(*N*-methyl-*N*-alkoxymethylaminomethyl)dialkoxysilanes and bis[*N*-methyl-*N*-(dialkoxysilylmethyl)amino]methanes

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(*N*-methyl-*N*-alkoxymethylaminomethyl)-dialkoxysilanes and bis[*N*-methyl-*N*-(dialkoxymethyl)amino]methanes were first obtained by the interaction of (*N*-methylaminomethyl)dialkoxy-R-silanes with chloromethyl alkyl ethers in yields of 40—67 % and 10—25 %, respectively.

Key words: (*N*-methyl-*N*-alkoxymethylaminomethyl) dialkoxysilanes, bis[*N*-methyl-*N*-(dialkoxymethyl)amino]methanes, chloromethyl alkyl ether.

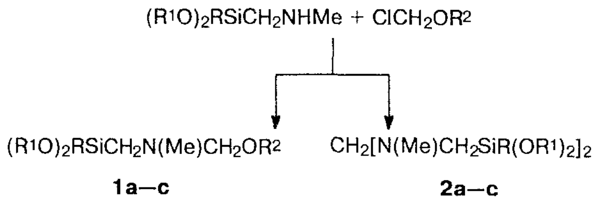
The sole example of organosilicon α-amino ethers, *N*-methoxymetyl-*N*-benzylaminomethyltrimethylsilane, has been obtained by the reaction between *N*-benzylaminomethyltrimethylsilane and formaldehyde.[1]

We performed the reaction between *N*-methylaminomethyldialkoxysilanes and chloromethyl alkyl ethers in the presence of triethylamine, *via* scheme 1.

In this reaction, along with the expected product of nucleophilic substitution of the chlorine atom (**1a—c**), bis[*N*-methyl-*N*-(dialkoxysilylmethyl)amino] methanes (**2a—c**) are also formed, possibly due to the subsequent reaction of nucleophilic O-substitution. The successive transformation of compounds **1a—c** into **2a—c** is confirmed by the following reaction:

$$(EtO)_3SiCH_2NHMe + \mathbf{1b} \longrightarrow \mathbf{2b}\ .$$

Scheme 1



a: $R = OMe$, R^1, $R^2 = Me$
b: $R = OEt$, $R^1 = Et$, $R^2 = Me$
c: $R = Me$, R^1, $R^2 = Et$

The obtained compounds **1a—c** and **2a—c** are colorless high boiling liquids with a slight specific odor. Their physicochemical characteristics, the elemental analyses data, and PMR spectra are summarized in Tables 1, 2.

Table 1. Characteristics of $R^2OCH_2N(Me)CH_2SiR(OR^1)_2$ and $CH_2[N(Me)CH_2SiR(OR^1)_2]_2$

Compound	R	R¹	R²	B.p./°C (*p*/Torr)	n_D^{20}	Yield (%)	Molecular formula	Found / Calculated (%) C	H	N	Si
1a	OMe	Me	Me	47—48/(1)	1.4141	46	$C_7H_{19}N_1O_4Si$	39.85 40.17	8.76 9.15	6.49 6.69	14.01 13.42
1b	OEt	Et	Me	66—68/(1)	1.4138	40	$C_{10}H_{25}N_1O_4Si$	47.35 47.78	9.88 10.02	5.28 5.57	12.01 11.17
1c	Me	Et	Et	83—84/(3)	1.4182	67	$C_{10}H_{25}N_1O_3Si$	51.38 51.02	10.88 10.70	5.68 5.95	12.22 11.93
2a	OMe	Me	—	112—114/(1)	1.4286	25	$C_{11}H_{30}N_2O_6Si_2$	38.42 38.57	8.65 8.83	8.08 8.18	15.96 16.40
2b	OEt	Et	—	141—143/(1)	1.4268	20	$C_{17}H_{42}N_2O_6Si_2$	47.48 47.85	9.66 9.92	6.77 6.57	13.89 13.16
2c	Me	Et	—	115—118/(1)	1.4325	10	$C_{15}H_{38}N_2O_4Si_2$	49.67 49.14	10.95 10.45	7.85 7.64	15.98 15.32

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Table 2. ^1H 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 %).

References

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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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