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LETTERS TO THE EDITOR

Dedicated to the 90th Anniversary of Academician M.G. Voronkov

1-(Pyridine-2-carboxymethyl)silatrane

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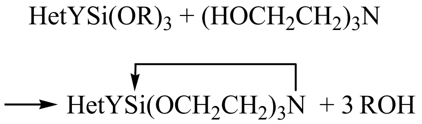
1-(*N*-Heterylalkyl)silatranes $Het(CH_2)_nSi(OCH_2CH_2)_3N$ and their physical and chemical properties have been systematically studied by us since the beginning of the nineteen nineties [1–3]. Generally, they are obtained by the reaction of transetherification of the corresponding (*N*-heterylalkyl)trialkoxysilanes with tris(2-hydroxyethyl)amine [2, 4].

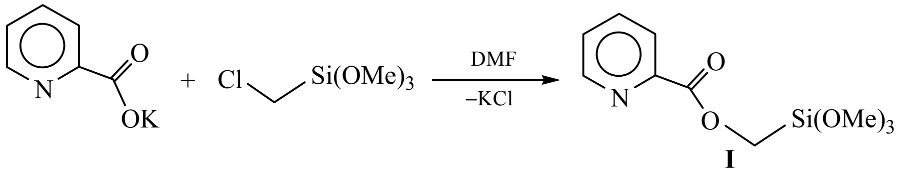


$$HetYSi(OR)_3 + (HOCH_2CH_2)_3N \longrightarrow HetYSi(OCH_2CH_2)_3N + 3\,ROH$$

Here, Het stands for a heterocyclic substituent, Y, for the hydrocarbon linker $(CH_2)_n$ (n = 1, 3) or SCH_2 connecting the heterocycle with the silicon atom of the silatranyl group.

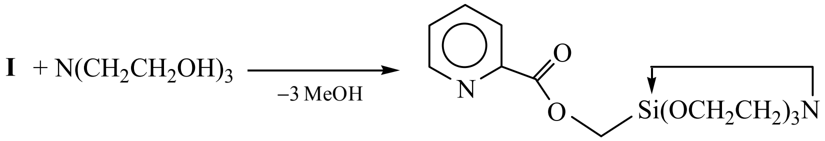
So far, *N*-silatranylmethyl derivatives of cyclic aminoacids were unknown. Here we describe the synthesis of the first representative of these compounds, 1-(pyridine-2-carboxymethyl)silatrane.

The precursor of 1-(pyridine-2-carboxymethyl)silatrane, the earlier unknown (pyridine-2-carboxymethyl)trimethoxysilane (I), was synthesized by the reaction of nucleophilic substitution of the chlorine atom of trimethoxy(chloromethyl)silane by the pyridine-2-carboxylic group in a polar solvent (DMF) in the presence of catalytic amounts of dibenzo-18-crown-6.



I

Transetherification of (pyridine-2-carboxymethyl)trimethoxysilane (**I**) with tris(2-hydroxyethyl)amine in the absent of the catalyst at 48–50°C affords 1-(pyridine-2-carboxymethyl)silatrane (**II**) in 80% yield.



II

The composition and structure of the synthesized compounds **I** and **II** are proved by the ^1H, ^{13}C, ^{29}Si NMR, IR spectroscopy, and elemental analysis.

(Pyridine-2-carboxymethyl)trimethoxysilane (I). To 5 g of potassium pyridine-2-carboxylate in 50 ml of DMF 5.63 g of trimethoxy(chloromethyl)silane was added dropwise in the presence of dibenzo-18-crown-6. The reaction mixture was stirred with a magnetic stirrer at 70–75°C for 9 h, the formed precipitate was filtered off, the filtrate was distilled in a vacuum. The yield of (pyridine-2-carboxymethyl)trimethoxysilane 2.11 g (28%), bp 136°C (2 mm Hg). IR spectrum, ν, cm^{-1}: 839, 1090, 2847 (Si–O–C), 1679 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.41 s (9H, OCH_3), 3.94 s (2H, OCH_2Si), 7.86 d (1H, H^3, ^3J 7.7 Hz), 7.60 t. d (1H, H^4, ^3J 7.7, ^4J 1.6 Hz), 7.24 d.d.d (1H, H^5, ^3J 7.7, ^3J 4.9, ^4J 1.0 Hz), 8.52 d (1H, H^6, $^3J_{HH}$ 4.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 50.82 (OCH_3), 52.19 (OCH_2Si), 147.90 (C^2), 124.90 (C^3), 136.79 (C^4), 126.65 (C^5), 165.35 [C(O)O]. Found, %: C 49.53; H 6.37; N 5.80; Si 11.91. $C_{10}H_{15}N_1O_5Si_1$. Calculated, %: C 49.79; H 6.22; N 5.81; Si 11.62.

1-(Pyridine-2-carboxymethyl)silatrane (II). To 1.41 g of (pyridine-2-carboxymethyl)trimethoxysilane 0.88 g of tris(2-hydroxyethyl)amine was added dropwise. The reaction mixture was stirred at 60–65°C for 1 h, the precipitate formed was filtered off and crystallized from the mixture hexane–chloroform (1:1). Yield 1.46 g (80%), mp 178–180°C. IR spectrum, ν, cm^{-1}: 570, 785, 915, 940, 1085, 1105 [$Si(OCH_2CH_2)_3N$]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.81 t (6H, NCH_2), 3.74 t (6H, OCH_2), 8.02 d (1H, H^3, $^3J_{HH}$ 7.7 Hz), 7.69 t (1H, H^4, ^3J 7.7 Hz), 7.31 d.d (1H, H^5, ^3J 7.7, ^3J 4.9 Hz), 8.61 d (1H, H^6, $^3J_{HH}$ 4.9 Hz), 3.83 s (2H, OCH_2Si). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 57.20 ($SiOCH_2$), 59.08 (OCH_2Si), 51.17 (NCH_2), 149.36 (C^2), 125.10 (C^3), 136.68 (C^4), 126.09 (C^5), 149.44 (C^6), 166.21 [C(=O)O]. ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –78.7 ppm. Found, %: C 50.01; H 6.20; N 8.75; Si 9.36. $C_{13}H_{18}N_2O_5Si_1$. Calculated, %: C 50.32; H 5.81; N 9.03; Si 9.03.

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