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LETTERS TO THE EDITOR

New Bis[diethynyl(hydrocarbyl)silyl]acetylenes

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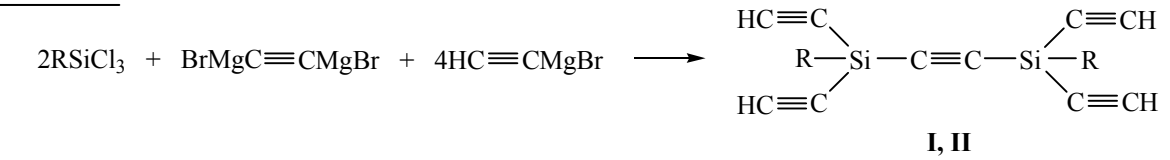
In the course of our studies in the field of unsaturated organosilicon compounds we have synthesized a series of ethynylsilanes possessing several terminal ethynyl groups, such as derivatives of dimethylethynylsilane [1], Si-di- and triethynyl-substituted disilylacetylenes [2–5], mono-, di- and triethynylsilanes with cyclic groups at the silicon atom [6–8], 2- and 3-aryl(propyl)(ethynyl)dimethylsilanes [9], 1,1-diethynylsilacycloalkanes [10], C- and Si-substituted benzyl(ethynyl)silanes [11]. These compounds were shown to be promising synthones in organic and organoelemental synthesis. Thus, diethynyl derivatives of silicon are starting monomers in the synthesis of polyunsaturated macromolecular and macrocyclic organoelemental hydrocarbons [4–6, 10, 12–14]. Mono-, di-, and triethynylsilyl derivatives were used for the preparation of various mono- and binuclear dendrimers [15–19].

Developing these studies, we have investigated the reaction of mono- and bis(bromomagnesium)acetylenes with halosilanes and prepared new Si-substituted disilylacetylenes. The reaction of (hydrocarbyl)trichlorosilanes with bis(bromomagnesium)acetylene and (bromomagnesium)acetylenes in the molar ratio 2:1:4 in THF affords bis[diethynyl(hydrocarbyl)silyl] (**I**, **II**).



I, II

R = Me (**I**), CH=CH$_2$ (**II**).

Similarly proceeds the reaction of tetrachlorosilane with mono- and bis(bromomagnesium)acetylene (molar ratio 2:1:6) with the formation of bis(triethynylsilyl)-acetylene (**III**). In all cases a considerable amount of polyunsaturated polymer products of intractable structure was formed.

III

Note that product **III** has seven closely located triple bonds and thus is highly energetic compound.

Disilylacetylenes **I–III** are colorless fine-crystalline compounds, soluble in organic solvents, stable at storage in the absence of air. Their structure was proved by the ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy and confirmed by elemental analysis.

Compounds **I–III** possess four or six terminal reactive ethynyl groups at the silicon atom and can be used for further reactions of addition, intermolecular reactions of condensation and polymerization, as well as for preparation of various organometallic compounds. Terminal ethynyl groups can act as predecessors of dendrite chains in the synthesis of binuclear polyunsaturated organosilicon dendrimers.

Bis[diethynyl(methyl)silyl]acetylene (I). To 10.8 g of methyltrichlorosilane a mixture of bromomagnesium-acetylene and bis(bromomagnesium)acetylene prepared from 7.2 g of Mg, 32.7 g of EtBr, and acetylene in 300 ml of freshly distilled THF was added dropwise. After heating to 45°C for 90 min the reaction mixture was cooled and decomposed with water and 5% HCl. The aqueous layer was separated, extracted with ether (3×30 ml), ethereal extracts were combined with the main organic layer, dried over $CaCl_2$, filtered, washed with anhydrous ether (2×30 ml), solvents were removed under reduced pressure. The crystals formed were crystallized from hexane. Yield 3.16 g (30%), mp 112°C. ^{1}H NMR, δ, ppm: 0.53 (CH_3); 2.56 (≡CH). ^{13}C NMR, δ_C, ppm: –2.51 (CH_3); 82.58 (–C≡), 95.64 (≡CH), 107.78 (C≡C). ^{29}Si NMR, δ_{Si}, ppm: –65.66. Found, %: C 68.15; H 4.80; Si 26.73. $C_{12}H_{10}Si_2$. Calculated, %: C 68.50; H 4.79; Si 26.70.

Bis[diethynyl(vinyl)silyl]acetylene (II). Yield 2.94 g (25%), mp 63–65°C. ^{1}H NMR, d, ppm: 2.45 (≡CH); 5.99 d.d (SiCH=, J^{cis} 13.5, J^{transc} 20.2 Hz), 6.04, 6.13 d.d (=CH_2, J^{gem} 3.4 Hz). ^{13}C NMR, δ_C, ppm: 82.63 (–C≡), 97.66 (≡CH), 108.56 (C≡C);130.05 (SiCH=), 136.84 (=CH_2). ^{29}Si NMR, δ_{Si}, ppm: –73.05. Found, %: C 70.04; H 4.51; Si 23.27. $C_{14}H_{10}Si_2$. Calculated, %: C 71.73; H 4.30; Si 23.97.

Bis(triethynylsilyl)acetylene (III). Yield 2.54 g (22%), mp 163–165°C. ^{1}H NMR, d, ppm: 2.48 (≡CH). ^{13}C NMR, δ_C, ppm: 80.95 (–C≡), 93.12 (≡CH), 94.67 (C≡C). ^{29}Si NMR, δ_{Si}, ppm: –85.78. Found, %: C 72.34; H 3.29; Si 23.89. $C_{14}H_6Si_2$. Calculated, %: C 73.05; H 2.63; Si 24.32.

^{1}H, ^{13}C, and ^{29}Si NMR spectra of 20 % $CDCl_3$ solutions were registered on a Bruker DPX 400 spectrometer at working frequencies 400.13 (^{1}H), 100.61 (^{13}C), and 79.46 MHz (^{29}Si), internal reference HMDS. Melting points were measured on a Koeffler heating block. All solvents were thoroughly dried**.**

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