==

Transetherification of Organosilicon Amines with Cellosolve and Trimethylsilanol

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

Gosudarstvennyi nauchno-issledovatel'skii institut khimii i tekhnologii elementoorganicheskikh soedinenii Federal State Unitary Enterprise, Moscow, Russia

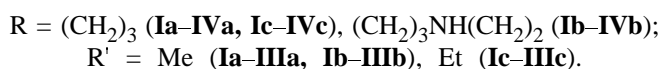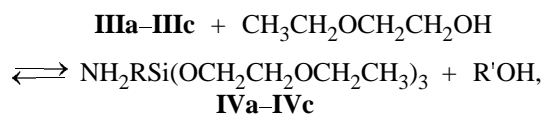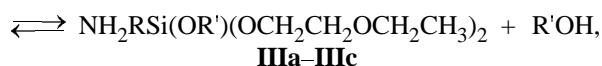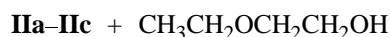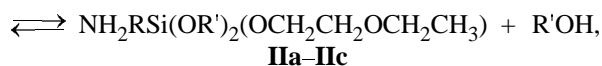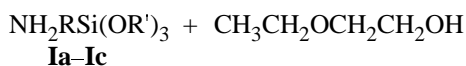**Abstract** — Kinetics of transetherification of (3-aminopropyl)trimethoxysilane, [3-*N*-(2-aminoethyl)amino-propyl]trimethoxysilane, and (3-aminopropyl)triethoxysilana with Cellosolve and trimethylsilanol were studied. The example of [3-*N*-(2-aminoethyl)aminopropyl]trimethoxysilane was used to show that the activation energies of the direct and reverse reactions are equal to each other both in the first and in the second stages, which points to independence of the equilibrium constant on temperature ($\Delta H \approx 0$). With methoxysilanes, the rate constant of the reverse reaction in the second stage of the transetherification with Cellosolve is higher than that of the direct reaction.

Aminoalkoxysilanes are widely used in organosilicon synthesis [1–8] and as adhesives for composite materials [9–13], which is associated with the high activity of the amino group in the organic substituent and of alkoxy groups on silicon. It should be noted that reactivity of alkoxy groups in aminoalkoxysilanes has scarcely been studied. Reactions of aminoalkoxysilanes with hydroxyl-containing compounds, specifically alcohols, silanols, and siloxanols, mimic a series of aminoalkoxysilane reactions in various reaction systems.
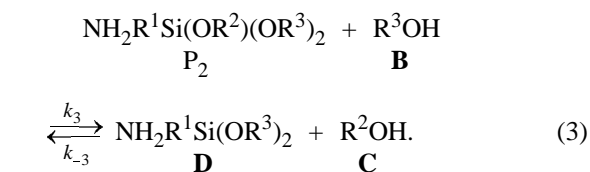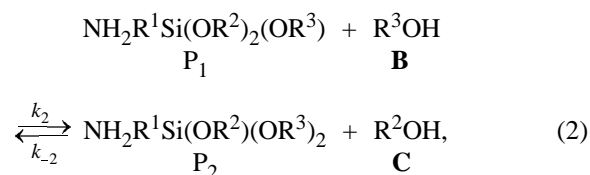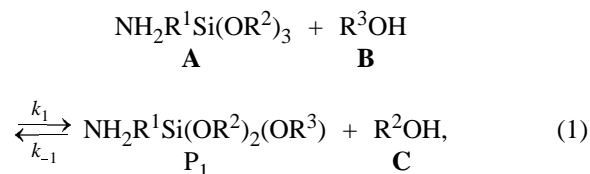
The present work is a continuation of our earlier studies [14].

Transetherification of organosilicon amines **Ia–Ic** with Cellosolve was performed at amine:Cellosolve molar ratios of 1:1, 1:2, 1:3, 1:4, and 1:6, with no catalysts, and the reaction mixtures were kept at room temperature. Reaction progress was controlled by GLC.

The reaction of aminoalkoxysilanes with Cellosolve occurs by the following scheme:

$$NH_2RSi(OR')_3 + CH_3CH_2OCH_2CH_2OH$$
$$\textbf{Ia–Ic}$$

$$\rightleftharpoons NH_2RSi(OR')_2(OCH_2CH_2OCH_2CH_3) + R'OH,$$
$$\textbf{IIa–IIc}$$

$$\textbf{IIa–IIc} + CH_3CH_2OCH_2CH_2OH$$

$$\rightleftharpoons NH_2RSi(OR')(OCH_2CH_2OCH_2CH_3)_2 + R'OH,$$
$$\textbf{IIIa–IIIc}$$

$$\textbf{IIIa–IIIc} + CH_3CH_2OCH_2CH_2OH$$

$$\rightleftharpoons NH_2RSi(OCH_2CH_2OCH_2CH_3)_3 + R'OH,$$
$$\textbf{IVa–IVc}$$

$$R = (CH_2)_3 \ (\textbf{Ia–IVa, Ic–IVc}), (CH_2)_3NH(CH_2)_2 \ (\textbf{Ib–IVb});$$
$$R' = Me \ (\textbf{Ia–IIIa, Ib–IIIb}), Et \ (\textbf{Ic–IIIc}).$$

The scheme involves series-parallel reversible reactions (Fig. 1) described by Eqs. (1)–(3).

$$NH_2R^1Si(OR^2)_3 + R^3OH$$
$$\textbf{A} \qquad\qquad \textbf{B}$$

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NH_2R^1Si(OR^2)_2(OR^3) + R^2OH, \qquad (1)$$
$$\textbf{P}_1 \qquad\qquad \textbf{C}$$

$$NH_2R^1Si(OR^2)_2(OR^3) + R^3OH$$
$$\textbf{P}_1 \qquad\qquad \textbf{B}$$

$$\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NH_2R^1Si(OR^2)(OR^3)_2 + R^2OH, \qquad (2)$$
$$\textbf{P}_2 \qquad\qquad \textbf{C}$$

$$NH_2R^1Si(OR^2)(OR^3)_2 + R^3OH$$
$$\textbf{P}_2 \qquad\qquad \textbf{B}$$

$$\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NH_2R^1Si(OR^3)_2 + R^2OH. \qquad (3)$$
$$\textbf{D} \qquad\qquad \textbf{C}$$

The rate equations for the series-parallel reversible reactions take forms (4)–(7).

$$w_\textbf{A} = -k_1[\textbf{A}][\textbf{B}] + k_{-1}[\textbf{P}_1][\textbf{C}], \qquad (4)$$

$$w_{\textbf{P}_1} = -k_2[\textbf{P}_1][\textbf{B}] + k_{-2}[\textbf{P}_2][\textbf{C}] + k_1[\textbf{A}][\textbf{B}]$$
$$- k_{-1}[\textbf{P}_1][\textbf{C}], \qquad (5)$$

Table 1. Yields, n_D^{20} values, and ^{1}H and ^{29}Si NMR spectra of synthesized compounds[a]

Comp. no.	Compound	Yield, %	n_D^{20}	^{1}H NMR spectrum, δ, ppm						^{29}Si NMR spectrum, δ_{Si}, ppm	
				Me$_3$Si	OMe	SiCH$_2$	CH$_2$	CH$_2$N	NH$_2$	SiCH$_2$	Me$_3$Si
Ib	(MeO)$_3$Si(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$			–	3.49	0.58	1.52	2.53, 2.58, 2.71	1.17	–42.24	
V	Me$_3$SiO(MeO)$_2$Si(CH$_2$)$_3$NH(CH$_2$)$_2$·NH$_2$	95.5	1.4315	0.05	3.41	0.50	1.49	2.51, 2.55, 2.68	1.04	–49.75	8.91
VI	(Me$_3$SiO)$_2$(MeO)Si(CH$_2$)$_3$NH(CH$_2$)$_2$·NH$_2$	92.5	1.4280	0.09	3.43	0.50	1.47	2.57, 2.63, 2.76	1.20	–57.67	8.15
VII	(Me$_3$SiO)$_3$Si(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$	68.5	1.4240	–0.01	–	0.35	1.41	2.48, 2.55, 2.67	1.21	–65.95	7.05

[a] δ_{Si} (SiCH$_2$), ppm: –42.11 (**Ia**), –43.15 (**IIa**), –44.08 (**IIIa**), –44.99 (**IVa**), –45.36 (**Ic**), –52.11 [Me$_3$SiO(EtO)$_2$Si(CH$_2$)$_3$NH$_2$], –58.95 [(Me$_3$SiO)$_2$(EtO)Si(CH$_2$)$_3$NH$_2$], –65.81 [(Me$_3$SiO)$_3$Si(CH$_2$)$_3$NH$_2$].

$$w_{P_2} = -k_3[P_2][\mathbf{B}] + k_{-3}[\mathbf{D}][\mathbf{C}] + k_2[P_1][\mathbf{B}]$$
$$- k_{-2}[P_2][\mathbf{C}], \qquad (6)$$
$$w_{\mathbf{D}} = k_3[P_2][\mathbf{B}] - k_{-3}[\mathbf{D}][\mathbf{C}]. \qquad (7)$$

With known equilibrium concentrations of all the components, the equilibrium constants can be calculated by Eqs. (8) and (9).

$$K_1 = [P_1][\mathbf{C}]/[\mathbf{A}][\mathbf{B}], \quad K_2 = [P_2][\mathbf{C}]/[P_1][\mathbf{B}],$$
$$K_3 = [\mathbf{D}][\mathbf{C}]/[P_2][\mathbf{B}], \qquad (8)$$

Fig. 1. Plot of molar fraction (n) vs. time for the components of the reaction mixture at the amine–Cellosolve ratio 1:6 (20°C). Compound: (*1*) **Ia**, (*2*) **IIa**, (*3*) **IIIa**, (*4*) **IVa**, (*5*) **Ib**, (*6*) **IIb**, (*7*) **IIIb**, (*8*) **IVb**, (*9*) **Ic**, and (*10*) **IIc**.

$$K_1 = k_1/k_{-1}, \quad K_2 = k_2/k_{-2}, \quad K_3 = k_3/k_{-3}. \qquad (9)$$

In view of the failure of isolation of the products of substitution of amines with Cellosolve in the pure state, we obtained mono-, di-, and trisubstitution products of compound **Ib** with trimethylsilanol, which have the same molecular weights as amines substituted with Cellosolve. The yields, n_D^{20} values, and ^{1}H and ^{29}Si NMR chemical shifts of the resulting compounds are listed in Table 1.

With the trimethylsilylated derivatives obtained, we constructed plots of n_a/n_d vs. S_a/S_d (the indices "a" and "d" relate to amine and dodecane, respectively) (Fig. 2), where n is the molar fraction of a compound, S is the peak area of the compound, and dodecane is the internal standard, and determined calibration factors (tan α are the slopes of the resulting straight lines). The linear dependence of tan α on the molecular weight (M) of amine [tan $\alpha = 4.77 \times 10^{-2}$ M (r 0.9894)] allows calculation of the contents of amines with various degree of substitution from their chromatographic peak areas by the formula $n = S$ tanα. This formula was used to calculate product concentrations for all the reactions studied.

Using experimental data, we found the equilibrium concentrations of the components in the system (Table 2) and, by Eqs. (4)–(9), the equilibrium constants of reactions (1)–(3) with compounds **Ia–Ic**, listed below.
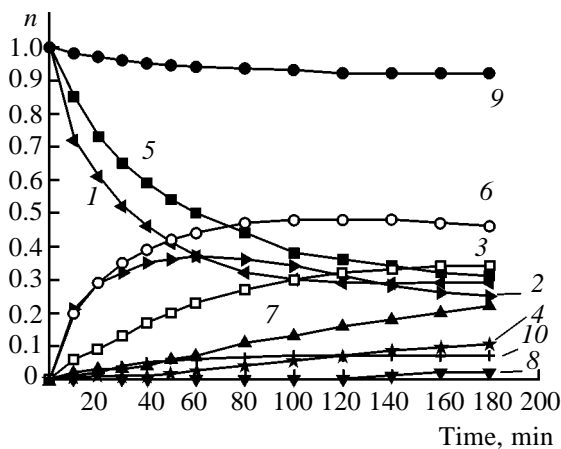
Table 2. Equilibrium concentrations of components and equilibration times at 20°C

$[B]_0/[A]_0$	Time, min	c_{A_0}, M	c_A, M	c_{P_1}, M	c_{P_2}, M	c_D, M
		(3-Aminopropyl)trimethoxysilane (**Ia**)				
1	210	3.363	1.821	1.590	0.216	0
3	205	2.720	0.920	1.199	0.551	0.051
6	217	2.153	0.620	0.849	0.603	0.082
		[3-N-(2-Aminoethyl)amino]propyltrimethoxysilane (**Ib**)				
1	1568	3.43	1.708	1.379	0.343	0
3	1571	2.34	0.796	1.048	0.452	0.044
6	1570	1.93	0.473	0.782	0.554	0.122
		[3-Aminopropyl]triethoxysilane (**Ic**)				
1	10315	3.033	1.535	1.189	0.294	0.015
3	10260	2.35	0.794	1.011	0.482	0.063
6	10155	1.91	0.493	0.785	0.529	0.103

Table 3. Rate constants (k, l mol^{-1} s^{-1}) of the direct and reverse reactions in transesterification of compounds **Ia–Ic** with Cellosolve at 20°C

Ia		Ib		Ic
$k_1 \times 10^5$ $(k_{-1} \times 10^5)$	$k_2 \times 10^5$ $(k_{-2} \times 10^5)$	$k_1 \times 10^5$ $(k_{-1} \times 10^5)$	$k_2 \times 10^5$ $(k_{-2} \times 10^5)$	$k_1 \times 10^5$ $(k_{-1} \times 10^5)$
4.25±0.46 (4.58±0.49)	3.27±0.10 (8.85±0.26)	3.23±0.56 (2.84±0.50)	1.85±0.11 (4.80±0.65)	1.90±0.38 (1.77±0.35)

	Ia	Ib	Ic
K_1	0.925	1.139	1.069
K_2	0.365	0.403	0.394
K_3	0.080	0.128	0.102

Further we calculated rate constants for the direct and reverse reactions (Table 3). In view of the low rates of formation of trisubstitution products, we failed to determine rate constant for reaction (3). For the same reason, we failed to determine rate constant for reaction (2) with (3-aminopropyl)triethoxysilane (**Ic**).

We also studied kinetics of transetherification of compound **Ib** with Cellosolve at 1:1, 1:3, and 1:6 ratios at 40 and 60°C.

Reaction rate constants and activation energies were calculated (Table 4).

As seen from the kinetic data, compounds **Ia** and **Ib** react much faster than **Ic**, which can be explained by steric reasons. At the same time, unlike what is observed with amine **Ic**, the rate constants of the reverse reactions with compound **Ia** are higher that those of the reverse ones. With compound **Ib**, $k_1 > k_{-1}$, whereas $k_2 < k_{-2}$.

The progress of transetherification of compound **Ib** with trimethylsilanol was followed by GLC by the consumption of starting amines and the formation of reaction products. The internal standard was dodecane,
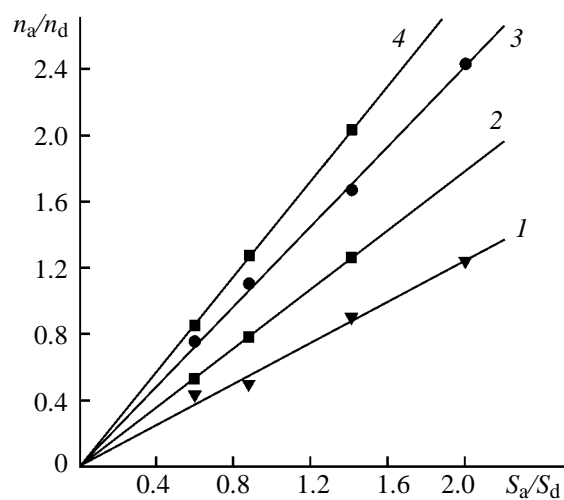

Fig. 2. Plots of n_a/n_d vs. S_a/S_d for compounds (*1*) **Ia**, (*2*) **V**, (*3*) **VI**, and (*4*) **VII**.

Table 4. Rate constants (l mol^{-1} s^{-1}) of the direct and reverse reactions in transetherification of compound **Ib** with Cellosolve and trimethylsilanol

Temperature, °C	Cellosolve		Trimethylsilanol	
	$k_1 \times 10^5$ ($k_{-1} \times 10^5$)	$k_2 \times 10^5$ ($k_{-2} \times 10^5$)	$k_1 \times 10^{-4}$	$k_2 \times 10^{-6}$
20	3.23 ± 0.56 (2.84 ± 0.50)	1.85 ± 0.11 (4.80 ± 0.65)	1.31[a]	–
40	4.37 ± 0.35 (3.83 ± 0.31)	2.57 ± 0.26 (6.43 ± 0.65)	2.69	2.86
60	8.90 ± 1.0 (7.81 ± 0.88)	4.71 ± 0.01 (11.79 ± 0.01)	4.76	3.78
E_a, kcal/mol	4.9[b] 4.9[c]	4.5[b] 4.4[c]	6.0	

[a] Reaction temperature 19°C. [b] Direct reaction. [c] Reverse reaction.

and the solvent was toluene. Under these conditions, almost no condensation of trimethylsilanol was observed, and the reaction occurred by the following scheme and involved no side processes.
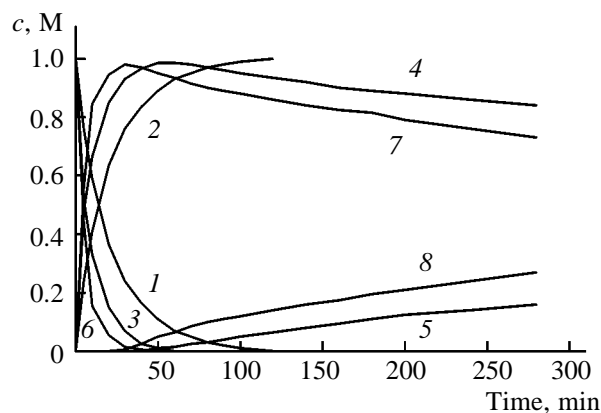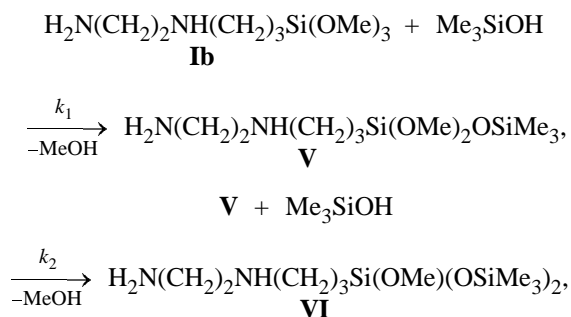
$$H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3 + Me_3SiOH$$
$$\textbf{Ib}$$

$$\xrightarrow[-MeOH]{k_1} H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_2OSiMe_3,$$
$$\textbf{V}$$

$$\textbf{V} + Me_3SiOH$$

$$\xrightarrow[-MeOH]{k_2} H_2N(CH_2)_2NH(CH_2)_3Si(OMe)(OSiMe_3)_2,$$
$$\textbf{VI}$$

Fig. 3. Plots of the concentration of compounds **Ib**, **V**, and **VI** vs. time for transetherification of compound **Ib** with trimethylsilanol at various temperatures. Temperature, °C: 19: (*1*) **Ib** and (*2*) **V**; 40: (*3*) **Ib**, (*4*) **V**, and (*5*) **VI**; and 60: (*6*) **Ib**, (*7*) **V**, and (*8*) **VI**. Compound **VII** was not formed within the observation time.

$$\textbf{VI} + Me_3SiOH \xrightarrow[-MeOH]{k_3} H_2N(CH_2)_2NH(CH_2)_3Si(OSiMe_3)_3.$$
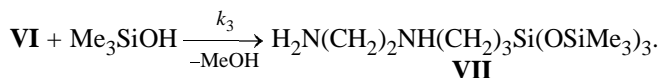$$\textbf{VII}$$

Figure 3 depicts the curves of diamine consumption and transetherification product formation.

Unlike the transetherification of isomeric (aminopropyl)triethoxysilane, we described in [14], the process in hand is a sequence of irreversible reactions, as judged from the fact that compound **VI** begins to form after the starting amine has been consumed completely. In this connection the rate constants were calculated by Eq. (10) for an irreversible second-order reaction [15].

$$k([\textbf{D}]_0 - [TMS]_0)t$$
$$- \ln \{[\textbf{D}]_0([TMS]_0 - x)\}/\{[TMS]_0([\textbf{D}]_0 - x)\}. \quad (10)$$

Table 4 lists the rate constants for the stages of transetherification of compound **Ib** with trimethylsilanol and the activation energies of the first stage, calculated by Arrhenius's equation.

Since in the presesent work we used the same transetherification conditions as in [14], except for reaction temperature, the rate constants of the first two stages of transetherification of compound **Ib** with trimethylsilanol at 70°C; the resulting values were compared with those for isomeric (aminopropyl)triethoxysilanes (Table 5).

As seen from Table 5, of the amines studied, (2-amino-1-methylethyl)triethoxysilane (**VIII**) is the most reactive toward trimethylsilanol.

Noteworthy is the fact that the silicon chemical shift is linearly related to the degree of substitution of

Table 5. Rate constants $(l\ mol^{-1}\ s^{-1})$ of the first and second stages of transetherification of amines with trimethylsilanol at 70°C

Comp. no.	$k_1 \times 10^4$	$k_2 \times 10^4$
Ib	6.166	0.043
Ic	0.630	0.080
VIII	10.000	0.450

methoxy or ethoxy groups by trimethylsiloxy or 2-ethoxyethoxy (Fig. 4). On complete trimethylsiloxy substituion, the silicon signal shifts upfield by 23.71 and 20.59 ppm for methoxy and ethoxy groups, respectively. On substitution of methoxy groups in **Ib** by 2-ethoxyethoxy, the difference is 2.8 ppm (Table 1).

EXPERIMENTAL

The ^1H and ^{29}Si NMR spectra were registered in $CDCl_3$ on a Bruker AM-360 instrument at 360 and 80 MHz.

Kinetic measurements were performed in the following way. A mixture of amine $(1 \times 10^{-2}\ mol)$ and decane $(0.5 \times 10^{-2}\ mol)$ and a solution of Me_3SiOH in toluene (8 M) were thermostated separately at a specified temperature. After 10 min, the solutions were mixed, and the mixture was stirred. Reaction progress was followed by GLC [chromatograph LKhM-80, column 2000×3 mm, packing SE-30 (5%) on Inerton AW-DMCS, carrier gas helium].

1-[3-*N*-(2-Aminoethyl)aminopropyl]-1,1-dimethoxy-3,3,3-trimethyldisiloxane (V). A mixture of 222 g of compound **Ib** and 90 g of Me_3SiOH was
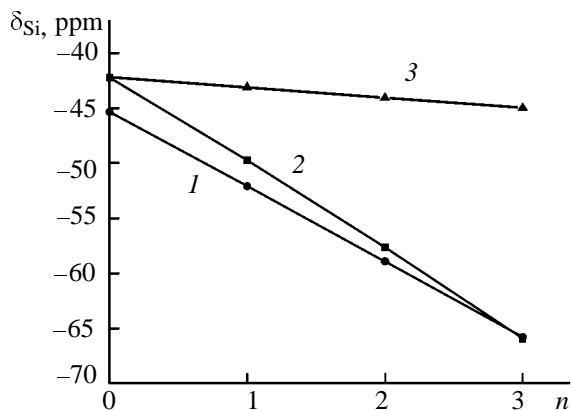

Fig. 4. Plot of silicon chemical shift δ_{Si} vs. substitution degree n for (*1*) trimethylsilylation of compound **Ic**, (*2*) trimethylsilylation of compound **Ib**, and (*3*) transetherification of compound **Ib** with Cellosolve.

stirred at 20°C until amine **Ib** had been consumed completely. Vacuum distillation gave 267.4 g of compound **V**, bp 109–111°C (1 mm).

3-[3-*N*-(2-Aminoethyl)aminopropyl]-3-methoxy-1,1,1,5,5,5-hexamethyltrisiloxane (VI). A mixture of 222 g of compound **Ib** and 185 g of Me_3SiOH was refluxed until silane **V** had been consumed completely. Vacuum distillation gave 312.7 g of compound **VI**, bp 110–115°C (1 mm).

[3-*N*-(2-Aminoethyl)aminopropyl]tris(trimethylsiloxy)silane (VII). A mixture of 222 g of compound **Ib** and 540 g of Me_3SiOH was refluxed until compound **VI** had been consumed completely. Vacuum distillation gave 271.3 g of compound **VII**, bp 127–130°C (1 mm).

REFERENCES

1. JP Pat. Appl. 97-143794, *Chem. Abstr.,* 1999, vol. 130, no. 110401.
2. Pozhidaev, Yu.N., Bol'shakova, S.A., Pestunovich, A.E., Vlasova, N.N., and Voronkov, M.G., *Dokl. Ross. Akad. Nauk,* 1997, vol. 355, no. 5, p. 653.
3. Vlasova, N.N., Zhila, G.Yu., Kirillov, A.I., and Voronkov, M.G., *Heteroatom. Chem.,* 1995, vol. 6, no. 2, p. 311.
4. Kopylov, V.M., Prikhod'ko, P.L., Kireev, V.V., Rudman, E.V., Korshunov, M.A., Mikhlin, V.S., and Kovyazin, V.A., USSR Inventor's Certificate no. 1 122 662, *Byull. Isobret.,* 1984, no. 41,
5. Kovyazin, V.A., Kopylov, V.M., Shkol'nik, M.I., Safrygina, I.A., Demina, N.M., and Ezhova, V.A., RU Patent 2 084 456, *Byull. Isobret.,* 1997, no. 20.
6. CZ Inventor's Certificate no. 221 786, *Ref. Zh. Khim.,* 1986, 4N77P.
7. US Patent 4 800 125, *Ref. Zh. Khim.,* 1989, 23T246P.
8. CZ Inventor's Certificate no. 215 229, *Ref. Zh. Khim.,* 1985, 17N176P.
9. US Patent 4 410 645, *Ref. Zh. Khim.,* 1984, 24M238P.
10. US Patent 4 435 474, *Ref. Zh. Khim.,* 1985, 4U246P.
11. US Patent 4 615 946, *Ref. Zh. Khim.,* 1987, 12T166P.
12. US Patent 4 704 419, *Ref. Zh. Khim.,* 1988, 14U129P.
13. RU Patent 2 028 986, *Byull. Isobret.,* 1995, no. 5.
14. Kovyazin, V.A. and Kopylov, V.M., *Zh. Obshch. Khim.,* 1992, vol. 62, no. 4, p. 842.
15. Emmanuel', N.M and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Mosocow: Vysshaya Shkola, 1969, p. 214.