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TETRAKIS(HYDROXYDIMETHYLSILYL)METHANE AND ITS DEHYDRATION WITH REARRANGEMENT. CRYSTAL STRUCTURE OF 2,2,4,4,6,6-HEXAMETHYL-5-(HYDROXYDIMETHYLSILYL)-1,3-DIOXA-2,4,6-TRISILACYCLOHEXANE *

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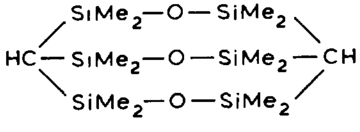
Summary

The compound $C(SiMe_2OH)_4$ has been made by treatment of $C(SiMe_2I)_4$ with AgOCN in moist ether. Upon heating or treatment with NaOMe/MeOH it undergoes rearrangement and dehydration to give the cyclic species $HOMe_2\text{-}Si\overline{CHSiMe_2OSiMe_2OSi}Me_2$, the crystal structure of which has been determined.

Introduction

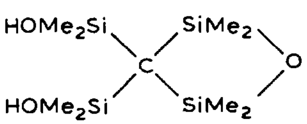
We recently reported the ready dehydration upon heating of tris(hydroxydimethylsilyl)methane, $(HOMe_2Si)_3CH$, to the cage siloxane I [1]. We have now prepared the related tetrakis(hydroxydimethylsilyl)methane (II) and found it also to undergo ready thermal dehydration but with a very different result, a 1,3-migration of a silyl group from carbon to oxygen leading to the formation of the trisiloxane derivative, IV.



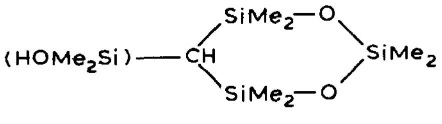
(I)

$C(SiMe_2OH)_4$

(II)



(III)



(IV)

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* Dedicated to Prof. R. Calas (a most courteous gentleman) on the occasion of his 70th birthday on 8th April 1984, in recognition of his outstanding contributions to organometallic chemistry during more than 30 years.

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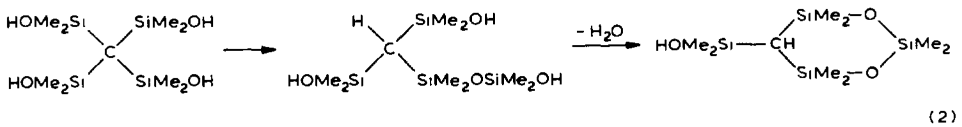
Results and discussion

Compound II was prepared by treatment of the corresponding iodide, $C(SiMe_2I)_4$, with silver cyanate in ether in the presence of water (eq. 1).

$$C(SiMe_2I)_4 + AgOCN + H_2O \xrightarrow{Et_2O} C(SiMe_2OH)_4 + AgI + HOCN \qquad (1)$$

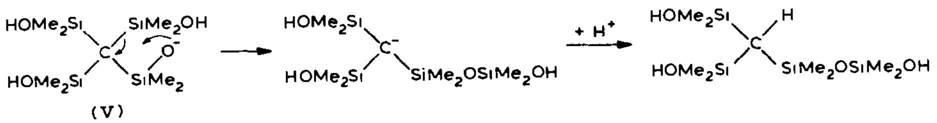
(This preparation was based on the observation that the cyanate $(Me_3Si)_3$-$CSiMe_2(OCN)$ is exceptionally readily hydrolysed [2].)

The tetrahydroxide II is a crystalline solid, insoluble in tetrachloromethane but readily soluble in acetone and ether. During a determination of its melting point it was found to decompose, and the decomposition was investigated by heating a sample in a sublimation apparatus at atmospheric pressure for 3 h at 130°C (use of various temperatures in the range 110–150°C gave similar results), during which white fern-like crystals formed on the cold finger. These accounted for 28% of the starting material. (The oily residue left in the sublimation flask, which is probably a mixture of siloxanes, gave a ^1H NMR spectrum which varied from experiment to experiment, and it was not further studied.) The sublimate had a m.p. of 55°C, and gave an elemental analysis and mass spectrum corresponding to a species produced by loss of one molecule of water from each molecule of II. The IR and ^1H NMR spectra indicated the presence of Si–OH bonds, and a broad IR band at 1020 cm^{-1} was consistent with the presence of Si–O–Si bonding. Initially it was thought possible that the product might be III, a derivative of the unknown 1-oxa-2,4-disilacyclobutane system, but the ^1H NMR spectrum showed five singlets for the methyl protons, which seemed inconsistent with structure III. In order to identify the product it was subjected to a single crystal X-ray diffraction study and this showed it to be 2,2,4,4,6,6-hexamethyl-5-(hydroxydimethylsilyl)-1,3-dioxa-2,4,6-trisilacyclohexane (IV). It seems likely that this is produced by an initial 1,3-migration of an $HOMe_2Si$ group from carbon to silicon (with a corresponding 3 to 1 migration of a hydrogen atom from oxygen to carbon) followed by an intramolecular dehydration, as depicted in eq. 2.



(2)

It is unlikely that the silyl and hydrogen migrations are simultaneous, and it is reasonable to assume that the silyl migration actually takes place within a silanolate ion (V) produced either by autoprotolysis of II, or possibly by interaction with traces of alkali on the surface of the glass vessel. The occurrence of this type of rearrangement in MeOH in the presence of NaOMe was reported recently for the silanols $(Me_3Si)_3C(SiMe_2OH)$, $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$, and $(PhMe_2Si)_3$-$C(SiMe_2OH)$, [3], and $(Me_3Si)_3C(SiPh_2OH)$ has recently been found to undergo the rearrangement (to give $(Me_3Si)_2CHSiPh_2OSiMe_3$) very readily under similar conditions, and even, more slowly, in refluxing MeOH alone [4]. The corresponding process in the case of V would be as in eq. 3.


(V)

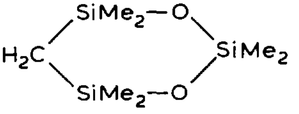
(3)

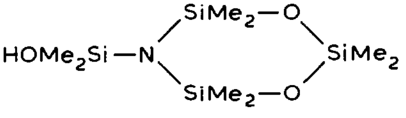
The driving force for such rearrangements is probably the release of steric strain, and they are facilitated by the stabilization of the formed carbanion by the three silyl groups attached to the central carbon atom. (The ease of the rearrangement varies considerably within the range of relevant hydroxylic tetrasilylmethane derivatives so far examined, and it is not yet clear what factors influence it.) In keeping with this interpretation, II was found to undergo complete conversion into IV within 10 min in an 0.2 *M* solution of NaOMe in MeOH at room temperature, and this provides the best route to IV at present.

The silanol IV was found to react with acetyl chloride to give the corresponding chloride (eq. 4).

$$\underset{\text{(IV)}}{\mathrm{HOMe_2Si\overline{CHSiMe_2OSiMe_2OSi}Me_2}} + \mathrm{CH_3COCl} \rightarrow \mathrm{ClMe_2Si\overline{CHSiMe_2OSiMe_2OSi}Me_2} \qquad (4)$$

It is noteworthy that the parent cyclic trisiloxane species, VI, is known, having been made by cohydrolysis of Me_2SiCl_2 and $(ClMe_2Si)_2CH_2$ and also by treatment of $(ClMe_2Si)_2CH_2$ with $Me_2Si(OK)_2$ [5], and shown to be remarkably thermally stable, 77% being recovered after 3 h at 550°C [6]. The structurally analogous tertiary amine VII is also known, and its crystal structure has been determined [7].


(VI)


(VII)

Structure of IV

The structure of IV is shown in Fig. 1, and the structural parameters are listed in Table 1. The packing diagram, Fig. 2, shows that there is, as expected, intermolecular hydrogen bonding, the OH group of one molecule interacting with the siloxane oxygen O(2) of another molecule; the O(3)–H bond length is 1.22 and the H · · · O(2′) distance is 1.80 Å.

The six-membered ring has a flattened (and somewhat distorted) chair conformation. The C(4) and C(7) methyl groups are non-equivalent to the C(5) and C(6) groups, and the C(8) likewise non-equivalent to the C(9) methyl group, and this, when account is taken of the equivalence of the C(2) and C(3) methyl groups, explains why five singlets appear in the SiMe region of the ^1H NMR spectrum.

As in $(Me_3Si)_3CH$ [8] and some related species [1,9,10], the Si–C–Si angles around the central carbon C(1) open to relieve the strain (the mean value is 114.9°, which compares with mean values for the corresponding angles in $(Me_3Si)_3CH$ (in the gas phase) of 116.3° [8] and $(Me_2PhSi)_3CH$ of 114.0° [9]), and the Si–C(1) bonds (mean 1.877 Å) are significantly longer than the Si–Me bonds (mean 1.834 Å), again as in $(Me_3Si)_3CH$, $(Me_2PhSi)_3CH$, and related species. The Si–O–Si angles, of

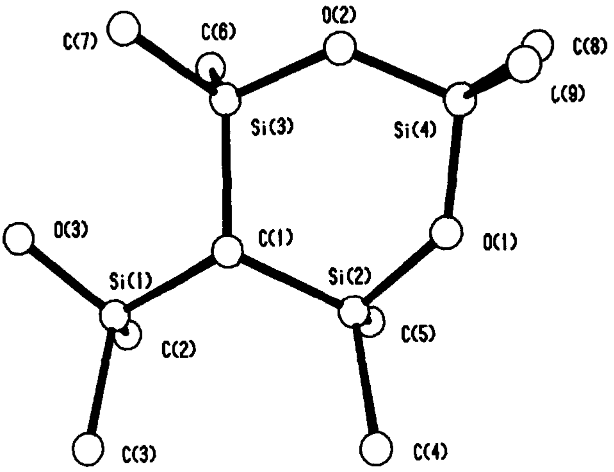


Fig. 1. Molecular structure of IV, with atom numbering scheme.

134.4(2) and 135.5(2)° are within the rather wide range observed for cyclic polysiloxanes [11].

The structure of IV seems to be fairly closely analogous to that of VII, which is described as having a "slight boat configuration" [7].

TABLE 1

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bonds			
Si(1)–C(1)	1.886(4)	Si(1)–O(3)	1.645(3)
Si(1)–C(2)	1.812(5)	Si(1)–C(3)	1.847(5)
Si(2)–O(1)	1.646(3)	Si(2)–C(1)	1.860(3)
Si(2)–C(4)	1.860(5)	Si(2)–C(5)	1.815(6)
Si(3)–O(2)	1.673(3)	Si(3)–C(1)	1.884(3)
Si(3)–C(6)	1.836(5)	Si(3)–C(7)	1.832(5)
Si(4)–O(1)	1.619(3)	Si(4)–O(2)	1.628(3)
Si(4)–C(8)	1.851(5)	Si(4)–C(9)	1.819(5)
Angles			
C(1)–Si(1)–O(3)	106.9(2)	C(1)–Si(1)–C(2)	115.5(2)
C(1)–Si(1)–C(3)	110.2(2)	O(3)–Si(1)–C(2)	107.0(2)
O(3)–Si(1)–C(3)	108.8(2)	C(2)–Si(1)–C(3)	108.1(2)
O(1)–Si(2)–C(1)	107.3(1)	O(1)–Si(2)–C(4)	105.6(2)
O(1)–Si(2)–C(5)	107.3(2)	C(1)–Si(2)–C(4)	112.1(2)
C(1)–Si(2)–C(5)	114.4(2)	C(4)–Si(2)–C(5)	109.6(3)
O(2)–Si(3)–C(1)	107.7(1)	O(2)–Si(3)–C(6)	107.5(2)
O(2)–Si(3)–C(7)	105.4(2)	C(1)–Si(3)–C(6)	112.4(2)
C(1)–Si(3)–C(7)	112.0(2)	C(6)–Si(3)–C(7)	111.4(3)
O(1)–Si(4)–O(2)	107.3(1)	O(1)–Si(4)–C(8)	110.0(2)
O(1)–Si(4)–C(9)	108.9(2)	O(2)–Si(4)–C(8)	108.7(2)
O(2)–Si(4)–C(9)	108.6(2)	C(8)–Si(4)–C(9)	113.1(3)
Si(2)–O(1)–Si(4)	135.5(2)	Si(3)–O(2)–Si(4)	134.4(2)
Si(1)–C(1)–Si(2)	117.2(2)	Si(1)–C(1)–Si(3)	113.6(2)
Si(2)–C(1)–Si(3)	114.0(2)		

Experimental

Preparation of $C(SiMe_2OH)_4$ (II)

A mixture of silver cyanate (0.45 g, 3 mmol), $C(SiMe_2I)_4$ (0.5 g, 0.65 mmol), diethyl ether (50 cm^3), and water (2.5 cm^3) was stirred for 2 h at room temperature. The solid was filtered off and the filtrate was evaporated under vacuum to leave a white solid, which was washed with n-pentane (2 × 5 cm^3) and dried under vacuum to give IV as a white solid (150 mg, 69%), m.p. 136–137°C (decomp.), (Found: C, 35.3; H, 9.4. $C_9H_{28}O_4Si_4$ calcd.: C, 34.6; H, 9.0%); ^1H NMR (in $(CD_3)_2CO$ relative to internal TMS), δ 0.37 (s, 24H, $SiMe_2$), 3.8 (br. s, 4H, SiOH); mass spectrum (m/z) 279 (78%, $[M - H_2O - Me]$), 263 (100, $[M - 2OH - Me?]$), 261 (95, $[M - 2H_2O - Me]$), 255 (17), 247 (20), 235 (25), 189 (32), 75 (15, $[HOMe_2Si^+]$), 73 (40, $[Me_3Si]^+$); several small peaks (of relative intensity < 5%) appear at mass higher than M^+, presumably as a result of intermolecular condensation.

Preparation of $HOMe_2Si\overline{CHSiMe_2OSiMe_2OSi}Me_2$ (IV)

(a) A sample of II (100 mg, 0.30 mmol) was heated for 3 h at 130°C in a sublimation apparatus at atmospheric pressure. Fern-like white crystals formed on the cold finger and an oily solid was left as a residue. The sublimate was shown by a single crystal X-ray study to be IV (25 mg, 28%), m.p. 55°C (Found: C, 36.3; H, 9.1. $C_9H_{26}O_3Si_4$ calcd.: C, 36.7; H, 8.9%); ^1H NMR (in CCl_4), δ 0.06 (s, 3H), 0.08 (s, 3H), 0.15 (s, 6H), 0.18 (s, 6H), 0.25 (s, 6H), 1.38 (br. s, removed on shaking with D_2O, 1H, OH) (tentative assigment of SiMe peaks: $OSiMe_2O$, δ 0.06 and 0.08;

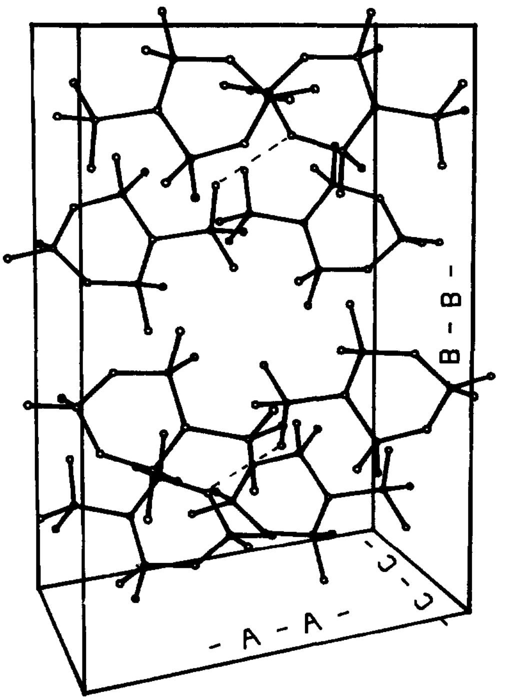


Fig. 2. Packing diagram for crystal of IV, showing the hydrogen bonding (broken line).

$OSiMe_2C$, δ 0.15 and 0.18; $HOMe_2Si$, δ 0.25; the methine CH peak was not detected, and is presumably hidden); IR, ν(SiO–H) 3500br, ν(SiOSi) 1020br cm^{-1}; mass spectrum (m/z) (main peaks only), 279 (75%, [M – Me]). 263 (100, [M – MeH – Me(?)]), 247 (12, [M – MeOH – Me(?)]), 189 (15, [M – Me_3SiOH – Me(?)]), 73(22). The residual oil from the sublimation had a complex ^1H NMR spectrum in the δ 0.0–0.5 ppm region.

(b) A sample of II (50 mg, 0.15 mmol) was dissolved in an 0.2 M solution of NaOMe/MeOH (ca. 2 cm^3) and the solution was stirred at room temperature for 10 min, then neutralized with aqueous HCl. The solvent was removed under vacuum, and the residue was extracted with CCl_4 (2 × 2 cm^3). The extract was dried ($MgSO_4$) and evaporated to give IV (33 mg, 74%), with properties identical with those given in (a) above.

Structure determination

Crystal data. $C_9H_{26}O_3Si_4$, $M = 294.7$, monoclinic, a 15.417(4), b 19.688(4), c 13.642(3) Å, β 122.23(2)°, U 3502.7 $Å^3$, $Z = 8$, D_c 1.12 g cm^{-3} $F(000) = 1280$. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 3.3 cm^{-1}. Space group $C2/c$ from systematic absences of hkl for $h + k$ odd, $h0l$ for l odd, and successful refinement.

Data were measured on an Enraf-Nonius CAD4 diffractometer using a roughly spherical crystal of diameter ca. 0.3 mm (crystallised from EtOH) sealed in a thin-walled glass capillary. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles for 25 reflections with $\theta \approx 15°$. Intensities for $hk \pm l$ reflections with $2 < \theta < 23°$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35 \tan \theta)°$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ, at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give minimum value of $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 60 seconds. Two standard

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Si(1)	4072(1)	3493(1)	4451(1)
Si(2)	2435(1)	4472(1)	2441(2)
Si(3)	2059(1)	2897(1)	2285(1)
Si(4)	412(2)	3872(1)	575(2)
O(1)	1225(3)	4457(2)	1370(3)
O(2)	907(3)	3145(2)	1189(3)
C(1)	2705(4)	3657(3)	3243(4)
O(3)	4123(3)	2703(2)	4871(4)
C(2)	5025(6)	3579(4)	4067(6)
C(3)	4432(6)	4064(4)	5686(6)
C(4)	2557(7)	5216(4)	3347(7)
C(5)	3199(6)	4612(5)	1807(7)
C(6)	2770(6)	2565(4)	1657(6)
C(7)	1802(6)	2230(4)	3033(7)
C(8)	216(7)	3876(4)	–887(6)
C(9)	–768(6)	3998(4)	551(7)

TABLE 3

SELECTED TORSION ANGLES (°)

O(3)–Si(1)–C(1)–Si(2)	−171.6(3)
Si(3)–C(1)–Si(2)–O(1)	38.6(4)
C(1)–Si(2)–O(1)–Si(4)	−29.6(5)
Si(2)–O(1)–Si(4)–O(2)	13.3(5)
O(1)–Si(4)–O(2)–Si(3)	−9.5(5)
Si(4)–O(2)–Si(3)–C(1)	23.3(5)
O(2)–Si(3)–C(1)–Si(2)	−36.4(4)

reflections monitored every hour showed no significant variation. Data were corrected for Lp effects but not for absorption, and after averaging any equivalent reflections 1739 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

The structure was solved by direct methods using the MULTAN program [12] Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least squares. The H atom on O(3) was located on a difference map and all other H atoms were placed at calculated positions (C–H 1.08 Å) and held fixed with a common isotropic temperature factor of B 8.0 Å^2. Refinement converged at $R = 0.068$, $R' = 0.081$, when the maximum shift/error was 0.04 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure solution and refinement was done on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 13. Final atom coordinates are listed in Table 2, bond lengths and angles are listed in Table 1, and some selected torsion angles in Table 3. Tables of temperature factors and final structure factors are available from the authors.

Acknowledgements

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