Table 2. ^{1}H chemical shifts in the NMR spectra of $R^2OCH_2N(Me)CH_2SiR(OR^1)_2$ and $CH_2[N(Me)CH_2SiR(OR^1)_2]_2$

Compound	$CDCl_3$, δ						
	R^2O—C	O—CH_2—N	N—CH_2—N	N—Me	N—CH_2Si	CH_3—Si	$Si(OR^1)$
1a	3.30 s	3.98 s	—	2.43 s	2.20 s	—	3.57 s
1b	3.29 s	3.94 s	—	2.42 s	2.18 s	—	1.23 t, 3.85 q
1c	1.18 s 3.49 q	3.98 s	—	2.39 s	2.11 s	0.17 s	1.21 t, 3.80 q
2a	—	—	2.68 s	2.27 s	2.04 s	—	3.58 s
2b	—	—	2.68 s	2.27 s	2.02 s		1.22 t, 3.86 q
2c	—	—	2.65 s	2.25 s	1.97 s	0.16 s	1.20 t, 3.79 q

Experimental

(*N*-methyl-*N*-alkoxymethylaminomethyl)dialkoxysylanes (1a—c) and bis[*N*-methyl-*N*-(dialkoxysilylmethyl)amino-]methanes (2a—c). A solution of 0.01 *M* chloromethyl alkyl ether in 20 mL of Et_2O was slowly added dropwise to a mixture of 0.01 *M* *N*-methylaminomethyldiethoxy-R-silane and 0.01 *M* triethylamine in 50 mL of absolute Et_2O with stirring in a dry argon atmosphere. The reaction mixture was stirred for 2 h at ~20 °C. The precipitate that appeared was filtered off and washed with Et_2O (2×30 mL). The Et_2O was removed from the filtrate and the residue was distilled *in vacuo*. Yield, constants and data of elemental analysis of the obtained compounds are given in Table 1.

Bis[*N*-methyl-*N*-(triethoxysilylmethyl)amino]methane (2b). A mixture of 2.07 g (0.01 *M*) *N*-methylaminomethyltriethoxysilane and 2.69 g (0.01 *M*) **1b** was kept under Ar for 4 h at 50—60 °C. Compound **2b** was isolated from the reaction mixture by vacuum distillation (96 %).

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N-(2-Thenyl)derivatives of aminoalkyltriethoxysilanes,-silatranes and 2,2-dimethyl-1,3-dioxa-6-aza-silacyclooctane

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The reactions of aminoalkylethoxysilanes and 2,2-dimethyl-1,3-dioxa-6-aza-2-silacyclooctane with 2-(chlormethyl)thiophene and its 5-chloroderivative lead to the corresponding *N*-(2-thenyl) derivatives. The *N*-methyl-*N*-(2-thenyl)aminomethyltriethoxysilane and 5-chlorothyenyl derivative formed are converted by triethanolamine into silatranes.

Key words: aminoalkylethoxysilanes, 2-(chlormethyl)thiophene, 2-(chlormethyl)5-chlorothiophene, *N*-methyl-*N*-(2-thenyl)-aminomethyltriethoxysilanes, *N*-methyl-*N*-(2-thenyl)aminomethylsilatrane, 2,2-dimethyl-1,3-dioxa-6-aza-2-silacyclooctane.

2-(Chlormethyl)thiophene has been known to react with liquid NH_3 to form a mixture of primary, secondary, and tertiary (2-thenyl)amines.[1]

We obtained the corresponding *N*-(2-thenyl)-derivatives by reacting aminoalkylethoxysilanes and 2,2-dimethyl-1,3-dioxa-6-aza-2-silacyclooctane with 2-(chloromethyl)thiophene and its 5-chlorine-substituted derivative.

The corresponding silatranes **11**, **12** are formed by mixing equimolar amounts of compounds **2**, **6** and triethanolamine.

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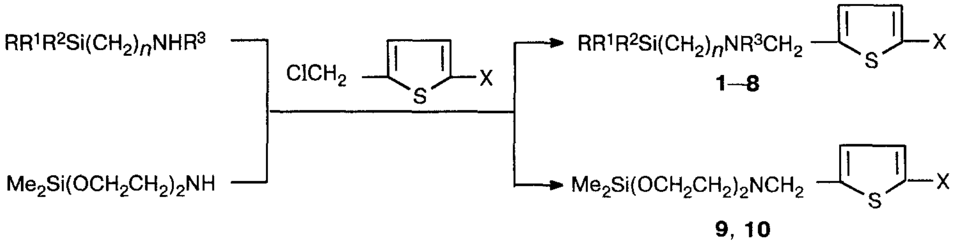
Scheme 1



1: R, R^3 = Me, R^1, R^2 = EtO, X = H, $n = 1$

2: R^3 = Me, R, R^1, R^2 = EtO, X = H, $n = 1$

3: R, R^1, R^2 = EtO, R^3, X = H, $n = 3$

4: R, R^3 = Me, R^1, R^2 = $EtOCH_2CH_2O$, X = H, $n = 1$

5: R, R^3 = Me, R^1, R^2 = EtO, X = Cl, $n = 1$

6: R^3 = Me, R, R^1, R^2 = EtO, X = Cl, $n = 1$

7: R^3 = Me, R, R^1, R^2 = EtO, X = Cl, $n = 3$

8: R, R^3 = Me, R^1, R^2 = $EtOCH_2CH_2O$, X = Cl, $n = 1$

10: X = H (**9**); X = Cl

Table 1. Physicochemical properties of silicon-containing thiophenes

Compound	B.p. /°C (p/Torr)	n_D^{20}	Yield (%)	Found/Calculated (%)						Empirical formula
				C	H	N	Si	S	Cl	
1	116—118 (1.5)	1.4822	66	52.66 52.70	8.49 8.48	5.60 5.12	10.86 10.27	11.57 11.73		$C_{12}H_{23}NO_2SiS$
2	117—120 (1.5)	1.4734	65	51.26 51.45	8.30 8.30	5.21 4.62	8.80 9.25	10.97 10.57		$C_{13}H_{25}NO_3SiS$
3	148—150 (1)	1.4812	23	52.74 52.96	8.41 8.57	4.84 4.41	9.90 8.85	10.26 10.10		$C_{14}H_{27}NO_3SiS$
4	167—171 (1.5)	1.4788	41	58.41 58.31	9.61 9.48	3.84 4.25	7.99 8.52	8.60 9.73		$C_{16}H_{31}NO_4SiS$
5	118—120 (1.5)	1.4922	45	—	—	—	—	10.42 10.41	11.99 11.51	$C_{12}H_{22}ClNO_2SiS$
6	117—120 (1)	1.4852	43	—	—	4.28 4.14	—	11.11 9.49	10.55 10.49	$C_{13}H_{24}ClNO_3SiS$
7	156—159 (1)	1.4908	33	—	—	4.20 3.98	—	10.11 9.71	10.55 10.07	$C_{14}H_{26}ClNO_3SiS$
8	178—182 (1)	1.4862	68	—	—	—	—	8.60 8.81	9.31 9.74	$C_{16}H_{30}ClNO_4SiS$
9	134—136 (1.5)	1.5169	23	51.50 51.32	7.40 7.44	5.42 5.44	11.38 10.91	13.39 12.46		$C_{11}H_{19}NO_2SiS$
10	156—158 (1.5)	1.5271	31	—	—	4.56 4.80	—	9.18 9.62	12.70 12.15	$C_{11}H_{18}ClNO_2SiS$
11	89—90*	—	83	50.08 49.65	7.20 7.05	—	8.83 8.93	9.39 10.20		$C_{13}H_{22}N_2O_3SiS$
12	95—97*	—	60	—	—	8.25 8.03	7.93 6.07	9.72 8.05	10.17 10.16	$C_{13}H_{21}N_2O_3SiS$

* M.p.

The physicochemical characteristics of the compounds obtained and the elemental analysis data are given in Table 1. The structure of the compounds obtained was confirmed by NMR-spectroscopy data (Table 2).

Table 2. Chemical shifts in the ^1H NMR spectra of organiosilicon derivatives of thiophene

Compound	CDCl$_3$, δ							
	CH$_3$—N	N—CH$_2$—Si	O—CH$_2$—C	CH$_3$—C	N—CH$_2$—C	CH$_3$Si	(OCH$_2$CH$_2$)$_3$N	Thiophene cycle
1	2.27 s	1.95 s	3.76 q	1.18 t	3.64 s	0.18 s	—	6.86 m, 7.14 m
2	2.15 s	1.88 s	3.71 q	1.08 t	3.53 s	—	—	6.74 m, 7.03 m
4	2.28 s	2.00 s	3.52 m 3.87 q	1.16 t	3.66 s	0.22 s	—	6.88 m, 7.18 m
5	2.31 s	1.99 s	3.80 q	1.22 t	3.61 s	0.22 s	—	6.68 m
6	2.30 s	2.02 s	3.87 q	1.25 t	3.60 s	—	—	6.67 m
7	—	1.60 m 2.63 m 2.70 m	3.80 q	1.23 t	3.84 s	—	—	6.90 m, 7.16 m
8	2.30 s	2.02 s	3.89 q	1.18 t	3.61 s	0.24 s	—	6.66 m, 6.69 m
9	—	—	—	—	3.85 s	0.14 s	2.70 t 3.74 t	6.63 m, 6.73 m
10	—	—	—	—	3.79 s	0.14 s	2.76 t 3.75 t	6.90 m, 7.16 m
11	2.31 s	1.80 s	—	—	3.78 s	—	2.76 t 3.75 t	6.90 m, 7.16 m
12	2.32 s	1.80 s	—	—	3.70 s	—	2.81 t 3.80 t	6.69 m

Experimental

***N*-Methyl(2-thenyl)aminomethylalkoxysilanes and 2,2-dimethyl-6-aza-2-silacylooktanes.** A mixture of the corresponding silane (0.02 mol) and triethylamine (0.025 mol) was added dropwise with stirring to 2-chloromethylthiophene (0.02 mol) or its 5-chloro derivative. The reaction mixture was heated for 1 h on a boiling water bath and kept for 14—20 h at room temperature. Then the mixture was filtered from the precipitate of triethylamine hydrochloride, which was washed with pentane (2 × 10 mL). The pentane was distilled off, and the residue was distilled *in vacuo*. The yield and physicochemical characteristics of the obtained compounds are given in Table 1.

1-(2-Thenyl)aminomethylsilatranes. A mixture of *N*-methyl-(2-thenyl)aminomethyltriethoxysilane (**2**) (0.01 mol) and triethanolamine (0.01 mol) was stirred until homogenization. The reaction mixture was kept for 1—2 h at 20 °C, then the ethanol that formed was evaporated *in vacuo*. The residue was recrystallized (compound **11** from mixture heptane—benzene, 3:1; compound **12** from benzene).

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