

Reaction of Tetrafluorosilane with Tris(2-hydroxyethyl)amine, Tris(2-trimethylsiloxyethyl)amine and Bis(2-trimethylsiloxyethyl)amine and Its *N*-methyl Derivative. 1,1-Difluoroquasisilatranes

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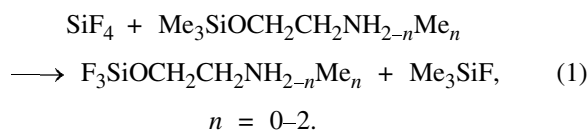
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Abstract—Reaction of tetrafluorosilane with tris(2-hydroxyethyl)- and tris(2-trimethylsiloxyethyl)amine results in formation of 1-fluorosilatrane and fluorosilatrane in 75 and 53% yield, respectively. Reaction of tetrafluorosilane with bis(2-trimethylsiloxyethyl)amine and its *N*-methyl derivative leads to the hitherto unknown 1,1-difluoroquasisilatranes ($N \rightarrow Si$) $F_2Si(OCH_2CH_2)_2NR$ ($R = H, Me$) containing donor–acceptor bond $N \rightarrow Si$ and pentacoordinate silicon atom. The structure of the synthesized compounds was proved by 1H , ^{13}C , ^{15}N , ^{19}F , ^{29}Si NMR and IR spectroscopy.

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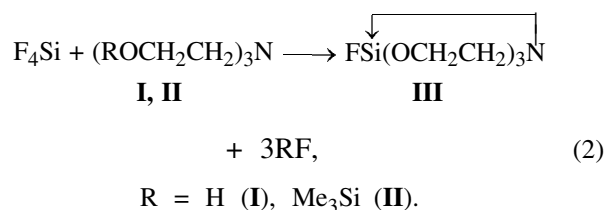
Earlier it was reported [1] that adducts $SiF_4 \cdot \beta$ or $SiF_4 \cdot 2\beta$ (β is a nitrogen base) are formed upon the gas-phase reaction of tetrafluorosilane with ammonia, primary and secondary aliphatic amines, or by bubbling SiF_4 through the benzene or ether solutions of aliphatic amines as well as of *N*-methyl derivatives of mono-, di-, and triethanolamine.

Later on, it was reported [2] that the reaction of SiF_4 with *O*-trimethylsilyl derivatives of ethanolamine, methyl-diethanolamine and dimethylethanolamine affords the corresponding *O*-trifluorosilyl derivatives containing the donor-acceptor bond $N \rightarrow Si$ (1).

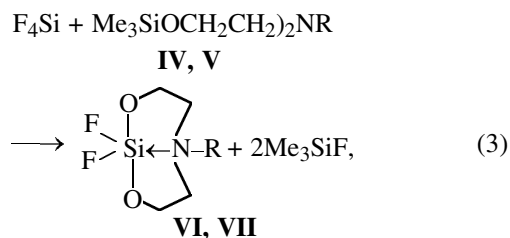


On the contrary to these findings, we observed that passing of gaseous SiF_4 into the hexane solution of tris(2-hydroxyethyl)amine **I** or tris(2-trimethylsiloxyethyl)amine **II** results in the formation of 1-fluorosilatrane **III** in 75 and 53% yield, respectively (2).

Melting points, IR and NMR spectra of 1-fluorosilatrane **III** correspond to the published data [3–8].



Reaction of tetrafluorosilane with bis(2-trimethylsiloxyethyl)amine **IV** or its *N*-methyl derivative **V** under similar conditions proceeds with elimination of trimethylfluorosilane and formation of new intracomplex bicyclic compounds ($N \rightarrow Si$) 2,2-difluoro-1,3-dioxo-6-aza-2-silacyclooctane **VI** or ($N \rightarrow Si$) 2,2-difluoro-1,3-dioxo-6-aza-6-methyl-2-silacyclooctane **VII** having the donor-acceptor bond $N \rightarrow Si$ and pentacoordinate silicon atom (3) (Table 1). We consider these



$R = H$ (**IV, VI**), Me (**V, VII**).

Table 1. 1-Fluorosilatrane **III** and 1,1-difluoroquasisilatranes **VI** and **VII**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	F	N		C	H	F	N
III	75	200 decomp.	37.08	6.22	9.45	7.24	C ₆ H ₁₂ NO ₃ FSi	37.29	6.26	9.83	7.25
VI	47	180	28.01	5.73	22.12	8.39	C ₄ H ₉ NO ₂ F ₂ Si	28.39	5.36	22.46	8.28
VII	35	162	33.23	6.17	20.43	7.82	C ₅ H ₁₁ NO ₂ F ₂ Si	32.77	6.0	20.75	7.64

Table 2. Parameters of ¹H, ¹³C, ¹⁵N, ¹⁹F, ²⁹Si NMR spectra of 1-fluorosilatrane **III** and 1,1-difluoroquasisilatranes **VI**, **VII** (in DMSO-d₆)

Comp. no.	δ _H , ppm (<i>J</i> , Hz)			δ _C , ppm			δ _{Si} , ppm	δ _F , ppm	<i>J</i> _{Si-F} , Hz	δ _N , ppm
	NR (SiR)	NCH ₂	OCH ₂	NR (SiR)	NCH ₂	OCH ₂				
III	–	2.92 ³ <i>J</i> 5.9	3.68	–	50.29	56.69 ³ <i>J</i> _{CF} 3.7	–100.2	–136.5	126.3	–348.4
VI	–	2.91; 2.71 <i>J</i> _{AB} 11.6 ³ <i>J</i> 6.1	3.72; 3.61 <i>J</i> _{AB} 10.2	–	43.63	57.71 ³ <i>J</i> _{CF} 4.6	–113.4	–136.1 <i>F</i> _{ax} –137.9 <i>F</i> _{eq} ² <i>J</i> _{FF} 23.5	132.2 <i>F</i> _{ax} 192.4 <i>F</i> _{eq}	–348.0
VII	2.47	³ <i>J</i> _{HNCH} 5.7 3.01; 2.76 <i>J</i> _{AB} 12.2 ³ <i>J</i> 5.9 ⁴ <i>J</i> _{HF} 2.2	3.76; 3.75 <i>J</i> _{AB} 10.9	42.62 ³ <i>J</i> _{CF} 6.5	53.00	56.69 ³ <i>J</i> _{CF} 4.3	–114.3	–137.7 <i>F</i> _{ax} –147.1 <i>F</i> _{eq} ² <i>J</i> _{FF} 22.5	129.3 <i>F</i> _{ax} 195.4 <i>F</i> _{eq}	–345.6

compounds as bicyclic analogues of silatranes and, therefore, they could be named as 1,1-difluoroquasisilatrane **VI** and 1,1-difluoro-5-methylquasisilatrane **VII**, respectively. Numeration of atoms in the cycle is the same as adopted for silatranes [3–5, 7, 8].

1,1-Difluoroquasisilatranes **VI** and **VII** are white crystalline compounds, odorless, insoluble in nonpolar solvents (hexane, benzene, toluene) but soluble upon heating in polar DMF and DMSO.

The composition and the structure of the synthesized 1,1-difluoroquasisilatranes **VI** and **VII** was proved by elemental analysis (Table 1), ¹H, ¹³C, ¹⁵N, ¹⁹F, ²⁹Si NMR spectroscopy (Table 2), and IR spectroscopy.

The NMR spectra of 1,1-difluoroquasisilatranes **VI** and **VII** demonstrated diastereotopy of the protons of OCH₂ and CH₂N groups as well as long-range (through three and four bonds) coupling constants of ¹⁹F nuclei with ¹H and ¹³C nuclei. The most interesting observation is nonequivalence of the ¹⁹F chemical shifts even at room temperature so far this effect was not observed for fluorosilanes having hypercoordinate silicon atom.

²⁹Si chemical shift in quasisilatranes **VI** and **VII** is shifted upfield by 17.7 and 18.6 ppm, respectively, as compared to that in F₂Si(OEt)₂ (–95.7 ppm [9]) having tetrahedral silicon atom. This also confirms the existence of intramolecular donor-acceptor interaction between the nitrogen and silicon atoms.

In ¹⁹F NMR spectra of 1,1-difluoroquasisilatranes **VI** and **VII** the average value of the ¹⁹F chemical shift is by ~15–18 ppm shifted downfield with respect to the tetracoordinate silicon compound (F₂Si(OEt)₂ –154.7 ppm [9]), which is also indicative of the donor-acceptor interaction N→Si in molecules **VI** and **VII**. Close values of the ¹⁹F and ²⁹Si NMR parameters along with much more pronounced (by 5 times) non-equivalence of fluorine atoms in compound **VII** testify that the presence of the methyl group at the nitrogen atom substantially increases the coordination bond N→Si. Coupling constants ²⁹Si–¹⁹F in the NMR spectra of trigonalbipyramidal molecules **VI** and **VII** for the axial fluorine atom are by 61–64 Hz less than in the model compound F₂Si(OEt)₂ (193.4 Hz [9]).

All these specific features of the NMR spectra are indicative of rather strong intramolecular N→Si in-

teraction and stereochemical rigidity of the quasisilatrane heterocycle **VI** and **VII**.

The ^{15}N chemical shift in the ^{15}N NMR spectrum of 1,1-difluoroquasisilatrane **VI** and **VII** are slightly (by 1 and 3 ppm, respectively) shifted downfield as compared to the ^{15}N chemical shifts in the spectra of the starting bis(2-hydroxyethyl)amine (−349.1 ppm) and methyl-bis(2-hydroxyethyl)amine (−348.4 ppm) [14] under the same conditions [10]. This small difference of the ^{15}N chemical shifts is apparently caused by slight deshielding of the nitrogen atom upon its protonation in alkyl amines [10] and oppositely directed (shielding) contribution of the cyclization effect [11].

IR spectrum of 1-fluorosilatrane **III** is identical to that given in the atlas of spectra [6]. It was reported earlier that the stretching vibrations of the Si–F bonds in compounds of pentacoordinate silicon containing one or two Si–F bonds and intramolecular bond $=\text{O}\rightarrow\text{Si}$ are mixed and are observed in relatively narrow frequency intervals [12]. In the spectra of 1,1-difluoroquasisilatrane **VI** and **VII** having coordination bond $\text{N}\rightarrow\text{Si}$ stretching vibrations $\nu(\text{Si}-\text{F})$ correspond to the bands at ~ 770 and $\sim 900\text{ cm}^{-1}$.

EXPERIMENTAL

IR spectra of the synthesized compounds were registered on a Specord IR-75 spectrometer in pellets with KBr. ^1H , ^{13}C , ^{15}N , ^{19}F , and ^{29}Si NMR spectra were recorded on a Bruker DPCE-400 spectrometer (at 400.13, 100.61, 40.56, 376.50, and 79.5 MHz, respectively) in $\text{DMSO}-d_6$, internal standard TMS.

1-Fluorosilatrane III. *a.* Gaseous tetrafluorosilane obtained by the reaction of 2 ml of conc. H_2SO_4 with powder-like mixture of 4.7 g of Na_2SiF_6 and 1.5 g of SiO_2 was passed into the solution of 4.28 g of tris(2-hydroxyethyl)amine in benzene during 3 h at -3 to 0°C . The precipitate formed was filtered, washed with dry ether and sublimed under vacuum. 0.84 g (75%) of compound **III** was obtained.

b. Tetrafluorosilane obtained as above was passed into the hexane solution of 15.66 g of tris(2-trimethylsiloxyethyl)amine during 3–4 h at -5 – 0°C . The yellowish precipitate formed was filtered, washed with dry ether and sublimed under vacuum. 3.78 g (53%) of compound **III** was obtained.

1,1-Difluoroquasisilatrane VI. Through the solution of 4.36 g of bis(2-trimethylsiloxyethyl)amine in 10 ml of hexane gaseous tetrafluorosilane was passed during 3 h at -5 – 0°C . The white precipitate formed was filtered and sublimed under vacuum. 1.39 g

(47%) of compound **VI** with mp 180°C was obtained.

1,1-Difluoro-5-methylquasisilatrane VII was synthesized similarly in the yield of 1.04 g (35%), mp 162°C .

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