Synthesis of methylvinylpolyfluoroalkoxysilanes by photoinitiated radical reaction of dialkoxy(methyl)vinylsilanes with perfluoro-4-methylpent-2-ene

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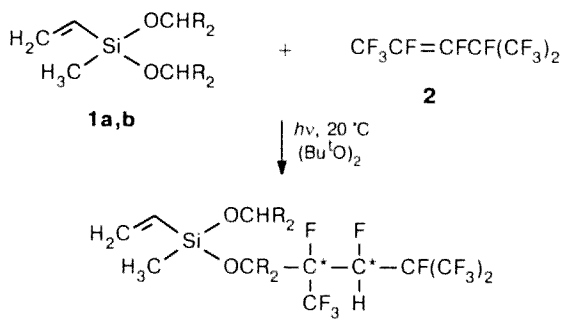
A new method was elaborated for the synthesis of vinylsilanes with polyfluoroalkoxy substituents at the silicon atom using the photoinitiated radical reaction of dialkoxy(methyl)vinylsilanes with perfluoro-4-methylpent-2-ene in the presence of di-*tert*-butyl peroxide at room temperature.

Key words: dialkoxy(methyl)vinylsilanes, perfluoro-4-methylpent-2-ene, radical addition.

The known methods for preparation of organofluorosilicon compounds (OFSC) containing fluorinated radicals linked to the silicon atom can be divided into several main groups: organometallic synthesis,[1–6] direct synthesis[7–9] (did not acquire successful development), hydrosilylation[10–12] (one of the basic methods for both laboratory-scale and industrial preparation of OFSC), and some other methods.[8,13] Many of the above methods are multistage and require difficultly accessible reagents. In addition, the methods for obtaining vinylorganosilanes with both the vinyl group and fluorocontaining substituents at the same silicon atom barely exist. The elaboration of such a method is the aim of the present study. These vinylsilanes can be used as the starting compounds for obtaining polymers with pendant polyfluoroalkoxysilyl groups attached to the polymer main chain.

UV irradiation of dialkoxy(methyl)vinylsilanes (**1**) in the presence of organic peroxides (*e.g.*, di-*tert*-butyl peroxide, DTBP) at −10—−20 °C results[14] in radical products with an unpaired electron at the α-carbon atom of the alkoxy group of **1**. The radicals generated from **1** react with perfluoro-4-methylpent-2-ene (**2**) through regiospecific addition at C(2) of perfluoroolefin 2.[14,15] The present work describes preparative synthesis of alkoxy(polyfluoroalkoxy)-substituted vinylsilanes (**3**) based on the photoinduced reaction of compounds **1** and **2** in the presence of DTBP (Scheme 1).

Scheme 1



R = H (**a**), CH_3 (**b**)

Photolysis of an equimolar mixture of **1a** or **1b** with **2** resulted in **3a** and **3b** in 90 and 99% yields, respectively (with respect to consumed **1a** and **1b**). No byproducts are formed, so the starting compounds can be recycled. It was shown previously[16] that alkoxy derivatives of vinylsilanes with an *iso*-structure generate radical products in the presence of radical initiators more readily than the alkoxy derivatives of normal structure. This fact can explain why the yield of adduct **3b** is higher than that of **3a**. Optimization of the photolysis conditions and investigation of the diastereomeric composition of the adducts formed were beyond the scope of the present study.

To identify products **3a** and **3b**, we synthesized methylvinylbis(1,1,3-trihydroperfluoro-2,4-dimethylpentyloxy)silane (**6**) by treating dichloro(methyl)vinylsilane (**4**) with 1,1,3-trihydroperfluoro-2,4-dimethylpentan-1-ol (**5**) (Scheme 2).

The comparative analysis of the ^{13}C and ^{19}F NMR spectra of model compound **6** and adducts **3a** and **3b** and identification of the structural fragments of these compounds allowed confirming the regiospecificity of the method proposed for synthesis of silanes **3**. The main parameters of the ^{13}C NMR spectra of **3a** and **6** are the same. For example, there are signals with the chemical shifts in the region of −5.83 to −6.6 ppm specific for CH_3—Si— groups and in the region of

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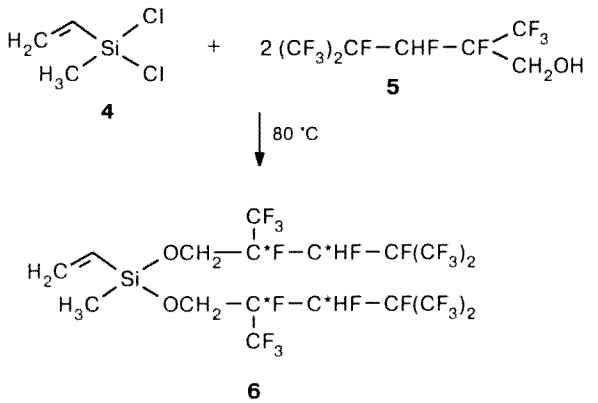
60.62—60.28 ppm specific for $-O\underline{C}H_2-CF-$ groups at the silicon atom.[17] The signals with the chemical shifts in the region of 135 and 133 ppm are characteristic of $CH_2=CH-Si-$ groups.

Scheme 2



A characteristic feature of the ^{13}C NMR spectrum of product **3a** is the presence of a signal with a chemical shift of 50.44 ppm, which is typical of the CH_3OSi- group (49.86 ppm for dimethoxy(methyl)vinylsilane), thus confirming the structure of **3a**.

The ^{13}C NMR spectrum of adduct **3b** matches those of **3a** and **6** in the main parameters. A characteristic feature of the spectrum of **3b** is the presence of the signals for $-Si-O\underline{C}H(\underline{C}H_3)_2$ groups (64.76 and 26.14 ppm, respectively), which confirms the structure of **3b**.

The analysis of the ^{19}F NMR spectra of the starting compounds and products **3a,b** and **6** supported the assumption that the addition of **1** to olefin **2** occurred at the $-CF=CF-$ bond. The ^{19}F NMR spectrum of the initial perfluoroolefin **2** contains signals corresponding to the $-CF=CF-$ group in the region of 59—62 ppm (*cis*-isomer) and 78—80 ppm (*trans*-isomer), which are absent in the ^{19}F NMR spectra of compounds **3a,b**. Furthermore, the presence of signals with characteristic chemical shifts[18] for the two $-C^*F-$ groups (101—104 ppm, four signals) and one $-C^*FH-$ group (133 ppm, two signals) of the fluorinated substituent in **3a,b** formation of the monosubstituted derivative. In fact, there are two such substituents in product **6**, which is reflected in its ^{19}F NMR spectrum: the number of signals for the corresponding groups is doubled (there are eight signals for $-C^*F-$ groups in the region from 105 to 110 ppm and four signals for $-C^*FH-$ groups in the region from 130 to 135 ppm).

Thus, a new method for introduction of fluorinated substituents in vinylorganosilanes retaining the vinyl group at the silicon atom was elaborated. Since monosubstituted adducts **3a,b** were obtained at the equimolar ratio of the corresponding dialkoxysilanes **1a,b** and perfluoroolefin **2**, one can suggest that disubstituted adducts like compound **6** can be formed in a ratio of **1a,b** to **2** of 1 : 2.

Experimental

The NMR spectra were recorded on a Bruker WP-200SY spectrometer (50.32 MHz and $SiMe_4$ as the external standard for ^{13}C and 188.4 MHz and CF_3COOH as the external standard for ^{19}F).

Photolysis of equimolar mixtures of **1** and **2** was performed by focused irradiation with a DRSh-250M lamp from a distance of 8 cm in a quartz flask in the presence of 0.5% DTBP. The process of photolysis and the composition, purity, and yield of adducts were monitored by GLC using a DKh-4 chromatograph on a column (2 m×3 mm) with 20% SKTFT-50 on Celite-545 (45—50 mesh) (helium as the carrier gas, 50 mL min^{-1}; katharometer as the detector). The purity of compounds **6** and **3a,b** was 98—99%.

Irradiation of a mixture of **1b** (5.31 g, 28 mmol) and **2** (8.41 g, 28 mmol) for 80 h and subsequent fractional distillation of the reaction mixture gave 3.41 g of **1b** (36% conversion), 5.58 g of **2** (34% conversion), and 4.83 g of **3b** (99% with respect to consumed **1b**), m.p. 103 °C (6 Torr). Found (%): C, 36.92; H, 3.9; F, 46.65; Si, 5.68. $C_{15}H_{20}F_{12}O_2Si$. Calculated (%): C, 36.89; H, 4.1; F, 46.72; Si, 5.73.

Similarly, irradiation of **1a** (3.31 g, 25 mmol) and **2** (7.50 g, 25 mmol) for 130 h yielded 2.71 g of **3a** (90% with respect to consumed **1a**), m.p. 140 °C (9 Torr), and the conversions of **1a** and **2** were 28 and 27%, respectively. Found (%): C, 30.71; H, 2.6; F, 52.71; Si, 6.40. $C_{11}H_{12}F_{12}O_2Si$. Calculated (%): C, 30.56; H, 2.78; F, 52.78; Si, 6.48.

Compound **6** was synthesized by heating dichloro(methyl)vinylsilane (1.8 g, 13 mmol) with 1,1,3-trihydroperfluoro-2,4-dimethylpentan-1-ol (38.18 g, 115 mmol) in toluene (50 mL) at 80 °C for 4 h. Fractionation of the reaction mixture gave **6** (3.05 g, 32%), m.p. 118 °C (11 Torr). Found (%): C, 28.13; H, 1.80; F, 62.10; Si, 4.22. $C_{17}H_{12}F_{24}O_2Si$. Calculated (%): C, 27.87; H, 1.64; F, 62.32; Si, 4.37.

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