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Reaction of Organylalkoxysilanes with Ethanolamine and Disproportionation of Transetherification Products

V. A. Kovyazin, V. V. Boev, V. M. Kopylov, and I. B. Sokol'skaya

State Research Institute of Chemistry and Technology of Organoelement Compounds,
sh. Entuziastov 38, Moscow, 111123 Russia
e-mail: vlkov@port.ru

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Abstract—Transetherification of organylalkoxysilanes with monoethanolamine was carried out. Disproportionation in mixtures containing organylalkoxysilanes with an amino group in the substituent was studied by means of NMR spectroscopy. It was shown that the disproportionation rate decreases with increase size of substituents on the silicon atom. The equilibrium composition of disproportionation products corresponds to the normal statistical distribution, except for mixtures containing tris(1-methylpropylideneaminooxy)(vinyl)-silane.

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Various methods for preparing organylalkoxysilanes containing an amino group in the alkoxy radical are sufficiently well documented [1–6]. These compounds attract special interest because of the presence of a highly reactive amino group and a Si–O bond in the alkoxy radical. Voronkov et al. [1, 2] have described the preparation of (2,2-diorganylaminoethoxy)alkoxysilanes $R_nSi(OCH_2CH_2NR^1R^2)_{4-n}$ by etherification of chlorosilanes with 2,2-diorganylaminoethanols. Analogous products can be prepared by dehydrocondensation of amino alcohols with hydride-containing alkoxysilanes [2, 3]. The transetherifications of tetraethoxysilane, methyltriethoxysilane, and dimethyldiethoxysilane under the action of amino alcohols, leading to $R_nSi(OCH_2CH_2NR^1R^2)_{4-n}$ ($R^1 = R^2 =$ H, Me; $n = 0, 1, 2$; R^1 = H, R^2 = Me, R = Me [4], as well as the reactions of triethoxy(vinyl)silane and triethoxy(phenyl)silane with monoethanolamine and some other amino alcohols, catalyzed by metallic sodium and giving $R(Si(OCH_2CH_2NR^1R^2)_3$ (R = Vi, Ph; $R^1 = R^2$ = H, Me; R^1 = H, R^2 = Me) [5], have been reported. The transetherification of organylalkoxysilanes under the action of monoethanolamine and its *N,N*-dialkyl derivatives, proceeding without catalysts and forming $R_{4-n}Si(OCH_2CH_2NR^1R^2)_n$ (R = alkyl, aryl; R^1 = H, Me, Et, R^2 = Me, Et; $n = 1$–3) has been described [1]. According to the patent [6], products of partial transetherification of $Si(OCH_2CH_2 \cdot NH_2)_4$ with nonanol undergo disproportionation.

Disproportionation affects significantly the composition of products in the synthesis of organylalkoxysilanes. It is known that the reaction involves not only alkoxy groups, but also Si–H and Si–Cl bonds. Hence oligoethylene glycol ethers catalyze disproportionation of triethoxysilane to tetraethoxysilane and monosilane [7]. Disproportionation of organyltrichlorosilanes $RSiCl_3$ (R = Me, CH=CH_2, Ph) and tetraethoxysilane, catalyzed by DMF, has been described [8]. The equilibrium compositions of disproportionation products differed significantly from the normal statistical distribution, which has been explained by different Si–Cl and Si–OEt bond energies.

In the present work we studied the specific features of transetherification of organylalkoxysilane with ethanolamine without catalyst, associated with the possible effect of the amino group, specifically, its catalytic action on the transetherification process and rearrangement of intermediate products.

To obtain both partial and complete transetherification products, we reacted organylalkoxysilanes with monoethanolamine at a varied reactant molar ratio. Complete transetherification is described by the following equation.

$$\underset{\mathbf{I}}{R_nSi(OR^1)_{4-n}} + n\underset{\mathbf{IV}}{HOCH_2CH_2NH_2} \longrightarrow \underset{\mathbf{VI\text{–}X}}{R_nSi(OCH_2CH_2NH_2)_{4-n}} + nR^1OH, \qquad (1)$$

R, R^1 = Me, n = 1 (**I, VI**); R = CH = CH_2, R^1 = Me, n = 1 (**II, VII**); R^1 = Et, n = 0 (**III, VIII**); R = $(CH_2)_3NH_2$, R^1 = Et, n = 1 (**IV, IX**); R = $(CH_2)_3NH(CH_2)_2NH_2$, R^1 = Me, n = 1 (**V, X**).

Physicochemical characteristics of products **VI**–**VIII** are consistent with reported data. Characteristics of new products **IX, X** are presented in Experimental.

Partial transetherification in the tetraethoxysilane–ethanolamine system (1 : 1 molar ratio) gave, after rectification, a number of products with different degrees of substitution.

$$Si(OC_2H_5)_4 + HOCH_2CH_2NH_2 \longrightarrow \underset{\textbf{XI–XIII}}{(C_2H_5O)_{4-n}Si(OCH_2CH_2NH_2)_n} + nC_2H_5OH, \quad (2)$$

$$n = 1\ (\textbf{XI}),\ 2\ (\textbf{XII}),\ 3\ (\textbf{XIII}).$$

The ratio of integral intensities of signals in the ^1H NMR spectrum of the transetherification product corresponds to compound **XI**, whereas the ^{29}Si NMR spectrum contains three signals at δ_{Si} –82.23, –82.27, and –82.31 ppm, which implies formation of three products. Since in the course of vacuum rectification we collected a fraction boiling at 90°C (5 mm Hg), bearing in mind the published boiling point of product **XI** [77–78°C (2 mm Hg) [3]), then a suggestion was made that this product undergoes disproportionation catalyzed by its own amino group to give a mixture of compounds with different degrees of substitution of the ethoxy groups by 2-aminoethoxy groups. The three signals in the ^{29}Si NMR spectrum probably relate to tetraethoxysilane and compounds **XI** and **XII**.

$$\underset{\textbf{XI}}{(C_2H_5O)_3Si(OCH_2CH_2NH_2)} \rightleftarrows \textbf{III} + \underset{\textbf{XI}}{(C_2H_5O)_3Si(OCH_2CH_2NH_2)} + \underset{\textbf{XII}}{(C_2H_5O)_2Si(OCH_2CH_2NH_2)_2}. \quad (3)$$

Lukevits et al. [3] showed that in the synthesis of (2-aminoethoxy)(diethoxy)methylsilane by dehydrocondensation of diethoxy(methyl)silane with monoethanolamine, the reaction mixture, together with the target product, contained bis(2-aminoethoxy)(ethoxy)-methylsilane. The formation of the latter compound was probably favored by a side disproportionation reaction. The same authors described the synthesis of compound **XI** from triethoxysilane and monoethanolamine, but mentioned no by-products. To confirm the possibility of disproportionation in such reaction systems, we undertook a ^{29}Si NMR study of a mixture of tetraethoxysilane and tetrakis(2-aminoethoxy)silane (**VIII**).

The choice of tetramethoxysilane as the second reaction component was motivated by the fact that the signal of its silicon atom is observed at δ_{Si} –79.1 ppm, while the signals of tetra(2-R-ethoxy)silanes (R = H, NH_2) fall in the range δ_{Si} –82.2 to –82.8 ppm. Such difference in the chemical shifts facilitates identification of disproportionation products. The reaction between tetramethoxysilane and tetrakis(2-aminoethoxy)silane (**VIII**) can be presented by the following scheme.

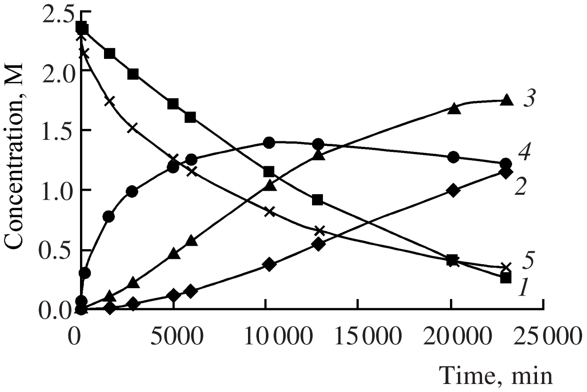

Fig. 1. Concentration–time curves for (*1*) tetramethoxysilane and compounds (*2*) **XV**, (*3*) **XVI**, (*4*) **XIV**, and (*5*) **VIII** in the course of the disproportionation reaction between tetramethoxysilane and compound **VIII** (20°C).

$$\underset{\textbf{VIII}}{Si(OCH_2CH_2NH_2)_4} + \underset{\text{TMOS}}{Si(OCH_3)_4} \rightleftarrows \underset{\text{TMOS}}{Si(OCH_3)_4} + \underset{\textbf{XIV}}{(CH_3O)_3Si(OCH_2CH_2NH_2)} + \underset{\textbf{XV}}{(CH_3O)_2Si(OCH_2CH_2NH_2)_2} + \underset{\textbf{XVI}}{(CH_3O)Si(OCH_2CH_2NH_2)_3} + \underset{\textbf{VIII}}{Si(OCH_2CH_2NH_2)_4}. \quad (4)$$

Figure 1 presents the concentration–time curves for the starting compounds and disproportionation products, measured by ^{29}Si NMR.

As seen from Fig. 1, disproportionation really takes place in the tetramethoxysilane–compound **VIII** reaction system at room temperature. At 60°C, this reaction reaches equilibrium in 12 h (Fig. 2), and the product ratio is close the normal statistical distribution: tetramethoxysilane : **XIV** : **XV** : **XVI** : **VIII** = 1 : 3.8 : 6.9 : 4.9 : 1.3 (calculated 1 : 4 : 6 : 4 : 1); δ_{Si}, ppm: –79.36 (tetramethoxysilane), –80.14 (**XIV**), –80.94 (**XV**), –81.73 (**XVI**, and –82.54 (**VIII**). The signals of the disproportionation products were assigned under the assumption that the chemical shift varies linearly with the degree of substitution of alkoxy groups (cf. [9]), except for tris(1-methylpropylidene-

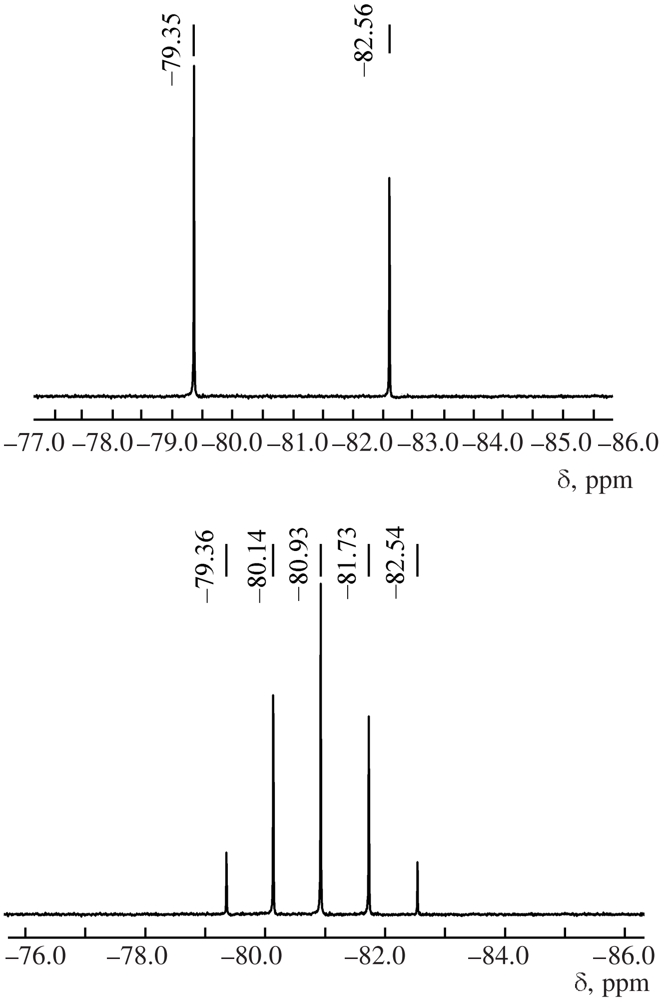

Fig. 2. ^{29}Si NMR spectra of the tetramethoxysilane–**VIII** (1 : 1 molar ratio) reaction mixture (a) before reaction and (b) after 12 h at 60°C.

aminooxy)(vinyl)silane. To assess the effect of substituent on the silicon atom on the reaction rate and compare the equilibrium product distributions with statistical, we studied disproportionation between various organylalkoxysilanes by ^{29}Si NMR spectroscopy. The objects for study were the following systems:

1). $ViSi(OCH_2CH_2NH_2)_3 : ViSi(OR)_3$,
(R = Me, Et, N=CMeEt)
2). $ViSi(ON{=}CMeEt)_3 : AlkNSi(OR)3$
[$Alk_N = H_2N(CH_2)_3$-, R = Et, Me; $Alk_N = H_2N(CH_2)_2NH(CH_2)_3$-, R = Me]
3). $RSi(OCH_2CH_2NH_2)_3 : Si(OMe)4$
[R = Vi, Me, $NH_2(CH_2)_3$-, $NH_2(CH_2)_2NH(CH_2)_3$-]

The simplest case is the disproportionation between tris(2-aminoethoxy)(vinyl)silane (**VII**) and other alkoxyvinylsilanes, because in such reaction systems only of three reversible reactions are possible. Each of them is characterized by the equilibrium constant K_i:

$$\underset{\textbf{VII}}{ViSi(OCH_2CH_2NH_2)_3} + \underset{\textbf{XVIIa–XVIIc}}{ViSi(OR)_3}$$
$$\overset{K_1}{\rightleftarrows} \underset{\textbf{XVIIIa–XVIIIc}}{ViSi(OCH_2CH_2NH_2)_3} + \underset{\textbf{XIXa–XIXc}}{ViSi(OCH_2CH_2NH_2)(OR)_2}, \quad (5)$$

$$\textbf{VII + XIXa–XIXc}$$
$$\overset{K_2}{\rightleftarrows} \underset{\textbf{XVIIIa–XVIIIc}}{ViSi(OCH_2CH_2NH_2)_2(OR)},$$

$$\underset{\textbf{XVIIIa–XVIIIc}}{ViSi(OCH_2CH_2NH_2)_2(OR)} + \underset{\textbf{XVIIa–XVIIc}}{ViSi(OR)_3}$$
$$\overset{K_3}{\rightleftarrows} 2ViSi(OCH_2CH_2NH_2)_2(OR)_2, \quad (6)$$

R = Me (**a**), Et (**b**), N=CMeEt (**c**).

It was found that for the above-mentioned vinylsilanes the composition of the disproportionation products at 60°C reaches the equilibrium state within 4 h. The mean equilibrium constants characteristic of the disproportionation of tris(2-aminoethoxy)(vinyl)silane with silanes of the general formula $ViSi(OR)_3$ (R = Me, Et, N = CMeEt) are presented below.

K_n	$ViSi(OMe)_3$	$ViSi(OEt)_3$	$ViSi(ON{=}CMeEt)_3$	Normal statistical distribution
K_1	9.11±2.49	7.84±0.92	127.24±29.79	9
K_2	2.56±0.49	2.74±0.22	12.12±2.59	3
K_3	3.43±0.38	2.86±0.10	11.56±2.14	3

The product distribution in the disproportionation of $ViSi(OMe)_3$ (**XVIIa**) and $ViSi(OEt)_3$ (**XVIIb**) with $ViSi(OCH_2CH_2NH_2)$ is close to statistical (Table 1). In the reaction of $ViSi(OCH_2CH_2NH_2)_3$ with ViSi· (ON=CMeEt) (**XVIIc**), significant deviation from the statistical distribution to silanes with mixed alkoxy groups is observed (Fig. 3, Table 1), and the equilibrium constant K_i is an order of magnitude higher than in the first two cases.

Comparison of the reactivities of vinylalkoxysilanes toward $ViSi(OCH_2CH_2NH_2)_3$ showed that the fastest reacting is ViSi(ON=CMeEt), and the difference in the consumption rates of $ViSi(OMe)_3$ and $ViSi(OEt)_3$ is evidently determined by the size of the alkoxy groups (the initial consumption rate ratio $w_{\textbf{XVIIc}} : w_{\textbf{XVIIa}} : w_{\textbf{XVIIb}}$ is ~85 : 18 : 1, and the ViSi· $(OCH_2CH_2NH_2)_3$ consumption rate ratio is 3.1 : 1.3 : 1, respectively).

Since ViSi(ON=CMeEt) exhibited quite a high reactivity in the disproportionation reaction, we checked

Table 1. Equilibrium product molar fractions (%) for the disproportionation $ViSi(OCH_2CH_2NH_2)_3$ with $ViSi(OR)_3$ at varied molar ratios of the starting components

Ratio	Distrubution	$ViSi(OCH_3)_3$	$ViSi(OC_2H_5)_3$	$ViSi[ON=C(CH_3)C_2H_5]_3$
(1 : 1)	Normal statistical		12.5 : 37.5 : 37.5 : 12.5[a]	
	Experimental	12.06 : 37.02 : 38.07 : 12.85	14.77 : 37.02 : 35.77 : 12.44	3.19 : 42.69 : 49.87 : 4.25
(1 : 3)	Normal statistical		1.56 : 14.06 : 42.19 : 42.19	
	Experimental	2.46 : 14.84 : 43.26 : 39.44	2.17 : 15.03 : 41.38 : 41.42	0 : 11.82 : 58.35 : 29.83
(3 : 1)	Normal statistical		42.19 : 42.19 : 14.06 : 1.56	
	Experimental	41.89 : 42.61 : 14.25 : 1.25	41.61 : 42.22 : 14.49 : 1.68	33.45 : 56.53 : 10.02 : 0
(2 : 3)	Normal statistical		6.4 : 28.8 : 43.2 : 21.6	
	Experimental	–	–	1.9 : 31.82 : 56.56 : 9.72
(3 : 2)	Normal statistical		21.6 : 43.2 : 28.8 : 6.4	
	Experimental	–	–	12.54 : 58.03 : 28.48 : 0.95
(0.33 : 0.67)	Normal statistical		3.59 : 21.89 : 44.44 : 30.08	
	Experimental	–	–	1.32 : 27.87 : 58.35 : 12.46
(0.67 : 0.33)	Normal statistical		30.08 : 44.44 : 21.89 : 3.59	
	Experimental	–	–	23.62 : 60.57 : 15.81 : 0

[a] The figures relate to compounds **VII, XVIIIa–XVIIIc, XIXa–XIXc**, and **XVIIa–XVIIc**, respectively.

the possibility of analogous reaction between $ViSi\cdot(ON{=}CMeEt)_3$ and carbofunctional aminoalkoxysilanes without a catalyst. The reaction was found to occur under the same conditions (4 h, 60°C) to form all possible products.

$$\underset{\mathbf{XVIIc}}{ViSi(ON{=}CMeEt)_3} + \underset{\mathbf{IV,\ V,\ XX}}{Alk_NSi(OR)_3} \rightleftarrows ViSi(ON{=}CMeEt)_3$$
$$+ ViSi(ON{=}CMeEt)_2(OR) + ViSi(ON{=}CMeEt)(OR)_2$$
$$+ ViSi(OR)_3 + Alk_NSi(OR)_3 + Alk_NSi(ON{=}CMeEt)(OR)_2$$
$$+ Alk_NSi(ON{=}CMeEt)_2(OR) + Alk_NSi(ON{=}CMeEt)_3, \quad (8)$$

$Alk_N = NH_2(CH_2)_3$, R = Et (**IV**), Me (**XX**); $Alk_N = NH_2(CH_2)_2NH(CH_2)_3$, R = Me (**V**).

Eighteen reversible reactions can proceed in such systems. Table 2 lists the equilibrium product ratios for the disproportionation of $ViSi(ON{=}CMeEt)_3$ with $Alk_NSi(OR)_3$ [$Alk_N = NH_2(CH_2)_3$-, R = Me,Et; $Alk_N = NH_2(CH_2)_2NH(CH_2)_3$-, R = Me].

As seen from Table 2, the distribution of the disproportionation products differs from the normal statistical distribution.

The initial consumption rates of the starting reagents at an equimolar initial ratio at 80°C are presented below.

Starting reagents	Initial consumption rate *w*, mol l^{-1} s^{-1}
1. $NH_2(CH_2)_3Si(OCH_3)_3$	–0.00485
2. $ViSi(ON{=}C(CH_3)C_2H_5)_3$	–0.069
1. $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	–0.00325
2. $ViSi(ON{=}C(CH_3)C_2H_5)_3$	–0.0056

It is evident that the disproportionation of tris(methylpropylideneaminooxy)(vinyl)silane with (3-aminopropyl)trimethoxysilane proceeds faster than with [3-*N*-(2-aminoethyl)aminopropyl]trimethoxysilane inspite of the presence of two amino groups in the diamine, which is probably caused by steric hindrances.

The disproportionation of tetramethoxysilane with silanes of the general formula $RSi(OCH_2CH_2NH_2)_3$ can be presented as follows.

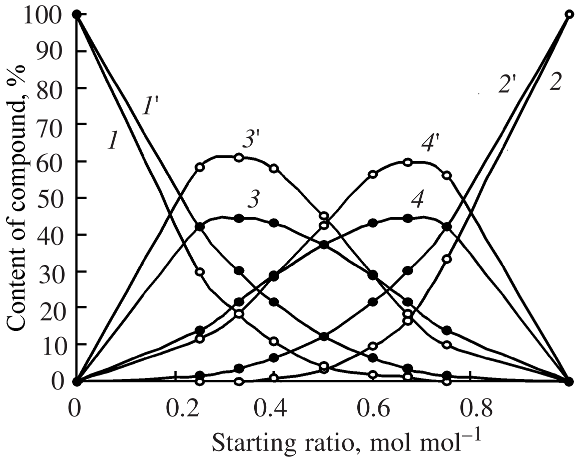

Fig. 3. Equilibrium product distribution curves for the disproportionation of $ViSi(OCH_2CH_2NH_2)_3$ (**VII**) with $ViSi(ON{=}CHMeEt)_3$ (**XVIIIc**). (*1–4*) Normal statistical distributions and (*1'–4'*) experimental curves for compounds (*1, 1'*) **VII**, (*2, 2'*) **XVIIIc**, (*3, 3'*) **XIXc**, and (*4, 4'*) **XVIIc**.

$$\mathrm{RSi(OCH_2CH_2NH_2)3 + Si(OMe)_4 \rightleftarrows RSi(OCH_2CH_2NH_2)_3}$$
$$\mathrm{+\ RSi(OCH_2CH_2NH_2)_2(OMe)}$$
$$\mathrm{+\ RSi(OCH_2CH_2NH_2)(OMe)_2 + RSi(OMe)_3 + Si(OMe)_4}$$
$$\mathrm{+\ Si(OCH_2CH_2NH_2)(OMe)_3 + Si(OCH_2CH_2NH_2)_2(OMe)_2}$$
$$\mathrm{+\ Si(OCH_2CH_2NH_2)_3(OMe) + Si(OCH_2CH_2NH_2)_4,} \quad (9)$$
$$\mathrm{R = Me,\ Vi,\ NH_2(CH_2)_3,\ NH_2(CH_2)_2NH(CH_2)_3.}$$

In this system, twenty one reversible reactions are possible. The composition of disproportionation products at a 1 : 1 molar ratio was always close to normal statistical (Table 3).

The ratio of the initial rates of consumption of organyltris(2-aminoethoxy)silanes in disproportionation with tetramethoxysilane $w_{\mathrm{VII}} : w_{\mathrm{VI}} : w_{\mathrm{IX}} : w_{\mathrm{X}}$, as determined by ^{29}Si NMR (Table 4) was ~7.5 : 6.1 : 1.1 : 1. The ratio of the rates of consumption of tetramethoxysilane in these reactions was 9.6 : 5.9 : 1 : 1.6, respectively. In all the cases, amino-containing silanes were consumed faster.

Hence, it was found that in mixtures containing organylalkoxysilanes with an amino group in the substituent there occurs disproportionation to form all possible products. The disproportionation rate decreases with increasing size of substituents on silicon. The highest activity is characteristic of tris(1-methylpropylidenaminooxy)(vinyl)silane. The disproportionation product distribution in the reaction mixtures containing this compound differs from normal statistical.

EXPERIMENTAL

The ^{1}H and ^{29}Si NMR spectra were taken on a Bruker AM-360 spectrometer (360 MHz for ^{1}H and 71 MHz for ^{29}Si) at 300 K in $\mathrm{CDCl_3}$.

Tris(2-aminoethoxy)(methyl)silane (VI). A mixture of 188 g of trimethoxy(methyl)silane and 265.9 g (5% excess) of monoethanolamine was heated with simultaneous distillation of methanol to 160°C. The reaction mixture was distilled in a vacuum to give 188.9 g of the target product (yield 57.5%).

Table 2. Equilibrium product molar fractions (%) for the disproportionation of $\mathrm{ViSi(ON{=}CMeEt)_3}$ with $\mathrm{Alk_NSi(OR)_3}$ [$\mathrm{Alk_N = NH_2(CH_2)_3}$, R = Me, Et; $\mathrm{Alk_N = NH_2(CH_2)_2NH(CH_2)_3}$-, R = Me] at varied molar ratios of the starting components

Ratio	Distribution	$\mathrm{NH_2(CH_2)_3Si(OC_2H_5)_3}$	$\mathrm{NH_2(CH_2)_3Si(OCH_3)_3}$	$\mathrm{NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3}$
(1 : 1)	Normal statistical	6.25 : 18.75 : 18.75 : 6.25 : 6.25 : 18.75 : 18.75 : 6.25 [a]		
	Experimental	13.66 : 30.26 : 3.49 : 0 : 1.6 : 4.01 : 18.31 : 28.67	0.81 : 15.98 : 24.31 : 5.42 : 2.54 : 25.61 : 22.84 : 2.49	0.93 : 21.67 : 24.14 : 3.11 : 1.84 : 19.53 : 20.87 : 7.91
(1 : 3)	Normal statistical	0.78 : 7.04 : 21.09 : 21.09 : 0.78 : 7.04 : 21.09 : 21.09		
	Experimental	0 : 1.26 : 13.04 : 4.71 : 0 : 7.49 : 32.41 : 41.09	0 : 0 : 6.93 : 12.7 : 0 : 5.59 : 38.69 : 36.09	–
(3 : 1)	Normal statistical	21.09 : 21.09 : 7.04 : 0.78 : 21.09 : 21.09 : 7.04 : 0.78		
	Experimental	39.91 : 28.65 : 0.19 : 0 : 2.24 : 13.53 : 11.84	22.04 : 41.35 : 8.59 : 0 : 3.64 :11.43 : 15.09 : 1.5 : 0	–

[a] The figures are arranged in an order corresponding to the product order in the right part of scheme (8).

Table 3. Equilibrium product molar fractions (%) for the disproportionation of tetramethoxysilane with organyltris(2-aminoethoxy)silanes $\mathrm{RSi(OCH_2CH_2NH_2)_3}$ [R = Me, Et, $\mathrm{NH_2(CH_2)_3}$-, $\mathrm{NH_2(CH_2)_2NH(CH_2)_3}$] at an equimolar ratio of the starting

Distribution	R = Vi	R = Me	R = $\mathrm{NH_2(CH_2)_3}$	R = $\mathrm{NH_2(CH_2)_2NH(CH_2)_3}$
Normal statistical	5.3 : 16.0 : 18.0 : 9.0 : 1.7 : 9.3 : 21.0 : 15.7 : 3.9 [a]			
Experimental	5.82 : 16.41 : 19.08 : 10.02 : 2.28 : 9.06 : 20.16 : 14.1 : 3.07	5.05 : 15.56 : 18.19 : 9.81 : 2.23 : 9.25 : 20.89 : 15.26 : 3.76	6.16 : 16.36 : 17.69 : 8.99 : 2.14 : 10.58 : 21.26 : 13.91 : 2.91	5.11 : 15.99 : 18.77 : 10.02 : 2.66 : 9.51 : 20.36 : 14 : 3.58

[a] The figures are arranged in an order corresponding to the product order in the right part of scheme (9).

Compounds **VII**–**X** were obtained analogously. Their physicochemical characteristics are listed in Table 5.

Disproportionation studies. Tetramethoxysilane and tris(2-aminoethoxy)(methyl)silane **VI** were mixed in a 1 : 1 molar ratio and kept for 6 h at 60°C, After that the reaction mixture was studied by means of ^{29}Si NMR spectroscopy. The disproportionations of tetramethoxysilane with tris(2-aminoethoxy)(vinyl)silane, tris(2-aminoethoxy)(3-aminopropyl)silane, and tris-(2-aminoethoxy) [3-*N*-(2-aminoethyl)aminopropyl]-silane were studied analogously. The silicon chemical shifts of the disproportionation products are listed in Table 6.

Trimethoxy(vinyl)silane and compound **VII** were mixed in 1 : 1, 3 : 1, and 1 : 3 molar ratios and kept at 60°C for 3 h. After that the reaction mixtures were studied by means of ^{29}Si NMR spectroscopy. The reactions of compound **VII** with triethoxy(vinyl)-silane and tris(1-methylpropylidenaminooxy)(vinyl)-silane were studied analogously. The silicon chemical shifts of the disproportionation products are listed in Table 7.

Table 4. Initial rates of consumption of the starting reagents at an equimolar initial ratio at 80°C

Starting reagents	Initial consumption rate w, mol l^{-1} s^{-1}
1. **VI**	–0.0411
2. $Si(OCH_3)_4$	–0.08654
1. **VII**	–0.10632
2. $Si(OCH_3)_4$	–0.06698
1. **IX**	–0.01537
2. $Si(OCH_3)_4$	–0.00697
1. **X**	–0.01423
2. $Si(OCH_3)_4$	–0.01101

Tris(1-methylpropylideneaminooxy)(vinyl)silane and (3-aminopropyl)trimethoxysilane {or [3-*N*-(2-aminoethyl)aminopropyl]trimethoxysilane} were mixed in a given ratio and kept at 60°C for 12 h. After that the reaction mixtures were studied by means of ^{29}Si NMR spectroscopy. The silicon chemical shifts of the disproportionation products are listed in Table 8.

Table 5. Physicochemical characteristics and ^{1}H NMR spectra of compounds **VI**–**X**

Comp. no.	bp, °C/mm Hg	Yield, %	n_D^{20}	Elemental composition, % (found/calculated)			
				C	H	N	Si
VI	164/9	57.5	1.4590 [a]	37.4/37.7	9.5/9.4	18.8/18.9	12.8/12.6
VII	157/3.5	83.0	1.4710	40.7/40.9	9.0/8.9	18.2/17.9	11.8/11.9
VIII	–	93.8	1.4688 [b]	36.0/35.8	9.2/9.0	21.2/20.9	10.5/10.4
IX	–	93.9	1.4798	40.9/40.6	9.4/9.8	21.8/21.1	10.8/10.5
X	–	91.3	1.4859	42.1/42.7	9.7/10.0	23.0/22.7	9.5/9.1

Comp. no.	Chemical shift of proton signals, δ, ppm (in CCl_3)			
	$OC\mathit{H}_2CH_2NH_2$	$OCH_2C\mathit{H}_2NH_2$	$OCH_2CH_2N\mathit{H}_2$	R
VI	2.89 t	1.93 t	0.66 s	(Me) –0.70 s
VII	3.55 t	2.58 t	1.15 s	(CH_2=CH) 5.80 s
VIII	2.93 t	1.94 t	0.58 s	–
IX	2.76 t	1.78 t	0.31 s	($C\mathit{H}_2Si$) –0.32 t ($C\mathit{H}_2$) 0.54 quintet ($C\mathit{H}2NH_2$) 1.65 t
X	2.76 t	1.78 t	0.43 s	($C\mathit{H}_2Si$) –0.32 t ($C\mathit{H}_2$) 0.60 quintet ($NH_2C\mathit{H}_2$) 1.73 t ($C\mathit{H}_2NHC\mathit{H}_2$) 1.60 t

[a] n_D^{20} 1.4600 [1]. [b] n_D^{20} 1.4688 [6]

Table 6. Silicon chemical shifts (δ_{Si}, ppm) of the disproportionation products of tetramethoxysilane with silanes of the general formula $RSi(OCH_2CH_2NH_2)_3$ [R = Vi, Me, $NH_2(CH_2)_3$-, $NH_2(CH_2)_2NH(CH_2)_3$-]

Compound	Degree of substitution, *n*				
$RSi(OCH_2CH_2NH_2)_{3-n}(OMe)_n$	*n* = 0	*n* = 1	*n* = 2	*n* = 3	*n* = 4
R = Me	–43.20	–42.31	–41.43	–40.56	–
R = Vi	–58.77	–57.87	–57.00	–56.16	–
R = $NH_2(CH_2)_3$	–45.63	–44.69	–43.78	–42.88	–
R = $NH_2(CH_2)_2NH(CH_2)_3$	–45.68	–44.76	–43.85	–42.95	–
$Si(OMe)_{4-n}(OCH_2CH_2NH_2)_n$	–79.63	–80.42	–81.23	–82.05	–82.87

Table 7. Silicon chemical shifts (δ_{Si}, ppm) of the disproportionation products of tris(2-aminoethoxy)(vinyl)silane with silanes of the general formula $ViSi(OR)_3$ (R = Me, Et, N = CMeEt)

Compound	Degree of substitution, *n*			
$ViSi(OR)_{3-n}(OCH_2CH_2NH_2)_n$	*n* = 0	*n* = 1	*n* = 2	*n* = 3
R = Me	–56.58	–57.46	–58.35	–59.27
R = Et	–59.55	–59.32	–59.11	–58.93
R = –N=C(Me)Et	–51.65	–54.76	–57.01	–58.66

Table 8. Silicon chemical shifts (δ_{Si}, ppm) of the disproportionation products of tris(methylpropylideneaminooxy)(vinyl)-silane with (aminoalkyl)alkoxysilanes $Alk_NSi(OR)_3$ (Alk_N = $NH_2(CH_2)_3$, R = Et, Me; Alk_N = $NH_2(CH_2)_2NH(CH_2)_3$, R = Me)

Compound	Degree of substitution, *n*			
$RSi(OMe)_{3-n}[ON{=}C(Me)Et]_n$	*n* = 0	*n* = 1	*n* = 2	*n* = 3
R = $NH_2(CH_2)_3$	–42.39	–40.59	–38.23	–35.34
R = $NH_2(CH_2)_2NH(CH_2)_3$	–42.48	–40.70	–38.27	–35.22
R = Vi	–55.97	–55.17	–53.72	–51.59

Two individual compounds were mixed in 1:1 molar ratio and ^{29}Si NMR spectra were taken immediately every 2 h over the course of 8 h (27°C, acquisition time 24 min).

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