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

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Abstract—A direct method of synthesis of 1-organylsilatranes by the reaction of organyltrichlorosilanes with tris(2-hydroxyethyl)amine was developed. 1-Organylsilatranes $RSi(OCH_2CH_2)_3N$ with R = Me, Et, Ph, $ClCH_2$, ICH_2, $Cl(CH_2)_3$ were prepared by this method in up to 72% yield.

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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 $RSi(OR')_3$ with tris(2-hydroxyethyl) amine (triethanolamine, TEA) [2–4].

$$RSi(OR')_3 + (HOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2)_3N + 3R'OH. \quad (1)$$

Reaction of the cleavage of polyorganylsilsesquioxanes or polyorganylsioxanoles with TEA [10–12].

$$1/n\ [RSiO_{1.5-m}(OH)_{2m}]_n + (HOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2)_3N + (1.5 + n)\ H_2O. \quad (2)$$

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

$$RSiX_3 + (Me_3SiOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2)_3N + 3\ Me_3SiX, \quad X = Cl, F. \quad (3)$$

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

$$HSi(OR)_3 + B(OCH_2CH_2)_3N \rightarrow HSi(OCH_2CH_2)_3N + B(OR)_3. \quad (4)$$

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

$$XSi(OMe)_3 + MeSi(OCH_2CH_2)_3N \rightarrow XSi(OCH_2CH_2)_3N + MeSi(OMe)_3, \quad X = ClCH_2, Cl_2CH, Vin, Ph, MeO, Cl. \quad (5)$$

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 ($RSi(OR')_3$, $[RSiO_{1.5}]_n$, $[RSiO_{1.5-m}(OH)_{2m}]_n$, $RSiF_3$) 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 $ClCH_2SiCl_3$ 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 $ClCH_2Sa$ by the reaction of $ClCH_2SiCl_3$ with TEA

Solvent	$ClCH_2SiCl_3$:N $(CH_2CH_2OH)_3$	Temperature, °C	Yield of $ClCH_2Sa$, %
$HCCl_3$	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_2CCl_2	1:2	0 to –5	72[a]
H_2CCl_2	1:2	20	68[a]
MeCN	1:1	–5	46

[a] Recalculated to the starting silane.

$$RSiCl_3 + (HOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2)_3N + 3\ HCl,$$

$$R = Me, Et, Ph, ClCH_2, ICH_2, Cl(CH_2)_3.$$

The above reaction of organyltrichlorosilanes with TEA in $HCCl_3$ 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 ICH_2Sa (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 $HSiCl_3$ and $SiCl_4$ and TEA failed. However, similar methods of synthesis of FSa from TEA and SiF_4 we described earlier [20].

EXPERIMENTAL

IR spectra were taken on a Specord IR 75 instrument from KBr pellets. ^1H and ^{13}C 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 $HCCl_3$ at 0–5°C in an inert atmosphere a solution of TEA in $HCCl_3$ was slowly added dropwise. The reaction mixture was stirred until warming to room temperature, $HCCl_3$ 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.

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Table 2. Yield, mp, and elemental analysis of RSa synthesized from $RSiCl_3$ 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	$C_7H_{15}NO_3Si$	44.42	7.99		7.40	14.84
Et	55	132–133 (heptane)	47.15	8.27		7.22	13.80	$C_8H_{17}NO_3Si$	47.26	8.43		6.89	13.82
Ph	40	209–210 (xylene)	56.87	7.04		5.76	10.72	$C_{12}H_{17}NO_3Si$	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	$C_7H_{14}ClNO_3Si$	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	$C_7H_{14}INO_3Si$	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	$C_9H_{18}ClNO_3Si$	42.93	7.21	14.08	5.56	11.16

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