ATRANES

COMMUNICATION 41. 1-(IODOALKYL)SILATRANES

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Previously we had reported the synthesis of the 1-(chloroalkyl)-silatranes [1] and 1-(bromoalkyl)silatranes [2]. The present paper is devoted to the synthesis of the previously unknown 1-(iodoalkyl)-silatranes and their comparison with the corresponding chloro and bromo derivatives.

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For this purpose we synthesized the difficultly accessible (iodoalkyl)trialkoxysilanes $I(CH_2)_n Si(OR)_3$ (R = CH₃, C₂H₅, n = 1 - 3) [3], which were reacted with triethanolamine [2] by the following scheme:

We were unable to obtain $1-(\beta-iodoethyl)$ silatrane by this procedure. An attempt to obtain the 1-(iodoalkyl)silatranes by the exchange reaction of the 1-(chloroalkyl)silatranes with NaI proved unsuccessful, since the (chloroalkyl)trialkylsilanes and (chloroalkyl)trialkoxysilanes are converted to the corresponding iodo derivatives when they are reacted with metal iodides.

The 1-(iodoalkyl)silatranes are either white or yellowish crystalline compounds that are odorless, soluble in acetone, ethanol, $CHCl_3$, DMSO or DMF, and insoluble in ether, hydrocarbons or water. The solubility of the 1-(haloalkyl)silatranes increases with increase in the length of the hydrocarbon chain between the halogen and silicon atoms, and also with increase in the atomic number of the halogen.*

* The (fluoroalkyl)silatranes, which will be the subject of the next communication, exhibit anomalous properties.

R	мр, °С	Frequencies of stretching vib- vibrations, cm ⁻¹			LD ₅₀ , mg/kg*	Chemical shifts, $ au$, ppm		
		۲CX	^v Si←N	*siog		CH2X	OCH2	CH₂N
I(CH ₂) ₃	167—168	545	594	799, 1018, 1100	29	9,54 (α) 8,04 (β)	6,22	7,17
ICH2 BrCH2 ClCH2 Cl(CH2)3	191—192 199—200 211—213 130—131	530 560 710 734	580 590 572 580	795, 1020, 1090 800, 1025, 1095 770, 1030, 1090 800, 1020, 1105	890 916 2800 2240	0, 18(1) 8,10 7,69 7,34 $9,48(\alpha)$ 8,14(3)	6,14 6,16 6,16 6,21	7,10 7,11 7,11 7,18
CH₃	151—152	_	570	772, 1020, 1095	3000	6,51 (γ) 10,12	6,22	7,21

TABLE 1. (Iodoalkyl)silatranes and Their Analogs RSi(OCH₂CH₂)₃N

*The toxicity was studied by A; T. Platonova, V. V. Bublis, and S. K. Suslova on white mice by the intraperitoneal injection of Tween emulsions,

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The toxicity of the haloalkylsilatranes increases in the same order, while both their melting point and hydrolytic stability decrease (Table 1).

The IR spectra of the 1-(iodoalkyl)silatranes resemble the spectra of the corresponding chloro and bromo derivatives [2, 4] (see Table 1). A change in the nature of the halogen atom in the α -haloalkylsilatranes is practically without effect on the position of the ν_{Si^*-N} and ν_{SiOC} frequencies, which remain the same as in silatrane itself and the 1-(haloalkyl)silatranes are also practically the same as the spectra of the corresponding alkylsilatranes [5]. However, for the 1-(α -haloalkyl)silatranes a linear relation is observed between the chemical shift of the protons of the XCH₂Si group and the electronegativity of the X substituent (see Table 1).

EXPERIMENTAL METHOD

The IR spectra were obtained on a UR-20 spectrophotometer (as KBr pellets and $CHCl_3$ solutions). The NMR spectra were taken on a Tesla BS487B spectrometer (80 MHz), using $CHCl_3$ as the solvent, and HMDS and cyclohexane as the internal standards.

(Iodomethyl)trimethoxysilane (I). With vigorous stirring, to a refluxing solution of 48.3 g (0.32 mole) of ignited NaI in 450 ml of absolute acetone was added 50.0 g (0.29 mole) of (chloromethyl)trimethoxysilane in drops. The mixture was refluxed for 29 h and then the acetone was distilled off. The salts (NaCl + NaI) were separated, while the residue was vacuum-distilled over powdered copper. We obtained 48.6 g (63.5%) of (I) with bp 74-75° (10 mm); n_D^{20} 1.4690; d_4^{20} 1.6238. Found: C 18.54; H 4.35; Si 10.87; I 48.58%; MR 44.97. C₄H₁₁O₃SiI. Calculated: C 18.32; H 4.22; Si 10.71; I 48.41%; MR 45.62.

 $\frac{(\gamma-\text{Iodopropyl})\text{trimethoxysilane (II)}}{\text{g (0.15 mole) of (}\gamma-\text{chloropropyl})\text{trimethoxysilane in 300 ml of acetone was refluxed for 3 h to give 17.5 g (39.5\%) of (II) with bp 79-80° (2 mm); nD²⁰ 1.4714;; d_4²⁰ 1.4755. Found: Si 9.81; I 43.78\%; MR 55.01. C₆H₁₅O₃SiI. Calculated: Si 9.68; I 43.73\%; MR 54.92.$

<u>1-(Iodomethyl)silatrane (III)</u>. A solution of 20.0 g (0.076 mole) of (iodomethyl)trimethoxysilane, 11.4 g (0.076 mole) of triethanolamine, and 0.1 g of KOH in 20 ml of o-xylene was heated until the formed methanol ceased to distill. Then the hot reaction mixture was treated with 20 ml of hexane. The obtained crystals were separated, washed with hexane, and dried in vacuo. We obtained 9.4 g (39%) of (III) with mp 187-188° (CHCl₃-heptane). Found: Si 9.12; I 42.94%. $C_7H_{14}NO_3SiI$. Calculated: Si 8.9; I 40.32%.

 $\frac{1-(\gamma-\text{Iodopropyl})\text{silatrane (IV)}}{\text{methoxysilane, 0.2 g of KOH, and 11.8 g (0.08 mole) of triethanolamine in o-xylene we obtained 15.0 g (54.4\%) of (IV) with mp 167-168° (CHCl₃-heptane). Found: Si 8.61; I 36.38\%. C₉H₁₈O₃NSiI. Calculated: Si 8.12; I 36.80\%.$

CONCLUSIONS

The previously unknown 1-(iodoalkyl)silatranes $I(CH_2)_n Si(OCH_2CH_2)_3 N$ (n = 1, 3) were synthesized. Their IR and NMR spectra were studied, and also their toxicity. The obtained results were compared with the corresponding data for the 1-(chloroalkyl)- and 1-(bromoalkyl)silatranes.

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