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Reaction of Organosilicon Amines with Dicarboxylic Anhydrides

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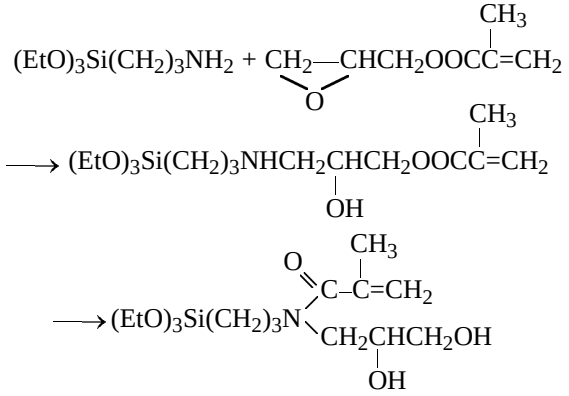
Abstract — Organosilicon amines react with cyclic dicarboxylic anhydrides to form previously unknown amido acids, which are converted into ammonium salts by the reaction with an equimolar amount of the amine. The structures of the compounds were studied by NMR spectroscopy.

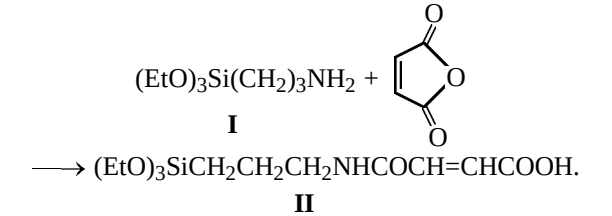
Carbofunctional organosilicon compounds are of interest as intermediates in synthesis. In particular, reactions of organosilicon amines allow preparation of a wide range of compounds from commercially available chemicals, e.g., of carbamates [1], thiocarbamates [2], sulfones, sulfoxides [3], etc. Addition of one or two glycidyl methacrylate molecules to 3-aminopropyltriethoxysilane gave silicon-containing amino acrylates [4, 5]. Opening of the epoxy ring is accompanied by isomerization and formation of amido alcohols [6]:



Products of reactions of amino alkoxysilanes with dicarboxylic anhydrides are mentioned in patents [7–11]. The reactions performed with amino silanes containing various numbers of nitrogen atoms at various anhydride : amine ratios could be the routes to compounds differing in the structure and functionality. However, published structural data for these products are lacking.

In this work we studied the reactions of carbofunctional amino alkoxysilanes with cyclic dicarboxylic anhydrides and the structures and conditions of formation of the resulting products.

All the reactions of amino alkoxysilanes with cyclic anhydrides are exothermic. The reaction of 3-aminopropyltriethoxysilane **I** with maleic anhydride was performed in the bulk, with gradual addition of maleic anhydride to the amine and with cooling.



II

Comparison of the ^{1}H NMR spectra of amino silane **I** and compound **II** suggests that the latter exists in the form of the ammonium salt $(EtO)_3SiCH_2CH_2CH_2 \cdot N^+H_2COCH{=}CHCOO^-$. In the spectrum of **I**, the NH_2 protons give a narrow singlet at δ 1.17 ppm. In the ^{1}H NMR spectrum of **II** (Fig. 1), two protons at the nitrogen atom also give a singlet, but this signal is considerably broadened and shifted downfield (δ

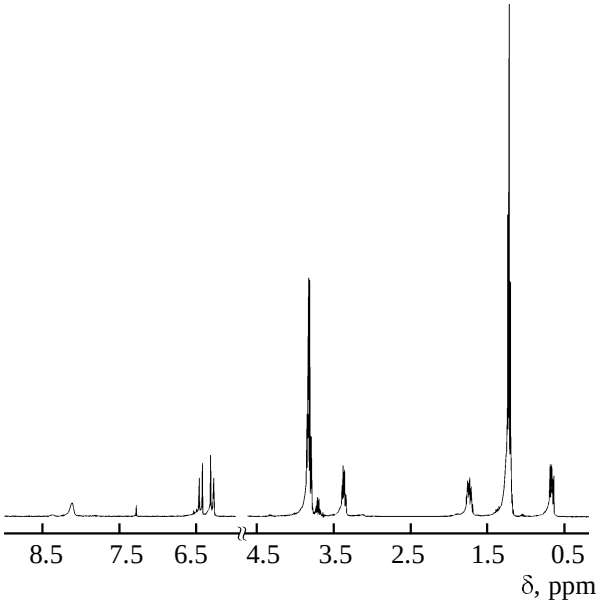


Fig. 1. ^{1}H NMR spectrum of **II**.

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Table 1. ^{1}H NMR spectra of amino silane **I**, diamine, and compounds **II**–**XIII** (δ, ppm)

Comp. no.	$SiCH_2$	CH_2	CH_2N	CH_3	CH_2O	NH_2	$^+NH_2$	NHCO	COOH	CH=CH	CH_3O
I	0.56	1.48	2.61	1.16	3.76	1.17	–	–	–	–	–
II	0.66	1.73	3.38	1.21	3.81	–	8.11	–	–	6.28, 6.43	–
III	0.62	1.74, 1.61	3.22, 2.83	1.18	3.79	–	7.61	9.50	–	5.83, 6.14	–
IV	0.53	1.56	3.11	1.18	3.76	–	–	6.30	–	5.48–5.79 methylcyclo-hexenylidene	–
V	0.64	1.80, 1.60	2.85	1.25	3.80	–	–	5.40	–	5.53–5.90 methylcyclo-hexenylidene	–
VI	0.61	1.70	3.31, 2.90	1.15	3.64	–	–	9.30	–	8.04, 7.77, 7.67, 7.39 phenylene	–
VII	0.45, 0.68	1.66	3.29, 2.69	1.20	3.74	–	6.65	–	–	7.46, 7.61 phenylene	
Diamine	0.58	1.52	2.53, 2.58, 2.71	–	–	1.17	–	–	–	–	3.49
VIII	0.69	1.82	3.01, 3.18, 3.63	–	–	–	8.48	–	–	6.05, 6.16	3.55
IX	0.58	1.74	2.95, 3.22	–	–	–	–	–	8.89	5.99, 6.33	3.48
X	0.62	1.53	2.63, 2.90, 3.80	–	–	–	–	7.35	–	7.70, 7.82 phenylene	3.50
XI	0.67	1.85	3.00, 3.35, 4.05	–	–	–	–	–	10.00	7.27–7.88 phenylene	3.40
XII	0.59	1.50	2.5–3.0	–	–	–	–	–	–	5.51–5.79 methylcyclo-hexenylidene	3.53
XIII	0.70	1.75	2.0–3.4	–	–	–	–	–	9.22	5.43–5.78 methylcyclo-hexenylidene	3.54

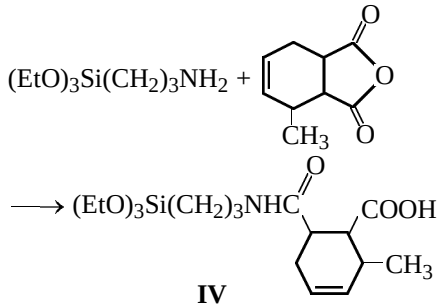
8.11 ppm). At the same time, protonation of the nitrogen atom strongly affects the position of the signals of the propylene group, especially of the CH_2N protons: their signal is shifted downfield by 0.77 ppm as compared to **I**. The signals of the two CH_2 groups more remote from the nitrogen atom are also shifted downfield but to a lesser extent (Table 1).

The ammonium form of **II** can react with amino silane **I**, which is a stronger base than the amido group in **II**. The reaction of **II** with **I** in an equimolar ratio gives product **III**.

$$\mathbf{II} + (EtO)_3SiCH_2CH_2CH_2NH_2$$
$$\longrightarrow (EtO)_3Si\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2NHCOCH{=}CHCOO^-$$
$$N^+H_3\overset{d}{C}H_2\overset{e}{C}H_2\overset{f}{C}H_2Si(OEt)_3.$$
III

Using the ^{1}H NMR data for **I** and **II**, we assigned the signals in the ^{1}H NMR spectrum of **III** (Fig. 2). The signals of the methylene groups of the propylene bridges are located at a sufficient distance from each other and can be identified as follows: *a*, *f*, 0.62; *b*, 1.61; *e*, 1.74; *c*, 2.83; and *d*, 3.22. As judged from the integral intensity, the broadened signal at δ 7.61 ppm is due to the NH^+ protons of the $^+NH_3$ group, and the singlet at δ 9.50 ppm, to the NHCO proton.

A similar reaction was performed with 3-methyl-1,2,3,6-tetrahydrophthalic anhydride:



IV

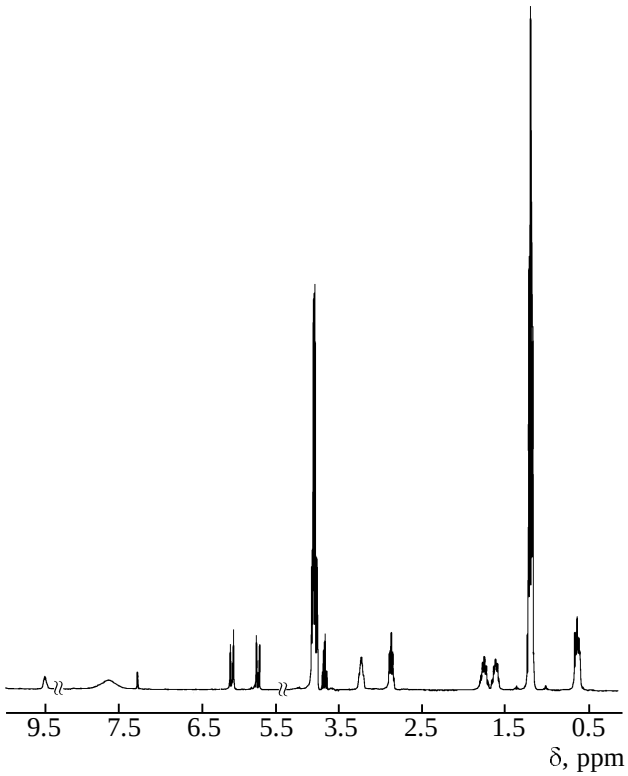
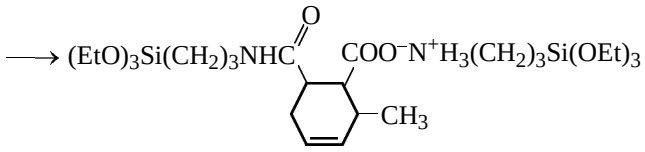


Fig. 2. ^{1}H NMR spectrum of **III**.

The reaction of **IV** with one more molecule of **I** yields neutral compound **V**.

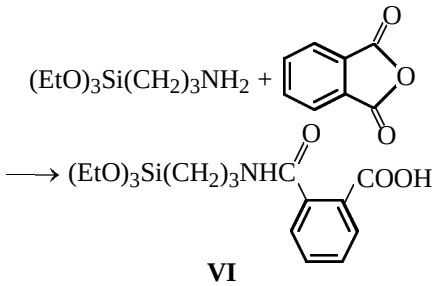
IV + $(EtO)_3SiCH_2CH_2CH_2NH_2$



V

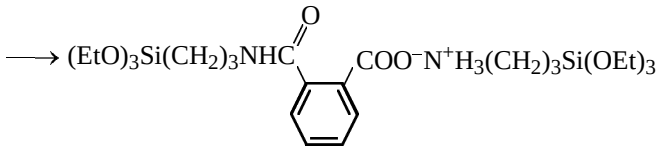
Similar results were obtained in the reaction of **I** with phthalic anhydride.

The ^{1}H NMR spectrum of **VI** contains two singlets of CH_2N protons: a triplet at 2.90 ppm and a multiplet at 3.31 ppm; the CH_2 group in the middle of the propylene chain gives a multiplet at 1.66–1.75 ppm. The fact that the CH_2N group gives two signals suggests



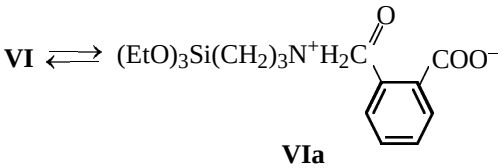
VI

VI + $(EtO)_3SiCH_2CH_2CH_2NH_2$



VII

that compound **VI** exists in two forms, acid and salt **VIa**, apparently occuring in an equilibrium:

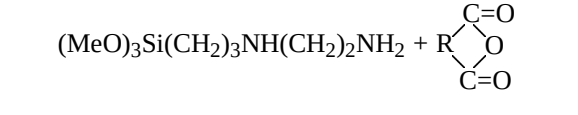


VIa

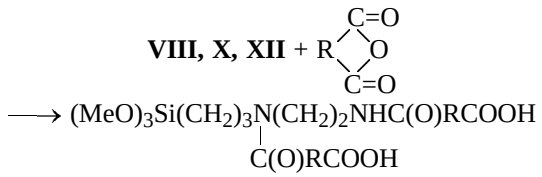
In **VIa**, the CH_2N group should give a triplet; therefore, from the ratio of the integral intensities of the two CH_2N signals, we can determine the ratio **VI** : **VIa** = 1.2 : 1.

Compounds **VII** and **III** appreciably differ in the positions of signals of the propylene group: whereas the CH_2Si groups in **III** give one signal (δ 0.60 ppm), in **VII** they give two multiplets (δ 0.45 and 0.68 ppm). The middle CH_2 groups in **VII** give two partially overlapping multiplets, in contrast to **III** where they are separated by 0.35 ppm. The CH_2N groups, as in **III**, give a triplet (δ 2.69 ppm) and a multiplet (δ 3.29 ppm).

An attempt to perform the reaction of 3-(2-aminoethyl)aminopropyltrimethoxysilane (diamine) with maleic anhydride in the bulk failed, because the heat evolution was so strong that cause tarring. To provide milder reaction conditions, the reactions of the diamine with dicarboxylic anhydrides were performed in ethyl acetate. The spectral characteristics of the products are listed in Table 1. The spectral data and the titration results show that the reactions of equimolar amounts of the diamine and anhydride yield neutral products, and at the ratio diamine : anhydride = 1 : 2 dicarboxylic acids are formed:



VIII, X, XII



IX, XI, XIII

Table 2. Yields, refractive indices, and elemental analyses of **II**–**XIII**

Comp. no.	Yield, %	n_D^{20}	Found, %				Formula	Calculated, %			
			C	H	N	Si		C	H	N	Si
II	99		48.45	7.53	4.41	8.98	$C_{13}H_{25}NO_6Si$	48.90	7.84	4.39	8.78
III	99	1.4587	49.01	8.78	5.05	10.46	$C_{22}H_{48}N_2O_9Si_2$	48.89	8.89	5.19	10.37
IV	98	1.4740	56.02	8.40	3.55	7.32	$C_{18}H_{33}NO_6Si$	55.81	8.53	3.61	7.24
V	99	1.4645	52.98	9.13	4.60	9.25	$C_{27}H_{56}N_2O_9Si_2$	53.29	9.21	4.61	9.21
VI	99	1.4950	55.42	7.43	3.55	7.48	$C_{17}H_{27}NO_6Si$	55.28	7.31	3.79	7.59
VII	98	1.4740	52.97	8.39	4.58	9.35	$C_{26}H_{50}N_2O_9Si_2$	52.88	8.47	4.75	9.49
VIII	97	–	45.23	7.36	8.66	8.89	$C_{12}H_{24}N_2O_6Si$	45.00	7.50	8.75	8.75
IX	96	–	45.77	6.14	6.55	6.87	$C_{16}H_{26}N_2O_9Si$	45.93	6.22	6.70	6.70
X	97	–	51.45	7.23	7.45	7.78	$C_{16}H_{26}N_2O_6Si$	51.89	7.03	7.56	7.56
XI	97	–	55.42	5.61	5.31	5.68	$C_{24}H_{30}N_2O_9Si$	55.60	5.79	5.41	5.41
XII	97	–	52.65	8.13	7.11	7.33	$C_{17}H_{32}N_2O_6Si$	52.58	8.25	7.22	7.22
XIII	96	–	56.13	7.41	4.98	5.23	$C_{26}H_{42}N_2O_9Si$	56.31	7.58	5.05	5.05

Compounds **IX**, **XI**, and **XIII** can be converted into the neutral form by the reaction with one diamine molecule or with two molecules of **I**.

Compounds **II**–**XIII** were identified by ^{1}H NMR spectroscopy; these substances are soluble in water and polar organic solvents.

IX, XI, XIII + $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2 \longrightarrow (MeO)_3Si(CH_2)_3N(CH_2)_2NHC(O)RCOO^-$
$C(O)RCOO^-N^+H_3(CH_2)_2N^+H_2(CH_2)_3Si(OMe)_3$

The high solubility in water and alcohols makes these compounds fairly promising for the use as dressing agents for treatment of mineral fillers. However, in industrial use of dressing agents, it is desirable to use as solvents lower alcohols, in particular, ethanol. In this connection, we performed the reactions of **I** and the diamine with maleic anhydride in absolute ethanol. The reaction of **I** with maleic anhydride in ethanol (molar ratio amine : maleic anhydride 2 : 1, 50% solution) gave a neutral reaction product. Hence, under these conditions maleic anhydride has no time to react with ethanol. Otherwise unchanged amino silane **I** would remain in the reaction mixture, imparting to it an alkaline reaction. A similar result was obtained in the reaction of the diamine with maleic anhydride in ethanol at the equimolar ratio of the diamine and maleic anhydride.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AM-360 spectrometer (360 MHz) in $CDCl_3$.

The acid numbers of the synthesized products were determined by titration with 0.1 N NaOH (phenolphthalein indicator).

(*E*)-Butenedioic acid 3-(triethoxysilyl)propylamide II. Maleic anhydride (98 g) was added with stirring and cooling to 221 g of amino silane **I**; the reaction temperature was maintained within the range 50–60°C. After adding the whole amount of the anhydride, the mixture was cooled to room temperature; 318 g of **II** was obtained as an amorphous solid, mp 38°C.

3-(Triethoxysilyl)propylammonium (*E*)-3-{*N*-[3-(triethoxysilyl)propyl]carbamoyl}propenoate III was prepared by the reaction of 221 g of **I** with 49 g of maleic anhydride with stirring and cooling. The reaction temperature was maintained within the range 50–60°C. After adding the whole amount of the anhydride, the mixture was cooled to room temperature, and 268 g of **III** was obtained as a viscous liquid.

Compounds **IV**–**VII** were prepared similarly.

(*E*)-3-{*N*-[3-(Triethoxysilyl)propylammonioethyl]carbamoyl}propenoate VIII was prepared

from 222 g of the diamine and 98 g of maleic anhydride in 320 g of ethyl acetate with stirring and cooling. The reaction temperature was maintained within the range 50–60°C. After adding the whole amount of the anhydride, the mixture was cooled to room temperature, and the solvent was distilled off at reduced pressure. Compound **VIII** (312 g) was obtained as an amorphous solid; mp 56–58°C.

Compounds **IX**–**XIII** were prepared similarly. The refractive indices of **III**–**VII** and analytical data for **II**–**XIII** are listed in Table 2.

ACKNOWLEDGMENTS

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