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LETTERS TO THE EDITOR

Organylbis-(1-silatranylmethyl)amines

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Silatranyl group $Si(OCHRCH_2)_3N$ is the strongest electron-donating substituent (σ^* –3.49) [1, 2]. This fact largely governs the physical and chemical properties of silatranes. In piperidinomethylsilatrane $(CH_2)_5NCH_2Si(OCHRCH_2)_3N$ the exocyclic nitrogen atom has a very low ionization energy even as compared with diazabicyclooctane (7.46 and 7.52, 9.65 eV, respectively) [1, 3]. At the same time the equilibirum constant of the reaction with phenol is very high (1100 and 537 l mol^{-1}, respectively) [1, 4]. When dialkylaminomethylsilatranes are dissolved in CCl_4 at room illumination, the formation of their hydrochlorides $[Alk_2N\overset{+}{H}Si(OCH_2CH_2)_3N]Cl^-$ in high yield starts even in 10–15 min [5].

Proceeding with these studies, we have prepared previously unknown organylbis(1-silatranylmethtyl)amines **IIa** and **IIb** according to the scheme

$$\underset{\textbf{Ia, Ib}}{AlkN[CH_2Si(OEt)_3]_2} + 2N(CH_2CH_2OH)_3$$

$$\rightarrow \underset{\textbf{IIa, IIb}}{AlkN[CH_2Si(OCH_2CH_2)_3N]_2} + 6EtOH.$$

Alk = Me (**Ia**, **IIa**), $PhCH_2$ (**Ib**, **IIb**).

For comparative evaluation of the electron-donating power of the exocyclic nitrogen atom in these compounds, we used the band of symmetric stretching vibrations of the CH_3 and CH_2 groups in the $CH_3(N)$ and $CH_2(N)$ moieties. According to nonempirical quantum-chemical calculations, the low-frequency shift of this band in the spectra of 2-(*N*-methylamino)ethanol and 2-(*N*,*N*-dimethylamino)ethanol (2807–2819 cm^{-1}) as compared to the vibration of the Me(C) group (2870 cm^{-1}) is caused by n, σ hyperconjugation in the N–CH_3 fragment between the unshared electron pair of nitrogen and the longest C–H bond in the *trans* position to this electron pair [6]. The protonation of nitrogen causes the high-frequency shift of this band. A similar trend was observed by us in going from dialkylaminomethylsilatranes to the corresponding hydrochlorides [5]. As the solvent polarity increases in going from C_7H_{16} to MeCN (the increase in the N→Si donor–acceptor interaction), the band of symmetric stretching vibrations of the $CH_3(N)$ group in the IR spectra of the monocyclic analogs of silatranes $RMeSi(OCH_2CH_2)_2NMe$ (R = Me, Ph) undergoes a high-frequency shift from 2780 to 2810 cm^{-1} [7]. In the absence of this interaction in the acyclic analog $(Me_3SiOCHRCH_2)_2NMe$ this band does not depend on the nature of solvent (2802–2805 cm^{-1}). These data show that the frequency of the symmetric stretching vibration in the compounds under study depends on the electron density on the nitrogen unshared electron pair. In the IR spectra of **IIa** and **IIb** the bands of symmetric stretching vibrations have lower frequencies as compared to **Ia** and **Ib** (2725–2730 and 2755–2760 cm^{-1}, respectively). This fact suggests the higher electron-donating power of the exocyclic nitrogen atom in **IIa** and **IIb**.

Methylbis(1-silatranylmethyl)amine (IIa). On mixing of **Ia** with triethanolamine in a 1 : 2 molar ratio, the mixture warmed up within 3–5 min and became homogeneous. It was left for 1 h at room temperature, the released ethanol was removed in a vacuum, and the solid residue was crystallized from benzene. Yield of **IIa** 78%, mp 138–140°C. IR spectrum, ν, cm^{-1}: 585, 905, 940, 1090, 1115 $[Si(OCH_2CH_2)_3N]$. ^1H NMR spectrum, δ, ppm: 1.60 s (NCH_2Si), 2.17 s (CH_3N), 2.83 t (NCH_2), 3.79 t (OCH_2). Found, %: C 44.12; H 7.28; N 10.45; Si 13.11. $C_{15}H_{31}N_3O_6Si_2$. Calculated, %: C 44.42; H 7.70; N 10.36; Si 13.85.

Benzylbis(1-silatranylmethyl)amine (IIb). This compound was prepared similarly. Yield 83%, mp 189–191°C. IR spectrum, ν, cm^{-1}: 585, 902, 915, 940, 1095, 1120 $[Si(OCH_2CH_2)_3N]$, 700, 745, 1600, 3020, 3050, 3080 (C_6H_5). ^1H NMR spectrum, δ, ppm: 1.94 s (NCH_2Si), 2.77 t (NCH_2), 3.52 s ($PhCH_2N$), 3.79 t (OCH_2), 7.15 m (Ph). Found, %: C 51.89; H 6.95; N 8.54; Si 10.62. $C_{21}H_{35}N_3O_6Si_2$. Calculated, %: C 52.36; H 7.32; N 8.72; Si 11.66.

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The IR spectra were recorded on a Specord IR-75 spectrometer in KBr pellets or in a thin layer. The ^{1}H NMR spectra were measured on a Jeol FX-90Q spectrometer for 20% solutions of **IIa** and **IIb** in CD_3CN against internal TMS.

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