ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 12, pp. 2520–2521. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © L.V. Zhilitskaya, N.O. Yarosh, M.G. Voronkov, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 12, pp. 2067–2068.

LETTERS TO THE EDITOR

1,1,4,4,7,7,10,10-Octamethyl-2,3-dibromo-1,4,7,10-tetrasilacyclododeca-5,8,11-triyne

L. V. Zhilitskaya, N. O. Yarosh, and M. G. Voronkov

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: lara zhilitskaya@irioch.irk.ru

Received April 5, 2011

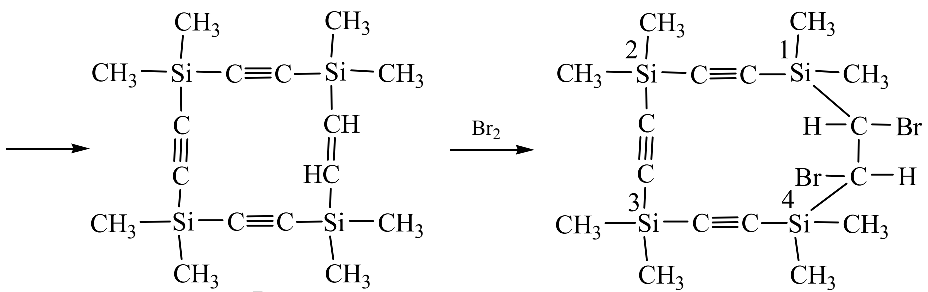
DOI: 10.1134/S1070363211120188

We have lately first synthesized two new classes of polyunsaturated macrocyclic silahydrocarbons, polydiorganylsilethynes $(R_2SiC{\equiv}C)_n$ [1–5] and polydimethylsilethenes $(Me_2SiCH{=}CH)_n$ [3, 6], as well as their hybrids containing both the double and triple bonds in the macrocycle [3, 7, 8]. In continuation of these studies we investigated the reaction of bromine addition to the endocyclic double bond of the macrocyclic skeleton of 1,4,7,10-tetrasilacyclododeca-2-ene-5,8,11-triyne (**I**) and obtained the corresponding dibromide in 43% yield.

1,1,4,4,7,7,10,10-Octamethyl-2,3-dibromo-1,4,7,10-tetrasilacyclododeca-5,8,11-triyne (**II**) is a colorless fine crystalline substance of mp 150°C, soluble in organic solvents, stable to storage in the absence of contact with atmospheric air. The formation of the obtained dibromide is the first example of the addition reaction to polyunsaturated macrocyclic silahydrocarbons [1–8], which are the subject of our systematic investigations.

In the ^{1}H NMR spectrum of dibromide **II** two doublets (δ 3.75 and 4.32 ppm, J_{HH} 10.15 Hz) corresponding to protons at the sp^3-hybridized endocyclic carbon atoms are present. Apparently, violation of symmetry of the molecule of macrocycle **II** as compared to the starting compound **I** results in splitting of the signals and complication of the spectrum [9]. Thus, the proton chemical shifts of the methyl groups at the silicon atoms are determined by the nature of the adjacent endocyclic bonds and are equal to δ (ppm): 0.55, 0.54, 0.50, 0.47, 0.40, 0.35, with total intensity of 24 protons, which corresponds to the total number of protons of the methyl groups. A similar picture is observed in the ^{13}C NMR spectrum. The chemical shifts of the C-atoms of the methyl groups are shifted upfield, δ_C, ppm: 1.05, 0.98, –0.67, –0.72, –1.04, –2.18. The chemical shifts of the sp^3-hybridized endocyclic carbon atoms correspond to two signals with δ_C 40.75 and 40.47 ppm, and the sp-hybridized carbon atoms are characterized by a set of downfield signals, δ_C, ppm: 115.55, 114.77, 113.62, 113.62, 112.33, 110.50). The ^{29}Si chemical shifts are determined by the nature of both the endo- and exocyclic substituents and contain four signals

$BrMgC{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CMgBr + FMe_2SiCH{=}CHSiMe_2F$



I **II**

corresponding to all silicon atoms in the molecule (δ_{Si}, ppm): Si^{2,3} –40.92, –41.33, and Si^{1,4} –12.27, –16.09.

1,1,4,4,7,7,10,10-Octamethyl-2,3-dibromo-1,4,7,10-tetrasilacyclododeca-5,8,11-triine (II). To the solution of 0.33 g (1 mmol) of compound **I** in 50 ml of dichloromethane the solution of 0.16 g (1 mmol) of bromine in 2 ml of dichloromethane was added dropwise at vigorous stirring and cooling to –5°C (acetone with dry ice). The solvents were removed in a vacuum and the residue was crystallized from hexane to give 0.21 g (43%) of compound **II**, mp 150°C. Mass spectrum: *m/z* 490 [M^+]. Found, %: C 40.30; H 5.28; Br 31.29; Si 23.54. $C_{16}H_{26}Si_4Br_2$. Calculated, %: C 39.17; H 5.34; Br 32.58; Si 22.91. (*M* 490).

NMR spectra were registered on a Bruker DRX-400 spectrometer (400 MHz) from 15% solutions in $CDCl_3$ with HMDS as an internal reference. Mass spectrum was obtained on an LKB-2091 chromato-mass spectrometer with direct probe anmission, ionizing voltage 60 eV, the temperature of the source 250°C.

REFERENCES

1. Voronkov, M.G. and Pavlov, S.F., *Zh. Obshch. Khim.,* 1973, vol. 43, no. 6, p. 1408.
2. Voronkov, M., Yarosh, O., and Zhilitskaja, L., *Phosphorus, Sulfur, Silicon, Relat. Elem*., 1992, vol. 65, p. 33.
3. Yarosh, O.G., Voronkov, M.G., and Brodskaya, E.I., *Russ. Chem. Rev*., 1995, vol. 64, no. 9, p. 839.
4. Yarosh, O.G., Zhilitskaya, L.V., Yarosh, N.K., Albanov, A.I., Klyba, L.V., and Voronkov, M.G., *Russ. J. Gen. Chem*., 2004, vol. 74, no. 8, p. 1185.
5. Zhilitskaya, L.V., Yarosh, N.O., Yarosh, N.K., and Voronkov, M.G., *Russ. J. Gen. Chem*., 2009, vol. 79, no. 3, p. 383.
6. Voronkov, M.G., Yarosh, O.G., and Turkina, G.Yu., *J. Organomet. Chem*., 1995, vol. 491, no. 1, p. 215.
7. Yarosh, O.G., Zhilitskaya, L.V., Yarosh, N.K., Istomina, E.E., Albanov, A.I., Chivashev, Yu.A., and Voronkov, M.G., *Russ. J. Gen. Chem*., 2004, vol. 74, no. 10, p. 1492.
8. Yarosh, O.G., Zhilitskaya, L.V., Istomina, E.E., Yarosh, N.K., Albanov, A.I., and Voronkov, M.G., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 7, p. 1094.
9. Gunther, H., *NMR Spectroscopy: An Introduction*, Chichester: John Wiley & Sons, 1980.