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LETTERS
TO THE EDITOR

Hydrocarbyltrialkoxysilanes Reaction with Fluoroptotatrane

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Of all 1-halogenosilatranes $XSi(OCH_2CH_2)_3N$ (XSa), 1-fluorosilatrane (X = F) is the most readily available. Several methods of its synthesis are known [1–6]. Previously, a new simple method of 1-fluorosilatrane (FSa) preparation was suggested, via the reaction of tris(2-hydroxyethyl)ammonium fluoride (fluoroprotatrane, FP) with tetraethoxysilane [7]. The reaction was performed by heating the mixture with distillating the formed ethanol off. The yield of FSa reached 90 %. The mechanism of that reaction was proposed based on quantum-chemical calculations [8].

Here, we report the study of FP reactions with hydrocarbyltrialkoxysilanes $RSi(OR^1)_3$ (R = Me, Vin, or Ph; R^1 = Me or Et). The equimolar mixture of FP (**I**) and phenyltrimethoxysilane (**II**) was heated upon stirring, and the formed methanol and benzene were distilled off and identified by chromato-mass spectrometry. The yield of FSa was of 88%.

The reaction of **I** with vinyltriethoxysilane **III** led to FSa with 91% yield. Both reactions proceeded via splitting of the C_{sp^2}–Si bond:

$$RSi(OR^1)_3 + F^-N^+H(CH_2CH_2OH)_3 \rightarrow FSi(OCH_2CH_2)_3N + RH + 3R^1OH,$$
$$R = Ph, Vin;\ R^1=Me, Et. \quad (1)$$

Under similar conditions, **I** reacted with methyltrimethoxysilane **IV** to give 1-methylsilatrane. In that case, the C_{sp^3}–Si bond remained intact:

$$MeSi(OMe)_3 + F^-N^+H(CH_2CH_2OH)_3 \rightarrow MeSi(OCH_2CH_2)_3N + 3MeOH + HF. \quad (2)$$

The composition and the structure of the prepared 1-fluorosilatrane and 1-methylsilatrane were confirmed by elemental analysis, ^1H, ^{13}C, ^{29}Si NMR, and IR spectroscopy. The IR and NMR spectra of 1-fluorosilatrane and 1-methylsilatrane were fully identical to the literature data [9–13].

Reaction of fluoroprotatrane (I) with phenyltrimethoxysilane (II). **I** was obtained by heating the mixture of 1.49 g of tris(2-hydroxyethyl)amine and 0.37 g of ammonium fluoride during 12 h at 90–95°C (until the ammonia evolution ceased). 1.98 g of **II** was added to the formed FP (yellow viscous liquid), and the mixture of methanol and benzene was distilled off. The residue was sublimed in vacuum at 1 mm Hg to yield 1.7 g (88%) of 1-fluorosilatrane. Found, %: C 37.26; H 6.13; N 7.21; F 10.16; Si 14.06. $C_6H_{12}NO_3FSi$. Calculated, %: C 37.29; H 6.26; N 7.25; F 9.83; Si 14.53. IR spectrum, ν, cm^{-1}: Si–F (748–802), Si–O (790–810) and C–O (1080–1150). ^1H, ^{13}C and ^{29}Si NMR spectra of FSa solution in CD_3CN: δ_H 2.94 and 3.76 ppm, δ_C 51.6 and 57.9 ppm, δ_{Si} –100.4 ppm.

Reaction of fluoroprotatrane I with vinyltriethoxysilane (III). 3.8 g of **III** was added to 3.38 g of **I**, and ethanol was distilled off. The obtained precipitate was sublimed in vacuum (1 mm Hg). Yield of FSa 3.5 g (91%), mp 330°C. Found, %: C 37.11; H 6.20; N 7.13; F 10.50; Si 14.11. $C_6H_{12}NO_3FSi$. Calculated, %: C 37.29; H 6.26; N 7.25; F 9.83; Si 14.53. Melting points, IR and NMR spectra of the prepared 1-fluorosilatrane coincided with those reported in the literature [9–13].

Reaction of fluoroprotatrane I with methyltrimethoxysilane (IV). A mixture of 1.69 g of **I** and 1.36 g of **IV** was heated with stirring until the distillation of the formed methanol and HF ceased. The obtained precipitate was crystallized from chloroform–heptane (1 : 1) to give 0.75 g (40%) of 1-methylsilatrane, mp 151–152°C. Found, %: C 44.13; H 8.12; N 7.68; Si

15.04. $C_7H_{15}NO_3Si$. Calculated, %: C 44.42; H 7.99; N 7.40; Si 14.84. IR spectrum, ν, cm^{-1}: Si–C (619), Si–O (770–817) and C–O (1080–1125). ^1H, ^{13}C and ^{29}Si NMR spectra of the solution of 1-methylsilatrane in $CDCl_3$: δ_H 2.79 and 3.75 ppm, δ_C 51.05 and 57.80 ppm, δ_{Si} –64.4 ppm.

IR spectra of the synthesized compounds were recorded with Specord IR-75 instrument in KBr. ^1H, ^{13}C and ^{29}Si NMR spectra were registered with Bruker DPX-400 spectrometer in CD_3CN or $CDCl_3$ solutions with TMS as an internal standard. Mass spectra were recorded with gas chromatograph Agilent 6850 equipped with mass-selective detector Agilent 6973N and capillary quartz column HP-5 MS.

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