

Received: November 2015

DOI 10.17677/fn20714807.2016.02.01

## A synthesis of a new fluoroorganosilicon compounds containing cyclobutane fragments and study of properties of obtained oligomers

Yarosh A.A., Sakharov A.M., Glazkov A.A.

**N.D. Zelinsky Institute of Organic Chemistry Russian Academy of Science,  
117991, Moscow, Leninsky prospect, 47,  
e-mail: [yar@ioc.ac.ru](mailto:yar@ioc.ac.ru), [as@zelinsky.ru](mailto:as@zelinsky.ru)**

**Abstract:** At interaction of perfluoroalkylvinyl ethers and butadiene there were synthesized a new polyfluorinated compounds - 1-vinyl-2- $\omega$ -cyanoperfluoroalkoxy-2,3,3-trifluorocyclobutanes. It was established that addition of butadiene to perfluoroalkylvinyl ether was going on under "head to head". There were obtained corresponded chlorosilyl derivatives. There were obtained polyfluoroorganosiloxanes at hydrolysis of these chlorosilyl derivatives. There were studied some properties of polyfluoroorganosiloxanes.

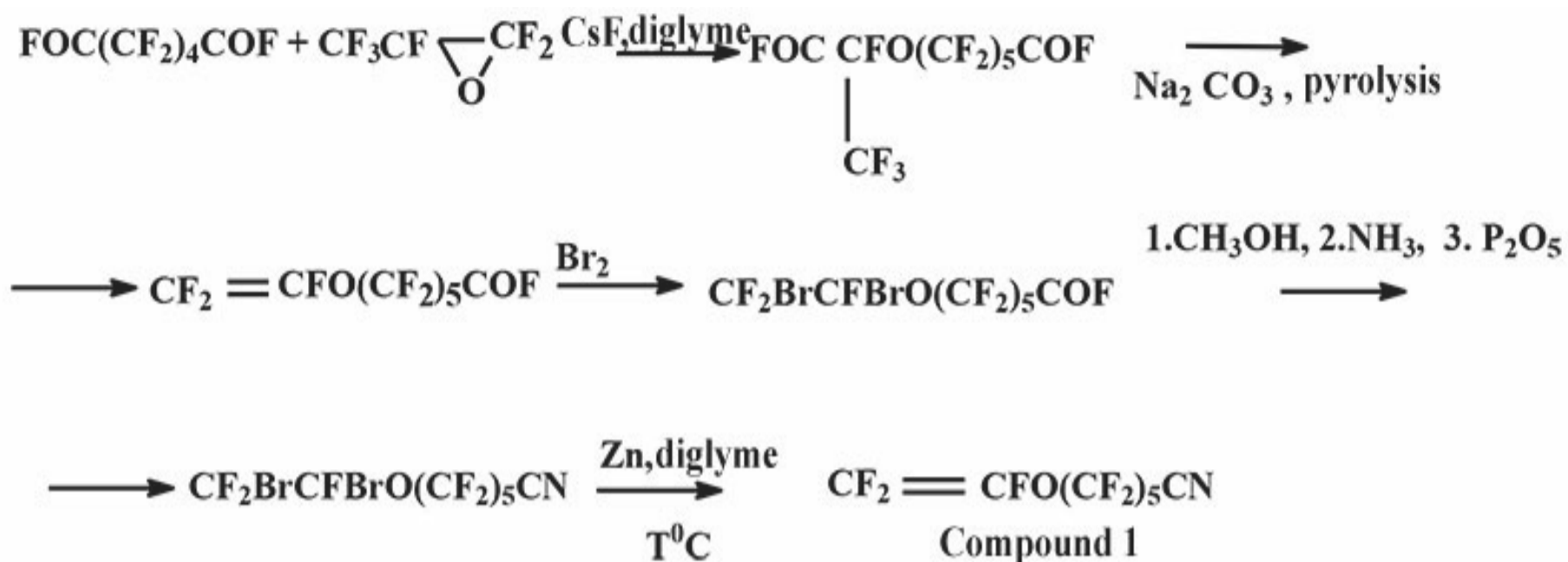
**Keywords:** perfluoroalkyl vinyl ethers, butadiene, cycloaddition, hydrosilylation, polyfluoroorganosiloxane, oligomer properties.

Production of aliphatic polyfluorinated organo-silicon compounds is of a great scientific and applicative interest. The main methods of synthesis of organo-silicon compounds containing fluorine's atom in organic radical were summarized in the monographs of V.A. Ponomarenko and their stuff. [1,2].

This work was devoted to the synthesis of polyfluoroorganosilanes and siloxanes containing nitrile groups. Offered method of synthesis of fluoroorgano silicon compounds supposed two steps: the first one is polyfluorinated cyclobutane derivative production containing multiple bond, the second one is application of well known hydrosilylation reaction of unsaturated compound.

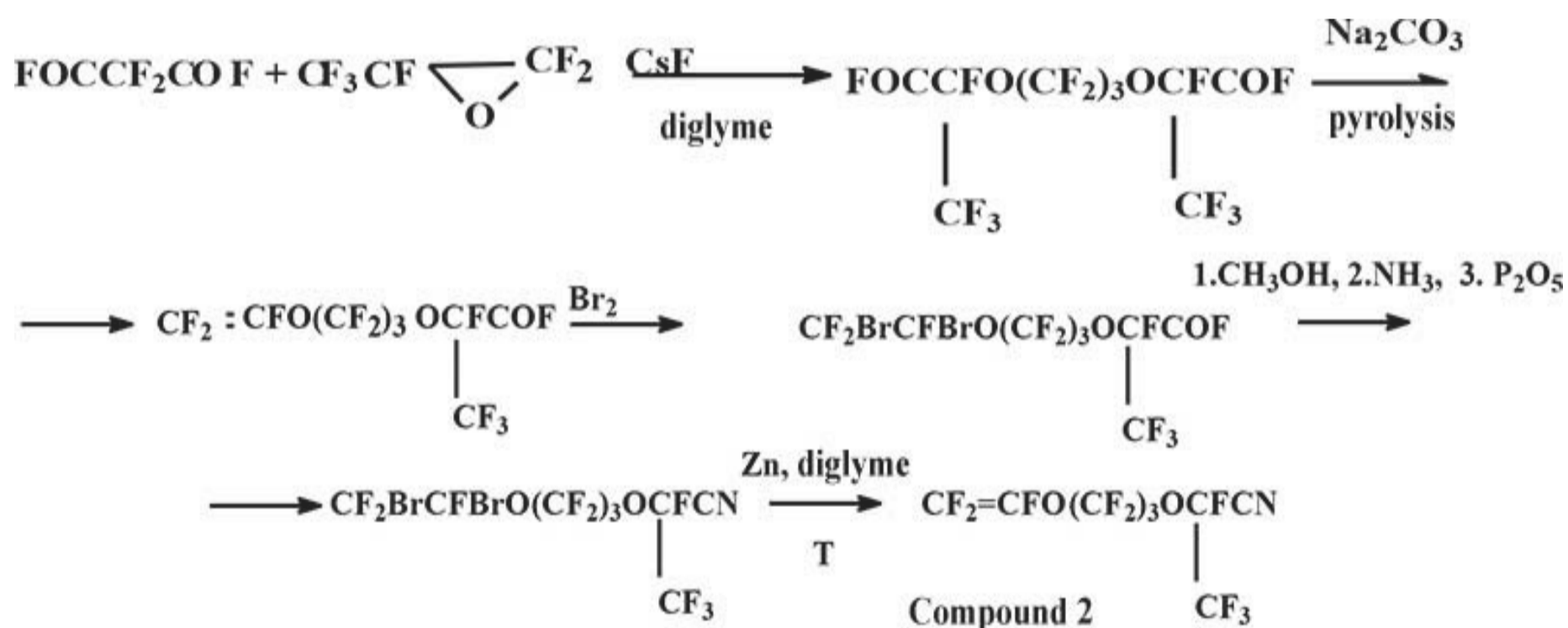
It is known that fluoro-containing alkenes could be added to nonfluorinated unsaturated compounds far easier than dimerized [3,4]. In the reaction of non-fluorinated dienes cycloaddition to fluoroalkenes, namely, to perfluoroalkylvinyl ether (PFAVE), it could be formed not only isomer (addition «head to head» or «head to tail»), but also their stereo isomers. The isolation and exact characterization of forming isomer is essentially complicated when they have a large molecular weight and high boiling point. That is why it seems appropriate to establish the principle of their formation and structure, low molecular weight analogues of these compounds.

In this work PFAVE was used as fluorinated dienes that contained nitrile group. The general method is described in the scheme below 1 [5,6]:



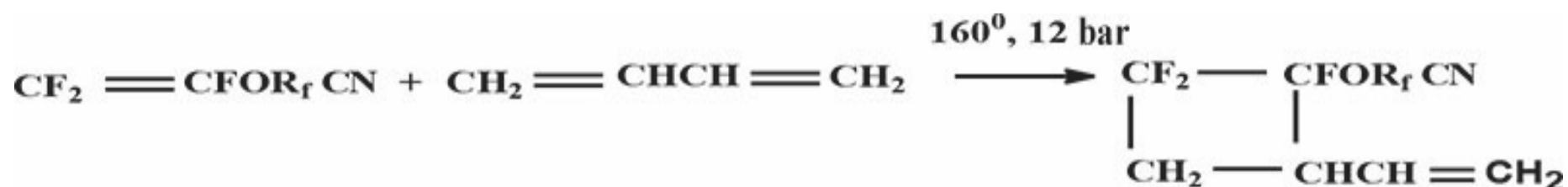
**Scheme 1**

Compound 2 was obtained analogically, scheme 2 [6]:



**Scheme 2**

A cycloaddition of PFAVE to butadiene could be done in two routes: «head to head» or «head to tail». <sup>1</sup>H and <sup>19</sup>F NMR spectra of cyclodimerization products show that it could be realized in experiment conditions, if there would be only one type of addition, namely "head to head" with equal content of *cis*- and *trans*- isomers relatively to the cycle [4] (scheme 3):



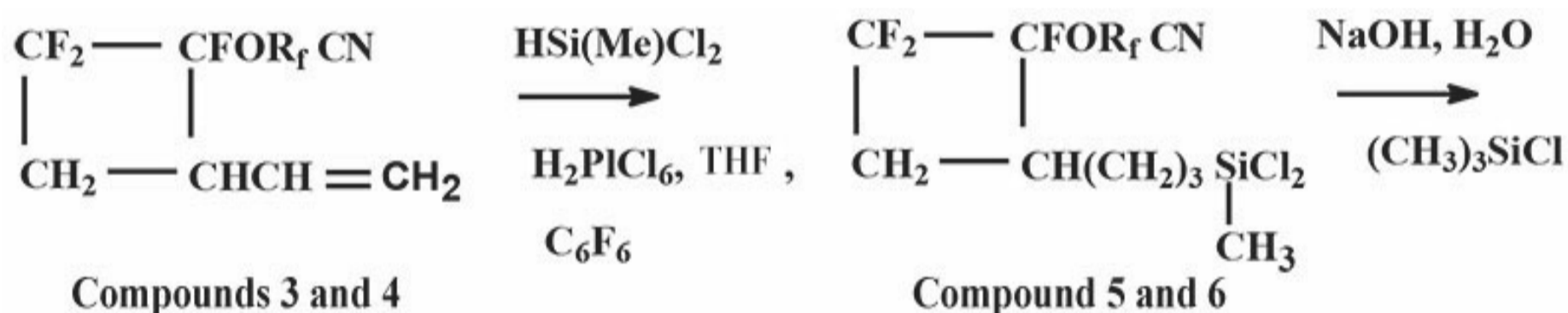
$R_f = -(CF_2)_5$  **Compound 3** ;  $-(CF_2)_3OCF(CF_3)$  **Compound 4**;

### Scheme 3

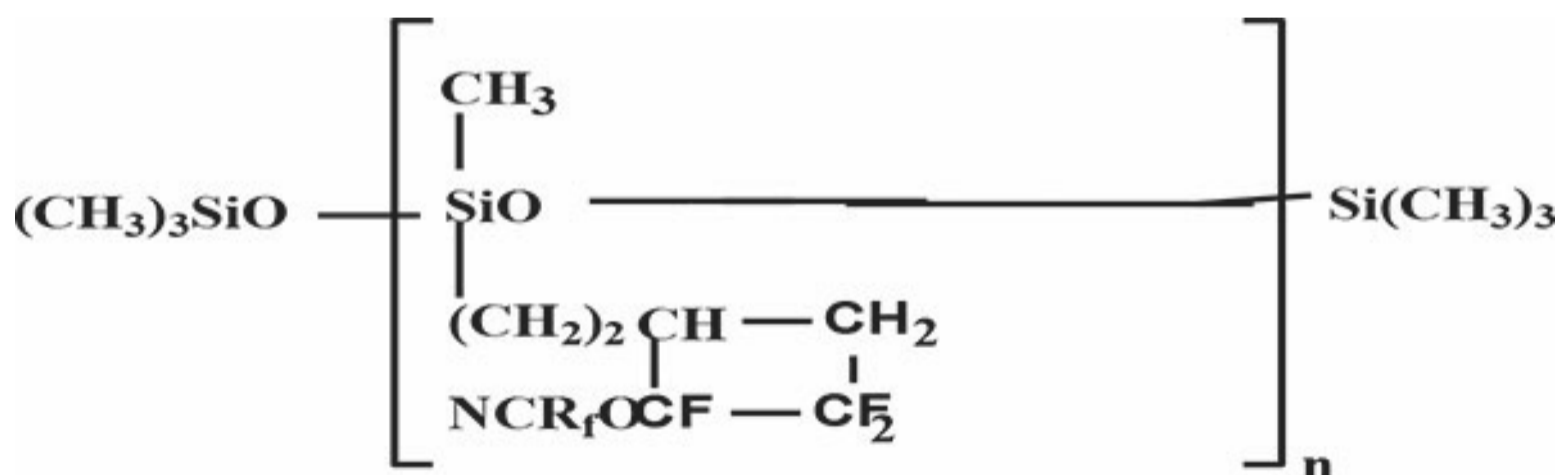
It was carried out the separation of *cis*- and *trans*-isomers -vinyl-2-perfluoropropoxy-2,3,3-trifluorocyclobutane by HPLC (High-performance liquid chromatography) method for accurate assignment of signals in NMR spectra and description of the stereochemical structure of obtained products. As a result, we managed to isolate preparative pure isomers in order to identify their  $^{19}F$  NMR spectra. It was established that the peak with early retention time corresponded to *cis*-isomer, and with late one corresponded to - *trans*-isomer [8].

It is known that electric field's dipole of neighboring bonds has a significant influence on chemical shift of  $^{19}F$  nucleus across the space, for example, so-called «*ortho*-effect» in fluorobenzenes. The size of this effect depends upon interatomic distance: as smaller interatomic distance between  $^1H$  and  $^{19}F$ , resonance atoms  $^{19}F$  is observed in weak field [9]. Based on it, the signals in the field -120 ppm could be referred to fluorine atom of -CF- group in *cis*-isomer, and the signals in the field -140 ppm could be referred to the same group in *trans*-isomer.

As a result of hydrosilylation of compounds 3 and 4 there were obtained corresponded dichlorosilanes and oligosiloxanes (scheme 4):



$R_f$  is mentioned above in Scheme 3



### Scheme 4

As a result of hydrolysis of methylchlorosilane derivatives there were synthesized oligomers with terminal silanol groups. The stabilization of last ones by trimethylchlorosilane gives a rise to oligomer formation with molecular weight 4500-5000 (ebullioscopy in  $C_6F_6$ ). The temperature of such oligomers consists of 260°C at 10% loss of weight, it is a result of dehydrofluorination at heating [10].

A reaction control was made by NMR spectroscopy. There were appeared signals in the area (ppm): 3.80 (OCH<sub>2</sub>); 1.02 (SiCH<sub>2</sub>); and 0.76 (SiCH<sub>3</sub>) in Proton magnetic resonance spectroscopy along with conversion increase. In the same time there were disappeared the signals in the area (ppm): 5.30 (=CH<sub>2</sub>) and 5.87 (=CH).

Obtained silanes and siloxanes could be used for creation of different composition on their basis, which one could have potentially useful properties in practice.

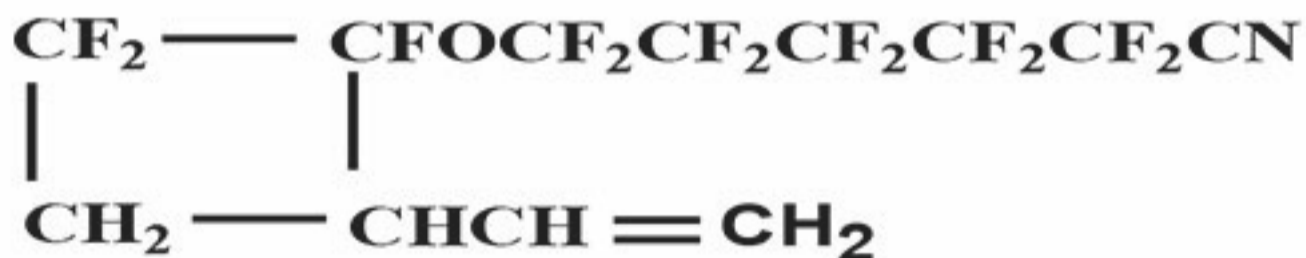
## Experimental

<sup>19</sup>F and <sup>1</sup>H NMR spectra are registered on spectrometer "Bruker WN-250" with frequency 235 (external standard CFC<sub>3</sub>) and 250 MHz (external standard TMS), accordingly. <sup>29</sup>Si spectra were registered on spectrometer «Bruker-AC-200P» with frequency 39.76 MHz (external standard TMS). IR-spectra were registered on spectrometer «Specord IR-75». HPLC was made on liquid chromatographer LC21CP «Bruker», equipped with refractometric detector on semi-preparative silicagel column IBM (10.0x250x5), eluent – hexane, 2 ml/min. GLC-analysis was made on chromatographer LHM-8MD (column 1000x3,5 mm, carrier Chromatone 0.160-0.200 mm, treated by 5% Silicon SE-30). A starting chlorosilanes were supplied by Acros Organics, (purity not less than 96%). A catalyst was made under the following method: 1 g of H<sub>2</sub>PCl<sub>6</sub>·xH<sub>2</sub>O was loaded into flask containing 100 ml of THF, preliminary distilled under CaH<sub>2</sub>, and obtained solution was kept in closed flask at room temperature within 168 hours.

A synthesis of compound 1 is described in [4]. The compound 2 was obtained by debromination in the presence of Zn-dust and metal iodine in diglime, similar to method [6]. Yield 87%, b.p.=105°C.

### General method for fluorocyclobutanes preparation 3 and 4:

0.05 mole of PFAVE and 0.05-0.006 mole of butadiene were loaded into steel autoclave with volume 50 ml. An autoclave was heated up to 120° and kept at this temperature within 6-8 hours. In addition autogenic pressure was increased to 10-12 atm. After cooling and pressure releasing the content of autoclave was purified by rectification. The yield of compounds 3 and 4 consisted of 70-75%.



### Compound 3

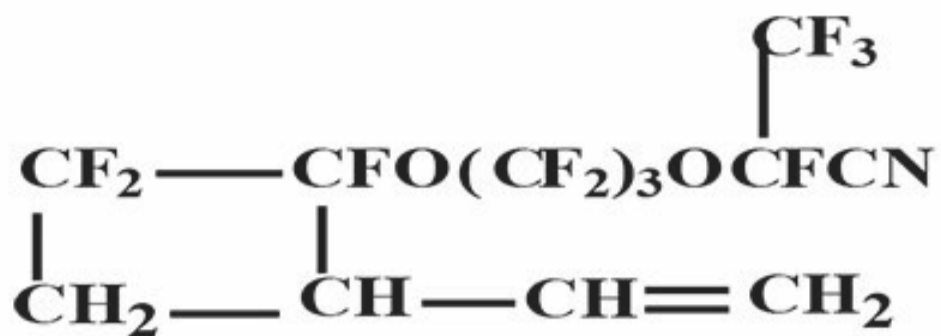
B.p.=71°C/10 torr. Elemental analysis: found, %: C 33.77; H 1.61; F 57.01. Calculated for C<sub>12</sub>H<sub>6</sub>F<sub>13</sub>NO, %: C 33.72; H 1.40; F 57.84.

<sup>1</sup>H NMR spectroscopy (δ, ppm): 5.80 m (1H CH=); 5.30 m (2H =CH); 3.30 m (1H CH in the cycle); 2.80 m and 2.45 m (2H CH<sub>2</sub> in the cycle).

<sup>19</sup>F NMR spectrum (δ, ppm): two AB-spectra: δ<sub>A</sub> -77.7, δ<sub>B</sub> -85.9, J<sub>AB</sub>= 152 Hz; δ<sub>A</sub> -80.1; δ<sub>B</sub> -84.9; J<sub>AB</sub>= 148 Hz; (2F OCF<sub>2</sub> *cis*- and *trans*-isomers); two AB-spectra: δ<sub>A</sub> -107.5, δ<sub>B</sub> -110.0, J<sub>AB</sub>= 208 Hz; δ<sub>A</sub> -108.2; δ<sub>B</sub> -212; J<sub>AB</sub>= 148 Hz; (2F CF<sub>2</sub> in the cycle, *cis*- and *trans*-

isomers); -105.3 m (2F CF<sub>2</sub>CN); -121.4 m (2F CF<sub>2</sub>CF<sub>2</sub>CN); -122.2-125.3 m (4 F -CF<sub>2</sub>CF<sub>2</sub>-); -121.0 m (*cis*); -138.9 m (*trans*) (1F CF-O).

IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2260 (CN).



**Compound 4**

B.p.=80°C/16 torr. Elemental analysis: found, %: C 32.61; H 1.57; F 55.37. Calculated for C<sub>12</sub>H<sub>6</sub>F<sub>13</sub>NO<sub>2</sub>, %: C 32,52; H 1,36; F 55,34.

<sup>1</sup>H NMR spectroscopy ( $\delta$ , ppm): 5.80 m (1H CH=); 5.30 m (2H =CH); 3.30 m (1H CH in the cycle); 2.80 m and 2.45 m (2H CH<sub>2</sub> in the cycle).

<sup>19</sup>F NMR spectrum ( $\delta$ , ppm): -78.1;78.9;81.5;82.0 (OCF<sub>2</sub>); 83.1 (CF<sub>3</sub>); 105.2; 109.2; 114.4; 118.0 (CF<sub>2</sub> in the cycle); 120.0 141.3 (CF in the cycle, *cis*- and *trans*); 115.0 CF-CN); 128.6 128.9 (CF<sub>2</sub>CF<sub>2</sub>). IR-spectrum,  $\nu$ , cm<sup>-1</sup>: 2260 (CN).

#### **Hydrosilylation of fluoro-containing cyclobutane by methyldichlorosilane.**

Into a four-neck flask equipped with stirring, dropping funnel, thermometer and reflux condenser was loaded 15.76 g (0.0355 mol) vinylcyclobutane 3. A flask was blown by argon. 0.5 ml 0.1N solution of H<sub>2</sub>PICl<sub>6</sub> in THF was added. Than 8.2 g (0.071 mol) of methyldichlorosilane was added at rapid mixing. The content of flask was heated to 60°C and kept within 2 hours. A reaction products were fractionated. It was obtained 16.1 g (80.8%) of compound 5. B.p.=90-91°C/1torr.

<sup>1</sup>H NMR spectroscopy ( $\delta$ , ppm.): 0.63 (Si-CH<sub>3</sub>); 0.70 -1.10 (Si-CH<sub>2</sub>); 1.5-2.00 (Si-CH<sub>2</sub> CH<sub>2</sub>); 2.20-2.70 (CH<sub>2</sub>-CH in the cycle). <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 78.1; -78.9; -81.5; -82.0 (OCF<sub>2</sub>) -83.1 (CF<sub>3</sub>); -105.3; -114.4; -118.0 (CF<sub>2</sub> in the cycle); -120.0; -141 (CF - in the cycle); -115.0 (CFCN); -128.6; -128.9 (CF<sub>2</sub>CF<sub>2</sub>).

<sup>29</sup>Si, NMR spectrum ( $\delta$ , ppm): 30.0. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1000-1200 (CF); 1410 (CH in SiCH<sub>3</sub>); 2260 (CN); 2800-3000 (CH).

A compound 6 was obtained analogically, yield 66,7%. B.p. = 105-107°C/1torr. Chemical shifts in <sup>1</sup>H, <sup>29</sup>Si NMR spectra of this compound were matched in a range of measurement accuracy in accordance with corresponded area of compound 6. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm.): -77.2; -78.5; -82.2; -83.1 (OCF<sub>2</sub>); -105.4 (CF<sub>2</sub>CN); -109.4; -109.6; -114.2; -118.1 (CF<sub>2</sub> in the cycle); -123.0; -124.4; -126.0 (CF<sub>2</sub>CF<sub>2</sub> CF<sub>2</sub>); -119.9; -141.9 and -141.2 (CF in the cycle).

IR-spectrum,  $\nu$ , cm<sup>-1</sup>: 2260 (CN).

## References

1. V.A. Ponomorenko, S.P. Krukovsky, A.Yu. Alybina. Fluorinated Heterochain Polymers. M. Nauka, p. 257, 1973.
2. V.A. Ponomorenko, M.A. Ignatenko. Chemistry of Fluorosilicone Organic Compounds. M. Nauka, p. 191, 1979.
3. J.D. Roberts, C.M. Sharts. Organic Reactions, **12**, M. Mir, 1965, p.7.
4. A.A. Glazkov, A.V. Ignatenko, S.P. Krukovsky, V.A. Ponomorenko. Izv. AN SSSR, ser. Khim., 1988, p. 2372 (Bull. of the Academy Sci., 1988, p.2137-2141).
5. A.A. Glazkov, A.V. Ignatenko, S.P. Krukovsky, V.A. Ponomorenko. Izv. AN SSSR, ser. Khim., 1979, p. 2515 (Bull. of the Academy Sci., 1979, p.2327-2330).
6. R. Sullivan. J.Org. Chem., 1969, v.34, p.1841.
7. P.R. Resnick. US Patent 4474899, Chem. Abstr., 1984, v. 101, P 231608.
8. A.A. Glazkov, V.M. Menshov, A.V. Ignatenko, S.P. Krukovsky, V.A. Ponomorenko. 6th Conference on Chemistry of Fluorosilicone Organic Compounds. Novosibirsk, 1990, abstract, p. 27.
9. J.W. Emsly, J. Feeney, L.H. Suteliff. Progress in NMR Spectroscopy, 1971, v.7, p.3.
10. A.A. Yarosh, A.A. Glazkov, L.I. Ignatishenko, A.M. Sakharov. 13th Andrianov's Conference on Fluorosilicone Organic Compounds: Synthesis, Properties, Applications. Proceedings, Moscow, 2015, PO 91, p. 169

*Recommended for publication by Prof. S. P. Krukovsky*