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1-(PYRIDYLMETHOXY)SILATRANES

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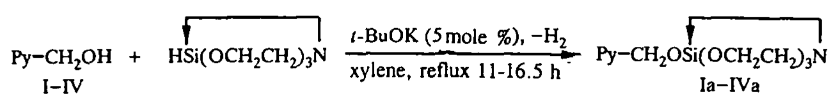
A series of 1-(pyridylmethoxy)silatranes was obtained by the dehydrocondensation of pyridinemethanols with 1-hydrosilatrane catalyzed by potassium tert-*butylate.*

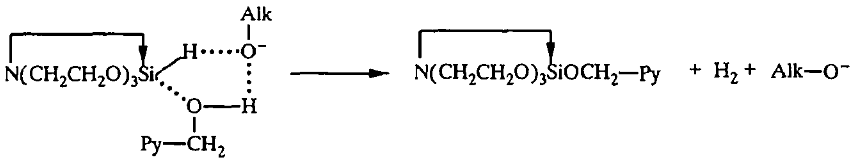
Silatranes are a unique class of compounds of pentacoordinated silicon and have been studied intensively in the past three decades [1-9]. New pyridylmethoxy-1-silatranes were sought in light of the considerable biological activity of many reported silatranes, especially, furyl and thienyl derivatives [10-12]. The present work was devoted to the synthesis and study of the title compounds.

A synthesis has been reported for 1-alkyloxy- and 1-aryloxysilatranes from 1-hydrosilatrane, which has a labile Si$-$H bond, upon reaction with several aliphatic and aromatic alcohols in the presence of base [13, 14]. In the present work, we show that the corresponding 1-substituted silatranes may be obtained by the reaction of pyridinemethanols with 1-hydrosilatrane upon heating in xylene at reflux in the presence of a strong base, namely, potassium *tert*-butylate (NaOH, KOH, and NaOEt do not catalyze these reactions).



I, Ia, II, IIa, III, IIIa) Py = 2,3,4-pyridyl, respectively; IV, IVa) Py = 6-methyl-2-pyridyl

The mechanism for base-catalyzed reactions of alcohols with hydrosilatrane may involve formation of an intermediate active complex with six electrons in the field of five atoms. The following scheme is described for the reactions of pyridinemethanols in the presence of alcoholates:



The corresponding dehydrocondensation products Ia-IVa were obtained by heating a mixture of 1-hydrosilatrane and pyridinemethanol I-IV (10% excess of alcohol) in xylene at reflux for 11-16.5 h in the presence of 5 mole % potassium *tert*-butylate. These products were identified by elemental analysis, PMR spectroscopy, and mass spectrometry. A downfield shift of the signal of the Py$-$C$\underline{H}_2$O group is observed relative to the corresponding pyridinemethanols due to formation of a bond of the oxygen atom of this group with the silatranyl silicon atom (see Table 2). The mass spectra of silatranes Ia-IVa display peaks for the corresponding molecular ions, while maximum strength is found for the peak of the $[(N(CH_2CH_2O)_3Si]^+$ ion.

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TABLE 1. Physical Indices of Silatranes Ia-IVa

Starting compound	Reaction time, h	Product	Chemical formula	Found, % / Calculated, %			mp, °C	Yield, %
				C	H	N		
I	16,5	Ia	$C_{12}H_{18}N_2O_4Si$	49,61 51,04	6,44 6,42	9,50 9,92	161...163	56
II	15	IIa	$C_{12}H_{18}N_2O_4Si$	50,38 51,04	6,76 6,42	9,54 9,92	120...122	44
III	11	IIIa	$C_{12}H_{18}N_2O_4Si$	49,83 51,04	6,65 6,42	9,67 9,92	157...160	48
IV	16	IVa	$C_{13}H_{20}N_2O_4Si$	52,03 52,68	6,97 6,80	9,22 9,45	130...134	25

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*Hygroscopic compounds.

TABLE 2. PMR Spectra of Silatranes Ia-IVa

Compound	Chemical shift, ppm							
	$N(CH_2)_3$, t	$(CH_2O)_3$, t	Py — CH_2O, s (starting alcohol)	pyridine ring, m				
	J = 6 Hz			H-2	H-6	H-4	H-3	H-5
Ia	2,89	3,87	4,91 (4,75)	—	8,44	7,61	6,93...7,22	
IIa	2,89	3,84	4,78 (4,71)	8,51	8,33	7,71	—	7,13
IIIa	2,88	3,91	4,80 (4,73)	8,44		—	7,33	
IVI*	2,87	3,87	4,89 (4,71)	—	—	6,71	6,71...7,56	

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*Signal of CH_3 group: 2.49 ppm, s.

TABLE 3. Mass Spectra of Silatranes Ia-IVa

Compound	m/z (I_{rel}, %)
Ia	282 (26, M^+), 252 (40), 251 (36), 198 (10), 175 (13), 174 (100, $N(CH_2CH_2O)_3Si^+$), 170 (23), 160 (18), 152 (11), 130 (11), 92 (12), 40 (13)
IIa	282 (27, M^+), 251 (8), 175 (15), 174 (100, $N(CH_2CH_2O)_3Si^+$), 160 (10), 130 (8), 92 (11)
IIIa	282 (29, M^+), 251 (5), 239 (11), 175 (14), 174 (100, $N(CH_2CH_2O)_3Si^+$), 160 (11), 152 (10), 132 (10), 130 (8), 92 (8)
IVa	296 (14, M^+), 266 (40), 265 (39), 184 (35), 174 (100, $N(CH_2CH_2O)_3Si^+$), 160 (25), 40 (70)

EXPERIMENTAL

The PMR spectra were taken on a Bruker WH-90/DS spectrometer in $CDCl_3$ with TMS as the internal standard. The mass spectra were taken on an MS-50 mass spectrometer at 70 eV and an HP-6890 CG/MS equipped with a 30-m × 250-μm × 25-μm HP-5 MS capillary column with temperature programming from 70 to 260°C at 10°C/min. The reaction mixtures were analyzed on a Chrom-4 chromatograph equipped with a flame ionization detector and 1.2-m × 3-mm glass column packed with 5% OV-17 on Chromosorb W-AW (60-80 mesh). The column temperature was 120-250°C and the nitrogen gas flow rate was 60 ml/min.

A xylene sample with bp 136-144°C was redistilled over $LiAlH_4$ prior to use. 1-Hydrosilatrane was synthesized from boratrane according to Zelchan [15]. Samples of the pyridinemethanols studied and potassium *tert*-butylate were obtained from Fluka and Aldrich.

General Method for the Synthesis of 1-(Pyridylmethoxy)silatranes Ia-IVa. A mixture of 40 ml dry xylene, 0.350 g (2 mmoles) 1-hydrosilatrane, 2.2 mmole pyridinemethanol I-IV, and 11 mg (0.1 mmole) potassium *tert*-butylate was prepared in a glass reactor equipped with a magnetic stirrer, probe outlet, and reflux condenser with a calcium chloride tube and heated at reflux. Probes were periodically taken using a microsyringe and analyzed by gas-liquid chromatography. At the end of the reaction, xylene was evaporated on a vacuum rotary evaporator and 40 ml dry chloroform was added to the residue. The mixture was filtered off. Hexane was added until the solution became cloudy. The mixture was left in a refrigerator for 5-6 h. The precipitate formed was filtered off and analyzed (Tables 1-3).

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