ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 4, pp. 669–671. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © Yu.V. Khoroshavina, G.A. Nikolaev, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 4, pp. 576–578.

Methyldichlorosilanes with Fluorinated Cyclic Substituents at Silicon

Yu. V. Khoroshavina and G. A. Nikolaev

Federal State Unitary Enterprise "Lebedev Research Institute of Synthetic Rubber,"
ul. Gapsal'skaya 1, St. Petersburg, 198035 Russia
e-mail: julhor@yandex.ru

Received August 12, 2010

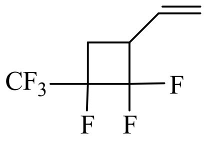
Abstract—Methyldichlorosilanes with fluorinated cyclic substituents at silicon are prepared by the reaction of hydrosilylation of the corresponding hexafluoroolefins with methyldichlorosilane.

DOI: 10.1134/S1070363211040086

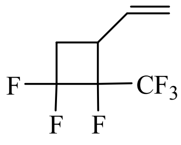
Fluorosiloxane rubbers are efficient in a wide temperature range from –60 to 250°C, they are characterized by high resistance to oils, fuels, greases, aliphatic, aromatic, and chlorinated hydrocarbons and are demanded in many fields of industry.

Polymethyl(hexafluoroalkyl)siloxane rubbers should substitute both the imported and domestic polymethyl (3,3,3-trifluoropropyl)siloxane rubbers [1–3]. The synthesis of the key monomers for production of fluorosiloxane rubbers: 2-(2,3,3-trifluoro-2-trifluoromethylcyclobutyl)ethylmethyldichlorosilane, 2-(2,2,3-trifluoro-3-trifluoromethylcyclobutyl)ethylmethyldichlorosilane, 2,2,3-trifluoro-3-trifluoromethyl-5-(dichloromethylsilyl)bicyclo[2.2.1]heptane, 2,3,3-trifluoro-2-trifluoromethyl-5-(dichloromethylsilyl)bicyclo[2.2.1]-heptane is based on the reaction of hydrosilylation of hexafluoroolefins with methyldichlorosilane.

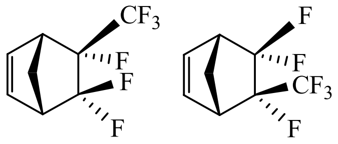
Recently we described the addition of hexafluoropropene to butadiene and cyclopentadiene proceeding as [2+2]-cycloaddition to butadiene and as [2+4]-cycloaddition to cyclopentadiene [4]. In the present work the obtained products, the mixture of the isomers 1-vinyl-2,3,3-trifluoro-2-trifluoromethylcyclobutane (**I**) and 1-vinyl-2,2,3-trifluoro-3-trifluoromethylcyclobutane (**II**), as well as the (exo/endo)-5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]heptene-2 (**III**) are investigated in the reaction of hydrosilylation with methyldichlorosilane in the presence of the Speier catalyst [5–9].



I

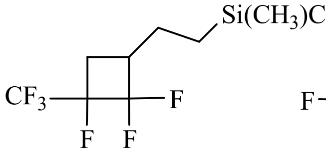


II

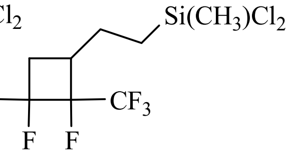


III

Hydrosilylation of the mixture of 1-vinylcyclobutanes **I** and **II** with methyldichlorosilane results in a mixture of isomers, 2-(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylmethyl-dichlorosilane (**IV**) and 2-(3-trifluoromethyl-2,2,3-trifluorocyclobutyl)ethylmethyldichlorosilane (**V**), which was further used without separation.



IV

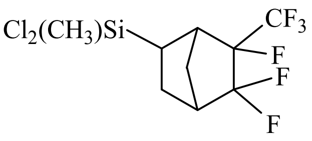


V

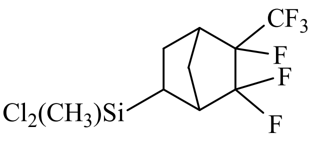
The investigation of the dependence of the product yield and the time of the reaction on the catalyst concentration has shown that its increase does not lead to the increase in the product yield or faster completion of the reaction, but at lower concentrations the degree of conversion of the olefin drops. Neither the protracted reflux increased the yield of the product. The data of the ^{1}H, ^{19}F, and ^{29}Si NMR spectroscopy confirm the formation of chlorosilanes **IV** and **V**.

The analysis of the ^1H NMR spectra shows that the addition of methyldichlorosilane proceeds by the Farmer rule. As compared with the spectra of the starting 1-vinylcyclobutanes **I** and **II** a signal at 0.44 ppm belonging to the SiMe group appears and two complex multiplets at 0.64 and 1.38 ppm belonging, respectively, to α- and β-protons of the $-CH_2CH_2-$ fragment. The signals of the protons of the cyclobutane ring at C^1 and C^4 are shifted upfield. The ^{19}F NMR spectrum does not differ from the spectra of the starting compounds, the geminal coupling constants also remain unchanged, thus proving the retention of the cyclobutane ring. In the ^{29}Si NMR spectrum the signals at 31.06 ppm for **IV** and 30.89 ppm for **V** appear, which are typical for dichlorosilanes with fluorinated substituents [10].

Because of low reactivity of bicyclic olefins [11], their hydrosilylation was performed with protracted reflux of the mixture of methyldichlorosilane, olefin, and catalyst, new portions of which were periodically added. The mixture of isomers: 2,2,3-trifluoro-3-trifluoromethyl-5-(methyldichlorosilyl)bicyclo[2.2.1]-heptane (**VI**) and 2,3,3-trifluoro-2-trifluoromethyl-5-(methyldichlorosilyl)bicyclo[2.2.1]heptane (**VII**) was obtained.

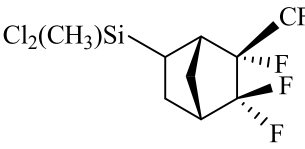


VI

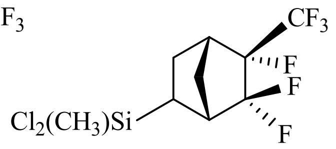


VII

The structure and composition of the obtained compounds were proved by the ^1H, ^{19}F, and ^{29}Si NMR spectra. The analysis of the ^{19}F NMR spectra proves the retention of the bicyclic substituent, although many authors mention that hydrosilylation of bicyclenes is often followed by isomerization, dimerization, or opening of one of the rings [7]. In the ^{19}F NMR spectrum the sets of signals from four different bicyclo [2.2.1]heptanes can be distinguished, since the addition of methyldichlorosilane can occur at both atoms of the C=C double bond C^2 and C^3 of the *exo*- and *endo*-isomers. The analysis of the intensity ratio of these sets of signals shows that in the *exo*-isomer the addition occurs to both atoms and the isomers **VIa** and **VIIa** are formed in 1:1 ratio.

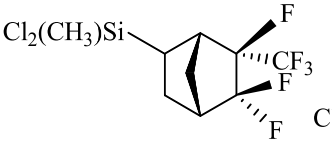


VIa

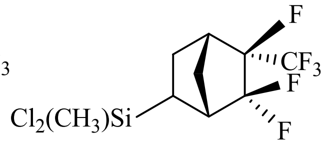


VIIa

The analysis of the spectrum of the endo-isomer shows that the addition occurs almost completely to one of the atoms of the double bond. Two possible isomers **VIb** and **VIIb** are formed in the ratio of 95:5.



VIb



VIIb

From the reasoning of steric availability of the carbon atoms and preferable *endo*-addition of the silyl group [7] it can be assumed that isomer **VIIb** is formed predominantly, that is, the addition of the bulky dichloromethyl group goes to the most sterically accessible carbon atom, whereas isomer **VIb** is the minor one.

Hydrosilylation of the mixture of 1-vinyl-2,3,3-trifluoro-2-trifluoromethylcyclobutane and 1-vinyl-2,2,3-trifluoro-3-trifluoromethylcyclobutane with methyldichlorosilane in the presence of the Speier catalyst follows the Farmer rule and leads to the mixture of 2-(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylmethyldichlorosilane and 2-(3-trifluoromethyl-2,2,3-trifluorocyclobutyl)ethylmethyldichlorosilane. Addition of methyldichlorosilane to 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]heptene-2 gives the mixture of 2,2,3-trifluoro-3-(*exo/endo*)trifluoromethyl-5-methyldichlorosilylbicyclo-[2.2.1]heptane and 2,3,3-trifluoro-2-(*exo/endo*)trifluoromethyl-5-methyldichlorosilylbicyclo-[2.2.1]heptane. Hydrosilylation of 5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]heptene-2 proceeds very slowly due to both the inductive effect of the fluorine atom and the location of the double bond in the interior of the rigid bicyclic framework structure.

EXPERIMENTAL

^1H, ^{19}F, and ^{29}Si NMR spectra were registered on a Bruker Spectrospin AM-500 spectrometer at working frequencies 500, 470.6, and 100 MHz using TMS and hexafluorobenzene as internal standards, solvents $CDCl_3$ and $(CD_3)_2CO$.

2-(2-Trifluoromethyl-2,3,3-trifluorocyclobutyl)-ethylmethyldichlorosilane (IV) and 2-(3-trifluoromethyl-2,2,3-trifluorocyclobutyl)ethylmethyldichlorosilane (V). A three-neck flask of 0.5 l capacity equipped with a mechanical stirrer, a dropping funnel, and a condenser was charged with 81 ml (89.4 g, 0.78 mol) of methyldichlorosilane, 1.5 ml of the Speier catalyst and the reaction mixture was refluxed for 2 h, then during 1 h 106.3 ml (142.8 g, 0.7 mol) of the mixture of 1-vinylcyclobutanes was added. After the completion of addition the reaction mixture was kept for 2 h at 150°C. By distillation 212 g (90%) of the mixture of 2-(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylmethyldichlorosilane (**IV**) and 2-(3-trifluoromethyl-2,2,3-trifluorocyclobutyl)ethylmethyldichlorosilane (**V**) was obtained. bp 55°C (2 mm Hg); n_D^{20} 1.4039; d_{20}^{20} 1.3573. Found, %: C 30.12; H 3.10; Cl 22.13; F 35.70; Si 9.05. $C_8H_{10}Cl_2F_6Si$. Calculated, %: C 30.25; H 3.01; Cl 22.10; F 35.60; Si 9.05. ^{1}H NMR spectrum (**IV** + **V**): 0.44 (3H, $SiCH_3$); 0.64 (2H, 1-CH_2); 1.38 (2H, 2-CH_2); 1.65 (1H, 1'-CH); 2.15 (2H, 4'-CH_2). ^{19}F NMR spectrum (**IV**): –78.58 (3F, 2-CF_3); AB quartet δ_A –103.66, δ_B –106.52, J_{AB} = 229 Hz, (2F, 3-CF_2); –193.53 (1F, 2-CF). ^{19}F NMR spectrum (**V**): –73.88 (3F, 3-CF_3); AB quartet δ_A –100.12, δ_B –116.58, J_{AB} = 225 Hz, (2F, 2-CF_2); –170.47 (1F, 3-CF). ^{29}Si NMR spectrum (**IV**): 31.06. ^{29}Si NMR spectrum (**V**): 30.89.

2,2,3-Trifluoro-3-trifluoromethyl-5-methyldichlorosilylbicyclo[2.2.1]heptane (VI) and 2,3,3-trifluoro-2-trifluoromethyl-5-methyldichlorosilylbicyclo[2.2.1]-heptane (VII). A three-neck flask of 0.5 l capacity equipped with a mechanical stirrer, a dropping funnel, and a condenser was charged with 94 ml (104 g, 0.9 mol) of methyldichlorosilane, 1.5 ml of the Speier catalyst, 110 ml (155 g, 0.72 mol) of 5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]heptene-2 (**III**) and the mixture was refluxed for 24 h, adding the new portion of the catalyst after each 8 hours. The reaction was monitored by GLC, the heating was stopped after 80% conversion of the olefin. By distillation 215 g (75%) of the mixture of 2,2,3-trifluoro-3-trifluoromethyl-5-methyldichlorosilylbicyclo[2.2.1]-heptane (**VI**) and 2,3,3-trifluoro-2-trifluoromethyl-5-methyldichlorosilylbicyclo[2.2.1]heptane (**VII**) was isolated. bp 65°C (2 mm Hg); n_D^{20} 1.4286; d_{20}^{20} 1.4497. Found, %: C 32.49, 32.40; H 3.02, 2,89; Cl 21.15, 21.13; F 34.74, 34.65; Si 8.79, 8.75. $C_9H_{10}Cl_2F_6Si$. Calculated, %: C 32.39; H 2.98; Cl 32.39; F 34.76; Si 8.65. ^{1}H NMR spectrum (**VI** + **VII**): 0.31(3H, Si-CH_3); 1.23 (1H, 5-CH); 1.41(1H, 6-CH *endo*); 1.44 (1H, 6-CH *exo*), J_{gem} = 6.22 Hz; 1.66 (1H, 7-CH *syn*); 1.81 (1H, 7-CH *anti*); 2.40–2.41 (2H, 4-CH and 1-CH). ^{19}F NMR spectrum (**VI** + **VII**): –68.17, –70.44, –71.77, –72.77 (CF_3); 3AB quartets δ_A –108.18, δ_B –118.14, J_{AB} = 235.5 Hz, δ_A –107.26, δ_B –113.26, J_{AB} = 260 Hz, δ_A –108.61, δ_B –117.65, J_{AB} = 250 Hz, (CF_2); –165.3, –170.06, –175.2, –176.9 (CF). ^{29}Si NMR spectrum (**VI** + **VII**): 29.38; 29.69; 29.93; 30.08.

ACKNOWLEDGMENTS

This work was performed with the financial support from the Federal Agency on Science and innovations, FSP no. 02.523.12.3025.

REFERENCES

1. Khoroshavina, Yu.V., Nikolaev, G.A., Lobkov, V.D., and Kormer, V.A., RF Patent no. 2 089 554, 1997.
2. Khoroshavina, Yu.V., Nikolaev, G.A., Lobkov, V.D., and Kormer, V.A., RF Patent no. 2 078 097, 1997.
3. Khoroshavina, Yu.V., Nikolaev, G.A., Lobkov, V.D., and Kormer, V.A., RF Patent no. 2 101 286, 1997.
4. Khoroshavina, Yu.V., Nikolaev, G.A., and Emel'yanov, G.A., Zh. Obshch. Khim., 2010, vol. 80, no. 11, p. 1846.
5. Ojima, I., Li, Z., and Zhu, J., *The Chemistry of Organic Silicon Compounds*, Chichester: Wiley, 1998, vol. 2.
6. Marciniec, B., *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd compl. revised and enlarged ed., Weinheim: Wiley-VCH, 2002, vol. 1.
7. Yur'ev, V.P. and Salimgareeva, I.M., *Reaktsii gidrosililirovanija olefinov* (Reactions of Hydrosilation of Olefines), Moscow: Nauka, 1982.
8. Ojima, I., *The Chemistry of Organic Silicon Compounds*, Chichester: Wiley, 1989, vol. 1.
9. Speier, J.L., Webster, J.A., and Barnes, G.H., *J. Am. Chem. Soc.*, 1957, vol. 79, p. 974
10. Boutevin, B., Pietrasanta, Y., and Youseff, B., *J. Fluorine Chem.*, 1986, vol. 31, p. 57.
11. Jurjev, V.P., Salimgareeva, I.M., and Kaverin, V.V., *J. Organomet. Chem.*, 1979, vol. 171, no. 2, p. 167.