Russian Journal of Organic Chemistry, Vol. 40, No. 9, 2004, pp. 1258–1264. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 9, 2004, pp. 1308–1314.
Original Russian Text Copyright © 2004 by Ladilina, Semenov, Kurskii, Khorshev, Domrachev.

Reactions of Primary Amines with Tetracyanoethylene

E. Yu. Ladilina, V. V. Semenov, Yu. A. Kurskii, S. Ya. Khorshev, and G. A. Domrachev

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina 49, Nizhnii Novgorod, 603950 Russia
e-mail: llena@imoc.sinn.ru

Received July 8, 2003

Abstract—Primary amines, 3-triethoxysilylpropylamine, 3-silatranylpropylamine, and cyclohexylamine, react with tetracyanoethylene in acetonitrile at room temperature via addition at the cyano group to afford the corresponding amidines. *N*-Cyclohexyltricyanoacrylamidine exists as a mixture of two of the three possible isomers, while *N*-(3-triethoxysilylpropyl)tricyanoacrylamidine and *N*-(3-silatranylpropyl)tricyanoacrylamidine exist mainly as a single isomer containing NH_2 group. *N*-(3-Triethoxysilylpropyl)tricyanoacrylamidine was used to prepare gels and films.

Transparent materials which are obtained from carbofunctional alkoxysilanes $(RO)_3Si(CH_2)_nX$ (R = Me, Et) by colloid chemistry methods may include fragments of an organic dye or a polyconjugated oligomer. The presence of a readily hydrolyzable trialkoxysilyl group provides the possibility for preparing fibers, films, and monoliths. Depending on the X chromophore, such materials exhibit second- or third-order nonlinear optical properties [1]. Hydrolysis of $(RO)_3Si(CH_2)_nX$ or its cohydrolysis with another trialkoxysilane $(RO)_3SiR'$ (R = Me, Et) or tetraethoxysilane $(EtO)_4Si$ gives rise to organosilicates with controlled properties, which can be used as specific adsorbents and heterogeneous catalysts [2]. The resulting organosilsesquioxane matrix possesses enhanced photo- and thermal stability as compared to organic polymers. This is important for both laser technologies and catalytic processes.

In the present article we report on the synthesis of a carbofunctional alkoxysilane containing a polarized conjugated organic group by reaction of 3-triethoxysilylpropylamine $(EtO)_3SiCH_2CH_2CH_2NH_2$ (**I**) with tetracyanoethylene; possible application of the product in the preparation of films and gels was also examined. In the recent time, tetracyanoethylene has been extensively used in the synthesis of nitrogen-containing organic compounds [3, 4]. Amine **I** is well known as fiber- and film-forming agent [5]. We expected that the triethoxysilyl fragment almost will not affect the reactivity of the amino group separated by three methylene units. Molecule **I** lacks [6] strong intramolecular donor–acceptor interaction between the nitrogen and silicon atoms (cyclic form with five-coordinate silicon atom), as is the case of 3-trifluorosilylpropylamine [7].

It is known [8] that primary and secondary amines react with nitriles to give amidines.

$$RNH_2 + R'C{\equiv}N \longrightarrow R'C(=NH)NHR$$

If the initial compound possesses a conjugated bond system and several cyano groups, the product could give rise to intramolecular charge transfer from the amino nitrogen atom of the amidine moiety to cyano group. Therefore, the resulting molecule could be an asymmetric chromophore exhibiting secon-order nonlinear optical properties. As such polycyano compound we used tetracyanoethylene. Its molecule is characterized by conjugated bond system, and reaction of an amine at one of the four cyano groups should considerably reduce the degree of symmetry. Addition of amines at a cyano group is facilitated by the presence of electron-acceptor substituents in the α-position with respect to that group [8]. There are almost no published data on the addition at cyano groups of tetracyanoethylene. This seems to be surprising, for each cyano group therein is attached to electron-acceptor tricyanovinyl fragment. Until present, it was believed [9, 10] that reactions of tetracyanoethylene with primary and secondary amines result only in replacement of one or two cyano groups. Reactions of tetracyanoethylene with substituted hydrazines were reported [11, 12]. The products were assumed to be formed in two steps. One of these is replacement of

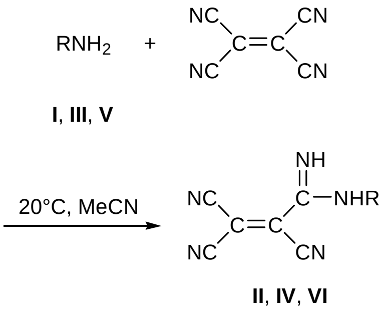
1070-4280/04/4009-1258 © 2004 MAIK “Nauka/Interperiodica”

one cyano group by amino, and the other is addition of NH_2 or RNH group at the C≡N bond. The authors did not determine which of these steps, substitution or addition, occurs first.

We have found that amine **I** reacts with tetracyanoethylene in acetonitrile at room temperature to give *N*-(3-triethoxysilylpropyl)tricyanoacrylamidine (**II**). After mixing of cooled colorless solutions of the reactants, the mixture remains homogeneous, but it quickly turns brown. The addition of the silicon-containing amine at the cyano group is confirmed by the following data. First, the process is not accompanied by separation of 3-triethoxysilylpropylammonium cyanide $(EtO)_3SiCH_2CH_2CH_2NH_3^+\,CN^-$ which should be formed as a result of replacement of the cyano group.

$$2\,RNH_2 \;+\; (NC)_2C{=}C(CN)_2 \;\longrightarrow\; RNHC(CN){=}C(CN)_2 \;+\; RNH_3^+\,CN^-$$

Second, the IR and ^1H and ^{13}C NMR spectra of the product are consistent with structure **II**. Thus our results differ from those reported in [10], according to which reactions of tetracyanoethylene with aliphatic amines involve only replacement of cyano group in the former. Therefore, we performed reactions of tetracyanoethylene with other amines, 3-silatranylpropylamine (**III**) and cyclohexylamine (**V**), and found that these reactions also followed mainly the addition pathway.



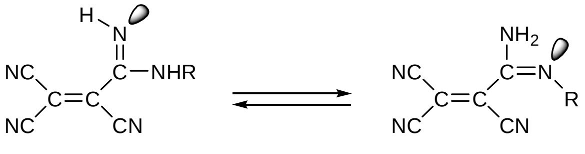
I, **II**, R = $CH_2CH_2CH_2Si(OCH_2CH_3)_3$, 85%;
III, **IV**, R = $CH_2CH_2CH_2Si(OCH_2CH_2)_3N$, 75%;
V, **VI**, R = *cyclo*-C_6H_{11}, 69%.

N-(3-Silatranylpropyl)tricyanoacrylamidine (**IV**) and *N*-(cyclohexyl)tricyanoacrylamidine (**VI**) were isolated as the major products which were readily soluble in acetonitrile. In addition, small amounts (6 and 2%, respectively) of insoluble light yellow powders were isolated. According to the IR spectral data, the insoluble minor products were 3-silatranylpropylammonium cyanide and cyclohexylammonium cyanide. Their formation indicates that substitution of cyano group nevertheless occurs, though the contribution of this pathway is small. The use of cyclohexylamine seems to be convenient, for the product of its reaction with tetracyanoethylene is fairly volatile, and it can be purified by vacuum sublimation. By contrast, amidines **II** and **IV** are characterized by larger molecular weights and low volatilities, so that they cannot be sublimed under reduced pressure. These products were purified by repeated washing with hexane and diethyl ether. In keeping with the ^1H and ^{13}C NMR data, compounds **II** and **IV** contained insignificant (~1%) amounts of impurities.

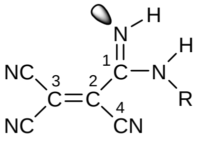
In the IR spectrum of amidine **VI** we observed two absorption bands with their maxima at 3220 and 3160 cm^{-1}, which correspond to stretching vibrations of unassociated N–H bonds in the amino and imino fragments, respectively. Compounds **II** and **IV** displayed three absorption bands in the same region of the IR spectrum, at 3340, 3240, and 3170 cm^{-1}, which are likely to belong to vibrations of both free and associated N–H bonds. Absorption bands due to stretching vibrations of the cyano groups in **II**, **IV**, and **VI** (2220–2150 cm^{-1}) are displaced to lower frequencies relative to the corresponding bands in the spectrum of tetracyanoethylene (2270 cm^{-1}). This may be interpreted in terms of some weakening of the C≡N bonds as a result of formation of polyconjugated system including the C=C and C≡N bonds and the amidine fragment NC(=NH). The latter is characterized by lower negative inductive and mesomeric effects as compared to the cyano group. A very high frequency and some broadening of the absorption band at about 1600 cm^{-1} in the IR spectra of all amidines **II**, **IV**, and **VI** must be noted. Presumably, this is the result of superposition of three bands corresponding to stretching vibrations of the double C=C and C=N bonds and bending vibrations of the N–H bonds. The ν(C=C) and ν(C=N) bands are slightly displaced to the low-frequency region (by about 20 cm^{-1}), while the δ(=N–H) and δ(N–H) bands are displaced to the high-frequency region due to p–π and π–π conjugation in the NC(=NH) and N=C–C=C fragments, respectively. It is known [13] that C=N stretching vibration bands are usually characterized by maximal intensity in the above spectral region. The IR spectra of **II**, **IV**, and **VI** also contained absorption bands belonging to vibrations of the organosilicon (triethoxysilyl or silatranyl) or cyclohexyl substituent.

The ^{13}C NMR spectra of compounds **II**, **IV**, and **VI** differ insignificantly. Each compound shows in the spectrum a signal from the amidine carbon atom (C=N). The presence of two signals from the C=C fragment and three signals from nonequivalent cyano groups indicates asymmetric structure of the products. Signals from protons in the substituent at the nitrogen atom in compounds **II**, **IV**, and **VI** almost do not change their positions relative to those observed in the ^{1}H NMR spectra of the initial amines. Exceptions are signals from protons of the methylene groups directly attached to the nitrogen atom. These signals shift downfield from δ 2.6 ppm to 3.5–3.7 ppm since the nitrogen atom in the product is a part of the amidine fragment which suffers from a strong electron-acceptor effect of the tricyanovinyl group. Signals from proton at the imino nitrogen atom are located in a weaker field, at δ 6.8–8.6 ppm. We failed to identify signals from protons in the amino group; probably, these signals are strongly broadened due to fast exchange or overlapped by signals from protons of the methylene bridges.

Amidines can exist as three isomers **A**, **B**, and **C**, two of which (**A** and **B**) are readily interconvertible tautomers [14].



A **B**



C

Differences in the positions and intensities of signals from the imino protons in amidines **II**, **IV**, and **VI** may be interpreted in terms of different isomer ratios for each compound. The =N–H signal in the ^{1}H NMR spectrum of **VI** is a doublet, indicating that isomers **A** and **C** prevail. In the spectra of **II** and **IV**, the corresponding signal is located in a weaker field, and its intensity is considerably lower than 1H; therefore, these compounds exist mainly as isomers **A** and **B**. This is confirmed by the presence in the IR spectra of **II** and **IV** of three bands corresponding to N–H stretching vibrations; such spectral pattern may be due not only to formation of associates (see above) but also to the presence of an appreciable fraction of isomer **B**. In the region 600–700 cm^{-1} we observed two weak absorption bands (670 and 630 cm^{-1} for compound **II** and 660 and 610 cm^{-1} for **IV**) which were absent in the spectra of the initial compounds. Analogous bands are typical of carboxylic acid amides [15]. The presence of these bands is indicative of structure **B** where the NH_2 group is linked to a fragment like the carbonyl group in amides, which exerts considerable negative inductive and mesomeric effects.

The electron absorption spectra of amidines **II** and **VI** contain a strong absorption band at about λ 320 nm, which may be assigned to n–π^* transition in the conjugated bond system of tricyanoacrylamidine. Red shift of that band in the spectrum of **VI** may be attributed to a slightly stronger positive inductive effect of the cyclohexyl group at the nitrogen, as compared to the 3-trialkoxysilylpropyl substituent in amidine **II**. Amidine **II** also showed in the spectrum several much weaker absorption bands at λ 400, 420, 470, 521, and 685 nm.

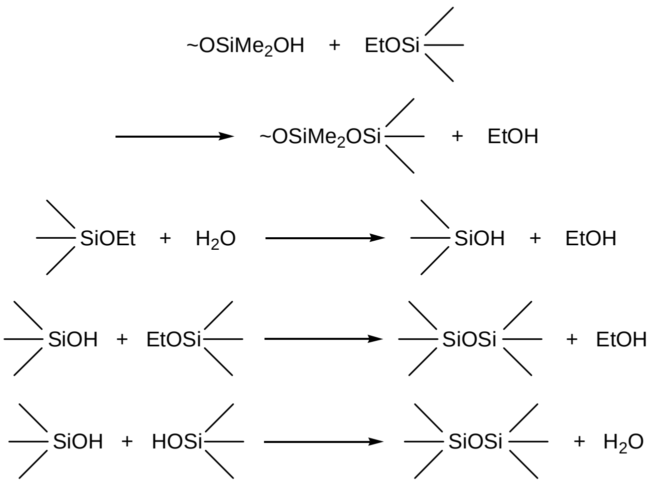
Molecule **II** comprises both tricyanoacrylamidine chromophore and alkoxysilyl group. The latter is capable of undergoing hydrolysis and condensation to afford cross-linked two- or three-dimensional polysiloxane structures. Therefore, compound **II** can be used for the preparation of chromophore-containing films and gels. Application of a solution of **II** in acetonitrile onto a silicate glass surface, followed by exposure to air over a period of 24 h, gave a brittle nontransparent film with an uneven thickness. With the goal of obtaining uniform elastic and transparent films we used a composition which, apart from compound **II**, contained oligodimethylsiloxane-α,ω-diols $HO(Me_2SiO)_nH$ (**VII**, n = 4, 5) and *N*-(3-triethoxysilylpropyl)-3-aminopropanenitrile $(EtO)_3Si$-$CH_2CH_2CH_2NHCH_2CH_2CN$ (**VIII**). Siloxanediols act as plasticizers which bind rigid three-dimensional organosilsesquioxane fragments $[RSiO_{1.5}]$ where R = $CH_2CH_2CH_2NHC(=NH)C(CN)=C(CN)_2$ or CH_2CH_2-$CH_2NHCH_2CH_2C\equiv N$ through flexible siloxane chains, thus preventing the resulting films from fissuring. Compound **VIII** was used to overcome incompatibility of permethylated siloxanediols **VII** with amidine **II** having a bulky polar organic group. *N*-(3-Triethoxysilylpropyl)-3-aminopropanenitrile (**VIII**) was synthesized by cyanoethylation of amine **I** with acrylonitrile [5].

The best films (with respect to their uniformity, transparency, adhesion, and thermal stability) were obtained by mixing components **II**, **VII**, and **VIII** at

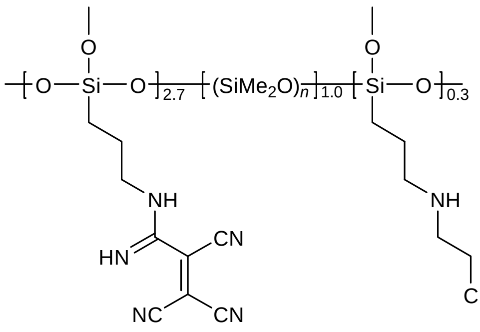
$$(EtO)_3SiCH_2CH_2CH_2NH_2 + CH_2{=}CHCN \longrightarrow (EtO)_3SiCH_2CH_2CH_2NHCH_2CH_2CN$$

VIII

a molar ratio of 2.7 : 1 : 0.3. The viscosity was controlled by adding a small amount of acetonitrile. After mixing, the composition was kept for 20–25 h at room temperature for maturing. During this time, partial condensation of siloxanediols with triethoxysilyl groups of compounds **II** and **VIII** occurred, which prevented possible disintegration upon subsequent curing. The maturing was accompanied by insignificant increase in the viscosity. Films were prepared both on modified glass (treated with hexamethyldisilazane) and on unmodified glass under conditions ensuring slow evaporation of the solvent. The composition applied to a support lose its fluidity in 20–25 h. The complete curing required 45–50 h at 20–25°C or 0.5 h at 150°C. The structurization process was monitored by IR spectroscopy. The spectra of uncured films contained absorption bands due to tricyanoacrylamidine fragment (2210, 1600 cm^{-1}), triethoxysilyl (1250, 1080, 800 cm^{-1}) and hydroxy groups (a strong broad band at 3300 cm^{-1}), and siloxane bonds (1040–1100 cm^{-1}). The curing process was accompanied by considerable decrease in the intensity of absorption bands belonging to stretching vibrations of hydroxy groups and increase in the relative intensity of the siloxane band, indicating complete formation of a siloxane matrix. The bands belonging to the tricyanoacrylamidine chromophore almost did not change in intensity. The structurization process may be represented by the following reactions:



The resulting films were red–brown, and the intensity of the color can be controlled by varying the fraction of amidine **II** at the expense of colorless compound **VIII**. The composition of the film is given by general formula **D**.



D

The electron absorption spectra of the films contained four bands (λ_{max} 320, 423, 490, and 694 nm) due to the presence of amidine chromophore. The fluorescence excitation spectrum consists of two bands, λ 271 and 364 nm (recorded at 430 nm), and of three bands, λ 368, 520, and 626 nm (recorded at 700 nm). In the fluorescence spectrum (excitation at λ 370 nm) we observed three emission bands with their maxima at λ 663, 422, and 443 nm and an intensity ratio of 28 : 2.5 : 2.5. The most intense bands in the near IR region were those with λ_{max} 1530, 1700, 1740, and 1920 nm. They were identified as first overtones of vibrations of the N–H (1530 nm) and C–H bonds (1700 and 1740 nm), O–H bonds of adsorbed water (1920 nm), and C≡N bond (1920 nm) [16]. The obtained films are characterized by a good thermal stability: heating to 200°C over a period of 30 min in air does not change their appearance and composition to an appreciable extent. Transparent red–brown films were also prepared from solutions of amidine **II** in ethyl cyanoacrylate with a concentration of 8–10%. In this case, no addition of organosilicon nitrile **VIII** was necessary. The composition applied to glass cured in 4 h. Films based on ethyl cyanoacrylate showed a lower thermal stability. Blushing and fissuring were observed on heating to 150°C. Thus, the sol–gel method involving only organosilicon components turned out to be superior.

It is known that, depending on the conditions of hydrolysis and cohydrolysis of alkoxysilanes, the resulting xerogels are transparent glasses or porous powders. Triethoxysilyl-substituted amidine **II** and nitrile **VIII** are slowly (in 4 days) hydrolyzed with a twofold amount of water in ethyl alcohol to give transparent gels. Removal of volatile compounds under reduced pressure on heating to 120°C leads to formation of xerogels **IX** and **X**.

$$2\,\mathbf{II} + 2.5\,H_2O \longrightarrow 2/n\,[(NC)_2C{=}C(CN)C({=}NH)NH(CH_2)_3SiO_{1.25}(OEt)_{0.5}]_n + 5\,EtOH$$

IX

$$\mathbf{VIII} + 1.5\,H_2O \longrightarrow 1/n\,[NCCH_2CH_2NH(CH_2)_3SiO_{1.5}]_n + 3\,EtOH$$

X

$$\mathbf{II} + Si(OEt)_4 + 2.5\,H_2O \longrightarrow 1/n\,[(NC)_2C{=}C(CN)C({=}NH)NH(CH_2)_3SiO(OEt)][EtOSiO_{1.5}]_n + 5\,EtOH$$

XI

$$\mathbf{VIII} + Si(OEt)_4 + 3\,H_2O \longrightarrow 1/n\,[NCCH_2CH_2NH(CH_2)_3SiO(OEt)][SiO_2]_n + 6\,EtOH$$

XII

Cohydrolysis of compounds **II** and **VIII** with an equimolar amount of tetraethoxysilane occurs at an appreciably higher rate. Nontransparent gels **XI** and **XII** are formed in 2 days; however, the complete syneresis is achieved by additionally keeping the gels at room temperature for 2 days.

The time of syneresis was determined from the ease of removal of alcohol from the gels under reduced pressure (alcohol was not removed in 2 days, while it was readily removed in 4 days). Xerogel **X** is a resin-like transparent material. The other substances are amorphous powders: colorless **XII** and black **IX** and **XI**. According to the data of elemental analysis (see table) and IR spectroscopy, the hydrolysis products contained unreacted ethoxy groups in an amount of 0.5 to 1.0 per silicon atom. The degree of both hydrolysis of nitrile **VIII** and its cohydrolysis with tetraethoxysilane was higher. In the IR spectra of the dried gels, the absorption bands belonging to organic substituents on the silicon remained almost unchanged. The strongest differences were observed in the spectral region corresponding to absorption of the triethoxysilyl group. An intense broadened band was located at 1100–1000 cm^{-1}; it was assigned to vibrations of siloxane bonds formed by hydrolysis of alkoxysilyl groups and subsequent condensation of Si–OH groups. The spectra lacked absorption in the region 3500–3300 cm^{-1} (SiO–H, H_2O), indicating that the condensation process was complete and that water was completely removed from the xerogel. We measured the specific surface of the obtained powder-like gels. As follows from the data in table, a non-zero value was obtained only for xerogel **XII**. The resulting gels were heated for 2 h at 600°C under argon. The pyrolysis products were characterized by a considerably greater porosity than the initial gels.

EXPERIMENTAL

The IR spectra of were recorded on a Specord 75IR spectrophotometer from samples prepared as liquid films between KBr plates or suspensions in mineral oil. The electron absorption spectra were measured on a Specord M40 spectrophotometer from 5-mm quartz cells. The near-IR spectra of flms applied to a quartz support were recorded on a Cary-500 Scan spectrometer. The fluorescence and fluorescence excitation spectra were obtained using an SFL-1211A (SOLAR TII) spectrofluorimeter. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 MHz) at 25°C using tetramethylsilane as internal reference; $CDCl_3$ and CD_3CN were used as solvents. The specific surfaces were determined by

Yields, specific surfaces, and elemental analyses of gels **IX**–**XII**

Comp. no.	Initial compounds	Yield, %	S_{sp}, m^2/g		Calculated, %			Formula	Found, %		
			before annealing	after annealing	C	H	Si		C	H	Si
IX	**II**	88	0	–	46.76	4.12	10.94	$C_{10}H_{10.5}O_{1.75}N_5Si$	46.80	4.80	10.48
X	**VIII**	63	0	30±2	44.14	6.79	17.20	$C_6H_{11}O_{1.5}N_2Si$	44.45	7.04	18.47
XI	**II** + EtO)$_4$Si, 1:1	97	0	–	41.92	4.87	15.08	$C_{13}H_{18}O_{4.5}N_5Si_2$	43.33	5.38	16.75
XII	**VIII** + (EtO)$_4$Si, 1:1	76	79±6	363±29	36.90	6.20	21.57	$C_8H_{16}O_4N_2Si_2$	36.04	5.70	18.90

thermal desorption of nitrogen using a GKh-1 chromatograph. *N*-(3-Triethoxysilylpropyl)-3-aminopropanenitrile (**VIII**) was analyzed on a Tsvet-530 chromatograph equipped with a 0.3×200-cm stainless steel column which was packed with 5% of KhS-2-1 on Chromaton N-AW-DMCS.

Acetonitrile (Reakhim) was boiled over P_2O_5 and distilled [17]; 3-triethoxysilylpropylamine (from *Altaikhimprom* Slavgorod Industrial Association) and cyclohexylamine were purified by distillation under reduced pressure; 3-silatranylpropylamine was prepared as described in [18], and tetracyanoethylene (98%, Aldrich) was used without additional purification.

***N*-(3-Triethoxysilylpropyl)-2,3,3-tricyano-2-propenimidamide (II).** A solution of 1.38 g (6.25 mmol) of amine **I** in 8 ml of acetonitrile was slowly added under stirring and cooling to a solution of 0.80 g (6.25 mmol) of tetracyanoethylene in 2 ml of acetonitrile. After 12 h, the solvent was removed, and the residue was washed with ether and hexane and dried under reduced pressure. Yield 1.85 g (85%). Brown viscous oily substance. Electron absorption spectrum, λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 320.5 (6.1×10^3), 400 (1.1×10^3), 420 (1.05×10^3), 470 (1.2×10^3), 521 (1.0×10^3), 685 (1.0×10^2). IR spectrum, ν, cm^{-1}: 3340, 3240, 3170 (NH); 2220, 2200, 2175 (C≡N); 1600 (C=C, C=N); 1240, 1170, 1110, 1080, 960, 780 [($CH_2CH_2CH_2$-$Si(OEt)_3$]. ^1H NMR spectrum, δ, ppm: 0.6 t (2H, $SiCH_2$), 1.2 t (9H, CH_3), 1.8 m (2H, CH_2), 3.6 m (2H, NCH_2), 3.8 q (6H, OCH_2), 7.5 s (1H, =NH). ^{13}C NMR spectrum, δ_C, ppm: 58.6 (C^3), 60.8 (C^2), 109.2 (C^4), 111.7 and 112.3 (3-C≡N), 142.9 (C^1), 7.4 ($SiCH_2$), 18.4 (CH_3), 23.8 ($SiCH_2\mathbf{C}H_2$), 50.2 (NCH_2), 59.0 (OCH_2). Found, %: C 51.92; H 6.48; Si 6.38. $C_{15}H_{23}O_3N_5Si$. Calculated, %: C 51.55; H 6.63; Si 8.04.

***N*-(3-Silatranylpropyl)-2,3,3-tricyano-2-propenimidamide (IV).** A solution of 0.43 g (3.36 mmol) of tetracyanoethylene in 6 ml of acetonitrile was added to 0.83 g (3.57 mmol) of 3-silatranylpropylamine, and the mixture was stirred for 10 min. After 2 days, a light material separated. The mixture was subjected to centrifugation, the solution was separated by decanting, and the solvent was removed under reduced pressure. The residue was washed with ether and dried to obtain 1.17 g (90%) of amidine **IV** as a dark brown very viscous material. IR spectrum, ν, cm^{-1}: 3340, 3220, 3150 (NH); 2220, 2190, 2150 (C≡N); 1600 (C=C, C=N); 1270, 1110, 990, 940, 910, 770, 760 [CH_2CH_2-$CH_2Si(OCH_2CH_2)_3N$]. ^1H NMR spectrum, δ, ppm: 0.5 m (2H, $SiCH_2$), 1.7 m (2H, CH_2), 2.8 m (6H, $NC\mathbf{H}_2CH_2O$), 3.6 m (2H, $NCH_2C\mathbf{H}_2CH_2$), 3.7 m (6H, OCH_2), 8.6 s (1H, =NH). ^{13}C NMR spectrum, δ_C, ppm: 57.6 (C^3), 58.9 (C^2), 109.4 (C^4), 112.5 and 113.1 (3-C≡N), 142.7 (C^1), 2.0 ($SiCH_2$), 15.4 ($SiCH_2\mathbf{C}H_2$), 51.0 ($OCH_2\mathbf{C}H_2N$), 57.7 (OCH_2), 65.9 ($SiCH_2CH_2$-$\mathbf{C}H_2N$). Found, %: C 49.08; H 6.50; Si 8.09. $C_{15}H_{20}O_3N_6Si$. Calculated, %: C 49.98; H 5.59; Si 7.79.

The light material was washed with acetonitrile and dried. It was identified as 3-silatranylpropylammonium cyanide, yield 0.05 g. IR spectrum, ν, cm^{-1}: 2730–2500 br, 1560 (RNH_2^+), 2170 ($C{\equiv}N^-$).

***N*-Cyclohexyl-2,3,3-tricyano-2-propenimidamide (VI).** A solution of 0.42 g (4.22 mmol) of cyclohexylamine in 7 ml of acetonitrile was added to 0.53 g (4.13 mmol) of tetracyanoethylene, and the mixture was stirred for 10 min. After 2 days, a small amount of a light material separated. The solution was removed from that material by centrifugation, and the solvent was distilled off under reduced pressure. The residue was washed with ether and dried to isolate 0.66 g (69%) of amidine **VI** as a dark green powder. The product was purified by sublimation. Yield 0.19 g, light yellow powder. Electron absorption spectrum, λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 320.5 (1.6×10^4). IR spectrum, ν, cm^{-1}: 3220, 3160 (NH); 2230, 2200 (C≡N); 1610 (C=C, C=N); 1080 (C–C, cyclohexyl); 720 (C–H, cyclohexyl). ^1H NMR spectrum, δ, ppm: 1.5 m (10H), 3.6 m (1H, NCH), 6.8 d (1H, =NH). ^{13}C NMR spectrum, δ_C, ppm: 59.4 (C^3), 60.5 (C^2), 109.2 (C^4), 111.9 and 112.1 (3-C≡N), 141.8 (C^1), 24.6, 24.7, 29.8, 33.5 (*cyclo*-C_6H_{11}). Found, %: C 63.79; H 6.21. $C_{12}H_{13}N_5$. Calculated, %: C 63.42; H 5.77.

The light material was washed with acetonitrile and dried. It was identified as cyclohexylammonium cyanide, yield 0.01 g. IR spectrum, ν, cm^{-1}: 2730–2500 br, 1560 (RNH_2^+), 2170 ($C{\equiv}N^-$).

***N*-(3-Triethoxysilylpropyl)-3-aminopropanenitrile (VIII).** Amine **I**, 30 g (0.136 mol), was added to 20 g (0.377 mol) of acrylonitrile, and the mixture was heated for 6 h at 120°C. Fractional distillation of the mixture under reduced pressure gave 24 g (65%) of compound **VIII** as a colorless liquid with bp 160°C (0.5 mm). IR spectrum, ν, cm^{-1}: 3320, 1600 (NH); 2250 (C≡N); 1175, 960, 780 (SiOEt). ^1H NMR spectrum, δ, ppm: 0.61 t (2H, $SiCH_2$), 1.20 t (9H, CH_3), 1.40 s (1H, NH), 1.53–1.61 m (2H, $CH_2C\mathbf{H}_2CH_2$), 2.49 t (2H, CH_2CN), 2.61 t [2H, $C\mathbf{H}_2N(CH_2)_2CN$], 2.90 t (2H, $NC\mathbf{H}_2CH_2CN$), 3.79 q (6H, OCH_2).

Preparation of gels. Organosilicon components (organotrialkoxysilanes and tetraethoxysilane), 0.5–

1.2 g, were dissolved in 1 ml of ethanol, a twofold amount of water was added to the solution, and the mixture was stirred and was kept at room temperature until formation of gel and its subsequent maturing. Ethyl alcohol and water were removed by heating to 70°C under reduced pressure. The residue was washed with acetonitrile, and the gel was kept in that solvent for 24 h and dried under reduced pressure.

This study was performed under financial support by the INTAS Foundation (project no. 03-51-5959), Russian Foundation for Basic Research (project no. 02-03-32165), Grant of President of the Russian Federation (project no. NSh 1652.2003.3), and Russian Academy of Sciences (package programs of the Presidium of the Russian Academy of Sciences “Fundamental Problems of Physics and Chemistry of Nanodimensional Systems and Nanomaterials” and “Target-Oriented Synthesis of Compounds with Specified Properties and Creation of Functional Materials Based Thereon”). The analyses were performed at the Analytical Center, Institute of Organometallic Chemistry, Russian Academy of Sciences, under financial support by the Russian Foundation for Basic Research (project no. 96-03-40042) and at the Institute of Physics, National Academy of Sciences of Belarus (Minsk).

REFERENCES

1. Levy, D. and Esquivias, L., *Adv. Mater. Opt. Electron.*, 1995, vol. 7, p. 120.
2. Corriu, R.J.P., *Angew. Chem., Int. Ed. Engl.*, 2000, vol. 39, p. 1376.
3. Sheverdov, V.P., Ershov, O.V., Nasakin, O.E., Chernushkin, A.N., Tafeenko, V.A., and Bulkin, V.V., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 291; Sheverdov, V.P., Ershov, O.V., Nasakin, O.E., Chernushkin, A.N., and Tafeenko, V.A., 2002, *Russ. J. Org. Chem.*, vol. 38, p. 1001.
4. Sheverdov, V.P., Ershov, O.V., Nasakin, O.E., Chernushkin, A.N., Efimov, R.N., and Tafeenko, V.A., *Russ. J. Gen. Chem.*, 2002, vol. 72, p. 820.
5. Chernyshev, E.A., Belyakova, Z.V., and Knyazeva, L.K., *Aminopropiltrietoksisilan. Obzornaya informatsiya. Ser. Elementoorganicheskie soedineniya i ikh primenenie* (Aminopropyltriethoxysilane. Survey Information. Ser. Organometallic Compounds and Their Application), Moscow: NIITEKhIM, 1985.
6. Elguero, J., Macquarrie, D.J., Fruckier, A., and Alkorta, I., *J. Organomet. Chem.*, 2001, vol. 625, p. 148.
7. Chernov, N.F., Bolgova, Yu.I., Trofimova, O.M., Albanov, A.I., Chipanina, N.N., Pestunovich, V.A., and Voronkov, M.G., *Dokl. Ross. Akad. Nauk*, 2000, vol. 375, p. 210.
8. Zil’berman, E.N., *Reaktsii nitrilov* (Reactions of Nitriles), Moscow: Khimiya, 1972, pp. 128–129.
9. Zefirov, N.S. and Makhon’kov, D.I., *Usp. Khim.*, 1980, vol. 49, p. 635.
10. McKusick, B.C., Heckert, R.E., Cairns, T.L., Coffman, D.D., and Mower, H.F., *J. Am. Chem. Soc.*, 1958, vol. 80, p. 2806.
11. Hecht, S.M., Werner, D., and Traficante, D.D., *J. Org. Chem.*, 1975, vol. 40, p. 1815.
12. Earl, R.A., Pugmire, R.J., Revankar, G.R., and Townsend, L.B., *J. Org. Chem.*, 1975, vol. 40, p. 1822.
13. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, New York: Wiley, 1974, 3rd ed. Translated under the title *Spektrometricheskaya identifikatsiya organicheskikh soedinenii*, Moscow: Mir, 1977, p. 203.
14. Clement, B. and Kämpchen, T., *Chem. Ber.*, 1986, vol. 119, p. 1101.
15. Pretsch, E., Clerc, T., Seibl, J., and Simon, W., *Tables of Spectral Data for Structure Determination of Organic Compounds*, Berlin: Springer, 1989, I105, I150.
16. *Pribory i metody analiza v blizhnei infrakrasnoi oblasti* (Instruments and Methods for Analysis in the Near IR Region), Moscow: Khimiya, 1977.
17. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents: Physical Properties and Methods of Purification*, New York: Intersci., 1955, 2nd ed.
18. Knyazev, S.P., Kirin, V.I., and Chernyshev, E.A., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1244.