-catalyzed equilibration in a 20:15:75 mixture of ether, alcohol, and benzene) gave 14% T_8 after 13 days; the filtrate then deposited T_{12} for 3-4 weeks before T_8 began precipitating again; additional yield of T_8 - T_{12} mixture, 10% after 4 months.

Phenyl- T_8 , Octaphenylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane.—Phenyltrichlorosilane (105.8 g., 0.50 mole) was dissolved in 500 ml. of benzene and shaken with water until hydrolysis was complete. After removing the acid layer and washing with water, 16.6 ml. (0.030 mole) of a commercial methanolic 30% benzyltrimethylammonium hydroxide solution was added. The mixture was refluxed 4 hr., allowed to stand 4 days, refluxed another 24 hr., and then cooled and filtered to give 57.0 g. (88%) of phenyl- T_8 . The mother liquors continued to deposit crystals, and subsequent small-scale runs (Fig. 1) indicated that a 98% yield would have been obtained on longer refluxing. The alternative procedures described above or reported earlier^{3,5} were found to give the same product. Purification could be effected by sublimation under vacuum at 250-300°, or by recrystallization from hot *o*-dichlorobenzene.

Pure phenyl- T_8 was a difficultly soluble solid which upon rapid heating melted and boiled momentarily at 495-500° before resolidifying to a colorless polymer. Impure phenyl- T_8 often could not be melted at all. The infrared spectrum showed $\nu_{Si-O-Si}$ at 1121 cm^{-1} , and no 730 cm^{-1} shoulder on the 740 cm^{-1} band. Two crystalline modifications were encountered. They first separated from benzene at room temperature as nearly cube-like rhombohedra, d 1.27 g./ml., and appeared to be isomorphous with cyclohexyl- T_8 .³ The powder pattern could be indexed on the basis of a rhombohedral cell where $a_{rh} = 11.0$ Å., $\alpha = 95^\circ$. This defined the substance as an octamer and left little room for choice as to the shape of the molecule. The more conspicuous lines in this pattern had *d*-spacings of 10.9 (vs), 8.1, 7.3, 4.76, 4.63, and 3.59 Å. The second form was obtained at higher temperatures. Its more conspicuous lines lay at 12.0, 10.6 (vs), 10.1, 9.4, 8.4, 7.7, and 3.88 Å. Other crystal forms have been reported.⁴

Phenyl- T_{10} , Decaphenylhexacyclo[9.9.1.1^{3,9}.1^{5,17}.1^{7,13}.1^{13,19}]decasiloxane.—The material obtained by fractionating the equilibrated phenylsilsequioxane mixtures was recrystallized from benzene-hexane: colorless crystals, readily soluble in most common solvents, m.p. 415-418°, $\nu_{Si-O-Si}$ ca. 1128 cm^{-1} . (The exact position of this maximum was obscured by the sharp 1133 cm^{-1} C_6H_5Si mode.) The most prominent X-ray reflections were at 12.3, 10.8 (vs), 4.78, and 4.63 Å.

Anal. Calcd. for $C_{60}H_{50}O_{10}Si_{10}$: C, 55.8; H, 3.9; mol. wt., 1290. Found: C, 55.6; H, 4.0; mol. wt. (ebullioscopic in trichloroethylene), 1245 \pm 60.

Phenyl- T_{12} , dodecaphenylheptacyclo[13.9.1.1^{3,13}.1^{5,17}.1^{7,21}.1^{9,19}.1^{17,23}]dodecasiloxane, was formed in 50-70% yields by allowing aqueous alkaline solutions of phenyltriethoxysilane or phenyltrichlorosilane hydrolysis products to stand in tetrahydrofuran for 4-6 months as indicated above, or by refluxing such solutions for 2-3 days.¹⁵ To purify the crude product, it was heated to 150° overnight to remove the solvent and decompose the traces of quaternary base present, and then recrystallized from toluene or sublimed under vacuum at 300°. Purified phenyl- T_{12} melted at 385° and slowly polymerized at higher temperatures; impure specimens usually melted sharply at temperatures 20-60° lower. The infrared (Fig. 2) showed only one $\nu_{Si-O-Si}$, centered near 1129 cm^{-1} , but again having the exact position of the maximum obscured by the sharp 1133 cm^{-1} C_6H_5Si mode. The crystal form obtained by drying the clathrates at 100-200° showed prominent inner reflections at 12.3 (vs), 11.8, 11.1 (vs), and 9.3

Å. That obtained by drying at 300° or by sublimation showed such reflections at 13.0, 12.0 (vs), 11.4, 10.6, 10.1, and 8.4 Å.

Anal. Calcd. for $C_{72}H_{60}O_{12}Si_{12}$: C, 55.8; H, 3.9; mol. wt., 1548. Found: C, 56.1; H, 4.3; mol. wt. (ebullioscopic in benzene), 1500 \pm 75.

Phenyl- T_{12} Clathrates.—Phenyl- T_{12} normally separated from solution in large, solvated crystals. The X-ray patterns of the crystals containing acetone, benzene, tetrahydrofuran, and toluene were found to be identical except for minor variations in the relative intensities of some of the reflections, indicating that the same host lattice was present in all cases. The most prominent lines in this pattern, which characterizes T_{12} as normally isolated from solution, lay at 14.2, 12.4 (vs), 5.25, 4.6, 4.35, 3.97, and 3.40 Å. The complexing ratios, determined by heating the air-dried crystals to 200°, appeared to be 1:2 for the benzene and tetrahydrofuran complexes, and 1:1 for the toluene adduct.

Anal. Calcd. for $C_{72}H_{60}O_{12}Si_{12} \cdot 2C_6H_6$ (benzene adduct): wt. loss, 9.2. Found: wt. loss, 9.1. Calcd. for $C_{72}H_{60}O_{12}Si_{12} \cdot 2C_4H_8O$ (tetrahydrofuran adduct): wt. loss, 8.5. Found: wt. loss, 8.7. Calcd. for $C_{72}H_{60}O_{12}Si_{12} \cdot C_7H_8$ (toluene adduct): wt. loss, 5.6. Found: wt. loss, 5.5.

Noncrystalline Phenyl-T Cage Compounds.—The small residue remaining after the removal of all crystallizable or methanol-insoluble constituents from the phenylsilsequioxane mixture obtained by equilibration in toluene was an amorphous resin, softening near 100°, which could be distilled under vacuum at 250-275° with partial polymerization. The infrared spectrum closely resembled those of phenyl- T_{10} and T_{12} ; $\nu_{Si-O-Si}$ came near 1128 cm^{-1} , and bands indicative of groups other than $C_6H_5SiO_{1.5}$ could not be detected with certainty. The molecular weight (found, osmometric in acetone, 1435 \pm 140) indicated species in the T_{10} - T_{12} range. It was considered likely that the material was largely the other strainless isomer of phenyl- T_{12} , e.g., dodecaphenylheptacyclo[11.11.1.1^{3,11}.1^{5,21}.1^{7,19}.1^{5,23}]dodecasiloxane (IV); however, the amounts available were insufficient for further studies.

The much larger residues remaining after similar fractionation of the products equilibrated in diglyme were dark yellow resins whose spectra generally resembled phenyl- T_{12} in the $\nu_{Si-O-Si}$ region, but in addition showed the bands of silanol groups, mostly not hydrogen-bonded to each other even in concentrated solutions. Their content was estimated as one SiOH per 10 C_6H_5Si 's. It is believed that these cage-like silanols probably arose *via* the hydrolysis of the corresponding alkoxyxilanes during the rather prolonged fractionation procedure, and that these in turn arose from alcoholic impurities or decomposition products in the diglyme used.

Linear Polycyclic Phenylsilsequioxanes.—The products that precipitated from solutions of 0.5 mole of phenyltriethoxysilane, 1.5 moles of water, and 0.015 mole of tetraethylammonium hydroxide in 500 ml. of methyl isobutyl ketone (MIBK) or acetone at room temperature varied somewhat in molecular size during the course of the reaction, as indicated by their intrinsic viscosities:

Solvent	Days standing	Crop	Yield, %	$[\eta]$, dl./g.
MIBK	8	1	14	0.14
MIBK	79	2	12	.17
MIBK	194	3	6	.25
Acetone	32	1A	22	.27
Acetone	63	2A	11	.10 ^a
Acetone	178	3A	19	.11 ^a

^a Sample purified and $[\eta]$ measured after standing for 1 year.

Similar preparations in ethanol-free acetone solutions (obtained by using a phenyltrichlorosilane hydrolysate resin instead of the triethoxysilane) gave polymers with $[\eta]$ 0.23-0.24 in the first crop, and phenyl- T_8 in the second. Use of double the quantity of base led to a lower precipitation rate (6.7% yield in 32 days) and considerable gel in the product.

These polyphenylsilsequioxanes were infusible solids, soluble in benzene, methylene chloride, and carbon disulfide, but insoluble in acetone or alcohol. X-Ray diffraction indicated the same laterally ordered polymer pattern as that shown by the *cis*-syndiotactic double-chain high polymers.^{6,7} The infrared spectra resembled those of the high polymers very closely, showing $\nu_{Si-O-Si}$ at 1044 and 1156 cm^{-1} , with a possible hidden shoulder in the 1135-1140 cm^{-1} region, and a second C_6H_5Si mode at 729 cm^{-1} . The base-line absorbancies of these peaks relative to those of nearby reference peaks were, in crop 1A: $A(1156)/A(1135)$, 0.98; $A(1044)/A(1135)$, 0.53; and $A(729)/A(740)$, 1.05. Measurements on the same instrument indicated exactly the same relative intensities in double-chain high polymers having $[\eta] \geq 4$. The ratios were all slightly lower in the polymers prepared in MIBK (crops 1-3), indicating the presence of 5-7% more cage-like structure in these than in the specimens prepared in acetone. Use of the relation $[\eta] = 1.12 \times 10^{-6} \bar{M}_w^{0.92}$, which was found to

hold for both the prepolymer fractions and the linear high polymers, indicated that typical $[\eta]$'s of 0.14, 0.20, and 0.28 dl./g. corresponded to \bar{M}_w 's of 28,000, 41,000, and 60,000, respectively. Osmotic measurements on a specimen of $[\eta]$ 0.20 showed \bar{M}_n 30,000, indicating $\bar{M}_w/\bar{M}_n = 1.37$. This polydispersity corresponds to the 1.4 value found in prepolymer specimens fractionated from a mixture having a "most probable" distribution by a single precipitation from a 10% solution in acetone.

Estimates of OH and OEt contents were made from absorption intensities in the regions corresponding to the strongest SiOH and SiOEt group modes,¹⁴ using the crystalline phenyl-T₃(OH)₂(OEt)₂, m.p. 55–57°,⁵ as the reference standard. A more sensitive measure of silanol plus silanolate was achieved by treating the polymer in benzene solution with trimethylchlorosilane and pyridine, whereby these groups were converted to SiOSiMe₃ groups, which were determined in the reprecipitated polymer from the intensity of the very strong band at 844 cm.⁻¹. The results on the material of crop 1 were

Group	No. per 1000 Ph-T	Method
SiO ⁻	4 ± 2	Titration
SiOH	10 ± 10	Infrared
SiO ⁻ + SiOH	15 ± 3	Trimethylsilylation
SiOEt	0 ± 30	Infrared

Since the observed $[\eta]$ and the usual \bar{M}_w/\bar{M}_n ratio indicated an \bar{M}_n of 20,400, or an average molecular size of 158 phenyl-T units for this specimen, and since it appears likely that SiOEt is 0.5–1.0 the content of SiOH, it would appear that the total content of silanol, silanolate, and alkoxy silane groups was 3–4 per molecule.

When a solution of this same specimen (1.00 g. in 10 ml. of benzene) was allowed to stand, precipitation of phenyl-T₈ occurred as previously reported,⁵ and at about the same rate; the conversion was 79% after 2 months, 92% after 6 months. However, when a similar solution which also contained a drop of acetic acid to neutralize the silanolate was allowed to stand, only the trace of phenyl-T₈ which had been originally present in the polymer crystallized out. No further rearrangement to T₈ occurred, and the intrinsic viscosity was unchanged after standing for 4 months.

A small sample of the phenylsilsesquioxane mixture remaining in acetone solution after the separation of crop 1A was recovered by precipitation into dilute aqueous HCl, followed by reprecipitation from acetone into water, drying overnight under vacuum at 35°, and for 0.2 hr. at 110°. Its infrared spectrum showed ν_{SiOSi} 's centered near 1135 and 1057 cm.⁻¹, and indicated OH and OEt contents of 1.8 and 2.3%, respectively, which are comparable to those reported previously for a similar product.⁵ Presumably, a quarter of this OH represented silanolate prior to neutralization, and some additional portion of it represented ethoxy hydrolyzed during the precipitation.

Kinetic Studies.—One-tenth gram samples of phenylsilsesquioxane were weighed into tared 13 × 100 mm. test tubes, fol-

lowed by phenyl-T₈ or -T₁₂ seed crystals; the solvent was 0.42 or 0.84 ml. of tetrahydrofuran or benzene, and 0.36 ml. of an ethanol-water-base solution (usually containing 6.05×10^{-5} mole of KOH). The stoppered tubes were placed in a 63° constant temperature bath for the desired reaction times, and then cooled to 0°. After 80 min. at room temperature to ensure completion of precipitation, the precipitates were centrifuged down, rinsed with two 1-ml. portions of solvent, dried at 200°, and weighed. The identities of the products were reconfirmed by their X-ray patterns in a number of cases. In general, the measurements of conversion as a function of time were reproducible, but fractions from different prepolymer preparations appeared to be converted to T₁₂ at different rates. Agitation of the reacting mixtures had no effect upon the precipitation rates. Higher rates of conversion to T₁₂ were observed in solutions containing both ethanol and water than in those that contained just one of these hydroxylic species. As the base, KOH gave faster conversion rates than NaOH or Me₄NOH; however, doubling its concentration from 0.078 mole/mole of phenyl-T to 0.156 mole/mole markedly reduced the rate of T₁₂ formation. In all cases, the conversions to T₈ or T₁₂ followed sigmoidal curves; representative examples are shown in Fig. 1.

In order to follow the changes occurring in the soluble fraction during the conversions of prepolymer to phenyl-T₁₂ in tetrahydrofuran, the dissolved phenylsilsesquioxanes were recovered by precipitation into dilute aqueous HCl, and their spectra determined. Representative examples are shown in Fig. 2. The material remaining in solution after the completion of T₁₂ precipitation was a low-melting, amorphous resin, contained about 2.5% each of OH and OEt groups, and showed an infrared spectrum (third curve on Fig. 2) that was unlike that of any of the fractions obtained after equilibrations in toluene or diglyme, but not inconsistent with that expected for a mixture of cage-like and very short-chain linear polycyclics.

The increase in cage-like structure during the course of this equilibration was followed by measuring the base-line absorbancy of the 1135 cm.⁻¹ C₆H₅Si group peak (which is superimposed upon the broader 1127 cm.⁻¹ ν_{SiOSi} mode) relative to that of the virtually invariant 697 cm.⁻¹ peak. This ratio, $A(1135)/A(697)$, was 2.9 in the ladder polymer, 4.0 in the lowest prepolymer fractions, 4.4 in the noncrystalline T₉-T₁₂ mixtures, 4.5 in T₈, 5.6 in T₁₂, and 5.7 in T₁₀. During the course of T₁₂ formation from unfractionated prepolymer ($[\eta]$ 0.085, prepared in toluene) the ratio went from 3.54 to 3.79 in 48 hr. (dotted line on Fig. 1), and was apparently approaching a final value of 3.80 as in a first-order reaction with a half-time of 10.5 hr.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

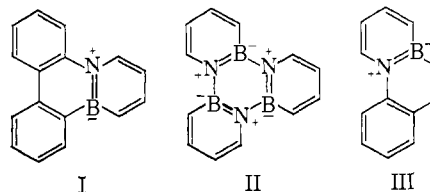
New Heteroaromatic Compounds. XXIII.¹ Two Analogs of Triphenylene and a Possible Route to Borazarene²

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We have prepared two boron-containing analogs of triphenylene, 14,13-borazarotriphenylene and 14,16,18-tribora-13,15,17-triazarotriphenylene. Hydrolysis of the latter with cold dilute alkali probably gives 2-hydroxy-borazarene.

Previous papers of this series have described a wide range of novel heteroaromatic compounds, derived from normal aromatic systems by replacing pairs of adjacent carbon atoms by boron and nitrogen. Here we report the preparation and properties of two further compounds of this type, 14,13-borazarotriphenylene (I) and 14,16,18-tribora-13,15,17-triazarotriphenylene (II).



The synthesis of I followed the route used previously⁵ to prepare 12,11-borazarophenanthrene (III). Con-

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