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CHEMISTRY OF METHYLENEDISILANES. SYNTHESIS OF CAGE COMPOUNDS BY HYDROLYSIS OF *sym*-TETRAFUNCTIONAL METHYLENEDISILANES*

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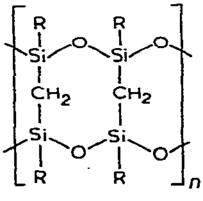
SUMMARY

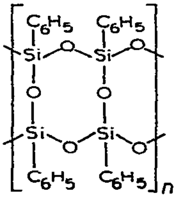
Crystalline, well defined, siloxanes were obtained on hydrolysis of *sym*-tetrafunctional methylenedisilanes ($RX_2SiCH_2SiX_2R$, $R=CH_3$ or C_6H_5, $X=Cl$ or OC_2H_5). These have in common a new closed cage structure, formed from three molecules of hydrolysed methylenedisilane, and containing two 2,4-dioxa-1,3,5-trisilacyclohexane units.

INTRODUCTION

Recent developments in polymer chemistry suggest that double chain or ladder polymers may be of importance in the future[1,2]. We have investigated routes to ladder structures based on polymer unit (I), and now report the first part of our work in this area.



(I)



(II)

The polymer under consideration (I) is structurally related to the well known phenyl-T polymer (II), described by Brown *et al.*[3] Phenyl-T may be prepared[3-5] from octakis(phenylsilsesquioxane), and a search of the literature for similar siloxane cage compounds, where some of the oxygen was replaced by methylene bridges, led us to the work of Wang *et al.*[6], and Clarke[7]. These workers claimed to have isolated a cage compound of structure (IVa) in very high yield, although Wang and his coworkers also discussed[6] and rejected a possible alternative structure (Va). This

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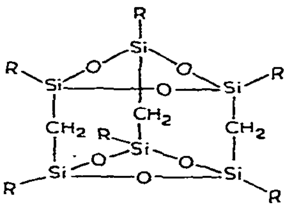
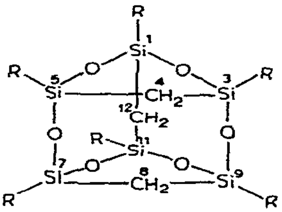
seemed a remarkable result because structure (IV) is closely related to the little known hexameric silsesquioxanes. The octamer cage structure is normally favoured[8] in the formation of oligosilsesquioxanes by hydrolysis routes.



(IV)

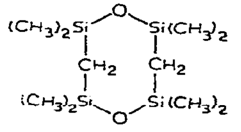
(IVa, $R=CH_3$; IVb, $R=C_6H_5$)



(V)

(Va, $R=CH_3$; Vb, $R=C_6H_5$)

Structure (IV) appeared to be the ideal precursor of polymer (I), because of (*a*) the known high reactivity[9] of cyclotrisiloxanes towards polymerisation catalysts and (*b*) Wang *et al.*'s claim[6] that the cyclosiloxane (VI) cannot be polymerised. We therefore decided to repeat the preparation of this cage compound and also attempt to prepare its phenyl analogue (IVb).



(VI)

RESULTS AND DISCUSSION

Preparation of the methyl cage compound, (IVa) or (Va)

This compound was prepared successfully and in high yield, as described in the published procedure[6], via methylenebis(trichlorosilane)[16], but the latter intermediate is not readily prepared in standard laboratory apparatus, and we developed a new route based on the formation of methylenebis(methylchlorosilane) in an *in situ* reaction between dibromomethane and methyldichlorosilane, eqn. (1). This

$$CH_2Br_2+CH_3SiHCl_2+2\,Mg \rightarrow CH_3SiHCl\text{–}CH_2\text{–}SiHClCH_3+2\,MgBrCl \qquad (1)$$

compound on chlorination gave the chlorosilane used by Clarke[7], and on treatment with ethanol gave the tetraethoxy derivative used by Wang *et al.*[6] to form the cage compound.

Preparation of the phenyl cage compound (IVb) or (Vb)

The phenyl cage was prepared from $Cl_3SiCH_2SiCl_3$ as follows:

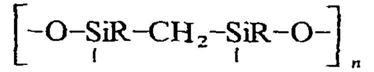
$$Cl_3Si\text{–}CH_2\text{–}SiCl_3+2\,C_6H_5MgBr \xrightarrow[(C_2H_5)_2O]{(2)}$$

$$C_6H_5SiCl_2\text{–}CH_2\text{–}SiCl_2C_6H_5+MgBrCl \xrightarrow[H_2O]{(3)} \text{(IVb) or (Vb)}$$

Difficulties experienced in purifying methylenebis(phenyldichlorosilane), associated with its high boiling point, were overcome by reducing the roughly distilled product with lithium aluminium hydride to the corresponding readily fractionated silane, $C_6H_5SiH_2–CH_2–SiH_2C_6H_5$, and re-chlorinating. In the hydrolysis step, eqn. (3), acetone had to be present in the hydrolysis medium before appreciable quantities of cage compound were obtained. Yields in this step were generally low (*ca.* 20%), and the remainder of the product of hydrolysis appeared as a soluble thermoplastic polymer.

Structures of the cage compounds

Element analyses, lack of reactivity towards methylmagnesium bromide. and lack of absorptions in the hydroxyl regions of their infrared spectra indicated that both compounds are cyclic polymers of formula:

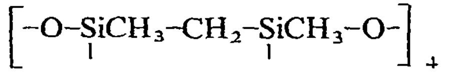


$$\left[-O-\underset{|}{Si}R-CH_2-\underset{|}{Si}R-O-\right]_n$$

Molecular weight determination by vapour pressure osmometry showed n to be 3 for the methyl cage, (IVa) or (Va). This technique failed with the phenyl compound, (IVb) or (Vb), because of its low solubility. However, mass spectrometry indicated that both compounds are trimeric with $n=3$, and therefore related to the relatively rare hexameric silsesquioxanes[11,12]. In the phenyl cage compound, the parent ion was by far the most abundant ion, and cleavage of the silicon–phenyl bond, to leave the cage intact, was the preferred mode of fragmentation in the mass spectrometer. A simplified fragmentation pattern is shown below:

$$\begin{tikzcd}
(Vb) \arrow[r] & \substack{M^+\ (100\%) \\ m/e\ 768} \arrow[r, "-CH_2", "m^*\ 740.2"'] \arrow[dr, "-C_6H_5", "m^*\ 622"'] & \substack{M^+ - CH_2\ (11\%) \\ m/e\ 754} \arrow[r, "-C_6H_5", "m^*\ 607.8"'] & \substack{M^+ - CH_2 - C_6H_5\ (6\%) \\ m/e\ 677} \\
& & \substack{M^+ - C_6H_5\ (40\%) \\ m/e\ 691} \arrow[r, "-C_6H_5", "m^*\ 545.6"'] & \substack{M^+ - 2\,C_6H_5\ (3\%) \\ m/e\ 614} \arrow[dll, "-3\,C_6H_5"'] \\
\substack{M^+ - 6\,C_6H_5\ (10\%) \\ m/e\ 306} & \substack{M^+ - 5\,C_6H_5\ (7\%) \\ m/e\ 383} \arrow[l, "-C_6H_5"'] & &
\end{tikzcd}$$

An interesting feature in the mass spectrum of the unpurified methyl cage compound was the parent ion of an impurity (*m/e* 528) corresponding to



$$\left[-O-\underset{|}{Si}CH_3-CH_2-\underset{|}{Si}CH_3-O-\right]_4$$ the octamer cage.

This impurity could also be detected in the sample by gas chromatography.

The fragmentation patterns were similar to those of carbon cage compounds[13], with ions containing the intact cage prominent.

Nuclear magnetic resonance spectroscopy (^1H NMR) at 100 MHz showed quite clearly that both compounds have cage structure (V), not (IV) as suggested by Clarke[7] and by Wang *et al.*[6]. The ^1H NMR spectra are shown in Figs. 1 and 2. Six lines were observed in the spectrum of the methyl cage compound (Fig. 1). Two lines of intensity ratio 3/1 would be predicted for a compound of structure (IV) and this structure is therefore improbable. Inspection of a model of structure (V) indicated

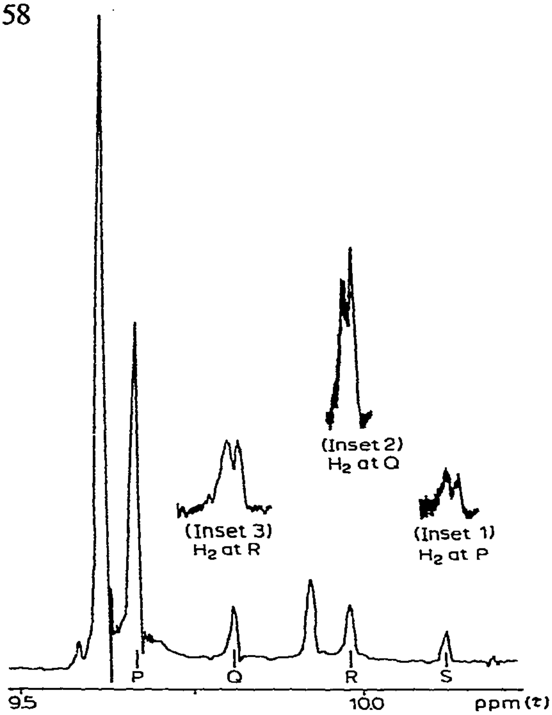


Fig. 1. ^1H NMR spectrum of the methyl cage compound (Va) (Solvent, benzene; sweep width, 250 Hz).

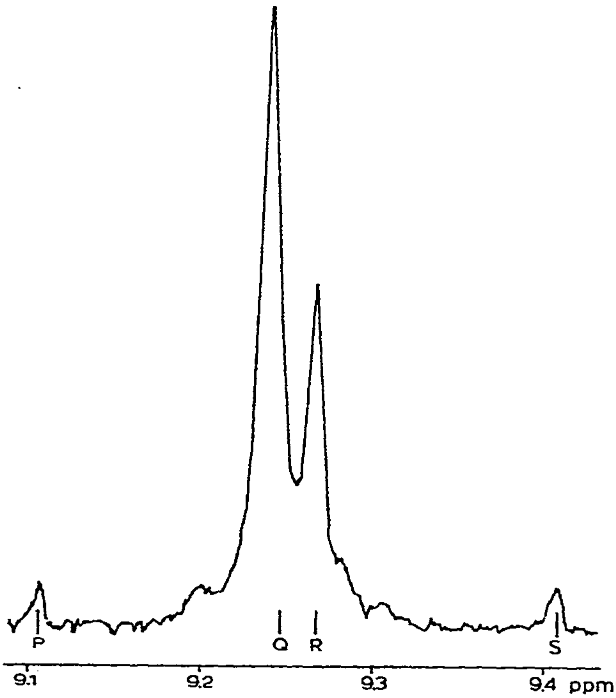


Fig. 2. ^1H NMR spectrum of the phenyl cage compound (Vb) (aromatic H omitted; solvent, $CDCl_3$; sweep width, 100 Hz).

that a seven line spectrum would be expected as follows:
(*a*) 2 lines arising from non-equivalence of methyl groups 3, 5, 7,9 and methyl groups 1 and 11;
(*b*) 1 line from methylene group 12;
(*c*) 4 lines forming an AB pattern arising from geminal coupling in methylene groups 4 and 8.

Although only six lines were observed in practice, the spectrum is still compatible with the structure (Va), because "spin-tickling" experiments (Fig. 1, insets 1–3) revealed that line P of the AB quartet (P, Q, R, S, Fig. 1) is overlapped by the singlet from methyl groups 1 and 11. The expected perturbations[14] of coupled spectral lines were observed on irradiating (H_2) at the various line positions of the AB quartet, *e.g.* irradiation of the hidden line at P induced line splitting at S (inset 1). The value of the coupling constant (J_{AB} 14.0 Hz) is also consistent[15] with coupling of geminal protons. Structure (Vb) was similarly indicated for the hexaphenyl cage compound, the lines P, Q, R, S (Fig. 2) forming the AB quartet (J_{AB} 14.3 Hz).

Structure (V) contains the ring systems of 1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisilacyclohexane and 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasilacyclooctane. These were formed in preference to cyclosiloxanes such as hexamethylcyclotrisiloxane on co-hydrolysis of an equimolar mixture of methylenebis(dimethylchlorosilane) and dimethyldichlorosilane[17], thus suggesting that a cage compound of structure (V) would be readily formed.

EXPERIMENTAL

General comments

Element analyses were carried out by the Analytical Department, Midland Silicones Ltd., Barry, Glam. Molecular weights were determined in toluene using a Mechrolab Model 301A Vapour Pressure Osmometer.

Infrared (IR) spectra were recorded (cm^{-1}) using a Perkin–Elmer 237 double beam spectrophotometer. Mass spectra were recorded at 70 eV on an A.E.I. Ltd. MS9 mass spectrometer. Nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Varian H.A. 100 high resolution spectrometer. Some results were also obtained with an A.E.I. R.S.2 instrument (60 MHz). τ values were measured relative to tetramethylsilane as internal standard, unless otherwise stated.

Gas chromatography (GLC) was carried out on an F and M 720 chromatograph using 8 ft. × $\frac{1}{4}$ in. columns of 10% phenyl/methyl silicone gum on chromosorb W support. The instrument was programmed at 20°/min over 70 to 300° with the detector at 350° unless otherwise stated.

Fractional distillations were carried out on a 24 in. × 8 mm Nester Faust NF 195 spinning-band column, which is rated at 28 theoretical plates by the manufacturers.

Methylenebis(trichlorosilane), $Cl_3SiCH_2SiCl_3$, was prepared by the published method[16]. Other chlorosilanes were manufactured at Midland Silicones Ltd. Ether and tetrahydrofuran (THF), Fisons SLR grades, were dried over sodium wire. Chlorine gas was dried with concentrated sulphuric acid and calcium chloride before use.

Methylenebis(methylchlorosilane). A mixture of magnesium turnings (50 g, 2.1 g-atom), methyldichlorosilane (800 g, 6.96 mole) and THF (750 ml) under dry argon was stirred and heated to reflux.

The reaction was initiated by adding a small quantity of dibromomethane (3–4 g, from 144 g, 0.71 mole) to the mixture and waiting for a rapid evolution of heat. The mixture was then cooled rapidly to 0° and maintained at this temperature, while the remainder of the dibromomethane was added to it over 2.5 h. The excess chlorosilane and most of the THF were subsequently distilled from the mixture, before adding dry pentane (500 ml) to precipitate any salts remaining in solution. After filtration, the product was isolated by fractional distillation of the filtrate on the spinning band column. The yield was 103 g, (72%), b.p. 53° (25 mm). (Found: C, 20.1; H, 5.76; Cl, 39.7; Si, 32.7. $C_3H_{10}Cl_2Si_2$ calcd.: C, 20.8; H, 5.78; Cl, 41.0; Si, 32.4%.) Infrared spectrum (cm^{-1}): 2950 m, 2918 sh, 2888 sh, 2856 sh, 2182 s, 1398 w, 1348 w, 1258 m, 1100 sh, 1058 m, 1005 sh, 882 m, 840 m, 790 m, 742 sh, 730 m. ^1H NMR spectrum: τ(SiH) 4.97 (sextet); $\tau(CH_3)$ 9.52 (doublet), $J(CH_3$–H) 3.3 Hz; $\tau(CH_2)$, 9.37 (doublet); $J(CH_2$–H) 3.3 Hz.

Methylenebis(phenylsilane). Phenylmagnesium bromide was prepared in the usual manner, from bromobenzene (460 g, 2.93 mole) and magnesium turnings (75 g, 3.12 g-atom) in dry ether (1000 ml), and added over 2 h to pure methylenebis(trichlorosilane) (400 g, 1.41 mole). The phenylation was stepwise, and closely followed by GLC. The mixture was then heated under reflux for 6 h, treated with dry pentane, and filtered to remove the magnesium salts. The filtrate was roughly fractionated under vacuum to yield methylenebis(phenyldichlorosilane) of about 90% purity (289 g, 57% yield), which was subsequently added over 2 h to a stirred mixture of lithium aluminium hydride (35 g, 0.92 mole) and diethyl ether (500 ml), while holding the reaction temperature at 20–30°, using an acetone/CO_2 cooling bath. The mixture was heated under reflux for 12 h, cooled to 0°, and then poured cautiously on to cracked ice.

The upper layer was dried over sodium sulphate before it was fractionated on the spinning-band column. The yield of the product, $C_6H_5SiH_2CH_2SiH_2C_6H_5$, was 81 g (46%), b.p. 98° (0.15 mm). (Found: C, 68.2; H, 7.75; Si, 24.5; mol.wt., 224. $C_{13}H_{16}Si_2$ calcd.: C, 68.5; H, 7.01; Si, 24.6%; mol.wt., 228.) Infrared spectrum (cm^{-1}): 3088 sh, 3065 m, 3028 w, 3012 w, 2138 s, 1590 w, 1483 w, 1430 s, 1355 w, 1330 w, 1298 w, 1118 s, 1046 m, 1025 w, 998 w, 940 s, 888 w, 846 s, 813 w, 766 m, 735 w, 699 s, 655 m.

Methylenebis(phenyldichlorosilane). Chlorine gas was passed into a solution, cooled to 20°, of methylenebis(phenylsilane) (81 g, 0.36 mole) in carbon tetrachloride (250 ml). When the reaction (followed by GLC) was complete, the mixture was degassed *in vacuo* (10 mm), to remove hydrogen chloride, and fractionated on the spinning-band still. The yield of the product was 122 g (93%), b.p. 204° (4.4 mm). (Found: C, 43.0; H, 3.32; Si, 15.2. $C_{13}H_{12}Cl_4Si_2$ calcd.: C, 42.6; H, 3.28; Si, 15.3%). Infrared spectrum (cm^{-1}): 3140 w, 3096 sh, 3080 m, 3060 m, 3025 sh, 3020 sh, 3008 sh, 2380 w, 1975 sh, 1958 w, 1905 sh, 1885 w, 1818 w, 1597 m, 1488 w, 1433 s, 1377 w, 1349 w, 1338 w, 1306 w, 1363 w, 1191 w, 1119 s, 1070 s, 1028 w, 998 m, 790 s, 748 s, 713 s, 692 s, 671 s. ^1H NMR spectrum: $\tau(C_6H_5)$ 2.66 (multiplet); $\tau(CH_2)$ 8.43 (singlet); the integration gave a proton ratio of 5:1 respectively.

Preparation of the methyl cage compound (Va)

This was prepared from methylenebis(methyldiethoxysilane) by Wang *et al.*'s method[6], and purified by sublimation *in vacuo* followed by recrystallisation from chloroform (yield 61%; m.p. 202°). (Found: C, 27.6; H, 6.20; Si, 42.1; mol.wt., 405.

$C_9H_{24}O_6Si_6$ calcd.: C, 27.3; H, 6.10; Si, 42.4%; mol.wt., 396.) The infrared spectrum did not differ from that published by Clarke[7]. ^1H NMR data, obtained from a saturated solution in benzene (approximately 5%) are collected in Table 1.

TABLE 1

^1H NMR DATA OF (Va)[a]

τ values	Multiplicity	Integrals (mm)	No. of protons		Assignment[b]
			Found	Calcd.	
9.61	Singlet	88	12	12	3,5,7,9-$(CH_3)_4$
9.67	Singlet[c]	51–3.7	6.4	6	1,11-$(CH_3)_2$
9.90[d]	AB quartet[e]	23.3+3.7	3.6	4	4,8-$(CH_2)_2$
9.93	Singlet	13.0	1.8	2	12-CH_2

[a] τ values were measured against benzene as internal standard. The integrals were corrected by assuming that the outermost lines of the AB quartet were of equal intensity (each ≡ 3.7 mm). [b] For numbering see structure of (V). [c] Overlapping low field line of AB. [d] Midpoint. [e] Analysis of the AB pattern gave τ_A 10.04 ppm, τ_B 9.76 ppm and J_{AB} 14.0 Hz.

Preparation of the phenyl cage compound (Vb)

Methylenebis(phenyldichlorosilane) (16.3 g, 0.05 mole) was added to a mixture of acetone (130 ml) and water (130 ml). A sticky solid separated from the mixture after it had been stirred gently for 24 h. This was recrystallised three times from acetone to yield white needles (4.7 g, 23%); m.p. 312–314°. (Found: C, 60.9; H, 4.60; Si, 21.7; mol.wt. mass spec., 768. $C_{39}H_{36}Si_6O_6$ calcd.: C, 61.0; H, 4.68; Si, 21.8%; mol.wt., 768.) The data obtained from a saturated solution (approximately 5%) in $DCCl_3$ are collected in Table 2.

TABLE 2

^1H NMR DATA OF (Vb)

τ values	Multiplicity	No. of protons		Assignment[a]
		Found	Calcd.	
2.15–2.79	Complex	31	30	Aromatic protons
9.24	Singlet	6	6	12-CH_2
9.26[b]	AB quartet[c]			4,8-$(CH_2)_2$

[a] For numbering see structure of (V). [b] Midpoint. [c] Analysis of the AB pattern gave τ_A 9.39 ppm, τ_B 9.13 ppm, and J_{AB} 14.3 Hz.

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REFERENCES

1 C. S. Marvel, *A.C.S. Polymer Preprints*, 5 (1964) 167.
2 J. F. Brown, Jr., *J. Polym. Sci., Part C*, 1 (1963) 83.
3 J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kieser and K. W. Krantz, *J. Amer. Chem. Soc.*, 82 (1960) 6194.
4 J. F. Brown, Jr., L. H. Vogt, Jr. and P. L. Prescott, *J. Amer. Chem. Soc.*, 86 (1964) 1120.
5 A. Guyot and R. Guidard, *C.R. Acad. Sci., Paris*, (1967) 1585.
6 P.-J. Wang, Y.-J. Zeng, C.-T. Huang and I. Lin, *J. Polym. Sci.*, 30 (1958) 525.
7 H. A. Clarke, *Brit. Patent* 675,041, 1952.
8 K. Olsson and C. Grönwall, *Ark. Kemi*, 17 (1961) 529.
9 D. W. Scott, *J. Amer. Chem. Soc.*, 68 (1946) 2297.
10 A. R. Finholt, A. C. Bond, Jr., K. E. Wilzbach and J. I. Schlesinger, *J. Amer. Chem. Soc.*, 69 (1947) 2692.
11 M. M. Sprung and F. O. Guenther, *J. Amer. Chem. Soc.*, 77 (1955) 3990.
12 A. J. Barry, W. H. Daudt, J. L. Domicone and J. W. Gilkey, *J. Amer. Chem. Soc.*, 77 (1955) 4248.
13 R. C. Fort, Jr. and P. von R. Schleyer, *Chem. Rev.*, 64 (1964) 286.
14 R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 37 (1962) 2071.
15 J. A. Elvidge, in D. W. Mathieson (Ed.), *Nuclear Magnetic Resonance for Organic Chemists*, Academic Press, London, 1967, p. 186.
16 W. I. Patnode and R. W. Schiessler, *U.S. Patent* 2,381,002, 1945.
17 N. S. Nametkin, T. Kh. Islamov, L. E. Gusel'nikov and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 6 (1968) 1329.