

Cyclodimethylsilethenes (Me₂SiCH=CH)_n

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Received 3 September 1994

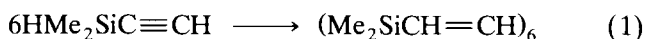
Abstract

Dodecamethylcyclohexasilethene (Me₂SiCH=CH)₆ (**1**) was synthesized by autohydrosilylation of HMe₂SiC≡CH in a tetrahydrofuran solution in the presence of H₂PtCl₆ under high dilution. An analogous reaction of Me₂Si(C≡CH)₂ or E-HC≡CMe₂SiCH=CHSiMe₂C=CH with E,E-Me₂Si(CH=CHSiMe₂H)₂ gave octamethylcyclotetrasilethene (Me₂SiCH=CH)₄ (**2**) and decamethylcyclopentasilene (Me₂SiCH=CH)₅ (**3**) respectively. The X-ray structure of **3** is presented.

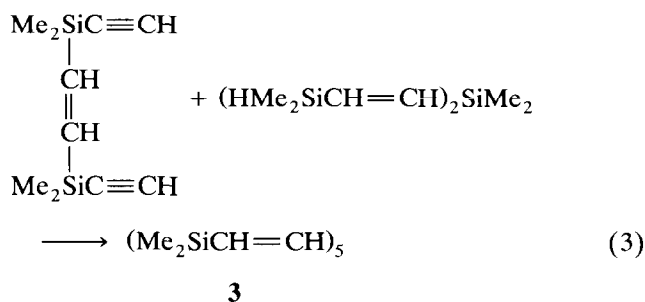
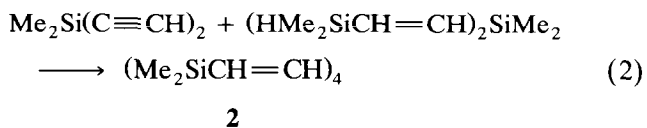
Keywords: Silicon; Silane; Macrocycla; Methyl; Alkene; Vinyl

1. Introduction

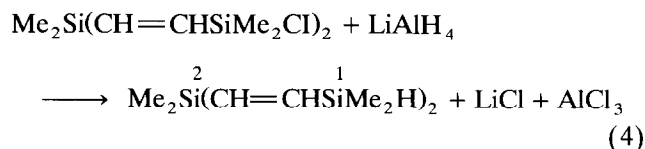
Proof of the existence of polyunsaturated organylsilanes of general formula (R₂SiCH=CH)_n was provided by one of the present authors as early as 1952 [1]. These compounds were given the name polydialkylsilethenes. Si-dodecamethylcyclohexasilethene (Me₂SiCH=CH)₆ (**1**), the first example of macrocyclic compounds of this type, was prepared by autohydrosilylation of dimethylethynylsilane in a tetrahydrofuran solution in the presence of H₂PtCl₆ under high dilution in 1989 [2]:



Continuing this research, we have synthesized the lower homologs **1** with $n = 4$ and $n = 5$, namely Si-octamethylcyclotetrasilethene (**2**) and Si-decamethylcyclopentasilene (**3**). They were obtained by intermolecular hydrosilylation of dimethyldiethynylsilane or E-1,2-bis(dimethylethynylsilyl)ethene respectively with E,E-dimethyl-bis(2-dimethylsilylvinyl)silane under the above conditions:



The silethene **3** ($n = 5$) was also isolated together with **1** from the products of dimethylethynylsilane autohydrosilylation. The identity of the samples **3** obtained by the two methods was confirmed by NMR spectroscopy, mass spectrometry, X-ray diffraction and melting-point (m.p.) determination. The starting E,E-dimethyl-bis(2-dimethylsilylvinyl)silane was obtained by reduction of E,E-dimethyl-bis(2-dimethylchlorosilylvinyl)silane with lithium aluminumhydride:



Details of the other initial reagents have been published previously [3,4].

The cyclodimethylsilethenes obtained are colorless high melting point crystals soluble in organic solvents. Their melting points, yields and analysis data are given in Table 1. The structure of **1–3** was proved by mass

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Table 1
Cyclodimethylsilethenes (Me₂SiCH=CH)_n

Compound	Yield (%)	M.p. (°C)	Found; calculated (%)			Mass spectrum <i>m/z</i>	General formula
			C	H	Si		
1	2.8	230	57.04; 57.06	9.67; 9.58	33.58; 33.36	504(1)	C ₂₄ H ₄₈ Si ₆
2	3.1	158	57.18; 57.06	9.72; 9.58	33.48; 33.36	336(5)	C ₁₆ H ₃₂ Si ₄
3	5.9	110	57.22; 57.06	9.64; 9.58	33.65; 33.36	420(8)	C ₂₀ H ₄₀ Si ₅

spectrometry (Table 1) and ¹H, ¹³C and ²⁹Si NMR spectroscopy (Table 2).

The molecular and crystal structure of decamethylcyclopentasilene **3** was determined by X-ray diffraction analysis [5]. The molecule **3** presents a comparatively flexible heterocycle with ten single Si–C bonds about which the rotation of Si–CH=CH–Si fragments is feasible. The considerable divergence in bond lengths and valency angles provides evidence of the disorder of at least some atoms in two or more positions.

Distortions in normal geometry are noticeable and distributed asymmetrically about the cycle sides although only alike Si–CH=CH–Si fragments are present in the molecule. The valence angles in the above compounds are grouped about values of 140, 150 and approximately 165°. This may be, in principle, due to the existence of a small number of different conformers **3** in the crystal cell given. In structure **3** the Si atoms show fairly high thermal parameters (*B*_{eq} ≈ 8 Å²). Disorder of the C atoms is expressed by high (*B*_{ii} up to 23 Å²) and clearly anisotropic temperature factors. The thermal ellipsoids of these atoms are extended normally to the Si...Si lines (Fig. 1). The observed conformation of cycle **3** is in Fig. 2 together with Si...Si...Si...Si pseudotorsional angles. Apart from possible fairly exact coincidence of the heterocycle **3** silicon apices on rotation about the approximate C₂ axes passing through both the Si(1)...Si(2) side center and the Si(4) atom, there is a possibility of a less exact superimposition of enantiomorphous heterocycles which brings into coincidence mean planes of Si(1)...Si(3)...Si(4)...Si(5) and Si(2)...Si(3)...Si(4)...Si(5) flattened cycle fragments. Thus the observed geometry of heterocycle **3** can be averaged over some conformers including enantiomorphous ones. Since the cycle **3** having ten Si–C single bonds is rather flexible, the orientation of Si–CH=CH–Si fragment

planes may change even, with retention of the silicon pseudoconfiguration. Therefore it seems rather difficult to draw a conclusion concerning the population of given crystallographic position with different conformers. It should be noted that the observed values of bond lengths and valence angles are within the ranges acceptable for averaged atomic positions. For instance, an approximately linear Si(3)C(5)C(6)Si(4) fragment with a C(5)–C(6) distance of 0.9 Å corresponds to the super-imposed enantiomorphous Si–CH=CH–Si groups with normal geometry.

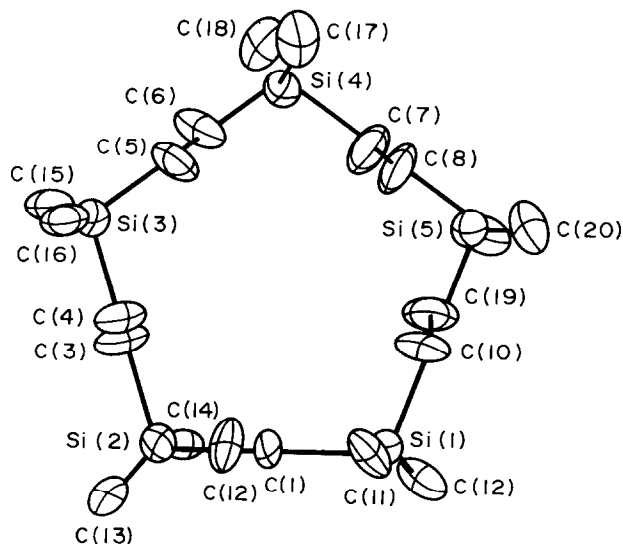


Fig. 1. General view of the disordered molecule **3** with atomic heat ellipsoids.

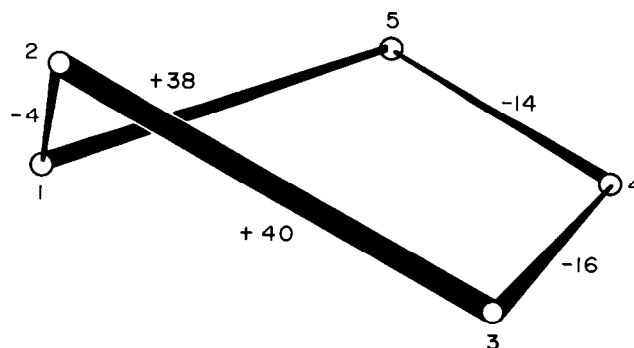


Fig. 2. Silicon pseudocycle in the structure **3** (Si...Si...Si torsional angles are given in degrees).

Table 2
NMR parameters of (Me₂SiCH=CH)_n

Compound	¹ H NMR, δ (ppm)		¹³ C NMR, δ (ppm)		²⁹ Si NMR, δ (ppm)
	CH ₃ Si	=CH	CH ₃ Si	=CH	
1	0.14	6.58			
2	0.17	6.66	-4.39	152.83	-17.9
3	0.13	6.56	-3.41	150.12	-15.5

2. Experimental details

2.1. Main data on X-ray structural experiments

The data are as follows: HW diffractometer; MoK₂ radiation source; ($2\theta_{\max}$) θ - 2θ scan values, 60°; $T = 20^\circ\text{C}$; number of reflections, 3915 (977 included in calculations); $a = 12.430(2)$ Å; $b = 23.811(1)$ Å; $c = 19.805(1)$ Å; $\beta = 90^\circ$; $V = 5802(1)$ Å³; $d_{\text{calc}} = 0.95$ g cm⁻³; $z = 8$; space group, P_{bca} ; $R = 0.051$; $R_w = 0.035$; Eclipse S/200 computer; INEXTL program.

NMR spectra were obtained on a JEOL FX 90Q spectrometer (15% solutions in CDCl₃; tetramethylsilane as internal standard). Mass spectra were recorded on a Varian MAT-212 gas-liquid chromatography mass spectrometer (ionizing voltage, 70 eV).

2.2. Si-dodecamethylcyclohexasilethene (1)

To a mixture of 50 ml of tetrahydrofuran (THF) and 0.1 ml of 0.2 N H₂PtCl₆ in 2-propanol, 8.4 g of HMe₂SiC≡CH in 15 ml of THF was added dropwise. The solvent was distilled under reduced pressure and the residue gave 0.18 g (2.2%) of **1** after distillation in a high vacuum (10⁻⁴ Torr) (Table 1).

2.3. Si-octamethylcyclotetrasilethene (2)

This was prepared in a similar way from a mixture of 5.4 g of Me₂Si(C≡CH)₂ and 10.9 g of *E,E*-Me₂Si(CH=CHSiMe₂H)₂. The yield of **2** is 0.5 g (3.1%) (Table 1).

2.4. Si-decamethylcyclopentasilolethene (3)

This was obtained analogously from a mixture of 9.6 g of *E*-HC≡CMe₂SiCH=CHSiMe₂C≡CH and 10.9 g of *E,E*-Me₂Si(CH=CHSiMe₂H)₂. The yield of **3** is 1.21 g (5.9%) (Table 1).

2.5. *E,E*-dimethyl-bis-(2-dimethylsilylvinyl)silane (4)

To a suspension of 3.0 g of LiAlH₄ in 250 ml of ether, 20.0 g of *E,E*-Me₂Si(CH=CHSiMe₂Cl)₂ in 20 ml of ether was added dropwise on stirring at 20°C. After stirring for 4 h the mixture was decomposed by a saturated NH₄Cl solution. After routine treatment and drying over CaCl₂ the ether was distilled off and 12.2 g (80%) of **4** was isolated from the residue by vacuum distillation. Boiling point, 94–95°C; 8 Torr; $n_D^{20} = 1.4648$; $d_4^{20} = 0.8389$. Anal. Found: C, 52.30; H, 10.43; Si, 35.92; C₁₀H₂₄Si₃ calc.: C, 52.54; H, 10.58; Si, 36.86%. ¹H NMR: δ 0.12 (CH₃Si¹), 0.16 (CH₃Si²), 6.66 (CH=), 4.09 (SiH). ¹³C NMR: δ -4.44 (CH₃Si¹), -3.47 (CH₃Si²), 150.71 (=CHSi¹), 148.65 (Si²CH=). ²⁹Si NMR: δ -21.39 (Si¹), -15.36 (Si²).

Acknowledgments

The authors would like to express their gratitude to Dr. Yu.E. Ovchinnikov and Dr. Yu.T. Struchkov for the X-ray diffraction analysis of **3**. We are also indebted to Dr. A.I. Albanov for NMR measurements.

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