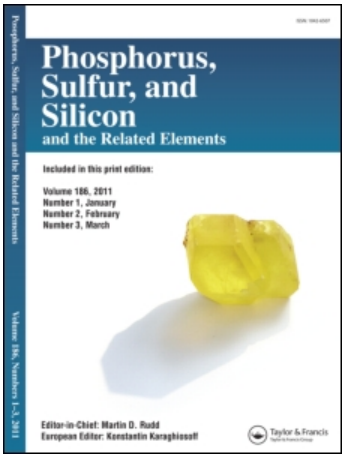

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Highly Unsaturated Macrocyclic Organosilicon Compounds

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HIGHLY UNSATURATED MACROCYCLIC ORGANOSILICON COMPOUNDS

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Abstract A series of 12-, 15-, 18-, 21-, 24-, 27- or 30-membered macrocyclic silahydrocarbons of general formula $(MeRSiC{\equiv}C)_n$, n = 4-10 and R = H, Me, $CH_2{=}CH$ were synthesized by reaction of $Me_2Si(C{\equiv}CMgBr)_2$, $Me(CH_2{=}CH)Si(C{\equiv}CMgBr)_2$, $BrMgC{\equiv}CMe_2SiC{\equiv}CSiMe_2C{\equiv}CMgBr$ or $BrMgC{\equiv}CMe_2SiC{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CMgBr$ with $MeHSiCl_2$, Me_2SiCl_2, $Me(CH_2{=}CH)SiCl_2$ or $(ClMe_2SiC{\equiv}C)_2SiMe_2$. 23-Membered spiromacrocyclic polyacetylenic silahydrocarbons containing 6 silicon atoms, 8 triple bonds and central Si or Ge atoms were prepared by reaction of $Me_2Si(C{\equiv}CSiMe_2C{\equiv}CMgBr)_2$ with MCl_4 (M = Si, Ge).

INTRODUCTION

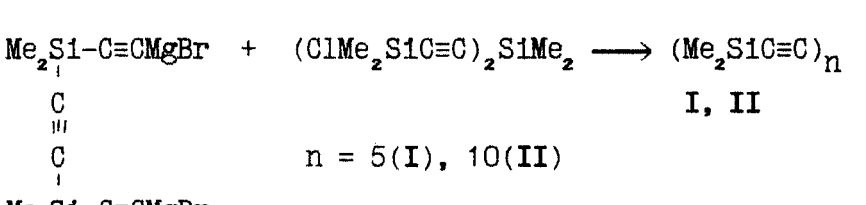
As early as the middle of this century we suggested to call the unknown that time silahydrocarbons of general formula $(H_2SiC{\equiv}C)_n$ cyclosilethynes.[1] The first cyclic silahydrocarbon of this type, permethyltetracyclosilethyne $(Me_2SiC{\equiv}C)_4$ was prepared by us in 1973 by reaction of dimethyldichlorosilane with calcium carbide in a molten salt system LiCl-KCl.[2] Later some other cyclic oligomers $(Me_2SiC{\equiv}C)_n$, n = 3-5 have been described.[3-8]

In several publications the synthesis of silaacetylenic polymers by reaction of diorganyldichlorosilanes with acetylene organometallic derivatives such as $C_2(MgBr)_2$,[9] C_2Na_2,[10,11] C_2Li_2[12] has been reported.

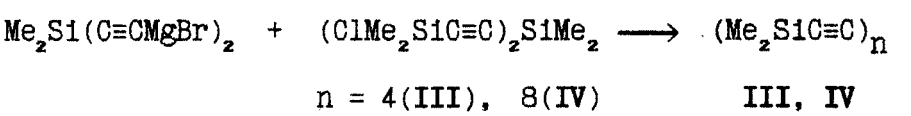
RESULTS AND DISCUSSION

During the last years by use of organomagnesium method we have prepared a number of new 12-30-membered polyacetylenic macrocyclic silahydrocarbons of general formula $(MeRC{\equiv}C)_n$ where n = 4-10; R = H, Me, CH_2=CH, which we called cyclodiorganylsilethynes.[13]

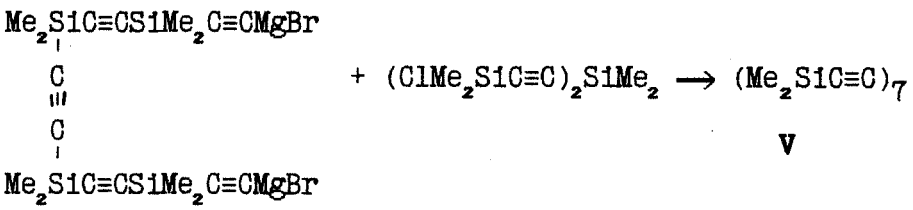
The reaction of bis(bromomagnesiumethynyldimethylsilyl)acetylene with dimethyl-bis(dimethylchlorosilylethynyl)silane in tetrahydrofuran under high dilution gave 15-membered decamethylcyclopentasilethyne, 1,1,4,4,7,7,10,10,13,13-decamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,5,8,11,14-pentaine (**I**) and 30-membered eicosamethylcyclodecasilethyne, 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22,25,25,28,28-eicosamethyl-1,4,7,10,13,16,19,22,25,28-decasilacyclotriaconta-2,5,8,11,14,17,20,23,26,29-pentaine (**II**).



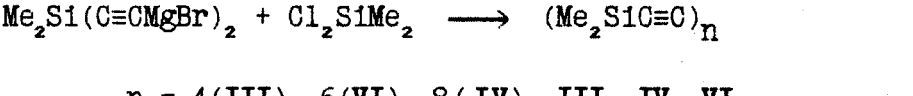
A similar reaction of dimethyl(bromomagnesiumethynyl)silane with dimethyl-bis(dimethylchlorosilylethynyl)silane leads to 12-membered octamethylcyclotetrasilethyne (**III**) and 24-membered hexadecamethylcyclooctasilethyne (**IV**):



The reaction of bis[(bromomagnesiumethynyldimethylsilyl)ethynyldimethylsilyl]acetylene with dimethyl-bis(dimethylchlorosilylethynyl)silane gave 21-membered tetradecamethylcycloheptasilethyne (**V**):

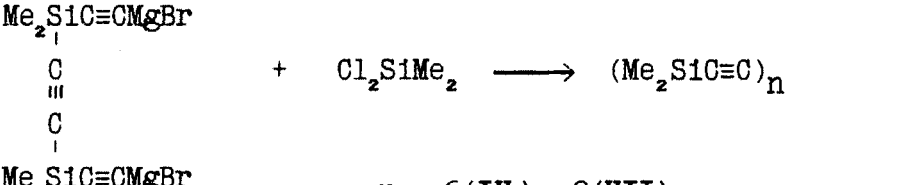


The silahydrocarbons **III**, **IV** and 18-membered dodecamethylhexasilethyne (**VI**) were obtained by reaction of dimethyl-bis(bromomagnesiumethynyl)silane with dimethyldichlorosilane:



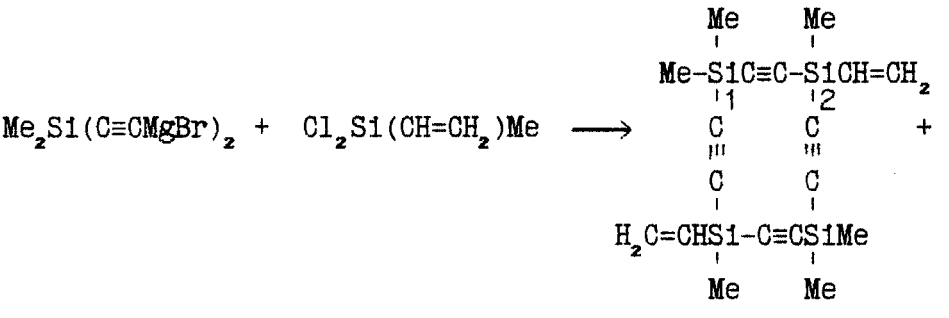
III, IV, VI

The silahydrocarbon **VI** and 27-membered octadecamethylcyclononasilethyne (**VII**) was obtained in an analogous way from bis(dimethylbromomagnesiumethynylsilyl)acetylene and dimethyldichlorosilane.

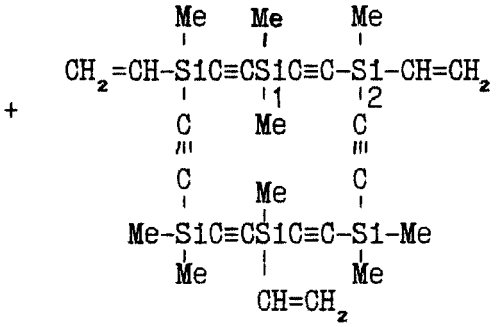


We have synthesized macrocyclic polyacetylenic silahydrocarbons containing exocyclic vinyl groups and Si-H bonds. In this manner, by reaction of dimethyl-bis(bromomagnesiumethynyl)silane with methyl(vinyl)dichlorosilane we

obtained 12-membered 1,4,4,7,10,10,-hexamethyl-1,7,-divinyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetraine (**VIII**) and 18-membered 1,4,4,7,10,10,13,16,16-nonamethyl-1,7,13-trivinyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5,8,11,14,17-hexaine (**IX**):

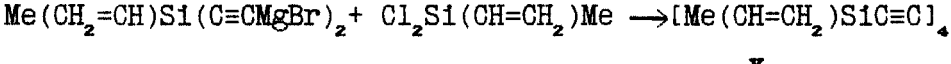


VIII



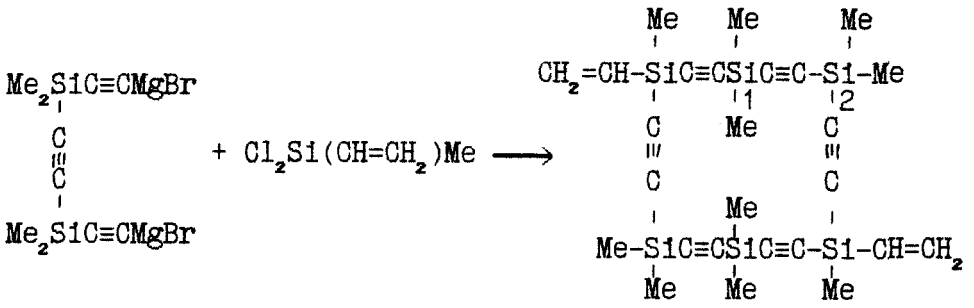
IX

An analogous reaction of methyl(vinyl)-bis(bromomagnesiumethynyl)silane with methyl(vinyl)dichlorosilane gave 12-membered cyclotetra(methylvinylsilethyne) (**X**):



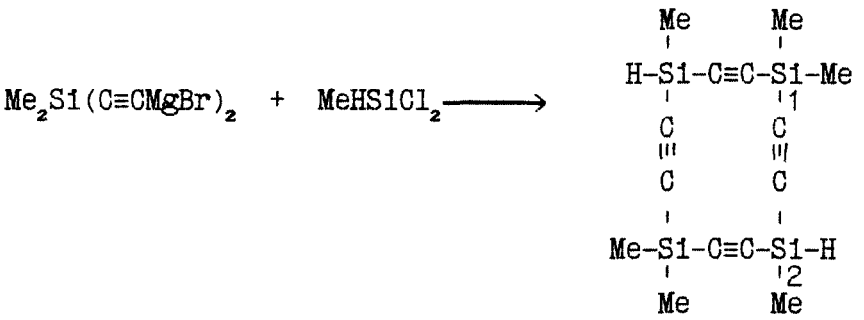
X

The reaction of bis(bromomagnesiumethynyldimethylsilyl)acetylene with methyl(vinyl)dichlorosilane led to 18-membered 1,4,4,7,7,10,13,13,16,16-decamethyl-1,10-divinyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5,8,11,14,17-hexaine (**XI**):



XI

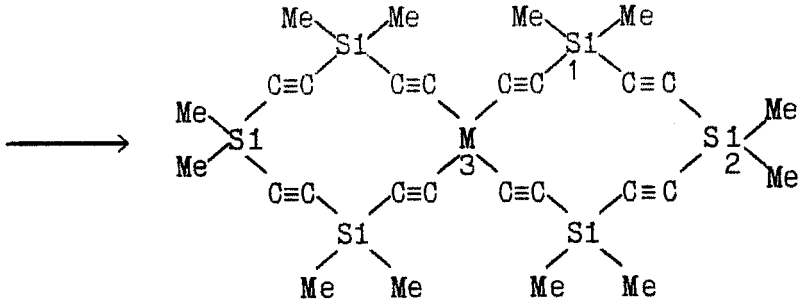
The 12-membered 1,4,4,7,10,10-hexamethyl-1,7-dihydro-1,4,-7,10-tetrasilacyclododeca-2,5,8,11-tetraine (**XII**) was isolated by reaction of dimethyl-bis(bromomagnesiumethynyl)-silane with methyldichlorosilane:



XII

Further we have first synthesized spiromacrocyclic polyacetylenic silahydrocarbon 3,3,6,6,9,9,15,15,18,18,21,-21-dodecamethyl-3,6,9,12,15,18,21-heptasilaspiro[11',11']-tricosa-1,4,7,10,13,16,19,22-octaine (**XII**) and its 12-membered germa analog 3,3,6,6,15,15,18,18,21,21-dodeca-methyl-3,6,9,15,18,21-hexasila-12-germa spiro[11',11']-tricosa-1,4,7,10,13,16,19,22-octaine (**XIV**). These compounds were obtained by reaction of bis[(bromomagnesiumethynyl-dimethylsilyl)ethynyl]dimethylsilane with tetrachlorosilane and tetrachlorogermane, respectively:

$2Me_2Si(C{\equiv}CSiMe_2C{\equiv}CMgBr)_2 + MCl_4 \longrightarrow$



XIII, XIV

M = Si(**XIII**), Ge(**XIV**)

The above compounds are colorless, high-melting crystalline substances stable in storage and heating to the melting point.

The melting points and yields of the silahydrocarbons obtained are presented in Table 1.

TABLE I Macrocyclic acetylenic silahydrocarbons

Compound	Yield, (%)	M.p., (°C)	Mass spectrum $[M]^+$
I	7.0	208	410(13)
II	1.2	217	820(28)
III	2.4	258	328(43)
IV	5.0	252	656(23)
V	3.8	163	574(17)
VI	5.0	268	492(19)
VII	2.5	190	738(2)
VIII	1.7	195	352(37)
IX	3.8	188	528(18)
X	2.0	176	376(25)
XI	4.5	215	516(32)
XII	4.3	185	300(58)
XIII	2.5	293	568(15)
XIV	2.0	299	610(5)

The melting points of permethylcyclosilethynes $(Me_2SiC{\equiv}C)_n$ fall in the following order of changing the cycle size (n): 6 > 4 >8 >10 >5 > 9 > 7. It is worth notice that the lowest melting points correspond to odd n values. This alternation of melting points of even and odd members of the homologous series is quite common.[14]

It should be noted that our melting points for compounds (**I**) (n = 5) and (**III**) (n = 4), 208 and 258°C, respectively, differ from the literature data[8] (255-257 and 207-209°C, respectively).

The structures of all the silahydrocarbons obtained were proved by mass spectrometry (Table 1) and ^1H, ^{13}C and ^{29}Si NMR spectrometry (Table 2).

The ^1H NMR spectra of cyclosilethynes $(Me_2SiC{\equiv}C)_n$ show one resonance signal of methyl groups attached to the silicon atom. The signal is slightly shifted downfields as the cycle size increases (by 0.06 ppm in going from n = 4 to n = 10). In the ^1H NMR spectra of cyclosilethynes **VIII-XII** there are two signals arisen from the methyl groups of non-equivalent $SiMe_2$, $Si(CH{=}CH_2)Me$ and SiHMe fragments.

The ^{13}C resonance signal of methyl groups attached to the silicon atom is present in a range from -0.96 to + 0.87 ppm and from -1.06 to -2.21 and -3.8 ppm in the $SiMe_2$, $Si(CH{=}CH_2)Me$, and SiHMe groups, respectively. The chemical shifts of acetylenic carbons in the $Me_2SiC{\equiv}$ group occur in the 111-116 ppm region whereas those for the $Me(CH{=}CH)SiC{\equiv}$ group are observed in higher fields (104-111 ppm). The 132 and 136 ppm resonance signals correspond to the vinylic CH= and CH_2= carbon atoms.

In the ^{29}Si NMR spectra the resonance signal of silicon in $SiMe_2$, $Si(CH{=}CH_2)Me$ and SiHMe groups is observed in ranges from -41.0 to -41.7, from -48.5 to -49 and at -41.0 ppm, respectively.

In the ^1H NMR spectra of spirocyclic compounds **XIII** and **XIV** there are two signals at 0.34 and 0.31 ppm. The former corresponds to the methyl groups at the silicon atoms nearest to spirocyclic silicon and germanium atoms.

TABLE II ^{13}C and ^{29}Si Spectral parameters of the compounds obtained

	^1H NMR, (δ, ppm)				^{13}C NMR, (δ, ppm)				^{29}Si NMR, (δ, ppm)				
	CH_3Si_1	CH_3Si_2	$CH{=}CH_2$	SiH	CH_3Si_1	CH_3Si_2	CH=	$=CH_2$	$Si_1C{\equiv}$	$Si_2C{\equiv}$	Si_1	Si_2	Si_3
I	0.35				0.12				111.23		-41.1		
III	0.30				-0.69				114.2		-41.7		
V	0.33				0.18				111.07		-41.2		
VI	0.34				0.87				111.55		-41.5		
VIII	0.30	0.35	6.05		-0.80	-2.10	131.98	136.10	113.29		-41.3	-49.0	
IX	0.34	0.39	6.07		0.11	-1.06	132.70	135.63	111.96	108.84	-41.0	-48.5	
X	0.37		6.06		-2.21		131.71	136.26	113.24		-48.7		
XI	0.33	0.39	6.07		0.18	-1.07	132.85	135.61	110.85 112.15	108.85	-41.2	-48.6	
XII	0.32	0.37		4.24	-0.96	-3.89			115.78	110.74	-41.0	-41.0	
XIII	0.34	0.31			-1.14	-0.87			116.69 114.42	113.22 106.67	-40.4	-41.4	-66.9
XIV	0.34	0.31			-1.08	-0.92			114.09 113.66	113.12 105.15	-40.7	-41.5	

The ^{13}C resonance signal of the methyl groups attached to these silicon atoms occurs within a range from -1.14 and -1.08 ppm for compounds **XIII** and **XIV**, respectively. The ^{13}C resonance of two methyl groups attached to other silicon atoms is observed at -0.87 and -0.92 ppm, respectively. The ^{13}C NMR signals of acetylenic carbons are shifted upfields on approaching the spirocyclic silicon (116.69, 114.42, 113.22 and 106,67 ppm) and germanium atoms (114.09, 113.66, 113.12 and 105.15 ppm).

The ^{29}Si NMR spectrum of spirocyclic compound **XIII** also shows the presence of silicon atoms of three types: central (δ = -66.9 ppm), 4 silicons nearest to the central atom (δ = -40.4ppm) and 2 silicons remote from the central silicon atom (δ = -41.4ppm). Analogously, in the ^{29}Si NMR spectrum of **XIV** the latter two types of silicon atoms give rise to the -40.7 and -41.5 ppm signals.

Mass spectra were run on a GLS-MS MAT-212 (Varian) instrument (ionizing voltage 70 eV). NMR spectra were recorded on a JEOL FX 90Q spectrometer (15% solution in $CDCl_3$, TMS). The ^{13}C resonance frequency is 13-22.49 MHz, pulse length 16 μs. NMR spectra were recorded by the pulse technique.

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