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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Reaction of γ-(Aminopropyl)siloxanes with Phenolphthalein as a Route to New Siloxane-containing Phenols

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Abstract—The reaction of γ-aminopropylorganosiloxanes with phenolphthalein yields monomeric and oligomeric *N*-alkylsiloxy-3,3-bis(4-hydroxyphenyl)phthalimidines. Their structures and compositions were confirmed by IR and NMR spectroscopy and by HPLC–MS. Studies by GLC and MALDI mass spectrometry showed that the action of the amine and of the water released in the reaction leads to the rearrangement of the siloxane bond in the course of the synthesis with the formation of linear and cyclic carbofunctional oligomeric siloxanephenols and mixed oligophenolaminosiloxanes. The possibility of modification of epoxy resins with the synthesized oligomers was revealed.

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Carbofunctional siloxane-containing phenols (CSPs) are demanded monomeric and oligomeric organosilicon compounds for the synthesis of copolymers [1] and block copolymers [2, 3] and for modification of organic polymers [4, 5]. CSP-based copolymers have diverse applications. They are used as modifiers of commercial polycarbonates and as materials for high-performance gas-permeable and pervaporation membranes, electrotechnical coatings, adhesive films for triplex, and conducting matrices for current sources, and also as various materials for medicobiological purpose [6].

The first representatives of organosilicon phenols with the Si–aryl bond were prepared by Speier et al. [7] by organometallic synthesis from halophenoxysilylchlorosilanes and chlorosilanes with the subsequent hydrolysis of the reaction products to the desired phenols. Later, such phenols were prepared by hydrosilation of alkenylphenols with hydridosilanes in the presence of H_2PtCl_6 as catalyst [8]. After that, the hydrosilation reaction was successfully applied to the synthesis of CSPs from unsaturated phenols or their silyl ethers and hydridoorganosilanes [9–12]. Mironov et al. [13] also suggested preparation of CSPs by intramolecular hydrosilation of vinylphenoxyhydridosilanes to cyclic products, followed by hydrolysis to obtain the desired organosilicon phenols.

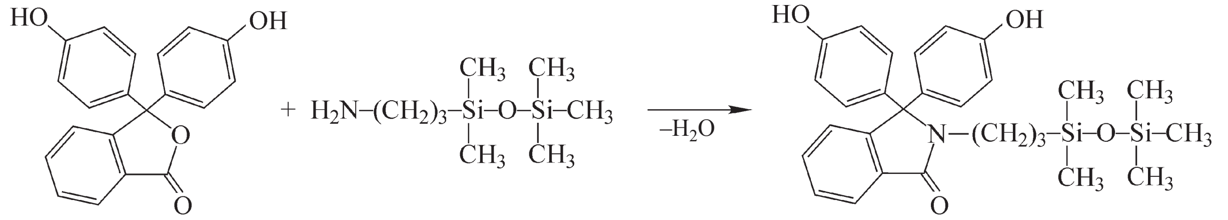
Continuing the search for facile routes to new CSPs, which are of interest as monomers for polycondensation copolymers and as modifiers for organic resins and polymers, we studied possible procedures for preparing phenols with a grafted siloxane group.

RESULTS AND DISCUSSION

For our experiments we chose γ-aminopropylorganosiloxanes and phenolphthalein, which is a readily available compound containing, along with two phenoxy groups, also a reactive lactone functional group.

It is known [14–16] that reactions of phenolphthalein with primary organic amines yield *N*-phthalimidines. However, we found no data on the corresponding reactions with organosilicon amines.

We expected that the use of aminoalkylsiloxanes in reaction with phenolphthalein would yield siloxane-containing bisphenols:



The reaction of γ-(aminopropyl)pentamethyldisiloxane with phenolphthalein was performed in dioxane and *o*-dichlorobenzene solutions. The reaction progress was monitored by IR spectroscopy and by the amount of low-boiling products collected in the Dean–Stark trap. In the course of the reaction, the intensity of the absorption band of the C=O bond in phenolphthalein at 1760 cm^{-1} decreases and a new absorption band of the C=O bond on phthalimidine appears at 1660 cm^{-1} (Fig. 1).

The reaction in dioxane (100°C) is slow. In 40 h, the conversion, as judged from changes in the intensities of the absorption bands at 1660 and 1760 cm^{-1}, did not exceed 10%.

With *o*-dichlorobenzene used as solvent, the conversion of the lactone carbonyl group into imidine group in 30 h at 140°C was 90–95%. Similar results were obtained when analyzing the reaction mixture by NMR (Fig. 2).

A GLC analysis of the low-boiling products revealed the presence of water, solvent, initial amine, and hexamethyldisiloxane. The presence of the latter suggests cleavage of the siloxane moiety. Similar rearrangements of siloxanes under the action of amines in the presence of proton-donor compounds (water) were described in [17].

An NMR analysis showed that the ratio of the integral intensities of the proton signals of the CH_3–Si (–0.1 to 0.1 ppm) and phthalimidine (7.3–7.8 ppm) groups decreased from 15 : 4 [for the product of reaction (1)] to 9 : 4 (for final reaction products). In the NMR spectrum, there are five signals from CH_3–Si≡ protons instead of two signals [≡C–Si$(CH_3)_2$O– and –OSi$(CH_3)_3$], which suggests the presence of several compounds in the reaction mixture.

An HPLC–MS analysis of the reaction mixture revealed five major components (Fig. 3). The isolated compounds were studied by ^{1}H NMR (products **I–V**).

Product I. Molecular weight (mass spectrum) 548.6; soluble in dioxane, acetone, ethanol, and THF; corresponds to *N*-(3-[(γ-aminopropyl)tetramethyldisiloxy]-propyl)-3,3-bis(4-hydroxyphenyl)phthalimidine.

Product II. Molecular weight (mass spectrum) 433.1; soluble in dioxane, acetone, and ethanol; corresponds to *N*-[3-(hydroxydimethylsilyl)propyl]-3,3-bis(4-hydroxyphenyl)phthalimidine.

Product III. Molecular weight (mass spectrum) 318.2, the NMR spectrum corresponds to the initial phenolphthalein.

Product IV. Molecular weight (mass spectrum) 847.4; poorly soluble in acetone and ethanol, soluble in dioxane and DMSO; corresponds to 1,3-bis([3,3-bis(4-hydroxyphenyl)phthalimidin-2-yl]propyl)tetramethyldisiloxane.

Product V. Molecular weight (mass spectrum) 505.5; soluble in dioxane, acetone, and ethanol; corresponds to the desired *N*-[3-(pentamethyldisiloxy)propyl]-3,3-bis-(4-hydroxyphenyl)phthalimidine.

Compounds **I–IV** can be formed by rearrangement upon cleavage of the siloxane bond with the water released in the course of the reaction (Scheme 1).

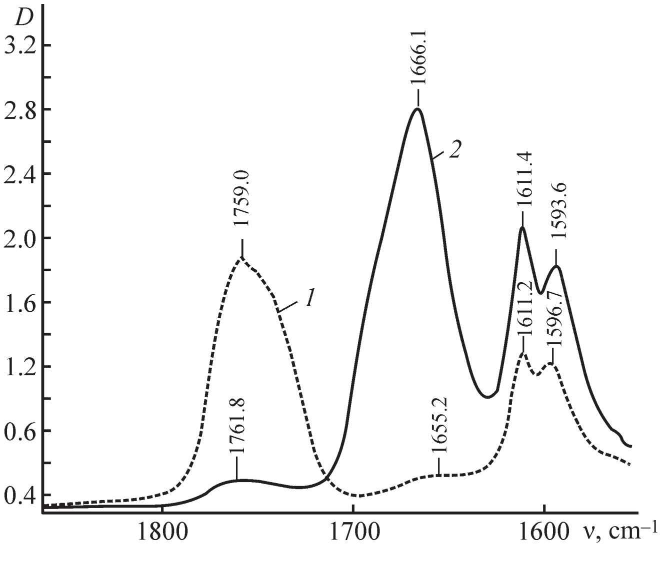


Fig. 1. IR spectrum of the products synthesized in (*1*) dioxane and (*2*) dichlorobenzene. (*D*) Optical density and (ν) wavenumber.

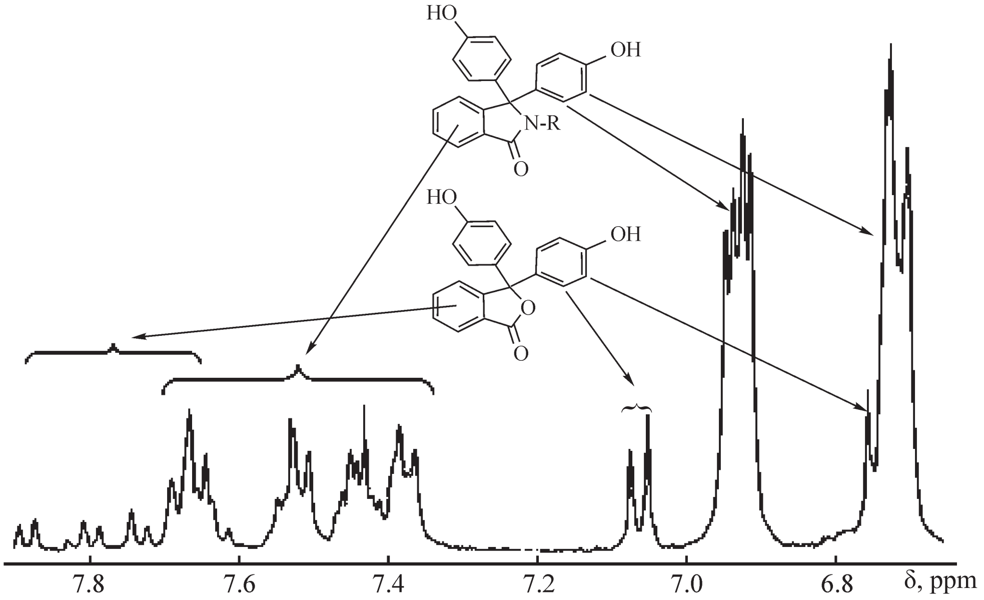
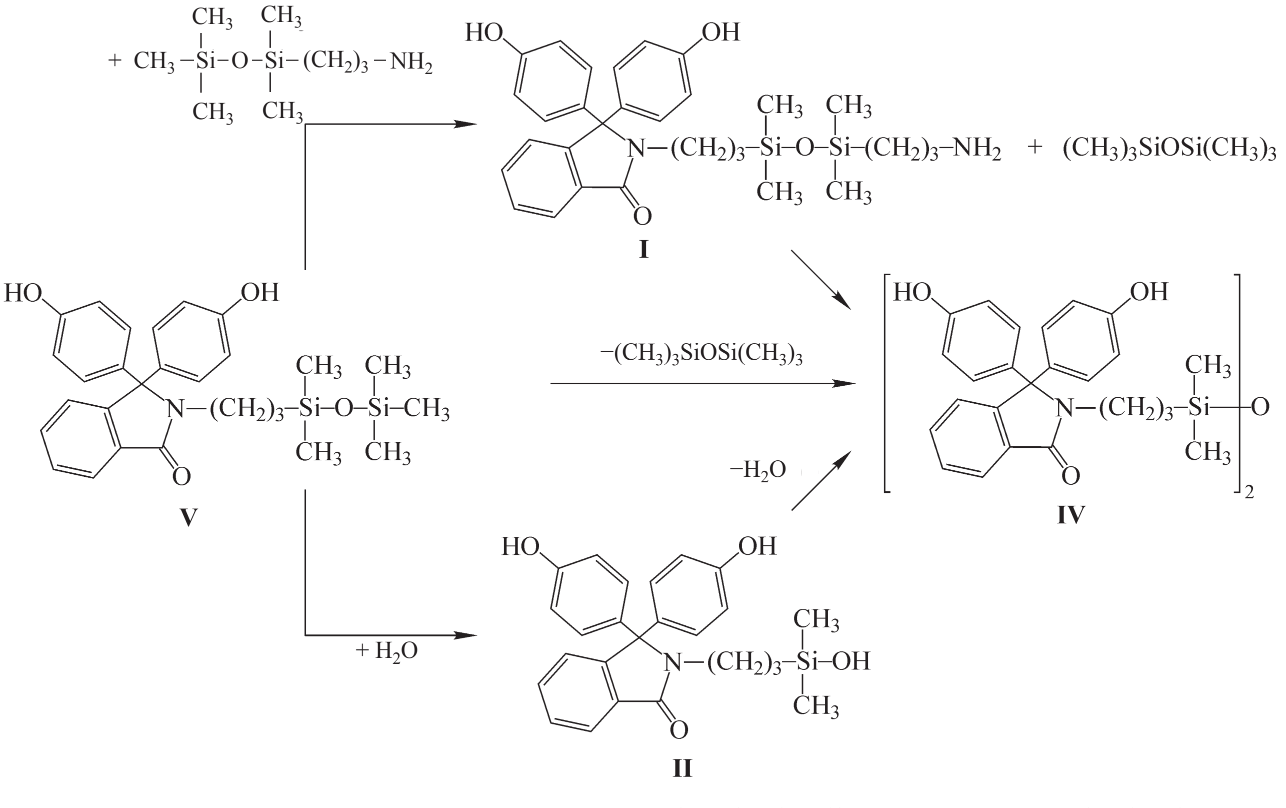


Fig. 2. NMR spectrum of products formed in the reaction of (γ-aminopropyl)pentamethyldisiloxane with phenolphthalein in *o*-dichlorobenzene. (δ) Chemical shift.

Scheme 1.



The reaction of 3-(γ-aminopropyl)heptamethyltrisiloxane with phenolphthalein was performed in an *o*-dichlorobenzene solution for 20 h at 140°C. The phenolphthalein conversion was 65% according to NMR data. The reaction yields a series of mixed oligomeric phenolaminosiloxanes. For example, in the MALDI mass spectrum (Fig. 4), there are peaks belonging to linear α,ω-bistrimethylsiloxy oligomers **VI** with MW = 89 + 417*n* + 117*m* + 73, to linear silanols **VII** with MW = 89 + 417*n* + 117(*m* + 1), to cyclic products **VIII**

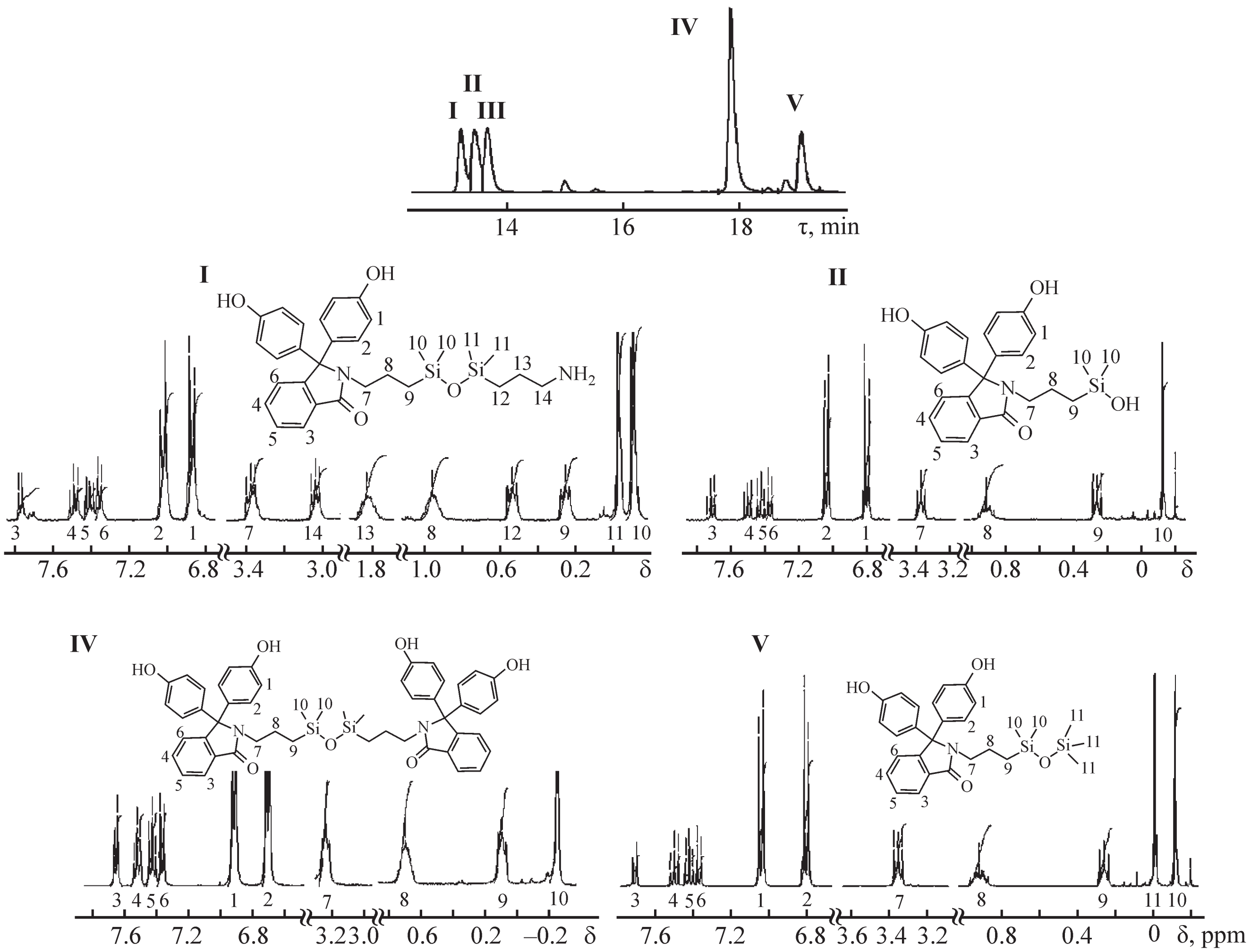


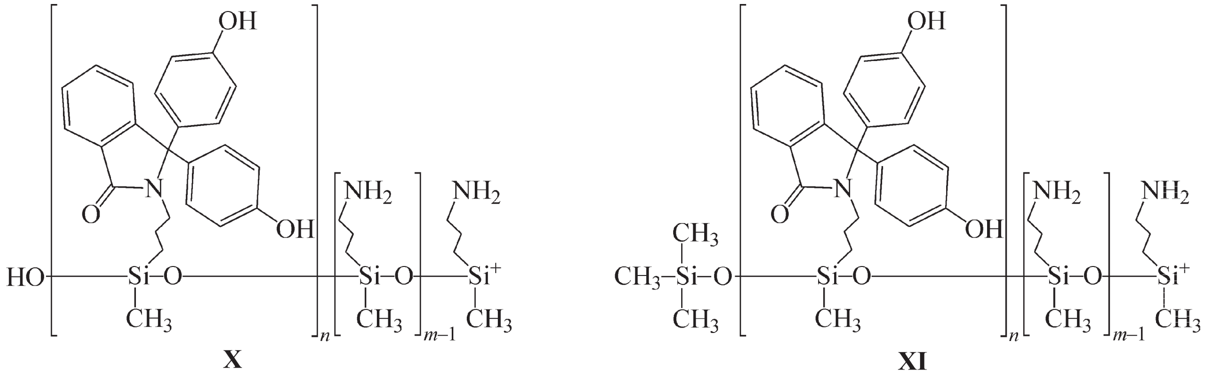
Fig. 3. Chromatogram of a mixture of products formed in the reaction of γ-(aminopropyl)pentamethyldisiloxane with phenolphthalein and NMR spectra opf products **I**, **II**, **IV**, and **V**. (τ) Retention time and (δ) chemical shift.

with MW = 417*n* + 117*m*, and to linear bissilanols **IX** with MW = 17 + 417*n* + 117(*m* + 1) (Scheme 2).

In the MALDI spectrum, there are also signals corresponding to ionized fragments of the molecules (in all the cases, *m* + *n* = 0–7) (Scheme 3).

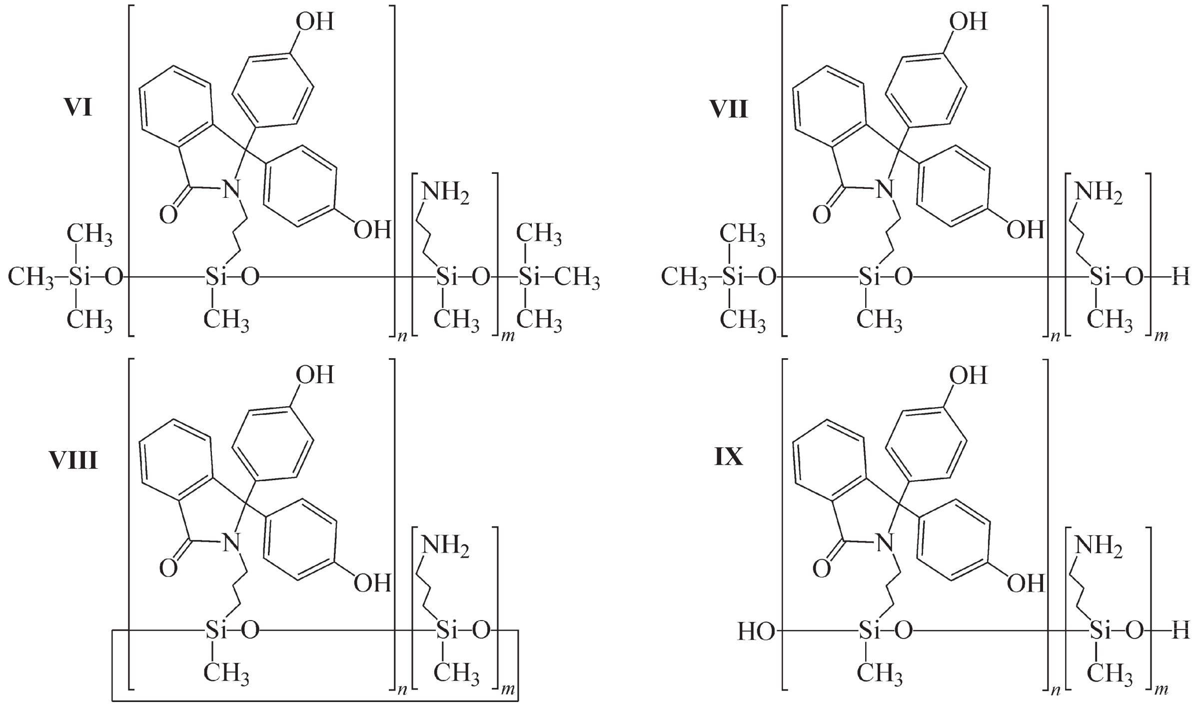
Compounds of structure **VI** were tested as modifier for a hot-curable epoxy compound. The TGA data showed that, on heating of the epoxy compound based on ED-20 epoxy resin and organosilicon modifier in air, the onset of the weight loss (5%) occurs above 350°C.

Scheme 2.



X **XI**

Scheme 3.



Thus, the reactions of γ-aminopropylsiloxanes with phenolphthalein yield *N*-alkylsiloxy-3,3-bis(4-hydroxyphenyl)phthalimidines. The phenolphthalein conversion under the synthesis conditions reaches 95%.

The siloxane fragments undergo rearrangements when heated in the presence of amino groups and of water released in the reaction. These rearrangements yield carbofunctional oligophenol(amino)siloxanes of different structures.

New di- and polyfunctional siloxanes containing aminopropyl and [3,3-bis(4-hydroxyphenyl)phthalimidin-2-yl]propyl groups were obtained and isolated by HPLC.

The polyfunctional amino- and phenolsiloxanes can be effective modifiers for epoxy resins.

EXPERIMENTAL

The Fourier transform IR spectra were recorded with a Nicolet 380 spectrometer in the range 400–4000 cm^{-1} at room temperature in the transmission mode using KBr pellets.

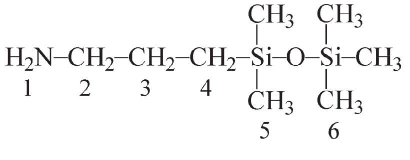
The ^1H NMR spectra of the products were recorded with a Bruker AT spectrometer operating at 360 MHz. $CDCl_3$ was used as solvent for organosilicon amines, and DMSO-d_6, for *N*-alkylsiloxyphthalimidines.

The purity of organosilicon amines and reaction products was evaluated by gas–liquid chromatography using a Kristallyuks 4000M chromatograph.

MALDI measurements were performed with a Bruker Ultraflex TOF/TOF spectrometer. The ScoutMTP MALDI ion source is equipped with a nitrogen laser (wavelength 337 nm) and PAN ion focusing system. Hydroxybenzoic acid was used as matrix. The target was prepared from an acetonitrile solution.

High-performance liquid chromatography was performed with a Vyodac C18 120A 250 × 4.6 mm column using a UV detector (220 nm). The mixture being analyzed was injected into the chromatograph as solution in acetonitrile. An acetonitrile–water mixture was used as eluent. The acetonitrile concentration was varied in the gradient from 5 to 100% in 30 min.

The initial (γ-aminopropyl)pentamethyldisiloxane



$$\underset{1}{H_2N}\text{–}\underset{2}{CH_2}\text{–}\underset{3}{CH_2}\text{–}\underset{4}{CH_2}\text{–}\overset{CH_3}{\underset{\underset{5}{CH_3}}{Si}}\text{–}O\text{–}\overset{CH_3}{\underset{\underset{6}{CH_3}}{Si}}\text{–}CH_3$$

was prepared in a 1-L two-necked flask equipped with a stirrer and a reflux condenser. The flask was charged with 124 g (0.5 mol) of bis(γ-aminopropyl)-tetramethyldisiloxane and 243 g (1.5 mol) of

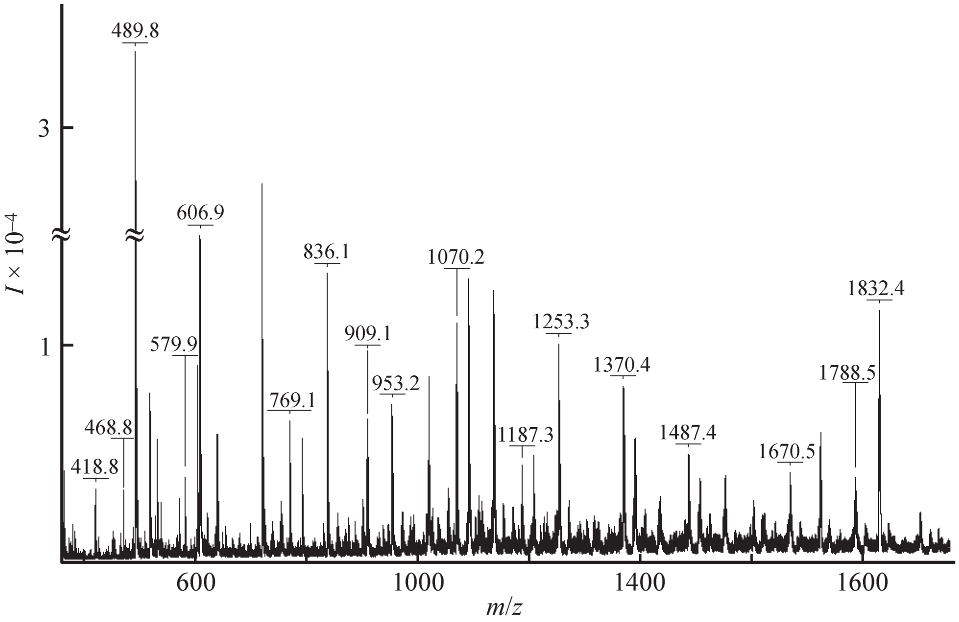
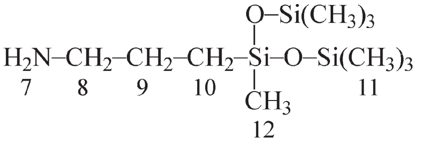


Fig. 4. MALDI mass spectrum of a mixture of products formed in the reaction of (γ-aminopropyl)heptamethyltrisiloxane with phenolphthalein. (*I*) Intensity.

hexamethyldisiloxane in the presence of 0.468 g of potassium siloxanolate. The reaction was performed at 90°C for 6 h. The reaction progress was monitored by gas chromatography. The diamine conversion was about 70%. The mixture was distilled at 95–105°C/2 mmHg to obtain 48.7 g of the product. The amine was analyzed by GLC. Purity 98.5%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.11 (H_1), 2.47–2.50 (H_2), 1.27–1.39 (H_3), 0.40–0.45 (H_4), –0.04 (H_5), –0.02 (H_6).

The initial 3-(γ-aminopropyl)heptamethyltrisiloxane



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad O\text{–}Si(CH_3)_3 \\ H_2N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Si\text{–}O\text{–}Si(CH_3)_3 \\ \;\,7 \qquad 8 \qquad\; 9 \qquad\; 10 \quad CH_3 \qquad\quad 11 \\ \qquad\qquad\qquad\qquad\quad\;\; 12 \end{array}$$

was prepared by the procedure described in [18]. The purity of the amine, determined by GLC, was 99%. The product was characterized by ^{1}H NMR, δ, ppm: 1.22 (H_7), 2.62–2.66 (H_8), 1.39–1.48 (H_9), 0.42–0.46 (H_{10}), 0.07 (H_{11}), –0.01 (H_{12}).

The reaction of phenolphthalein with (γ-aminopropyl)-pentamethyldisiloxane was performed in a 250-mL four-necked flask purged with nitrogen and equipped with a stirrer, a thermometer, and a Dean–Stark trap. The flask was charged with 31.8 g (0.1 mol) of phenolphthalein, 41.9 g (0.2 mol) of (γ-aminopropyl)-pentamethyldisiloxane, 50 mL of dichlorobenzene, and 10 mL of toluene (for azeotropic distillation of the water released in the reaction). The Dean–Stark trap was filled with toluene. The reaction was performed at 140°C for 30 h. Toluene, dichlorobenzene, and excess amine were distilled off on a rotary evaporator at 140°C/2 mmHg. A powdered product (49 g) was obtained. The phenolphthalein conversion was 95%.

The reaction of phenolphthalein with 3-(γ-amino-propyl)heptamethyltrisiloxane was performed in a 250-mL four-necked flask purged with nitrogen and equipped with a stirrer, a thermometer, and a Dean–Stark trap. The flask was charged with 15.9 g (0.05 mol) of phenolphthalein, 27.96 g (0.1 mol) of 3-(γ-aminopropyl)-heptamethyltrisiloxane, 50 mL of dichlorobenzene, and 10 mL of toluene (for azeotropic distillation of the water released in the reaction). The Dean–Stark trap was filled with toluene. The reaction was performed at 140°C for 20 h. The phenolphthalein conversion was 65%.

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