

Direct Synthesis of 1-Organylsilatranes from Organyltrichlorosilanes and Tris(2-hydroxyethyl)amine

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Received January 29, 2009

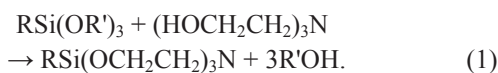
Abstract—A direct method of synthesis of 1-organylsilatranes by the reaction of organyltrichlorosilanes with tris(2-hydroxyethyl)amine was developed. 1-Organylsilatranes $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ with $\text{R} = \text{Me, Et, Ph, ClCH}_2, \text{ICH}_2, \text{Cl}(\text{CH}_2)_3$ were prepared by this method in up to 72% yield.

DOI: 10.1134/S1070363209050107

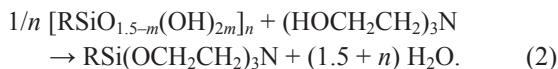
For almost half a century silatranes attract attention due to their unusual molecular structure [1–4], high specific biological activity [2, 5–8] and wide applications in medicine and agriculture [9].

The main methods of synthesis of silatranes are as follows:

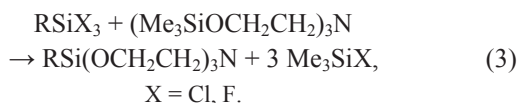
Reactions of reetherification of the Si-substituted triethoxysilanes $\text{RSi}(\text{OR}')_3$ with tris(2-hydroxyethyl)amine (triethanolamine, TEA) [2–4].



Reaction of the cleavage of polyorganylsiloxanes or polyorganylsioxanols with TEA [10–12].



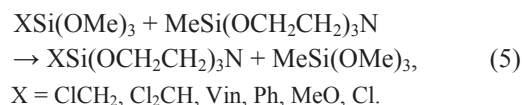
Condensation of Si-substituted trichloro- [13, 15] and trifluorosilanes [12, 14, 16] with tris(2-trimethylsiloxyethyl)amine.



The exchange reaction of triethoxysilane and its Si-substituted derivatives with boratrane [17].



Transsilylation of silatranes with Si-substituted trialkoxysilanes [18].



Reactions (4) and (5) are less common but very attractive methods for synthesis of silatranes.

It is noteworthy that all starting Si-organyl reagents used in the synthesis of silatranes ($\text{RSi}(\text{OR}')_3$, $[\text{RSiO}_{1.5}]_n$, $[\text{RSiO}_{1.5-m}(\text{OH})_{2m}]_n$, RSiF_3) are preliminarily synthesized from the isostructural Si-substituted organyltrichlorosilanes RSiCl_3 . Therefore, all the aforementioned methods of synthesis are practically two- or even three-step processes.

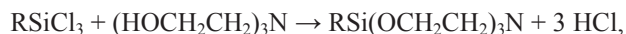
We have planned to work out a simplest and economic direct method of synthesis of 1-organylsilatranes (RSa) starting from organyltrichlorosilanes and TEA. So far nobody tried to synthesize 1-organylsilatranes by this method. The only exception is our earlier described method of synthesis of 1-chloromethylsilatrane (ClCH_2Sa) from $\text{ClCH}_2\text{SiCl}_3$ and TEA [19].

On this example, we have studied the effect of the solvent character, temperature of the reaction (from –20 to +60°C), and the molar ratio of the reagents on the yield of silatranes (Table 1).

The optimal conditions found for the synthesis of ClCH_2Sa (solvent HCCl_3 , the ratio of the reagents, and the temperature of the reaction) were used for synthesis of other 1-organylsilatranes by the general scheme.

Table 1. Optimization of the conditions of synthesis of ClCH₂SiSa by the reaction of ClCH₂SiCl₃ with TEA

Solvent	ClCH ₂ SiCl ₃ :N (CH ₂ CH ₂ OH) ₃	Temperature, °C	Yield of ClCH ₂ SiSa, %
HCCl ₃	1:1	–20	62
HCCl ₃	1:1	0 to –5	66
HCCl ₃	1:2	0 to –5	70 ^a
HCCl ₃	1:4	0 to –5	66 ^a
HCCl ₃	1:4	20	68 ^a
HCCl ₃	1:2	61	63 ^a
HCCl ₃	1:4	61	45 ^a
H ₂ CCl ₂	1:2	0 to –5	72 ^a
H ₂ CCl ₂	1:2	20	68 ^a
MeCN	1:1	–5	46

^a Recalculated to the starting silane.

The above reaction of organyltrichlorosilanes with TEA in HCCl₃ at the temperature of 0–5°C results in the corresponding 1-organylsilatranes in up to 66% yield (Table 2). The order of mixing has practically no effect on the yield of RSa. The low yield of ICH₂SiSa (33%) and PhSa (40%) is probably due to splitting of the Si–C bond by the liberated HCl.

Our numerous attempts to synthesize XSa with X = H, Cl from HSiCl₃ and SiCl₄ and TEA failed. However, similar methods of synthesis of FSa from TEA and SiF₄ we described earlier [20].

EXPERIMENTAL

IR spectra were taken on a Specord IR 75 instrument from KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 spectrometer at working frequencies 400 and 100 MHz respectively, with HMDS as an internal standard.

General procedure for the synthesis of RSa. To a stirred solution of organyltrichlorosilane in HCCl₃ at 0–5°C in an inert atmosphere a solution of TEA in HCCl₃ was slowly added dropwise. The reaction mixture was stirred until warming to room temperature, HCCl₃ and hydrogen chloride were distilled off, the solid residue was heated under a vacuum (1–2 mm Hg) at 110–120°C, and the formed 1-organylsilatrane was extracted with an appropriate solvent.

ACKNOWLEDGMENTS

This work was performed with a financial support from the Council of grants of the President of RF (NSh-255.2008.3).

Table 2. Yield, mp, and elemental analysis of RSa synthesized from RSiCl₃ and TEA

R	Yield, (%)	mp, °C	Found, %					Formula	Calculated, %				
			C	H	Cl(I)	N	Si		C	H	Cl(I)	N	Si
Me	50	151–152 (chloroform–heptane)	44.47	7.94		7.40	15.10	C ₇ H ₁₅ NO ₃ Si	44.42	7.99		7.40	14.84
Et	55	132–133 (heptane)	47.15	8.27		7.22	13.80	C ₈ H ₁₇ NO ₃ Si	47.26	8.43		6.89	13.82
Ph	40	209–210 (xylene)	56.87	7.04		5.76	10.72	C ₁₂ H ₁₇ NO ₃ Si	57.34	6.82		5.57	11.17
ClCH ₂	66	215–217 (chloroform–heptane)	37.43	6.25	15.72	6.21	12.37	C ₇ H ₁₄ ClNO ₃ Si	37.58	6.31	15.85	6.26	12.55
ICH ₂	33	190–191 (chloroform–heptane)	27.10	4.93	40.00	4.44	9.05	C ₇ H ₁₄ INO ₃ Si	26.68	4.48	40.26	4.35	8.91
Cl(CH ₂) ₃	50	130–131 (chloroform–heptane)	43.26	7.80	14.54	5.68	11.20	C ₉ H ₁₈ ClNO ₃ Si	42.93	7.21	14.08	5.56	11.16

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