## New Route to 1,1-Difluoro-5-methylquasisilatrane

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**Abstract**—A new route to 1,1-difluoro-5-methylquasisilatrane (N $\rightarrow$ Si) F<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe is elaborated: the reaction of chlorinated methyltrifluorosilanes F<sub>3</sub>SiCH<sub>3-n</sub>Cl<sub>n</sub> (n = 1-3) as well as trifluoro(3-chloropropyl) silane and trifluoro(propenyl)silane with *N*-methyl-bis(2-hydroxyethyl)amine. The reactivity of the silanes F<sub>3</sub>SiCH<sub>3-n</sub>Cl<sub>n</sub> increases with the number of chlorine atoms, that is, with the electronegativity of the CH<sub>3-n</sub>Cl<sub>n</sub> group.

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For a long time the reactions of splitting of theC–Si bond have attracted the attention of organosilicon chemists [1–3]. Our systematic studies in this field have shown that the cleavage of the Ph–Si bond in the phenyltrifluorosilane PhSiF<sub>3</sub> and phenyl(methyl) difluorosilane PhMeSiF<sub>2</sub> by various nucleophiles are of substantial synthetic interest [4–9]. In particular, it was found that that the reaction of PhSiF<sub>3</sub> with mono-, bis-, and tris(2-hydroxyethyl)amines (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>NR<sub>3-n</sub> (n = 1-3) readily afforded 1,1,1-trifluorohyposilatranes (N→Si) F<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>NR<sub>2</sub> (R<sub>2</sub> = H<sub>2</sub>, HMe, Me<sub>2</sub>) (**A**), 1,1-di-fluoroquasisilatranes (N→Si) F<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH (**B**), and 1-fluorosilatrane FSi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (**C**) [7–10].



Nowadays, the compounds of hypervalent silicon continue to attract the interest of many researchers due to the unusual ability of the silicon atom to increase its coordination number to five or six [11-15].

As early as in 1987, it was shown that the C–Si bond in the C-chlorinated trifluoro(methyl)silanes  $Cl_n(H)_{3-n}CSiF_3$  (n = 1-3) could be split by the action of

phenylmercury acetate PhHgC(O)OMe with the formation of the C-chloromethyl derivatives of phenylmercury [4, 5].

$$Cl_n(H)_{n-3}CSiF_3 + MeC(O)OHgPh$$
  
→  $Cl_n(H)_{n-3}CHgPh + MeC(O)OSiF_3,$   
 $n = 1-3.$ 

Based on this observation and looking for new synthetic routes to intracomplex compounds of hypervalent silicon we have elaborated an original method of synthesis of 1,1-difluoro-5-methylquasisilatrane by the reaction of the C-chlorinated trifluoro(methyl)silanes  $Cl_n(H)_{3-n}CSiF_3$ , where n = 1 (I), 2 (II), 3 (III), with *N*-methylbis(2-hydroxyethyl)amine (IV).

The reaction of trifluoro(chloromethyl)- (I) or trifluoro(trichloromethyl)silane (III) with *N*-methyl-bis-(2-hydroxyethyl)amine (IV) proceeds with the cleavage of the C–Si and Si–F bonds, evolution of HF, methyl chloride or chloroform, and the formation of 1,1-difluoro-5-methyl-quasisilatrane (N $\rightarrow$ Si) F<sub>2</sub>Si· (OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe (V) in 77% (*n* = 1) or 93% (*n* = 3) yield.

$$Cl_{n}(H)_{3-n}CSiF_{3} + (HOCH_{2}CH_{2})_{2}NMe$$

$$I, III IV$$

$$\rightarrow Cl_{n}(H)_{3-(n+1)}C + F_{2}Si(OCH_{2}CH_{2})_{2}NMe, \quad (1)$$

$$V$$

$$n = 1, 3.$$

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 $Cl(CH_2)_3SiF_3 + (HOCH_2CH_2)_2NMe \rightarrow F_2Si(OCH_2CH_2)_2NMe + PrCl + HF.$ 

$$Cl_{2}HCSiF_{3} + (HOCH_{2}CH_{2})_{2}NMe \xrightarrow{-HF, -Cl_{2}CH_{2}} F_{2}Si(OCH_{2}CH_{2})_{2}NMe + Cl_{2}CH(F)Si(OCH_{2}CH_{2})_{2}NMe.$$
(2)  

$$II IV V VI$$

tivelv).

The reaction of trifluoro(dichloromethyl)silane (II) with *N*-methylbis(2-hydroxyethyl)amine (IV) results in breaking not only the C–Si but also the Si–F bond with the formation of 1,1-difluoro-5-methylquasisilatrane (N $\rightarrow$ Si) F<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe (V) (60%) and 1-fluoro-1-dichloromethyl-5-methylquasisilatrane (N $\rightarrow$ Si) Cl<sub>2</sub>CH(F)Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe (VI) (22%).

The reactivity of the C-chlorinated trifluoro(methyl)silanes  $Cl_n(H)_{3-n}CSiF_3$  (I–III) in reactions (1) and (2)

(48%) and propyl chloride.

In the series  $Cl(CH_2)_mSiF_3$  the electronegativity of the  $Cl(CH_2)_m$  group decreases with the number of the methylene groups (*m*) [ $\sigma^* = 1.05$  (*m* = 1),  $\sigma^* = 0.13$  (*m* = 3)], but reaction (3) still occurs (3). Yet trifluoro(chloropropyl)silane  $Cl(CH_2)_3SiF_3$  does not react with mercury salts [4, 5].

The reaction of *N*-methylbis(2-hydroxyethyl)amine **(IV)** with trifluoro(propenyl)silane **VIII** proceeds in a similar way.

$$F_{3}SiCH=CHMe + (HOCH_{2}CH_{2})_{2}NMe$$

$$VIII IV$$

$$\rightarrow F_{2}Si(OCH_{2}CH_{2})_{2}NMe + MeCH=CH_{2} + HF. (4)$$

$$V$$

The structure of compounds V and VI was proved by  ${}^{1}$ H,  ${}^{13}$ C,  ${}^{19}$ F,  ${}^{29}$ Si NMR spectroscopy

In the <sup>1</sup>H NMR spectrum of quasisilatrane **VI** the protons of the OCH<sub>2</sub> and NCH<sub>2</sub> groups are nonequivalent and resonate as AB-quartets (<sup>2</sup>*J*<sub>HH</sub> 11.1 and 12.1 Hz, respectively), with each component split into a triplet with <sup>3</sup>*J*<sub>HH</sub> 6.1 Hz. In the upfield part of the AB-multiplet of each group of protons a long-range interaction with the fluorine atom is observed (<sup>4</sup>*J*<sub>F-Si-N(O)-C-H</sub> ~ <sup>5</sup>*J*<sub>F-Si-O(N)-C-C-H</sub> = = 2.4 Hz).

In the <sup>13</sup>C NMR spectrum of quasisilatrane VI only the NMe and  $CHCl_2$  carbon atoms are split by the coupling with the fluorine atom, whereas the signals of the carbon atoms of the atrane rings remain singlets.

In the  ${}^{13}$ C NMR spectrum of quasisilatrane V the spin–spin coupling is observed also for the OCH<sub>2</sub>

carbon (J 4.4–4.6 Hz), but only with one, apparently, the equatorial, fluorine atom.

increases with the number of chlorine atoms (n),

that is, with the electronegativity of the  $C(H)_{3-n}Cl_n$ 

group, where n = 1, 2, 3 ( $\sigma^* = 1.05, 1.94, 2.65$  respect-

(VII) with *N*-methylbis(2-hydroxyethyl)amine (IV)

both the C-Si and Si-F bonds are split with the

formation of 1,1-difluoro-5-methylquasisilatrane (V)

In the reaction of trifluoro(3-chloropropyl)silane

The presence of narrow signals and long-range coupling constants in the <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>29</sup>Si NMR spectra of compounds V and VI is determined by the stereochemical direction of the bonds and is indicative of the existence of stereodynamically rigid molecules of the studied guasisilatranes in solution.

## EXPERIMENTAL

<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13, 100.61, 376.50, 79.5 MHz, respectively) in CDCl<sub>3</sub> and DMSO $d_6$ , internal reference TMS.

C-Chlorinated derivatives of trifluoro(methyl)silane  $F_3SiCCl_nH_{3-n}$  (n = 1-3), trifluoro(3-chloropropyl)silane  $F_3Si(CH_2)_3Cl$ , and trifluoro(propenyl)silane  $F_3SiCH=CHMe$  were synthesized by the Swarts reaction of SbF<sub>3</sub> with the corresponding C-chlorinated derivatives of tri-chloro(methyl)silane, trichloro(3-chloropropyl)silane, or trichloro(propenyl)silane.

**1,1-Difluoro-5-methylquasisilatrane (V).** *a. Reac*tion (1), n = 1. To the solution of 1.87 g of ClCH<sub>2</sub>SiF<sub>3</sub> in 10 ml of anhydrous benzene (5°C) 1.43 g of freshly distilled *N*-methylbis(2-hydroxyethyl)amine was added dropwise. The reaction mixture was stirred with a magnetic stirrer at room temperature for 20–30 min, the formed precipitate was filtered off and sublimed in a vacuum. Yield 1.96 g (77%), mp 160–161°C. Found, %: C 33.15; H 6.30; F 20.56; N 7.28. C<sub>5</sub>F<sub>2</sub>H<sub>11</sub>NO<sub>2</sub>Si. Calculated, %: C 32.76; H 6.05; F 20.74; N 7.64.

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(3)

*b. Reaction (1), n* = 3. To the solution of 0.23 g of *N*-methylbis(2-hydroxyethyl)amine in 7 ml of anhydrous benzene (5°C) 0.47 g of Cl<sub>3</sub>CSiF<sub>3</sub> was added dropwise. The reaction mixture was stirred with a magnetic stirrer at room temperature for 5–10 min, the formed precipitate was filtered off and sublimed in a vacuum. Yield 0.39 g (93%), mp 160–161°C. Found, %: C 32.56; H 5.87; F 21.06; N 7.79. C<sub>5</sub>F<sub>2</sub>H<sub>11</sub>NO<sub>2</sub>Si. Calculated, %: C 32.76; H 6.05; F 20.74; N 7.64.

*c. Reaction (2), n* = 2. To the solution of 0.49 g of *N*-methylbis(2-hydroxyethyl)amine in 7 ml of anhydrous benzene (5°C) 0.82 g of Cl<sub>2</sub>CHSiF<sub>3</sub> was added dropwise. The reaction mixture was stirred with a magnetic stirrer at room temperature for 10–20 min, the formed precipitate was filtered off and sublimed in a vacuum. Yield 0.53 g (60%), mp 160–161°C. Found, %: C 32.45; H 5.81; F 20.78; N 7.26. C<sub>5</sub>F<sub>2</sub>H<sub>11</sub>NO<sub>2</sub>Si. Calculated, %: C 32.76; H 6.05; F 20.74; N 7.64. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 2.60 (NCH<sub>3</sub>), 2.77, 2.97 d. t (2H, NCH<sub>2</sub>, <sup>2</sup>J 12, <sup>3</sup>J 6.0 Hz), 3.91, 3.97 d.t (2H, OCH<sub>2</sub>). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 43.28 (NCH<sub>3</sub>, <sup>3</sup>J<sub>FC</sub> 6.5 Hz), 53.86 (NCH<sub>2</sub>), 57.35 (OCH<sub>2</sub>, <sup>3</sup>J<sub>FC</sub> 4.6 Hz). <sup>19</sup>F NMR spectrum,  $\delta_{F}$ , ppm: –149.50 d (F<sub>eq</sub>, <sup>2</sup>J<sub>FF</sub> 29.4, <sup>1</sup>J<sub>SiF</sub> 197.2 Hz), –143.21 d (F<sub>ax</sub>, <sup>2</sup>J<sub>FF</sub> 29.4, <sup>1</sup>J<sub>SiF</sub> 129.7 Hz). <sup>29</sup>Si NMR spectrum:  $\delta_{Si}$  –113.6 ppm.

Crystallization of the reaction mixture from chloroform gave compound **VI**. Yield 0.19 g (22%), mp 280°C (decomp.). Found, %: C 28.67; H 4.61; Cl 28.90; F 7.86; N 5.57. C<sub>6</sub>Cl<sub>2</sub>FH<sub>12</sub>NO<sub>2</sub>Si. Calculated, %: C 29.04; H 4.87; Cl 28.57; F 7.60; N 5.60. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 2.60 d (3H, NCH<sub>3</sub>, <sup>4</sup>J 1.5 Hz), 2.78, 2.96 d. t. d (2H, NCH<sub>2</sub>, <sup>2</sup>J 12.1, <sup>3</sup>J 6.1, <sup>4(5)</sup>J 2.3 Hz), 3.92, 3.99 d. t. d (2H, OCH<sub>2</sub>, <sup>2</sup>J 11.1, <sup>4(5)</sup>J 2.5 Hz); 5.28 d (1H, CHCl<sub>2</sub>, <sup>3</sup>J<sub>HF</sub> 2.6 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 43.36 (NCH<sub>3</sub>, <sup>3</sup>J<sub>FC</sub> 6.1 Hz), 54.02 (NCH<sub>2</sub>), 58.02 (OCH<sub>2</sub>), 63.64 d (CH, CHCl<sub>2</sub>, <sup>2</sup>J<sub>CF</sub> 67.7 Hz). <sup>19</sup>F NMR spectrum:  $\delta_{F}$  –143.15 ppm ( $F_{ax}$ , <sup>1</sup>J<sub>SiF</sub> 279.2 Hz). <sup>29</sup>Si NMR spectrum:  $\delta_{Si}$  –99.2 ppm.

*d. Reaction (3).* To the solution of 0.61 g of *N*-methylbis(2-hydroxyethyl)amine in 8 ml of anhydrous benzene (5°C) 0.97 g of Cl(CH<sub>2</sub>)<sub>3</sub>SiF<sub>3</sub> was added dropwise. The reaction mixture was stirred with a magnetic stirrer at room temperature for 25–35 min, the formed precipitate was filtered off and sublimed in a vacuum. Yield 0.53 g (48%), mp 160–161°C. Found, %: C 33.05; H 6.41; F 20.96; N 7.54. C<sub>5</sub>F<sub>2</sub>H<sub>11</sub>NO<sub>2</sub>Si. Calculated, %: C 32.76; H 6.05; F 20.74; N 7.64. The evolved Me(CH<sub>2</sub>)<sub>2</sub>Cl was identified chromatographically. *e. Reaction (4).* Gaseous  $F_3SiCH=CHMe$  was passed through the solution of 1.14 g of *N*-methylbis-(2-hydroxyethyl)amine in 10 ml of anhydrous hexane (-20°C) for 20 min. The reaction mixture was stirred at room temperature for 20 min, the formed precipitate was filtered off and sublimed in a vacuum. Yield 1.77 g (87%), mp 160–161°C. Found, %: C 32.43; H 6.32; F 20.46; N 7.45.  $C_5F_2H_{11}NO_2Si$ . Calculated, %: C 32.76; H 6.05; F 20.74; N 7.64.

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