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1-(HETERYLOXY)SILATRANES*

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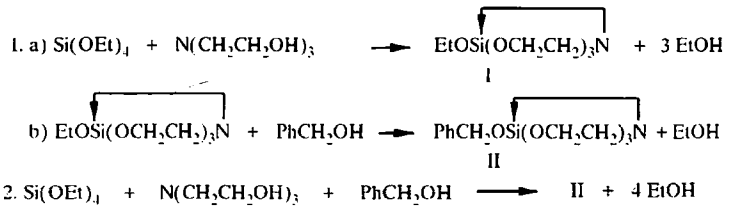
Novel heterocyclic 1-derivatives of silatranes have been obtained. The optimal synthetic method for the indicated compounds is transesterification of tetraethoxysilane by an equimolar mixture of triethanolamine and a heterocyclic (or aromatic) hydroxyl-containing compound.

1-(Organyl)silatranes continue to attract attention of researchers [1,2]. The paper [3] was devoted to synthesis of N-heterocyclic silatranes by dehydrocondensation of pyridine methanols with 1-hydrosilatrane, which has a labile Si–H bond; we obtained three isomeric 1-(pyridylmethoxy)silatrane in satisfactory yields (44-56%). However the yield of the corresponding silatrane from 6-methyl-2-pyridine methanol was rather low (25%). Since heterocyclic derivatives of silatranes are potentially biologically active compounds [4], in this work we have continued the search for more efficient methods for synthesis of compounds in this class.

Many 1-(organyloxy)silatranes are obtained by transesterification of lower alkoxysilanes by higher alcohols or other hydroxyl-containing organic compounds [5]. But it remains unclear which transesterification method is optimal: sequential synthesis of the lower alkoxysilatrane and its reaction with the higher hydroxy derivative, or transesterification by the method first proposed by Voronkov and Zelchan [6], in a single step using a three-component system tetraalkoxysilane–triethanolamine–higher alcohol. The objective of our work was to select the optimal method from these two possibilities, to compare it with the previously used method [3], and also to synthesize a series of novel 1-heterocyclic silatranes based on our results.

To determine the optimum transesterification method, we chose the synthesis of 1-(benzyloxy)silatrane, which we carried out by two methods: sequentially in two steps (reactions 1a,b), and in a single step (reaction 2).



The ethoxysilatrane I was obtained by reaction 1a twice in 61% and 66% yields. The yield of 1-(benzyloxy)silatrane II from silatrane I according to reaction 1b was 71% based on the ethoxysilatrane, i.e., 45% based on the starting tetraethoxysilane. By the reaction 2 (reaction time ~1 h), silatrane II was obtained in 75% yield. Thus we determined that the one-step method is more efficient. Using the data obtained, we synthesized several 1-(heteryloxy)silatranes by transesterification in three-component mixtures.

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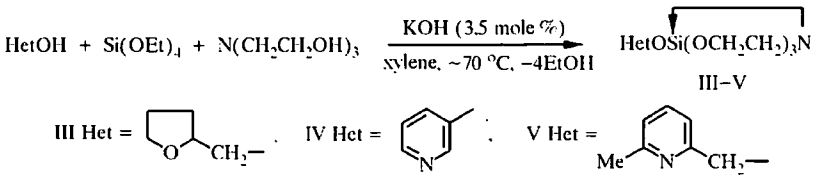

The reactions were carried out in xylene in the presence of KOH catalyst (3.5 mole %) under a stream of argon by heating on an oil bath, with distillation of the ethanol formed at ~70°C into a graduated test tube until the calculated amount of alcohol was obtained. The reaction time was 2 h to 3.5 h. As the heterocyclic hydroxyl derivatives, we used compounds with different structures, including saturated oxygen-containing or N-heteroaromatic rings, and also with different reacting groups (CH_2OH or OH): 2-tetrahydrofurfuryl alcohol, 3-hydroxypyridine, and 6-methyl-2-pyridine methanol. The corresponding silatranes III-V were obtained in the following yields: III, 49%; IV, 17%; V, 60%. We were unable to synthesize silatrane from 2-hydroxypyridine using the indicated method. Probably the low reactivity in the target reaction and the thermal instability of the

TABLE 1. Characteristics of Synthesized Silatranes I-V

Compound	mp, °C	Found, % / Calculated, %			Yield, %
		C	H	N	
I	100*	43.61 / 43.81	7.77 / 7.80	6.68 / 6.40	61-66
II	187-190*[2]	54.68 / 55.49	6.76 / 6.75	5.02 / 4.98	71*[3]; 75*[4]
III	176-179	47.90 / 47.99	7.63 / 7.69	5.13 / 5.09	49
IV	188-189	48.23 / 49.24	5.98 / 6.01	10.12 / 10.44	17
V	170-172	52.68 / 52.68	6.88 / 6.80	9.40 / 9.45	60

* 100-102°C [5].

*[2] 190-192°C [5].

*[3] Based on the starting $EtOSi(OCH_2CH_2)_3N$; 45% based on $Si(OEt)_4$.

*[4] Based on starting $Si(OEt)_4$.

TABLE 2. PMR Spectra of Silatranes $R\text{-}OSi(CH_2CH_2)_3N$ I-V

Compound	Chemical shift, δ (ppm); spin-spin coupling constant J (Hz)			
	CH_2N, t	CH_2O, t	J	R
I	2.82	3.82	5.6	1.18 (3H, t, J = 7.0, CH_3); 3.67 (2H, q, J = 7.0, CH_2)
II	2.80	3.80	6.2	4.73 (2H, s, CH_2); 6.80-7.44 (5H, m, Ph)
III	2.82	3.80	6.0	1.50-2.09 (4H, m, two 3-H, two 4-H) 3.24-4.21 (5H, m, 2-H, two 5-H, CH_2)
IV	2.96	3.92	6.0	7.10 (1H, dd, J_1 = 8.2, J_2 = 4.6, 5-H) 7.33 (1H, m, J_1 = 8.2, J_2 = 2.8, J_3 = 1.8, 4-H) 8.10 (1H, dd, J_1 = 4.6, J_2 = 1.8, 6-H) 8.39 (1H, d, J = 2.8, 2-H)
V	2.87	3.85	6.0	2.49 (3H, s, CH_3) 4.88 (3H, s, CH_2) 6.92 (1H, m, 5-H) 7.46-7.58 (2H, m, 3-H, 4-H)

TABLE 3. Mass Spectra of Silatranes I-V

Compound	m/z (I_{rel}, %)
I	219 (10, M^+), 204 (13, $[M-Me]^+$), 188 (5), 174 (100, *$[SiA]^+$), 160 (5), 148 (6), 132 (8), 118 (5), 102 (7), 89 (6), 79 (7), 63 (12), 45 (15, $[EtO]^+$), 42 (10), 30 (2)
II	281 (18, M^+), 250 (2), 238 (5), 206 (4), 174 (100, $[SiA]^+$), 160 (5), 130 (7), 116 (4), 102 (7), 91 (21, $[PhCH_2]^+$), 77 (6, Ph), 63 (7), 51 (4), 45 (6), 42 (6), 30 (2)
III	275 (2, M^+), 244 (2), 232 (2), 204 (15, $[M-C_4H_7O]^+$), 192 (5), 174 (100, $SiA]^+$), 162 (5), 148 (5), 130 (6), 116 (4), 102 (6), 89 (5), 79 (6), 71 (5, $[C_4H_7O]^+$), 63 (7), 55 (5), 43 (13), 41 (12), 31 (2)
IV	268 (21, M^+), 237 (5), 174 (100, $[SiA]^+$), 152 (5), 138 (5), 130 (6), 102 (5), 88 (4), 78 (4), 63 (5), 45 (6)
V	296 (15, M^+), 281 (1, $[M-Me]^+$), 266 (27), 265 (26), 198 (10), 184 (25), 174 (100, $[SiA]^+$), 160 (18), 106 (7, $[MeC_5H_3NCH_2]^+$), 77 (7, $[C_5H_3N]^+$), 63 (8), 42 (9), 30 (2)

* $[SiA]^+ = [Si(OCH_2CH_2)_3N]^+$.

hydroxypyridines lead mainly to decomposition of these compounds and not forming the desired products. Compounds III and IV could not be synthesized by the dehydrocondensation method used earlier [3].* This result suggests that transesterification is a more efficient method for preparation of the indicated compounds.

The synthesized silatranes I-V were characterized by elemental analysis, PMR, and mass spectrometry (Tables 1-3); the results correspond to the proposed structure of the compounds. The PMR spectra of atranes I and II are close to those given in the literature [7]. We give more detailed characteristics for silatrane V.

We recorded the ^{29}Si NMR spectra of silatranes III and V; the magnitude of the chemical shift in both cases was -94.7 ppm, which is typical for five-coordinate silicon compounds [7].

EXPERIMENTAL

The NMR spectra were recorded on Bruker WH-90/DS (90 MHz) and Varian 200 Mercury (200 MHz) spectrometers for solutions in $CDCl_3$, internal standard HMDSO. The mass spectra were obtained on an HP 6890 GC/MS chromatograph/mass spectrometer equipped with an HP-5 MS capillary column (30.0 m × 250 μm × 0.25 μm), for temperature programming from 70°C to 260°C (10°C/min). Xylene (bp 136-144°C) was distilled before use over $LiAlH_4$. The tetraethoxysilane, triethanolamine, and benzyl alcohol were purified by vacuum distillation, after which their properties corresponded to literature data. The 2-tetrahydrofurfuryl alcohol, 2- and 3-hydroxypyridines, and also the 6-methyl-2-pyridine methanol were obtained from Fluka and Aldrich.

General Procedure for Synthesis of 1-(Organyloxy)silatranes II-V. A 50 ml glass flask with a rectifying column, a condenser, and a graduated test tube and equipped with a magnetic stirrer was purged with argon and then dry xylene (14 ml), the hydroxy derivative (0.01 mol), KOH (0.02 g), triethanolamine (1.33 ml, 0.01 mol), and tetraethoxysilane (2.23 ml, 0.01 mol) was placed inside it. The mixture was heated on an oil bath (120-130°C) with stirring. At ~70°C the ethanol formed was distilled into a graduated test tube until the calculated amount was obtained (2.35 ml). At the end of the reaction, the hot reaction mixture was rapidly filtered to remove the insoluble residue or decanted to remove the oily residue. On cooling, crystals of 1-(organyloxy)silatrane were precipitated from the filtrate, and these crystals were filtered off and washed on the filter with petroleum ether. The compounds obtained were recrystallized from ethylacetate and analyzed after drying in a vacuum desiccator (Tables 1-3).

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