Reactions of 1-hydro- and 1-halosilatranes with metal salts

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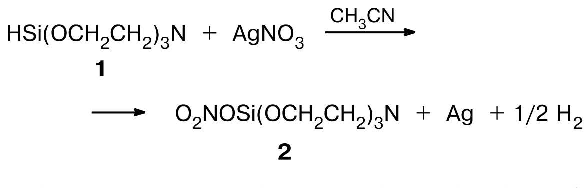
1-Hydrosilatrane reduces $AgNO_3$ and $CuCl_2$ in CH_3CN to form metallic silver and CuCl, respectively; other reaction products are the silatranyl nitrate $O_2NOSi(OCH_2CH_2)_3N$ and the 1-chlorosilatrane $ClSi(OCH_2CH_2)_3N$.

Key words: 1-hydrosilatrane, 1-halosilatrane, silatranyl nitrate, reduction, silver nitrate, cupric chloride.

1-Hydrosilatrane (**1**),[1] like other tetra- and pentacoordinate silicon compounds containing the Si—H bond,[2] is a reducing agent. Products obtained by reduction of benzyl bromide, benzoyl chloride, azoxybenzene, and some carbonyl compounds with 1-hydrosilatrane (**1**) have been isolated and characterized.[1] However, it remains unclear what happens to compound **1** as a reducing agent. There is some evidence that the silatranyl group keeps intact in redox processes. 1-(Organylthioalkyl)silatranes are oxidized with H_2O_2 into the corresponding sulfoxides or sulfones.[3] In the study of the electrochemical behavior of 1,1´-bis(silatranyl)ferrocene,[4] the redox potential of iron has been found to vary substantially with the nature of the organosilicon substituent in ferrocene. However, the reported data[4] have confirmed the structure of the starting 1,1´-bis(silatranyl)ferrocene only, throwing no light upon whether the silatranyl group is retained under these conditions.

Here, we studied redox reactions of compound **1** with $AgNO_3$ and $CuCl_2$. The reaction of 1-hydrosilatrane **1** with $AgNO_3$ (used in equimolar amounts) started immediately upon mixing in acetonitrile, giving rise to gaseous H_2 and metallic Ag.



$$\underset{\mathbf{1}}{HSi(OCH_2CH_2)_3N} + AgNO_3 \xrightarrow{CH_3CN} \underset{\mathbf{2}}{O_2NOSi(OCH_2CH_2)_3N} + Ag + 1/2\ H_2$$

The process was exothermic and completed in a few minutes. The 100% conversion of the starting reagents was proven by ^1H NMR data. The precipitate of silver was separated by decanting and the solvent was removed to give silatranyl nitrate (**2**) as a viscous yellowish oil.

Table 1. ^1H, ^{13}C, and ^{29}Si NMR spectra of compounds **2** and **3** in CD_3CN

Compound	δ				
	^1H		^{13}C		^{29}Si
	OCH_2	NCH_2	OCH_2	NCH_2	
2	3.86	3.07	57.76	50.59	−98.02
2*	3.86	3.08	57.74	50.61	−97.91
2**	3.85	3.07	57.76	50.59	−97.98
3***	3.96	3.00	—	—	−86.1

* Obtained from $BrSi(OCH_2CH_2)_3N$ and $LiNO_3$.
** Obtained from $ClSi(OCH_2CH_2)_3N$ and $AgNO_3$.
*** In $CDCl_3$.

Compound **2** is very sensitive to moisture traces. All attempts to isolate its crystals for X-ray diffraction analysis failed. Structure **2** was confirmed by ^1H, ^{13}C, and ^{29}Si NMR data (Table 1). The ^{29}Si chemical shift appears in the range characteristic of 1-alkoxysilatranes[5] and is close to the value for *E*-*o*-difluoromethoxybenzylideneiminoxysilatrane containing the =N—O—Si bond.[6] The IR spectrum of compound **2** shows intense bands at 1075 and 1380 cm^{-1} due to the Si—OC and $O—NO_2$ groups, respectively.[7] The difference between the chemical shifts $\delta(CH_2O) - \delta(CH_2N)$ in the ^1H NMR spectra of silatranes usually approaches 1 ppm.[5] However, this difference for compound **2** is appreciably smaller (~0.8 ppm). An analogous value has been obtained at the quaternization of the exocyclic N atom of 1-dialkylaminomethylsilatranes[8] and for sulfonium salts of the silatrane series.[3,5] Such a deviation Δδ is probably due to the electron-withdrawing effect of the NO_3 group ($\sigma^* = 3.76$).[9] It is not improbable that considerable polarization of the $O_2NO—Si$ bond can give rise to solvated silatranyl cation of the type $(O_2NO)^-(solv)[Si(OCH_2CH_2)_3N]^+$ (solv stands for the

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solvent). For the nitrile-stabilized silatranyl cation $[(CD_3CN)Si(OCH_2CH_2)_3N]^+TFPB^-$ (TFPB is tetrakis[3,5-bis(trifluoromethyl)phenyl] borate), $\Delta\delta$ is 0.74 ppm.[10] The ^{29}Si chemical shift for this cation is δ –94.9.

We also synthesized compound **2** by metathesis reactions of 1-chloro- and 1-bromosilatranes with metal salts.

$$XSi(OCH_2CH_2)_3N + MNO_3 \xrightarrow{MeCN} \underset{\mathbf{2}}{O_2NOSi(OCH_2CH_2)_3N} + MX$$

M = Li, Ag; X = Cl, Br

The IR and NMR data for the products obtained were identical with those for compound **2**.

1-Hydrosilatrane (**1**) reacted with $CuCl_2$ much more slowly: the reaction was completed over several hours.

$$\underset{\mathbf{1}}{HSi(OCH_2CH_2)_3N} + CuCl_2 \xrightarrow{MeCN} \underset{\mathbf{3}}{ClSi(OCH_2CH_2)_3N} + CuCl + 1/2\ H_2$$

The physicochemical characteristics and spectroscopic data for compound **3** (see Table 1) are identical with those for 1-chlorosilatrane.[11]

Redox reactions with compound **1** as a reducing agent remain poorly investigated. The results we presented here can be used to develop new methods for the synthesis of silatranes and obtain further data on the structure of the silatranyl cation.

Experimental

NMR spectra were recorded on a Bruker-400 spectrometer in CD_3CN (20% solutions) with Me_4Si or cyclohexane as the internal standard. IR spectra were recorded on a Specord IR75 spectrometer (in KBr pellets). 1-Hydro-, 1-chloro-, and 1-bromosilatranes were prepared as described earlier.[11,12] Solvents were purified according to known procedures.[13] All syntheses were carried out under dry argon.

Reactions of 1-hydro- and 1-halosilatranes with metal salts (general procedure). A solution of an appropriate salt (0.001 mol) in MeCN (30 mL) was added dropwise to a solution of an appropriate silatrane (0.001 mol) in thoroughly dried acetonitrile (10 mL). After the reaction was completed (monitoring by ^1H NMR spectroscopy), the solution was decanted and concentrated *in vacuo* and the residue was dried *in vacuo*. Compound **2**. Found (%): C, 30.07; H, 4.78; N, 11.98. $C_6H_{12}N_2O_6Si$. Calculated (%): C, 30.50; H, 5.12; N, 11.86. Compound **3** was recrystallized from CH_2Cl_2. The yield was 79%. Compound **3** decomposed above 200 °C without melting. Found (%): C, 34.41; H, 5.88; N, 6.51. $C_6H_{12}ClNO_3Si$. Calculated (%): C, 34.36; H, 5.77; N, 6.68.

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