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# New Polyunsaturated Silahydrocarbons

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**Abstract—**12-Membered highly unsaturated macrocyclic silahydrocarbon containing exocyclic methyl and benzyl groups is synthesized by the reaction of benzylmethyldi(bromomagnesiumethynyl)silane with dimethyldichlorosilane. Hydrosilylation of benzyl(triethynyl)silane with trichlorosilane with subsequent reaction of the formed adduct with trimethylsilylmagnesium bromide leads to the spherical dendrimer ($N_C = 3$) containing the benzyl group at the central Si atom, –CH=CH– groups in the inner sphere and numerous triple bonds on the periphery. NMR spectra of the obtained compounds were studied.

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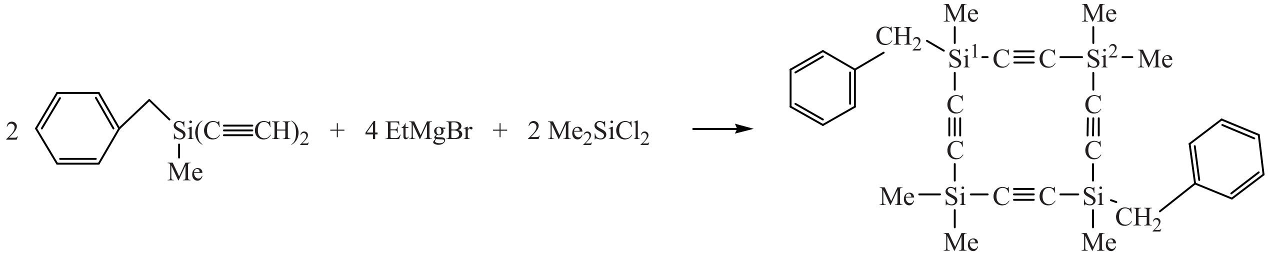
In continuation of our studies of polyunsaturated macrocyclic and dendrimer silahydrocarbons [1–9] we have synthesized new representatives of these classes of compounds. For their design we have used benzylmethyl(diethynyl)- and benzyl(triethynyl)silane as synthons [10].

By the reaction of benzylmethyl(diethynyl)silane with ethylmagnesium bromide and dimethyldichlorosilane in the molar ratio of 2:4:2 in the mixture of ether and tetrahydrofuran under the conditions of high dilution the 12-membered highly unsaturated macrocyclic silahydrocarbon containing exocyclic methyl and benzyl groups, 1,4,4,10,10-hexamethyl-1,7-dibenzyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (**I**) has been synthesized in 12% yield (Scheme 1).

In the mass spectrum of compound **I** the peak of the molecular ion is present. Its fragmentation proceeds with the expulsion of either methyl or benzyl radical giving rise, in the latter case, to the peak of maximum intensity. In the mass spectrum the peak of ion with *m*/*z* 91(26) is observed, which has the structure of tropylium cation as indicated by the presence of the peak of cyclopentadienyl cation with *m*/*z* 65(10) formed after elimination of acetylene molecule from the ion with *m*/*z* 91. The abstraction of trimethylsilyl group from $[M^+]$ is a general route of fragmentation of macrocyclic silahydrocarbons [11]. Other characteristic processes of fragmentation are weakly pronounced (Table 1).

The two-step synthesis: hydrosilylation of benzyl (triethynyl)silane with trichlorosilane and the subsequent reaction of the formed adduct with trimethylsilylmagnesium bromide (1:3:9) affords in 30% yield the three-branched organosilicon dendrimer containing a benzyl group at the central silicon atom, three –CH=CH– groups in the inner sphere and numerous C≡C triple bonds on the periphery, benzyltris[tris(trimethylsilylethynyl)silylvinyl]silane (**II**) (Scheme 2).

**Scheme 1.**



**I**

**Table 1.** Constants of synthesized compounds **I, II**

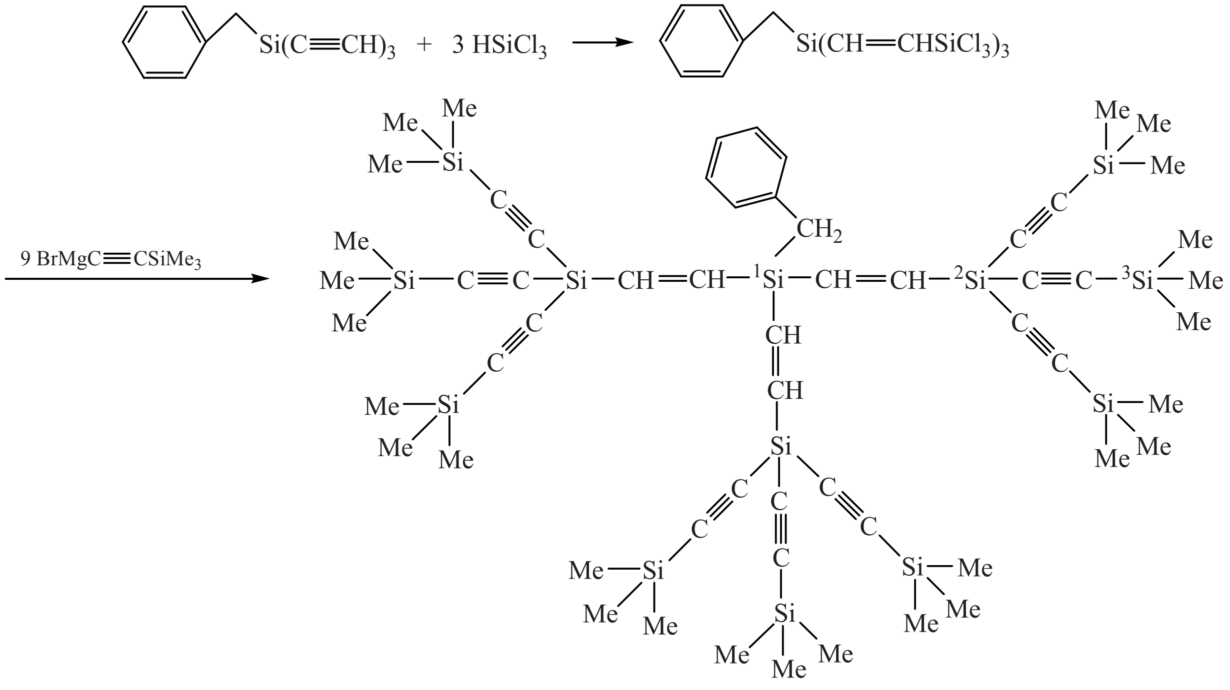
| Comp. no. | Yield, % | mp, °C | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | Si | | C | H | Si |
| **I**[a] | 11 | 186–187 | 68.65 | 6.12 | 22.87 | $C_{28}H_{32}Si_4$ | 69.93 | 6.70 | 23.36 |
| **II** | 30 | 146–148 | 58.91 | 8.07 | 30.50 | $C_{58}H_{94}Si_{13}$ | 60.23 | 8.19 | 31.58 |

[a] Mass spectrum, *m*/*z* , ion: 480(3), $[M]^+$; 465(2), $[M - 15]^+$; 389(100), $[M - C_7H_7]^+$; 316(4), $[M - 164]^+$; 97(7), $[C{\equiv}CSiMe_3]^+$; 91(26), $[C_7H_7]^+$; 83(14), $[C{\equiv}CSiMe_2H]^+$; 73(48), $[SiMe_3]^+$.

**Table 2.** $^1H$, $^{13}C$, $^{29}Si$ NMR spectra of synthesized compounds **I, II**

| Comp. no. | $^1H$ NMR spectrum, δ, ppm | | | | | $^{13}C$ NMR spectrum, $δ_C$, ppm | | | | | | $^{29}Si$ NMR spectrum, $δ_{Si}$, ppm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Si_1Me$ | $Si_2Me$ | CH=CH, (*J*, Hz) | $CH_2$ | $C_6H_5$ | $Si_1Me$ | $Si_2Me$ | CH=CH | C≡C | $CH_2$ | $C_6H_5$ | $Si_1$ | $Si_2$ | $Si_3$ |
| **I** | 0.22 | 0.34 | – | 2.35 | 7.2 (*m*) | –3.74 | –1.29 | – | 115.41,<br>112.64 | 24.52 | 124.63(*p*),<br>127.98(*o*),<br>128.36(*m*),<br>136.62(*i*) | –42.06 | –42.56 | – |
| **II** | 0.05 | – | 6.31 d,<br>6.44 d,<br>($J_{trans}$ 21.77) | 2.20 | 6.83 (*m*) | –0.31 | – | 149.16,<br>147.19 | 115.86,<br>104.01 | 23.17 | 124.31(*p*),<br>127.07(*o*),<br>127.95(*m*),<br>144.51(*i*) | –16.01 | –76.71 | –60.44 |

**Scheme 2.**



**II**

Some key parameters of dendrimer **II** having regular structure were determined [12]. The number of generation G = 1; index of branching or the number of dendrons growing from the core, $N_C = 3$; index of branching of the units, the number of branches formed by each of the repeated units $N_B = 3$. The number of terminal groups: $Z = N_C N_B^G = 9$.

The degree of polymerization and theoretical mass cannot be calculated using the earlier employed method since dendrimer **II** simultaneously contains in the chain the bonds of different multiplicity.

The synthesized polyunsaturated silahydrocarbons **I, II** are crystalline compounds stable at storage, soluble in organic solvents. Their yields and physicochemical constants are given in Table 1 and their structure is proved by the data of $^1$H, $^{13}$C and $^{29}$Si NMR spectroscopy (Table 2).

The presence of numerous multiple bonds in the molecules **I, II** provides wide possibilities for their use as precursors of more complex nanodimensional structures.

## EXPERIMENTAL

NMR spectra were registered on a Bruker DRX 400 instrument (400 MHz) for 15% solutions in $CDCl_3$ with HMDS as an internal reference. Mass spectrum was obtained on a LKB 2091 chromatomass spectrometer using the system of direct injection into the ion source, ionizing voltage 60 eV, the temperature of the source 250°C.

All solvents used in this work were thoroughly dried.

**1,4,4,10,10-Hexamethyl-1,7-dibenzyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (I).** To 50 ml of dry ether, benzylmethyldi(bromomagnesiumethynyl)-silane prepared from 1 g of Mg, 4.4 g of EtBr and 3.68 g of benzylmethyl(diethynyl)silane in 75 ml of THF and, simultaneously, 2.6 g of dimethyldichlorosilane in 50 ml of ether were added dropwise with stirring. After mixing for 1 h the mixture was decomposed with water and 5% HCl. Aqueous layer was separated in a separating funnel and thrice extracted with ether in portions of 30 ml. The ether extracts were combined with the main organic layer and dried over calcinated $CaCl_2$. The dryer was filtered off, twice washed with dry ether in portions of 30 ml, and the solvent was distilled off under reduced pressure (water-jet pump). From the residue, 1.06 g (11%) of compound **I** was isolated by sublimation in a high vacuum ($10^{-3}$ mm Hg) (Table 1).

**Benzyltris[tris(trimethylsilylethynyl)silylvinyl]-silane (II).** To 1.94 g of benzyl(triethynyl)silane and 0.1 ml of 0.2 N solution of $H_2PtCl_6$ 4.06 g of trichlorosilane was added dropwise at stirring. The mixture was kept for 1 h at 90°C, then cooled and the Iotsitch reagent prepared from 2.4 g of Mg, 10.9 g of EtBr and 9.8 g of trimethylethynylsilane in 100 ml of THF was added dropwise. After heating to 45°C during 30 min the mixture was decomposed with water and 5% HCl. Further treatment was similar to that described above. After removal of solvents 3.4 g (30%) of compound **II** was isolated by crystallization from hot hexane.

## ACKNOWLEDGMENTS

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