Russian Journal of General Chemistry, Vol. 75, No. 7, 2005, pp. 1094–1097. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 7, 2005, pp. 1157–1160.
Original Russian Text Copyright © 2005 by O. Yarosh, Zhilitskaya, Istomina, N. Yarosh, Albanov, Voronkov.

Novel Highly Unsaturated Macrocyclic and Macrobicyclic Silahydrocarbons Containing Si–H Bonds and Exocyclic Vinyl Groups

O. G. Yarosh, L. V. Zhilitskaya, E. E. Istomina,
N. K. Yarosh, A. I. Albanov, and M. G. Voronkov

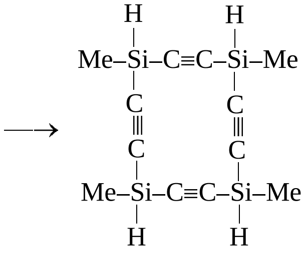
Favorskii Irkutsk Iinstitute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia

Received March 31, 2004

Abstract — The first representative of cycloorganylhydrosilalkynes $(C{\equiv}CSiHR)_n$, tetramethylcyclotetrasilethyne, was prepared by organomagnesium synthesis. The same procedure was used to synthesize 15-membered polyunsaturated silahydrocarbons containing both triple and double bonds in the ring and an exocyclic vinyl group. Organomagnesium synthesis was also used for preparing previously unknown polyunsaturated macrobicyclic silahydrocarbons containing a $–CH_2CH_2–$ bridge. The ^1H, ^{13}C, and ^{29}Si NMR and IR spectra of the synthesized compounds were studied.

Proceeding with investigations into highly unsaturated silahydrocarbons [1–3], we synthesized a series of 12- and 15-membered macrocyclic and 26-membered macrobicyclic compounds of this type. Thus, the reaction of bis(bromomagnesioethynyl)methylsilane with dichloro(methyl)silane in THF under conditions of high dilution gave a previously unknown tetramethylcyclotetrasilethyne $(C{\equiv}CSiHMe)_4$, viz. 1,4,7,10-tetramethyl-1,4,7,10-tetrahydro-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (**I**), the first representative of the $(C{\equiv}CSiHR)_n$ homologous series.

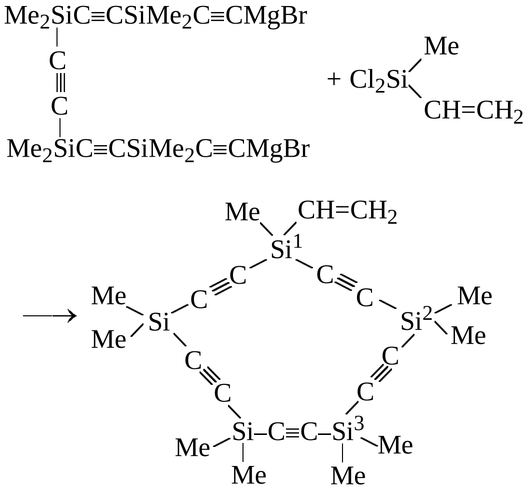
$MeSiH(C{\equiv}CMgBr)_2 + MeSiHCl_2$



I

Tetramethylcyclotetrasilethyne presents interest from the synthetic viewpoint, since the hydrogen atom on silicon is readily substituted by other groups, which opens up the way to compounds like $(C{\equiv}CSiXR)_n$ (X = Hlg, OH, OR, OCOR, NR'R", hydrocarbonyl, etc.).

In the same way, bis(bromomagnesioethynyldimethylsilylethynyldimethylsilyl)ethyne was reacted with dichloro(methyl)(vinyl)silane to synthesize 1,4,4,7,7,-10,10,13,13-nonamethyl-1-vinyl-1,4,7,10,13-pentasilacyclopentadeca-2,5,8,11,14-pentayne (**II**).

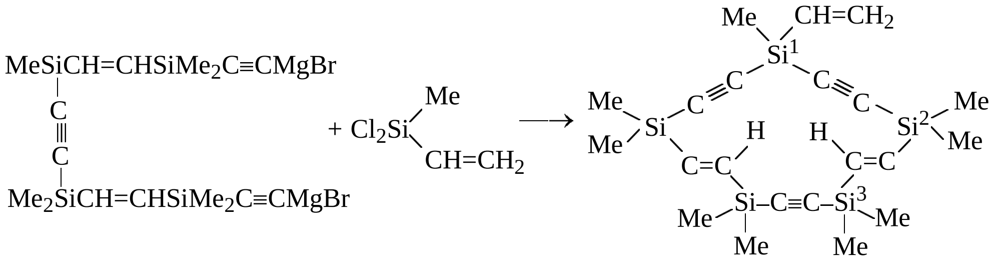


II

The reaction of bis[[2-(*E*,*E*)-bromomagnesioethynyldimethylsilylvinyl]dimethylsilyl]ethyne with dichloro(methyl)(vinyl)silane gave 1,4,4,7,7,10,10,13,13-nonamethyl-1-vinyl-1,4,7,10,13-pentasilacyclodeca-5,11-diene-2,8,14-triyne (**III**).

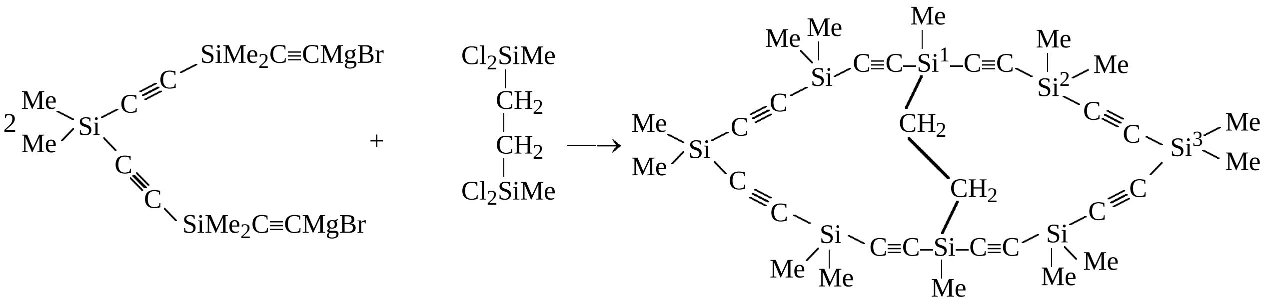
The reaction of bis(bromomagnesioethynyldimethylsilylethynyl)dimethylsilane with 1,2-bis[dichloro-

1070-3632/05/7507-1094 ©2005 Pleiades Publishing, Inc.



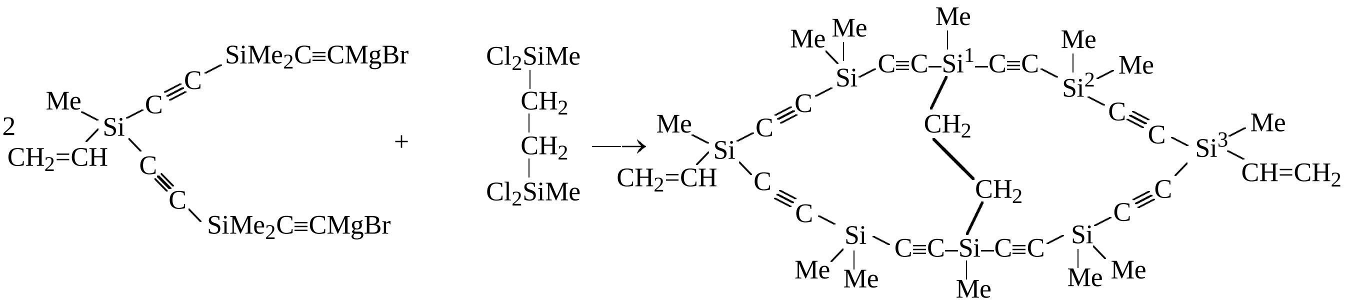
III

(methyl)silyl]ethane gave 1,4,4,7,7,10,10,13,16,16,19,19,22,22-tetradecamethyl-1,4,7,10,13,16,19,22-octasilabicyclo[11.11.2]hexacosa-2,5,8,11,14,17,20,23-octayne (**IV**).



IV

The same reaction of bis(bromomagnesioethynyldimethylsilylethynyl)(methyl)(vinyl)silane with 1,2-bis[dichloro(methyl)silyl]ethane provided 1,4,4,7,10,10,13,16,16,19,22,22-dodecamethyl-7,19-divinyl-1,4,7,10,13,16,19,22-octasilabicyclo[11.11.2]hexacosa-2,5,8,11,14,17,20,23-octayne (**V**).



V

The starting (*E*,*E*)-bis[[2-(ethynyldimethylsilyl)vinyl]dimethylsilylethyne (**VI**) was prepared by the reaction of (*E*)-1-(ethynyldimethylsilyl)-2-chlorodimethylsilylethene with bis(bromomagnesio)ethyne.

$$2HC\equiv CSiMe_2CH=CHSiMe_2Cl + BrMgC\equiv CMgBr \longrightarrow HC\equiv CSiMe_2CH=CHSiMe_2C\equiv CSiMe_2CH=CHSiMe_2C\equiv CH$$

VI

Compounds **I**–**V** are colorless crystals with high melting points (129–212°C), that sublime in a high vacuum (with compound **I**, vacuum ~1 mm Hg, 100°C; Table 1). They all are stable when handled and heated to the melting point. Their structure was proved by ^{1}H, ^{13}C, and ^{29}Si NMR (Table 2) and IR spectral data. Compound **VI** is a low-melting crystalline substance (Table 1), its ^{1}H, ^{13}C, and ^{29}Si spectra are given in Table 2.

The IR spectrum of compound **I** shows a strong Si–H absorption band at 2170 cm^{-1}. The vinyl groups in compounds **II**, **III**, and **V** give a weak absorption band at 1590 cm^{-1}. It is interesting to note that the C≡C band of compound **I** at 2050 cm^{-1} is weak, and in the spectra of the other macrocycles no absorption of this bond, as well as of the disubstituted CH=CH bond, is observed at all. The Si–C bands are on their usual places (850 and 1250 cm^{-1}).

The ^{1}H NMR spectrum of compound **I** shows an SiH proton signal [quintet, $^{3}J(CH_3SiH)$ 3.7 Hz, $^{1}J^{29}(SiH)$ 22.8 Hz] and an SiMe proton signal [d, $^{3}J(CH_3SiH)$ 3.7 Hz, $^{2}J(^{29}SiCH)$ 12.2 Hz]. The in-

Table 1. Physicochemical characteristics of compounds **I**–**VI**

Comp. no.	Yield, %	mp, °C	[*M*], *m/z* (I_{rel}, %)	Found, %			Formula	Calculated, %		
				C	H	Si		C	H	Si
I	22	129	272 (18)	52.61	5.97	40.78	$C_{12}H_{16}Si_4$	52.87	5.92	41.21
II	11	190	422 (2)	59.26	7.05	33.15	$C_{21}H_{30}Si_5$	59.63	7.15	33.31
III	23	134	426 (15)	59.36	8.31	32.44	$C_{21}H_{34}Si_5$	59.07	8.03	32.90
IV	6	214	654 (34)	57.98	7.15	33.78	$C_{32}H_{46}Si_8$	58.64	7.07	34.29
V	9	212	674 (12)	60.69	6.74	32.73	$C_{34}H_{46}Si_8$	60.46	6.27	33.27
VI[a]	62	30	–	59.52	8.39	29.35	$C_{18}H_{30}Si_4$	60.26	8.43	30.31

[a] bp 118–120°C (1 mm Hg).

Table 2. Parameters of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compounds **I**–**VI**

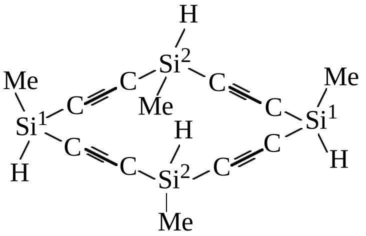
Comp. no.	^{1}H NMR spectrum, δ, ppm						^{13}C NMR spectrum, δ_C, ppm						
	MeSi^{1}	MeSi^{1}	MeSi^{1}	VinSi	$SiCH_2$	SiCH=	MeSi^{1}	MeSi^{2}	MeSi^{3}	VinSi	$SiCH_2$	SiCH=	SiC≡
I[a]	0.38 d	–	–	–	–	–	–4.18	–	–	–	–	–	112.15
II	0.38 d	0.33	0.32	6.05, 6.08, 6.10	–	–	–0.85	–1.53	–1.73	132.49 (CH), 135.64 (CH_2)	–	148.49 111.60	108.26, 110.30,
III	0.38 d	0.33	0.32	6.03, 6.05, 6.07	–	6.70	–1.24	–1.57	–1.70	132.96 (CH), 135.48 (CH_2)	–	148.33, 148.08	109.07, 114.05, 112.97
IV	0.29 d	0.30	0.35	–	0.91	–	–0.23	–2.19	–0.33	–	8.61	–	109.54, 110.50, 110.69, 111.59
V	0.31 d	0.33	0.36	6.02,	0.90 6.05, 6.09	–	–1.53	–2.17	–0.35	132.47 (CH), 135.66 (CH_2)	8.61	–	108.48, 109.64, 111.52, 112.04
VI[b]	0.23 d	0.24	–	–	–	6.69, 6.72 (*AB* quartet, *J* 22.25 Hz)	–1.69	–1.52	–	–	–	148.17, 149.31 149.31	113.29

Table 2. (Contd.)

Comp. no.	^{29}Si NMR spectrum, δ_{Si}, ppm		
	Si^1	Si^2	Si^3
I[a]	–61.59	–64.55	–
II	–48.79	–41.55	–41.48
III	–49.55	–26.80	–25.64
IV	–36.62	–41.38	–
V	–36.61	–41.17	–48.55
VI[b]	–	–	–

Other signals: [a] ^{1}H NMR spectrum, δ, ppm: 4.24 (SiH); [b] ^{1}H NMR spectrum, δ, ppm: 2.43 (≡CH); ^{13}C NMR spectrum, δ_C, ppm: 88.28 (SiC≡), 94.47 (≡CH).

tensity ratio of these two signals is 1:3. As judged from the fact that the ring SiH protons of **I** appear as a symmetric quintet that is formed by a superposition of two quartets of equal intensity. The conformation of the ring is close to planar, and the methyl groups at neighboring silicon atoms are *trans* to each other.



The difference in the chemical shifts of the Si^1H and Si^2H proton signals, roughly equal to $J(CH_3SiH)$ of 3.7 Hz, will give rise to the observed quintet. This suggestion is confirmed by the presence of two ^{29}Si signals (Table 2).

The synthesis of (*E*)-1-(ethynyldimethylsilyl)-2-(chlorodimethylsilyl)ethane has been described in [4].

EXPERIMENTAL

The NMR spectra were measured on a Bruker DPX-400 spectrometer (400 MHz) for 15% solutions in $CDCl_3$, internal reference HMDS. Gas chromatography–mass spectrometry of compounds **I**–**III** was performed on a Hewlett–Packard HP-5971A instrument, ionizing energy 70 eV, column Ultra-2, oven temperature 70–280°C programmed at a rate of 20 deg min^{-1}. The mass spectra of compounds **IV** and **V** were obtained on an LKB-2091 instrument with direct sample inlet, ionizing energy 60 eV, source temperature 250°C.

Tetramethylcyclotetrasilethyne (I). To 50 ml of absolute ether, we simultaneously added dropwise with stirring $MeHSi(C{\equiv}CMgBr)_2$ prepared from 2.43 g of Mg, 10.9 g of EtBr, and 4.7 g of $MeHSi(C{\equiv}CH)_2$ in 75 ml of THF, and 5.75 g of $MeHSiCl_2$ in 50 ml of ether. The mixture was stirred for 1 h and then decomposed with water and 5% HCl. After usual workup and drying over calcined $CaCl_2$, the solvents were removed at reduced pressure, and the residue was sublimed in a vacuum (1 mm Hg, 100°C) to isolate 1.5 g (22%) of compound **I** (Table 1).

Compounds **II**–**V** were prepared in a similar way (Table 1).

(*E*,*E*)-Bis[[2-(ethynyldimethylsilyl)vinyl]dimethylsilylethyne (VI). Through a solution of the Grignard reagent prepared from 2.43 g of Mg and 10.9 g of EtBr in 100 ml of THF we passed a dry and pure acetylene until a thick suspension formed, after which a solution of 20 g of $HC{\equiv}CSiMe_2CH{=}CHSiMe_2Cl$ in 50 ml of ether was added dropwise with stirring. Further workup was performed as described above. Yield 12.5 g (62%) (Table 1).

ACKNOWLEDGMENTS

The work was financially supported by the *Leading Scientific Schools* Program (grant no. NSh-1129-2003.3).

REFERENCES

1. Yarosh, O.G., Voronkov, M.G., and Brodskaya, E.I., *Usp. Khim.*, 1995, vol. 64, no. 9, p. 896.
2. Voronkov, M.G., Zhilitskaya, L.V., Yarosh, O.G., Albanov, A.I., and Klyba, L.V., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 12, p. 2006.
3. Voronkov, M.G., Zhilitskaya, L.V., Yarosh, O.G., Burnashova, T.D., Albanov, A.I., and Klyba, L.V., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 4, p. 578.
4. Yarosh, O.G., Turkina, G.Yu., Albanov, A.I., and Voronkov, M.G., *Metalloorg. Khim.*, 1998, vol. 1, no. 3, p. 708.