of iodine per tin atom changing from 0.506 to 0.992.

All the evidence we have presented indicates distinct bis oxide and hydroxide structures, which leads us to suppose that the band at 3646 cm.$^{-1}$ cannot be explained simply as an OH stretching frequency; this work is being continued.

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Crystalline Methylsilsesquioxanes

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Received July 16, 1962

The sublimates obtained by the base-catalyzed pyrolysis of methyl silicone gels have been fractionated and the major components characterized. These were found to be crystalline silsesquioxanes $(CH_3SiO_{1.5})_x$, where $x = 8$, 10, and 12. In addition, small amounts of incompletely condensed crystalline nonamers $(CH_3)_9Si_9O_{13}(OR)$ and numerous non-crystalline minor components were detected. The octasilsesquioxane obtained ("methyl-T_8") was identical with the octamethylpentacyclo-$[9.5.1.1^{3,9}.1^{5,15},.1^{7,13}]$-octasiloxane which has been reported previously. Infrared and n.m.r. spectra indicated that the nonamers were 15-alkoxypentacyclo-$[9.7.1.1^{3,9}.1^{5,17}.1^{7,13}]$-nonasiloxanes, the decamer was a hexacyclo-$[9.9.1.1^{3,9}.1^{5,17}.1^{7,15}.1^{13,19}]$-decasiloxane, and the dodecamer was probably a heptacyclo-$[13.9.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{17,23}]$-dodecasiloxane. The known methyl-T_6, T_8, T_{10}, and T_{12} compounds thus appear to constitute a homologous series of prismatic cage-like polycyclics, which can be regarded as the cyclic analogs of the linear double chain polymers found in the phenylsilsesquioxane series. The relative molar concentrations of methyl-T_6, T_8, T_{10}, T_{12}, and T_{14} in equilibrated solutions were in the ratio 0:1:2:1:0, indicating that the decamer is the most stable member of the series.

Introduction

The methylsilsesquioxanes are polycyclic polysiloxanes which may be regarded as total condensation products of methylsilanetriol, $CH_3Si(OH)_3$. This series of compounds is known to contain several distinct crystalline species in addition to the expected resins and gels. Reported examples of crystalline methylsilsesquioxanes include the hexamer, methyl-T_6 $(CH_3SiO_{1.5})_6$[2]; the octamer, methyl-T_8[2-5]; a "dodecamer"[5]; and four unidentified species from the pyrolysis of methyl-T gel.[5]

The present investigation was undertaken in order to characterize the unidentified crystalline members of the series, and to determine the structural and stability relations among the group as a whole. It was hoped that this might shed some light upon the structural nature of the network polymers found when trifunctional monomers such as $CH_3Si(OH)_3$ undergo polycondensation.

Results and Discussion

Following the general procedure of Barry, *et al.*,[5] base-containing methyl silicone gels were prepared by hydrolyzing methyltriethoxysilane with KOH–water–methanol mixtures, and then pyrolyzed at 325–400° *in vacuo* to yield sublimates containing methylsilsesquioxanes. The relative proportions of the sublimate components varied somewhat with the conditions used for preparing the gels. It also was noted that some of the "gels" were largely methyl-T_8 even before pyrolysis. However, the higher silsesquioxanes appeared to be formed by rearrangement of the gel rather than T_8; heating methyl-T_8 with alkali under the reaction conditions yielded no other volatile products.

The sublimates were partially separated by crystallization, and then analyzed by g.l.c. (gas–liquid chromatography). They were found to contain 66–91% methyl-T_8; 2–9% methyl-T_{10}; 1–17% methyl-T_{12}; 1–9% methyl-T_9(OR), where R = methyl or ethyl; and 3–11% of an oil which contained about 30 minor components. No methyl-T_6 could be detected, either by g.l.c. or by infrared spectroscopy.

The methyl-T_8 obtained was identical with that reported by various other investigators.[2-5] The methyl-T_{10} appeared to be the same as the "Compound B" obtained by Barry, *et al.*,[5] and reported as a "dodecamer" on the basis of borderline molecular weight determinations. The methyl-T_{12} is probably the same as their unidentified "Compound C" or "D." The methyl-$T_9(OC_2H_5)$ appeared to be their "Compound F." No species corresponding to "Compound E" was obtained. However, it is not certain that the unidentified compounds C, D, and E could not all have been methyl-T_{12}; polymorphism and mixed crystal formation are both quite prevalent among the silsesquioxanes.

The presence of methyl-$T_9(OCH_3)$ and methyl-$T_9(OC_2H_5)$ in the product indicated that exchange with methanol occurred during the hydrolysis, and also

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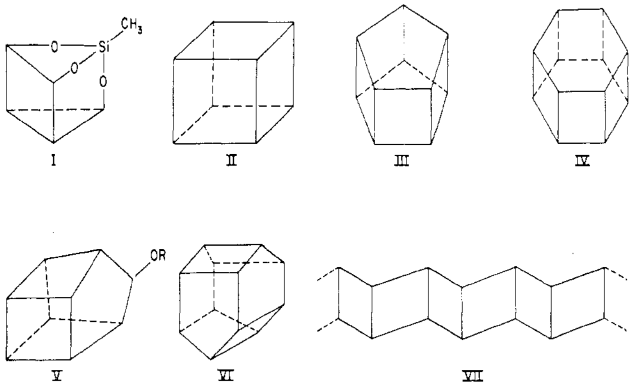

Fig. 1.—Proposed skeletal arrangements in the crystalline methylsilsesquioxanes: I, T_6; II, T_8; III, T_{10}; IV, T_{12}; V, T_9(OR); VI, possible alternative structure for T_{12}; VII, skeletal arrangement observed in linear polyphenylsilsesquioxanes.

that the sublimates did not consist solely of completely condensed siloxanes. Presumably, the oily mixtures of minor by-products contained other alkoxylated species, and perhaps products resulting from methyl group migration during the pyrolysis.[6]

The infrared spectra of the methyl-T_8, T_9(OR), T_{10}, and T_{12} compounds showed only one strong band in the 900–1250 cm.$^{-1}$ region. This came at 1122–1128 cm.$^{-1}$ and was of normal width ($\Delta\nu_{1/2} \sim 40$ cm.$^{-1}$) for an SiOSi asymmetrical stretching vibration. By contrast, methyl-T_6 showed a pair of much sharper bands at 1057 cm.$^{-1}$ (vs) and 1085 cm.$^{-1}$ (s). The shifting and sharpening of these bands in methyl-T_6, which contains cyclotrisiloxane rings (Fig. 1-I), is a characteristic feature of cyclotrisiloxane spectra.[7–9] The absence of this feature in the T_8–T_{12} spectra indicated that cyclotrisiloxane rings were not present in any of these compounds.

This finding eliminated most of the conceivable alternative polycyclic arrangements of trifunctional silicone units and limited the structural possibilities to one each for the T_8, T_9(OR), and T_{10} species. The one allowed arrangement for our methyl-T_8 involves the cube-like pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane skeleton (Fig. 1-II). This structure has been deduced previously from considerations of molecular symmetry[2–4] and from X-ray crystallography.[5,10] The one allowed arrangement for our methyl-T_9(OR) species involves the 15-alkoxypentacyclo-[9.7.1.1^{3,9}.1^{5,17}.1^{7,13}]-nonasiloxane arrangement (Fig. 1-V). This structure has been suggested previously for the *n*-butoxy derivative.[3] The one allowed arrangement for our methyl-T_{10} is the pentagonal prism-like structure (Fig. 1-III), namely, decamethylhexacyclo-[9.9.1.1^{3,9}.1^{5,17}.1^{7,15}.1^{13,19}]-decasiloxane. For methyl-T_{12}, however, there are two possible structures which do not contain cyclotrisiloxane (or smaller) rings. These are the heptacyclo-[13.9.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{17,23}]-dodecasiloxane structure (Fig. 1-IV) and the heptacyclo-[11.11.1.1^{3,11}.1^{5,21}.1^{7,19}.1^{9,17}.1^{15,23}]-dodecasiloxane arrangement (Fig. 1-VI). Molecular models using oxygens having 155° bond angles[11] showed that both of these structures could be constructed without appreciable strain. Evidence in favor of Fig. 1-IV was provided by the n.m.r. spectrum, which showed only a single proton resonance signal, and by the infrared, which showed only a single C–Si stretching band at 774 cm.$^{-1}$. It is not absolutely certain, however, that the band splittings in structure VI (Fig. 1) would be large enough to be detected by either of these methods.

Aside from this slight uncertainty about the methyl-T_{12} assignment, it would appear that the known species, methyl-T_6, T_8, T_{10}, and T_{12}, represent a homologous series of prism-like cage structures in which 3, 4, 5, or 6 cyclotetrasiloxane rings are fused together in a cylindrical arrangement (Fig. 1, structures I–IV). Such structures may be regarded as the cyclic analogs of the double chain linear silsesquioxane structure (Fig. 1-VII) found in the phenylsilsesquioxane series.[12,13]

In order to estimate the stability relations in this series of compounds, methyl-T_{10} was equilibrated with KOH in a dilute solution in refluxing toluene, and the distribution of low molecular weight silsesquioxanes determined by g.l.c. The relative molar proportions of T_6, T_8, T_{10}, T_{12}, and T_{14} in solution were in the ratio 0:1:2:1:0. This distribution of relative stabilities is quite similar to that found in the phenylsilsesquioxane series by other procedures.[14]

The major factors determining the relative thermodynamic stabilities in the T_6–T_{14} series probably are SiOSi bond angle distortion and intramolecular group–group interactions. Simple trigonometric calculations show that in prism-like structures where all the OSiO angles are tetrahedral and all the SiOSi angles equal, the SiOSi angles must be 129.5, 148.5, 154, 154, and 151.5° in T_6, T_8, T_{10}, T_{12}, and T_{14}, respectively. Since the preferred SiOSi angle appears to be near 155°,[11] this could indicate essentially no angular strain in T_{10} and T_{12}, slight strain in T_8 and T_{14}, and severe stain in T_6. The calculations and molecular models also indicate that steric interactions between the methyls and intramolecular dipole–dipole repulsions should start becoming appreciable in the dodecamer, and should be quite severe in the higher members of the prismatic series. Thus, it does not appear difficult to account for a maximum stability in the T_{10} species, and lower stability in the smaller and larger cage compounds.

Experimental

G.l.c. analyses were run on an F & M Model 500 programmed unit equipped with a thermal conductivity cell and a 1-m. column packed with the high boiling residue from Dow-Corning No. 710 methyl phenyl silicone oil. The program was run at

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11°/min. from 100–227°, with a helium flow rate of 60 ml./min. and inlet and detector temperatures at 300°. Melting points were taken in sealed capillaries; all reported values are corrected. X-Ray powder patterns were taken using CrKα radiation.

Preparation.—Hydrolysates were prepared from methyltriethoxysilane (2.00 moles, Dow Corning purified grade, 99.95% pure by g.l.c.) and water (15.5 moles), using KOH (0.20 mole) as the catalyst and methanol (3.5 l.) as solvent. Variations in the procedures used in combining these reactants are listed in Table I. After drying, the alkaline gels were heated *in vacuo* (0.5 mm.); first at 325° (48 hr.), then at 400° (24 hr.). The sublimates obtained were mixtures of colorless crystalline solids and pale yellow viscous oils (Table II). They were extracted with acetone to separate the oils and the higher silsesquioxanes from the very insoluble methyl-T_8, and the acetone extracts then were concentrated to separate the crystalline species from the oils. The over-all compositions of the sublimates were estimated by g.l.c. analysis of the acetone extracts. The results obtained, which are estimated to be reliable to ±15%, are listed in Table III.

TABLE I

PREPARATION OF KOH CONTAINING METHYL-T HYDROLYSATES

Method	Sequence of addn.[a]	Temp. of hydrolysis, °C.	Days standing at 25°	Yield, %	Prod. type[b]
Ref. 5	?	?	3	93.5	P
1	DBCA	10–15	3	46	P[d]
			34	50	P[d]
2	DBAC	−30	2	100	R[e]
3	DBCA	25–30	3	63	P[d]
			33	30	P[d]
4	DBCA	25–30	8	35	P
				65	R
5	DBAC	20–25	1	100	R
6	DABC[c]	10–15	1	100	R[e]
7	DBAC	30	0.1	100	R

[a] Sequence of addition (A, $CH_3Si(OC_2H_5)_3$; B, H_2O; C, KOH; D, CH_3OH). [b] P, precipitate which separated from mixture; R, residue left by evaporating solution or gel. [c] Aqueous KOH solution added to AD mixture. [d] X-Ray indicated precipitate was predominantly methyl-T_8. [e] X-Ray indicated precipitate was predominantly amorphous.

TABLE II

PYROLYSIS OF METHYL-T HYDROLYSATES

Prep. method (Table I)	Product type	Yield of sublimate %	Sublimate fraction sol. in acetone
Ref. 5	Ppt.	55.5	60
	1st and 2nd ppt.	96	11
3	1st ppt.	93	9
	2nd ppt.	98	
4	Ppt.	96	29
	Res.	53	33
5	Res.	34	34
7	Res.	37	33

TABLE III

COMPOSITION OF SUBLIMATES[a]

Hydrolysate prep. method	Methyl-T_8	Methyl-T_{10}	Methyl-T_{12}	Methyl-$T_9(OCH_3)$	Oil mixture[c]
1	89	4	2.7	0.3	4
3	91	2	<1	<1	6
4[b]	69	7	17	4	3
5	66	9	6	8	11
7	67	8	5	9	11

[a] Weight per cent. [b] Combined fractions. [c] Includes the methyl-$T_9(OC_2H_5)$ which was not determined separately.

Methyl-T_8, Octamethylpentacyclo-$[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]$-octasiloxane.—The material obtained was identical in its general properties and X-ray diffraction pattern with the octamethyloctasilsesquioxane reported by earlier investigators.[2–5,10] The g.l.c. retention time was 11.4 min.

Anal. Calcd. for $C_8H_{24}O_{12}Si_8$: C, 17.9; H, 4.5; mol. wt., 537.0. Found: C, 17.9; H, 4.5; mol. wt. (mass spectrum), 536.

Methyl-T_{10}, Decamethylhexacyclo-$[9.9.1.1^{3,9}.1^{5,17}.1^{7,15}.1^{13,19}]$-decasiloxane.—This was the first compound to separate upon concentrating the acetone extract; it was readily obtained pure (one g.l.c. peak, retention time 14.2 min.) by recrystallization from acetone; m.p. 332.6–334.0°. The compound was soluble in carbon tetrachloride and in hot acetone, cyclohexane, or toluene. Slow crystallization gave a pseudo-hexagonal crystal form which corresponded in its birefringence to the "Compound B" reported previously.[5] Rapid crystallization gave a rhombohedral form. Both forms gave the same X-ray powder pattern; the most prominent reflections were at 9.25 (vs), 8.76 (vs), 8.48 (s), 6.22 (m), 5.42 (m), 4.96 (m), 4.58 (m), 4.33 (s), 3.90 (m), 3.80 (s), 3.59 (s), 2.87 (m), 2.73 (m), and 2.70 (m) Å. The infrared spectrum (in CS_2) showed a single SiOSi asymmetrical stretching band at 1127 cm.$^{-1}$, and no detectable OH, OCH_3, or OC_2H_5. The n.m.r. spectrum (in CCl_4) indicated that all protons were equivalent. The mass spectrum was similar to that of methyl-T_8 in showing a weak parent peak and a very strong peak corresponding to the loss of one methyl from the polysiloxane nucleus.

Anal. Calcd. for $C_{10}H_{30}O_{15}Si_{10}$: C, 17.9; H, 4.5; mol. wt., 671.2. Found: C, 17.9; H, 4.7; mol. wt., 703, 674 (ebullioscopic in cyclohexane); 670 (mass spectrum).

Methyl-T_{12}, Dodecamethylheptacyclo-$[13.9.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{17,23}]$-dodecasiloxane.—This was the second compound to separate upon concentrating the acetone extract of the sublimate; it also was readily obtained pure (one g.l.c. peak, retention time 18.2 min.) by recrystallization from acetone; rectangular platelets, m.p. 260.9–261.4°. Its solubility pattern generally paralleled that of methyl-T_{10}; it also was moderately soluble in methanol. The X-ray pattern showed prominent reflections at 10.26 (s), 9.70 (s), 8.79 (vs), 5.59 (m), 5.14 (m), 4.73 (s), 4.37 (m), 4.10 (m), 3.87 (m), and 3.65 (m) Å. The infrared spectrum (in CS_2) showed a single siloxane band at 1127 cm.$^{-1}$, and no detectable OH, OCH_3, or OC_2H_5. The n.m.r. spectrum (in CCl_4) showed that all protons were equivalent.

Anal. Calcd. for $C_{12}H_{36}O_{18}Si_{12}$: C, 17.9; H, 4.5; mol. wt., 805.4. Found: C, 18.0; H, 4.4; mol. wt. (ebullioscopic in cyclohexane), 825.

Methyl-$T_9(OCH_3)$, 15-Methoxynonamethylpentacyclo-$[9.7.1.1^{3,9}.1^{5,17}.1^{7,13}]$-nonasiloxane.—This was the third compound to separate upon concentrating the acetone extract; however, it could only be obtained in 60% purity (T_{10} and T_{12} g.l.c. peaks in addition to main peak at 11.4 min.) by recrystallization from acetone. Purification by g.l.c. removed the T_{10} and T_{12}, but, unlike methyl-T_8, T_{10}, and T_{12}, it decomposed slightly in the detector cell. Thus, the product isolated by g.l.c. was 90% pure, m.p. 134.5–135.2°. The X-ray pattern showed prominent reflections at 9.03 (vs), 8.49 (vs), 7.93 (m); 6.28 (m), 4.76 (m), 4.51 (s), 4.31 (s), 3.86 (s), 3.49 (m), and 2.88 (m) Å. The infrared spectrum showed strong siloxane absorption at 1125 cm.$^{-1}$, a shoulder near 1094 cm.$^{-1}$ characteristic of $SiOCH_3$ groups, and a weak absorption at 795 cm.$^{-1}$, in addition to the usual strong C–Si stretching band at 774 cm.$^{-1}$; there was no indication of OH or OC_2H_5 groups.

Anal. Calcd. for $C_{10}H_{30}O_{14}Si_9$: C, 19.2; H, 4.8; mol. wt., 627.2. Found (sample 90% pure): C, 20.2 ± 0.5; H, 5.1 ± 0.2; mol. wt. (mass spectrum), 626.

Methyl-$T_9(OC_2H_5)$, 15-Ethoxynonamethylpentacyclo-$[9.7.1.1^{3,9}.1^{5,17}.1^{7,13}]$-nonasiloxane.—This compound was present in unpurified crops of methyl-T_8, T_{12}, and $T_9(OCH_3)$, but could not be separated by fractional crystallization. A small sample was isolated by g.l.c.; however, this procedure introduced a few per cent of new impurities from decomposition in the detector cell. It melted quite sharply at 135°; g.l.c. retention time, 13 min. The reflections from the X-ray pattern were at 9.06 (m), 8.35 (m), 7.99 (s), 7.16 (w), 4.74 (w), 4.60 (w), 4.47 (w), 4.36 (w), 4.14 (w), 4.05 (w), 3.89 (w), and 3.78 (w) Å. The infrared spectrum (in CS_2) showed a strong siloxane absorption at 1125 cm.$^{-1}$, a shoulder near 1085 cm.$^{-1}$ characteristic of the $SiOC_2H_5$ group, and a weak absorption at 788 cm.$^{-1}$ on the side of the 774 cm.$^{-1}$ band.

Anal. Calcd. for $C_{11}H_{32}O_{14}Si_9$: mol. wt., 641.2. Found: mol. wt. (mass spectrum), 640 ± 5.

Relative Thermodynamic Stabilities.—A solution containing 0.50 g. of methyl-T_{10} and 0.050 ml. of 0.1610 *N* ethanolic KOH (equilibration catalyst) in 25 ml. of toluene was refluxed for 84 hr. The composition of the solution was determined by g.l.c. at 24-hr. intervals; equilibrium was attained within 24 hr. G.l.c. detected only five volatile components, almost equally spaced as to retention times. The first, second, third, and fifth of these corresponded in retention times to T_8, $T_9(OC_2H_5)$, T_{10}, and T_{12}, respectively. It was assumed that the fourth peak was due to a $T_{11}(OC_2H_5)$ species. In addition, a non-volatile oil, presumably of higher polymers, was present. The over-all composition (% by weight; reliable to ±15%) of the equilibrated species was found to be 8% methyl-T_8, 7% methyl-$T_9(OC_2H_5)$, 19% methyl-T_{10}, 6% "methyl-$T_{11}(OC_2H_5)$," 10% methyl-T_{12}, and 50% non-volatile oil. There were no peaks with retention times expected for such species as methyl-T_6, methyl-$T_7(OC_2H_5)$, methyl-$T_{13}(OC_2H_5)$, or methyl-T_{14}; if any of those species were present their concentrations were below 0.15%. Thus, at equilibrium in 2% solution in toluene at 110° the relative molar concentrations of the completely condensed species, methyl-T_6, -T_8, -T_{10}, -T_{12}, and -T_{14}, were in the ratios <0.01: 1.2:2.3:1.0:<0.01, respectively.

Acknowledgments.—L. H. V. wishes to thank his thesis advisor, Professor Walter H. Bauer, Dean of the School of Science, Rensselaer Polytechnic Institute, and Drs. D. M. White and H. L. Finkbeiner of the General Electric Research Laboratory for their valuable comments and suggestions during this work. Dr. F. J. Norton, Messrs. E. M. Hadsell, H. W. Middleton, L. M. Osika, and Miss D. V. McClung, of this Laboratory, performed the analytical measurements. Special thanks are due to the Houston Research Laboratory of the Shell Oil Company for the high temperature mass spectrometric data.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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Phosphine Sulfides and Selenides: The Phosphorus–Sulfur and Phosphorus–Selenium Stretching Frequencies

BY RALPH A. ZINGARO

Received August 23, 1962

The fundamental P=X stretching frequency, where X is a sulfur or selenium atom, has been assigned in 15 phosphine sulfides and 13 phosphine selenides. The effect of coördination with halogen molecules on this vibration also has been observed. A statistically significant correlation has been shown to exist between the position of the P=S band and the nature of the substituents attached to the phosphorus atom.

Introduction

Prior to the investigations of Hooge and Christen,[1] who reported the spectra of trimethyl- and triethylphosphine sulfides, no additional spectra of $R_1R_2R_3P{=}S$ molecules, in which the three R- substituents are all linked directly to the phosphorus atom *via* carbon atoms, have been reported. Gore[2] and Daasch and Smith[3] have investigated a number of thiophosphates and McIvor, Grant, and Hubley[4] have investigated the monothionopyrophosphates.

The highest observed frequency for the P–S fundamental vibration is that at 860 cm.$^{-1}$ for $PS(NH_2)_3$,[5] while the lowest observed value is that at 535 cm.$^{-1}$ reported for triethylphosphine sulfide.[1] A proposed range for the P=S vibration of 840–600 cm.$^{-1}$ has been suggested.[6]

In some recent studies[7] on the effect of halogen complexing on the spectra of phosphine oxides and sulfides, tentative assignments were made for the P=S frequencies in a few phosphine sulfides. It is now established that when three phosphorus–carbon links are present these frequencies lie beyond the range of rock salt and a revision of these earlier assignments is necessary.

Thomas and Chittenden[8] have reported the range from 473–577 cm.$^{-1}$ as the region of the P=Se fundamental vibration in five phosphorus–selenium bonded compounds and 568–835 cm.$^{-1}$ as that of the P=S vibration, but we have no details as to the structures of

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