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Syntheses and Properties of Isocyanatodisiloxanes and Their Alkoxy-Substituted Derivatives

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Isocyanatooligosiloxanes and their alkoxy derivatives were synthesized. The hydrolysis of triisocyanato(methyl)silane followed by distillation provided 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane in good yield. The reaction of 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane with ethanol, isopropyl alcohol, and *t*-butyl alcohol proceeded selectively to afford partially alkoxy substituted isocyanatodimethyldisiloxanes, $(RO)_n(NCO)_{4-n}Me_2Si_2O$ ($R = Et$, $n = 1$—4; $R = Pr^i$, $n = 1$—4; and $R = Bu^t$, $n = 1$—2). On the other hand, the hydrolysis of tetraisocyanatosilane provided a mixture of isocyanatooligosiloxanes. Hexaisocyanatodisiloxane was isolated by distillation from the reaction mixture with some impurities produced by the disproportionation of hexaisocyanatodisiloxane on heating. The reaction of hexaisocyanatodisiloxane with alcohols provided partially alkoxy-substituted isocyanatodisiloxanes, $[(RO)_n(NCO)_{3-n}Si]_2O$ ($R = Et$, $n = 2$—3; $R = Pr^i$, $n = 1$—3; and $R = Bu^t$, $n = 1$—2), selectively and in high yield.

In the interest of nature conservation, the fabrication and application of novel halogen-free compounds has been badly needed for both industrial and household chemicals to depress the production and release of halides. The replacement of chlorosilanes has delayed the industrial applications to the improvement and modification of the surface properties. Isocyanatosilanes are now focused on as suitable candidates of "chlorine-free" silanes because there is no evolution of hydrogen chloride on hydrolysis. They have been applied as a curing and crosslinking agent for resins and a surface treatment agent for organic and inorganic materials for a long time.[1]

The application and utilization of isocyanatosilanes was prevented by the low yield and low selectivity of the reaction of silver cyanate with chlorosilanes.[2] The isocyanatosilane derivatives have been synthesized since the discovery of the bulk production of tetraisocyanatosilane,[3] about forty years after the first synthesis of isocyanatotrimethylsilane.[4] We are interested in the syntheses and application of novel isocyanatosilanes because of their versatility not only as pseudo halosilanes but as heterocumulenes; in addition, they show lower and higher reactivities on substitution reaction compared to that of chlorosilanes and alkoxysilanes, respectively. Unsubstituted (hydro), methyl-, and phenylisocyanatosilanes react with alcohols step by step to form alkoxysilanes in almost quantitative yield,[5] i.e. $RSi(NCO)_{3-n}(OR')_n$ ($R = H$, Me, Ph; $R' = Et$, Pr^i, Bu^t, $n = 1$—3) and $Si(NCO)_{4-n}(OR')_n$ ($R' = Et$, Pr^i, Bu^t, $n = 1$—4).

Surface coating on substrates should be achieved more effectively with sila-functional oligo- or polysiloxanes having hydroxy, alkoxy, acetoxy, or isocyanato group than with the monomeric silanes by the chemical coating, methods such as dip, spin, and spray dry coating except for chemical vapor deposition process. In this work, therefore, the syntheses of isocyanatooligosiloxanes and their alkoxy derivatives were investigated according to Eqs. 1, 2, 3, and 4.

$$\underset{\underline{1}}{2\ MeSi(NCO)_3} + H_2O \xrightarrow{THF} \underset{\underline{2}}{[(OCN)_2MeSiO]_2O} + 2\ HNCO \qquad (1)$$

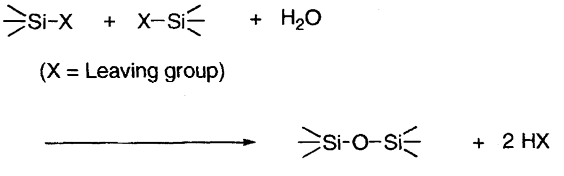
$$\underset{\underline{3}}{2\ Si(NCO)_4} + H_2O \xrightarrow{THF} \underset{\underline{4}}{[(OCN)_3Si]_2O} + 2\ HNCO \qquad (2)$$

$$\underset{\underline{2}}{[(OCN)_2MeSi]_2O} + (p+q)\ ROH \xrightarrow{Et_3N\ /\ THF} \underset{\underline{5}\text{ - }\underline{14}}{(OCN)_{2-p}(RO)_pMeSiOSiMe(OR)_q(NCO)_{2-q}} + (p+q)\ HNCO \qquad (3)$$

$$\underset{\underline{4}}{[(OCN)_3Si]_2O} + (p+q)\ ROH \xrightarrow{Et_3N\,/\,THF} \underset{\underline{15}\,-\,\underline{24}}{(OCN)_{3-p}(RO)_pSiOSi(OR)_q(NCO)_{3-q}} + (p+q)\ HNCO \qquad (4)$$

Results and Discussion

Preparation of 1,1,3,3-Tetraisocyanato-1,3-dimethyldisiloxane (2) and Hexaisocyanatodisiloxane (4). Syntheses of disiloxanes from sila-functional silanes are schematically shown by three routes Eqs. 5, 6, and 7 : 1) hydrolysis of silane (Eq. 5), 2) condensation reaction between silanes with different sila-functional groups (Eq. 6), and 3) oxidation of disilane (Eq. 7). The first route is the most common strategy among three routes but a mixture of oligosiloxanes must be provided. The second one will be desirable because no side reactions take place. The third one is most preferable if disilanes are available. In this work, we chose the first route with isocyanatosilanes, not only because disiloxanes are conveniently prepared, but also because the hydrolysis and condensation can be controlled with the moderate reactivity of isocyanatosilanes compared with the corresponding chlorosilanes.



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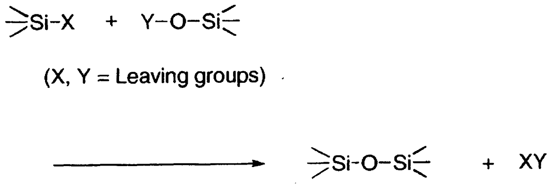

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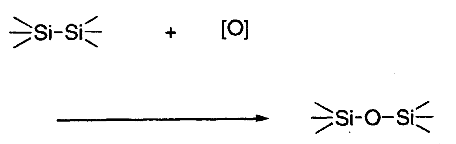
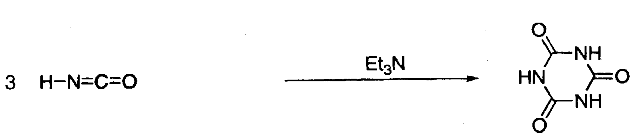


(7)

The results on the hydrolysis of **1** under controlled conditions followed by gas chromatography analysis are summarized in Table 1 and Scheme 1. Uncontrolled hydrolysis of **1** yielded a mixture of oligosiloxanes. The ratio of the oligosiloxanes varied with the solvent and the molar ratio of water to **1**. In Run 1, **2** was produced in 44% with a recovery of 50% of **1**. With the increase of the molar ratio of water to **1**, the amount of **1** decreased with an increasing yield of oligosiloxanes (**2**, trisiloxane,[6] and the others). A maximum yield of **2** was obtained in Run 3. When the hydrolysis of **1** was carried out in the other solvent systems (Runs 5 and 6), the compositions of the hydrolysates were almost the same, which indicates the independence of the polarity of solvent on hydrolysis. Compound **2** was isolated by a fractional distillation under reduced pressure, since a selective production of **2** was difficult under these hydrolysis conditions. This compound **2** was confirmed by gas chromatograph analysis to show a single peak.

The hydrolysis of **3** gave a mixture of **3**, **4**, trisiloxane, and the siloxane oligomers as shown in Table 2. The formation of trisiloxane and the others was depressed by the hydrolysis of **3** in diethyl ether and benzene with a recovery of **3** more than 50% in Runs 3 and 4. Isolation of **4** by fractional distillation resulted in the disproportionation of **4** on heating: The purity of **4** was 90% to be contaminated with **3**, trisiloxane, and the other siloxanes. Compound **4** was found to be thermally unstable and also to undergo disproportionation in the presence of triethylamine to provide a mixture of **3**, **4**, trisiloxane, and the other oligosiloxanes. This compound **4** was insoluble in the common organic solvents except for tetrahydrofuran, acetnitrile, and acetone.

Syntheses of Alkoxyisocyanato-1,3-dimethyldisiloxanes. The alkoxyisocyanato-1,3-dimethyldisiloxanes were synthesized by the reaction of **2** with alcohols in order to clarify the fundamental alcoholysis of **2**. The alcoholysis of isocyanato(methyl)silanes underwent a stepwise substitution of isocyanato group to produce alkoxyisocyanatosilanes.[5] The substitution reaction was easily controlled by the amount of alcohols in the feed in the presence or absence of triethylamine to form the alkoxysilanes with different degrees of substitution of isocyanato group. Triethylamine shifts the equilibrium to the formation of product due to the quantitative precipitation of cyanuric acid as shown in Eq. 8.



(8)

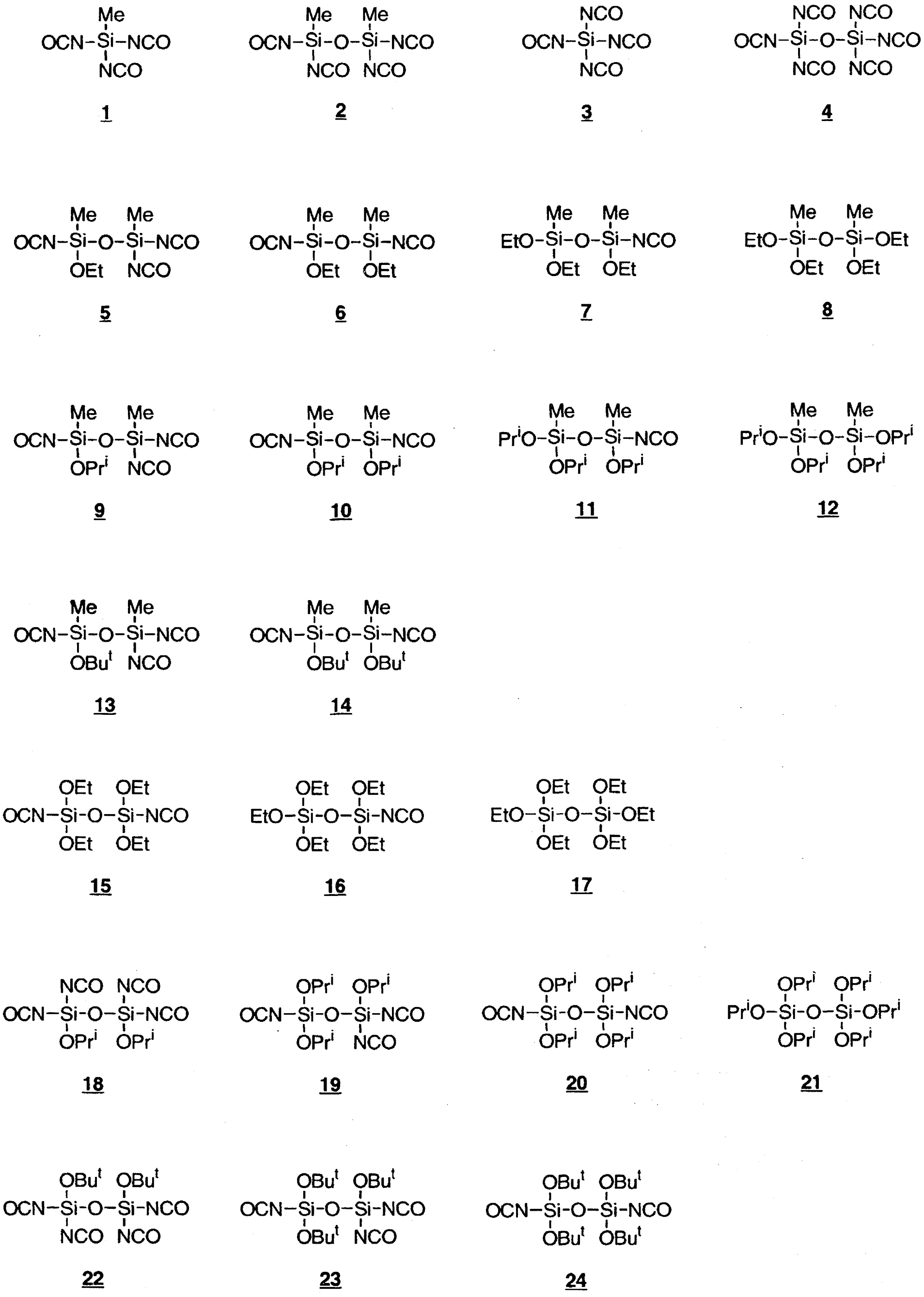
The results for the reaction of **2** with alcohol are summarized in Table 3. Ethoxy derivatives **5** and **6** were synthesized selectively and quantitatively under the conditions shown in Runs 1 and 2, respectively. The reaction was incomplete in Runs 3 and 4. The compounds **7** and **8** were synthesized by the reaction of ethanol with **2** in the presence of triethylamine in Runs 5 and 6. In Runs 7, 8, 9, and 10, the isopropoxy derivatives **9**, **10**, **11**, and **12** were synthesized by the reaction of isopropyl alcohol with **2** in the molar ratios of 1, 2, 3, and 4, respectively. The addition of triethylamine was necessary for the syntheses of **11** and **12**. In the reaction of *t*-butyl alcohol with **2** in Runs 11 and 12, the reaction rate decreased compared to the rates of ethanol and isopropyl alcohol: a longer reflux time and an addition of triethylamine were neccessary for the selective syntheses of **13** and **14**, respectively. In Runs 13 and 14, tri- and tetra-*t*-butoxyisocyanatosilane were not synthesized under these conditions.

The substitution of alcohols became more difficult with the increasing number of alkoxy groups substituted and with the bulkiness of the alkoxy group, which is correlated with the increase of steric hindrance. On the other hand, the decrease

Table 1. Results on the Preparation of **2** by the Hydrolysis of **1**[a]

Run	Solvent	Molar ratio	Relative yield[b] (%)			
		$H_2O/\mathbf{1}$	**1**	**2**	Trisiloxane[c]	Others[d]
1	THF	0.25	50	44	6	0
2	THF	0.375	20	57	20	3
3	THF	0.5	8	58	27	7
4	THF	0.625	0	38	32	30
5	Diethyl ether/THF (40/2)	0.5	13	60	22	5
6	Chloroform/THF (40/2)	0.5	12	55	26	7

a) Scale of operation: **1**, 3.4 g (0.02 mol); solvent, 40 ml. The reaction mixture was subjected to reflux for 2 h after the hydrolysis at 0 °C. b) Calculated based on gas chromatograph (GC) peak area. c) 1,1,3,5,5-Pentaisocyanato-1,3,5-trimethyltrisiloxane. d) Oligosiloxanes except for **2** and trisiloxane.



Scheme 1. Structures and numbers of compounds.

Table 2. Results on the Preparation of **4** by the Hydrolysis of **3**[a)]

Run	Solvent	Hydrolysis temperature (°C)	Relative yield[b)] (%)			
			3	**4**	Trisiloxane[c)]	Others[d)]
1	THF	−20	40	24	20	16
2	Acetonitrile	0	33	21	29	17
3	Diethyl ether	0	51	29	13	7
4	Benzene	10	55	29	10	6

a) Scale of operation: **3**, 3.9 g (0.02 mol); solvent, 40 ml; water, 0.18 g (0.01 mol). The reaction mixture was subjected to reflux for 3 h after the hydrolysis. b) Calcd based on GC peak area. c) Octaisocyanatotrisiloxane. d) Oligosiloxanes except **4** and trisiloxane.

Table 3. Reaction of **2** with Alcohol[a)]

Run	Alcohol (ROH)	Molar ratio of ROH/**2**	Products	Yield (%)
1	EtOH	1	**5**	82
2		2	**6**	82
3		3	**6, 7**	—
4		4	**7, 8**	—
5		3[d)]	**7**	74
6		4[d)]	**8**	80
7	$\mathrm{Pr}^i\mathrm{OH}$	1	**9**	80
8		2	**10**	82
9		3[d)]	**11**	72
10		4[d)]	**12**	76
11[b)]	$\mathrm{Bu}^t\mathrm{OH}$	1	**13**	82
12		2[d)]	**14**	73
13[c)]		4	**14**	80
14		4[d)]	**14**	73

a) Scale of operation: **2**, 2.7 g (0.01 mol); THF, 40 ml. The reaction mixture was subjected to reflux for 2 h after the addition of alcohol at 0 °C. b) Reflux time: 9 h. c) Reflux time: 37 h. d) The reaction was carried out in the presence of triethylamine (0.20 g, 0.002 mol) was added.

of the substitution rate allowed the exclusive formation of 1, 3-dialkoxy derivative instead of the production of a mixture of 1,3- and 1,1-dialkoxy derivatives. Attempts to synthesize 1,1-dialkoxy derivatives led to the formation of 1,3-derivatives.

The formation of 1,3-dialkoxy derivative was also monitored by the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **2**, **5**, and **6**. A single signal was observed in each NMR spectrum of **2**, which is ascribed to $CH_3Si(NCO)_2O$– group. The new signals which appeared in the NMR spectra of **5** support the existence of two types of silicons in a molecule, i.e. $CH_3Si(NCO)_2O$– and $CH_3Si(NCO)(OEt)O$–. A single signal was observed in each NMR spectrum of **6** which was ascribed to $CH_3Si(NCO)(OEt)O$– group; this result shows that $CH_3Si(NCO)(OEt)OSi(CH_3)(NCO)(OEt)$ (**6**) was isolated and its isomer, $CH_3Si(OEt)_2OSi(CH_3)(NCO)_2$, was not formed. A similar spectral change was observed in a series of the other alkoxy derivatives. The NMR spectral and experimental results indicate that substitution of the second alkoxy group is controlled by the steric factor and possibly the reactivity on the silicon as the center of nucleophilic substitution reaction.

Syntheses of Alkoxyisocyanatodisiloxanes. In the reaction of **4** with alcohols, it is desirable to produce the target compound selectively, since the close boiling points of alkoxyisocyanatodisiloxanes form an azeotropic mixtures on distillation. In this work, therefore, the optimum reaction conditions such as the molar ratio of alcohol to **4**, catalyst, solvent, reaction temperature, and reaction time were investigated: Triethylamine was fed to promote the condensation of isocyanic acid to cyanuric acid after the addition of alcohol to prevent the degradation of **4** catalyzed by the amine.

Table 4 summarizes the results for the reaction of **4** with alcohols. When four equivalent amounts of ethanol were added to **4** in diethyl ether, ethanol was consumed to provide a mixture with oligoethoxyisocyanatosiloxanes other than disiloxanes. Thus **15** was isolated by fractional distillation. Under the reaction condition of Run 2, an azeotropic mixture of **16** and **17** was recovered because of their close boiling points. The disiloxane **17** was formed as a major product on the reflux for 20 h in the presence of twenty molar amounts of ethanol in THF. The other compounds,

Table 4. Reaction of **4** with Alcohol[a)]

Run	Alcohol (ROH)	Molar ratio of ROH/**4**	Products	Yield (%)
1	EtOH	4[g)]	**15**	45
2		10[g)]	**16, 17**	—
3[b)]		20	**17**	71
4	$\mathrm{Pr}^i\mathrm{OH}$	2	**18, 19**	—
5[c)]		10	**20**	70
6[d)]		30[h)]	**21**	60
7[e)]	$\mathrm{Bu}^t\mathrm{OH}$	2.3	**22**	73
8		4	**22, 23**	—
9[f)]		30[i)]	**24**	28

a) Scale of operation: **4**, 6.5 g (0.02 mol); THF, 40 ml. The reaction mixture was subjected to reflux for 1 h after the addition of alcohol at 0 °C and stirring for 1 h. b) Scale of operation: **4**, 0.05 mol; THF, 100 ml. Reflux time: 20 h. c) Scale of operation: **4**, 0.06 mol; THF, 120 ml. d) Reflux time: 2 h. e) Scale of operation: **4**, 0.06 mol; THF, 120 ml. f) Scale of operation: **4**, 0.03 mol; THF, 60 ml. Reflux time: 50 h. g) Ether was used in place of THF. h) The reaction was carried out in the presence of triethylamine (2.0 g, 0.02 mol) was added. i) The reaction was carried out in the presence of triethylamine (3.0 g, 0.03 mol) was added.

$(EtO)_n(NCO)_{6-n}Si_2O$ ($n = 1, 2, 3$, and 5 (**16**)), were not isolated, but they were confirmed to be in the reaction mixture. A mixture of **18** and **19** was produced even when the molar ratio of isopropyl alcohol to 5 was 2.0. The compounds **20** and **21** were prepared by the reaction of a large excess amount of isopropyl alcohol against **4** and a long reflux time. When **4** was subjected to the reaction with *t*-butyl alcohol, **22** and **24** were produced selectively. The steric hindrance of *t*-butyl group prevented the substitution of six isocyanato groups even under severe reaction conditions.

The ^{13}C and ^{29}Si NMR spectra of **18**,[7] **20**, and **21** showed an interesting feature compared to the spectra series of **2**, **5**, and **6**. With the increase of the isopropoxy group attached, the signal ascribed to the methyne carbon shifted to higher field while that of silicon shifted to lower field in ^{13}C and ^{29}Si NMR spectra, respectively. The same feature was observed in other compounds: **15**, **17**, **22**, and **24**.

An observation of one signal in each ^{29}Si NMR spectrum of **15**, **18**, **20**, and **22** indicates a symmetrical structure for these compounds. The alkoxy group replaces the isocyanato group in 1,3- and 1,1,3,3-fashions to show the absence of the structural isomers.

Experimental

General Procedure. The ^1H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) spectra were measured on JEOL JNM-PMX60Si, JNM-FX90Q, and JNM-FX-400 spectrometers in chloroform-*d*. Infrared (IR) spectra were recorded on a Hitachi infrared spectrometer 260-50 by a carbon tetrachloride solution method. Mass (MS) spectra were acquired on a Shimadzu GCMS-QP2000A mass spectrometer. The silicon content was determined by a wet method as follows: A sample of 0.1 g was weighed in a flask and then heated in the presence of ammonium nitrate (0.8 g), ammonium sulfate (0.8 g), and sulfuric acid (15 ml). The residue was poured into ice (100 g) carefully, followed by filtration. The residue was subjected to firing in a crucible, followed by weighing to be calculated as SiO_2.

Syntheses of 2. All reactions were carried out under dry nitrogen atmosphere. A mixture of water and solvent (20 mL) was added dropwise into a mixture of **1** (3.4 g, 0.02 mol) and solvent (20 mL) at 0 °C, followed by reflux for 2 h and evaporation of the solvents. 1,1,3,3-Tetraisocyanato-1,3-dimethyldisiloxane (**2**) was isolated by a fractional distillation under reduced pressure. Yield: 0.84 g (31%). Bp 128.1—129.9 °C (13 Torr, 1 Torr = 133.322 Pa). IR 2950, 2310, 1280, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.50$ (s, 6H); ^{13}C NMR (22.6 MHz) $\delta = -0.5$ (s), 123.0 (s); ^{29}Si NMR (79.5 MHz) $\delta = -59.4$; MS *m/z* 255 (M^+-15). Found: Si, 20.7%. Calcd for $C_6H_6N_4O_5Si_2$: Si, 20.8%.

Synthesis of 4. All reactions were carried out under dry nitrogen atmosphere. A mixture of water (0.18 g, 0.01 mol) and solvent (20 ml) was added dropwise into a mixture of **3** (3.9 g, 0.02 mol) and solvent (20 ml) at 0 °C, followed by reflux for 3 h and then evaporation of solvents. Hexaisocyanatodisiloxane **4** was isolated by distillation under reduced pressure. Yield: 0.81 g (25%). Bp 123.2—128.3 °C (4.5 Torr). IR 2300, 1080 cm^{-1}. ^{13}C NMR (22.6 MHz) $\delta = 123.2$ (s). ^{29}Si NMR (79.5 MHz) $\delta = -110$ (s). MS *m/z* 324 (M^+).

Preparation of Alkoxyisocyanato-1,3-dimethyldisiloxanes (5—14). All reactions were carried out under nitrogen atmosphere. Into a mixture of THF (20 mL) and **2** (2.7 g, 0.01 mol), a mixture of alcohol and THF (20 mL) was added dropwise at 0 °C. Triethylamine (0.20 g, 0.002 mol) was added as a catalyst before the reflux in some cases. The reaction mixture was subjected to reflux for 1 h, followed by filtration of white solids. Solvents were removed under reduced pressure. 1,3-Dimethylakoxyisocyanatosilanes (**5—14**) were isolated by distillation under reduced pressure.

1-Ethoxy-1,3,3-triisocyanato-1,3-dimethyldisiloxane (5). Yield: 2.3 g (82%). Bp 110.5—111.3 °C (16 Torr). IR 2980, 2310, 2290, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.32$ (s, 3H), 0.46 (s, 3H), 1.23 (t, 3H), 3.75 (q. 2H); ^{13}C NMR (22.6 MHz) $\delta = -3.0$ (s), -0.4 (s), 18.1 (s), 59.6 (s), 123.5 (s); ^{29}Si NMR (79.5 MHz) $\delta = -59.9$ (s), -53.9 (s); MS *m/z* 258 (M^+-15). Found: Si, 20.5%. Calcd for $C_7H_{11}N_3O_5Si_2$: Si, 20.5%.

1,3-Diethoxy-1,3-diisocyanato-1,3-dimethyldisiloxane (6). Yield: 2.3 g (82%). Bp 92.7—93.4 °C (12 Torr). IR 2950, 2300, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.30$ (s, 6H), 1.22 (t, 6H), 3.73 (q, 4H); ^{13}C NMR (22.6 MHz) $\delta = -2.9$ (s), 18.0 (s), 59.2 (s), 123.4 (s); ^{29}Si NMR (79.5 MHz) $\delta = -54.9$ (s); MS *m/z* 261 (M^+-15). Found: Si, 20.2%. Calcd for $C_8H_{16}N_2O_5Si_2$: Si, 20.3%.

1,1,3-Triethoxy-3-isocyanato-1,3-dimethyldisiloxane (7). Yield: 2.1 g (74%). Bp 100.6—101.2 °C (19 Torr). IR 2980, 2300, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.08$ (s, 3H), 0.28 (s, 3H), 1.20 (t, 9H), 3.71 (q, 6H); ^{13}C NMR (22.6 MHz) $\delta = -5.7$ (s), -2.8 (s), 18.0 (s), 18.3 (s), 58.4 (s), 58.9 (s), 123.2 (s); ^{29}Si NMR (79.5 MHz) $\delta = -55.0$ (s), -50.1 (s); MS *m/z* 264 (M^+-15). Found: Si, 20.1%. Calcd for $C_9H_{21}NO_5Si_2$: Si, 20.1%.

1,1,3,3-Tetraethoxy-1,3-dimethyldisiloxane (8). Yield: 2.2 g (80%). Bp 82.3—82.9 °C (10 Torr). IR 2980, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.05$ (s, 6H), 1.17 (t, 12H), 3.70 (q, 8H); ^{13}C NMR (22.6 MHz) $\delta = -5.6$ (s), 18.3 (s), 58.2 (s); ^{29}Si NMR (79.5 MHz) $\delta = -50.5$ (s); MS *m/z* 267 (M^+-15). Found: Si, 19.9%. Calcd for $C_{10}H_{26}O_5Si_2$: Si, 19.9%.

1,1,3-Triisocyanato-3-isopropoxy-1,3-dimethyldisiloxane (9). Yield: 2.3 g (80%). Bp 107.6—108.1 °C (12 Torr). IR 2980, 2320, 2290, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.31$ (s, 3H), 0.47 (s, 3H), 1.22 (d, 6H), 4.20 (m, 1H); ^{13}C NMR (22.6 MHz) $\delta = -2.4$ (s), -0.3 (s), 25.4 (s), 67.3 (s), 123.7 (s); ^{29}Si NMR (79.5 MHz) $\delta = -60.5$ (s), -56.1 (s); MS *m/z* 272 (M^+-15). Found: Si, 19.5%. Calcd for $C_8H_{13}N_3O_5Si_2$: Si, 19.5%.

1,3-Diisocyanato-1,3-diisopropoxy-1,3-dimethyldisiloxane (10). Yield: 2.5 g (82%). Bp 110.0—111.1 °C (14 Torr). IR 2950, 2300, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.26$ (s, 6H), 1.18 (d, 12H), 4.18 (m, 2H); ^{13}C NMR (22.6 MHz) $\delta = -2.3$ (s), 25.3 (s), 66.7 (s), 123.2 (s); ^{29}Si NMR (79.5 MHz) $\delta = -56.8$ (s); MS *m/z* 289 (M^+-15). Found: Si, 18.4%. Calcd for $C_{10}H_{20}N_2O_5Si_2$: Si, 18.5%.

1-Isocyanato-1,3,3-triisopropoxy-1,3-dimethyldisiloxane (11). Yield: 2.3 g (72%). Bp 103.2—104.1 °C (14 Torr). IR 2980, 2300, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.07$ (s, 3H), 0.23 (s, 3H), 1.15 (d, 18H), 4.15 (m, 3H); ^{13}C NMR (22.6 MHz) $\delta = -4.4$ (s), -2.2 (s), 25.4 (s), 25.6 (s), 65.3 (s), 66.2 (s), 122.6 (s); ^{29}Si NMR (79.5 MHz) $\delta = -57.2$ (s), -53.5 (s); MS *m/z* 306 (M^+-15). Found: Si, 17.4%. Calcd for $C_{12}H_{27}NO_5Si_2$: Si, 17.5%.

1,1,3,3-Tetraisopropoxy-1,3-dimethyldisiloxane (12). Yield: 2.6 g (76%). Bp 115.3—115.9 °C (22 Torr). IR 2980, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.05$ (s, 6H), 1.13 (t, 24H), 4.13 (m, 4H); ^{13}C NMR (22.6 MHz) $\delta = -4.2$ (s), 25.6 (s), 64.8 (s); ^{29}Si NMR (79.5 MHz) $\delta = -53.8$ (s); MS *m/z* 323 (M^+-15). Found: Si, 16.6%. Calcd for $C_{14}H_{24}O_5Si_2$: Si, 16.6%.

1-*t*-Butoxy-1,3,3-triisocyanato-1,3-dimethyldisiloxane (13). Yield: 2.5 g (82%). Bp 129.3—129.9 °C (22 Torr). IR 2980, 2330, 2300, 1110 cm^{-1}; ^1H NMR (60.0 MHz) $\delta = 0.32$ (s, 3H), 0.46 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (22.6 MHz) $\delta = -0.8$ (s), -0.3 (s), 31.5 (s), 75.4 (s), 123.1 (s); ^{29}Si NMR (79.5 MHz) $\delta = -61.2$ (s), -60.8 (s); MS *m/z* 286 (M^+-15). Found: Si, 18.4%. Calcd for $C_9H_{15}N_3O_5Si_2$: Si, 18.6%.

1,3-Di-*t*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane (14). Yield: 2.7 g (80%). Bp 135.4—136.7 °C (24 Torr). IR 2980, 2300, 1110 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 0.27$ (s, 6H), 1.33 (s, 18H); ^{13}C NMR (22.6 MHz) $\delta = -0.5$ (s), 31.6 (s), 74.9 (s), 123.2; ^{29}Si NMR (79.5 MHz) $\delta = -62.3$ (s); MS *m/z* 317 (M^+-15). Found: Si, 16.7%. Calcd for $C_{12}H_{24}N_2O_5Si_2$: Si, 16.9%.

Preparation of Alkoxyisocyanatodisiloxanes (15, 17, 20, 21, 22, and 24). All reactions were carried out under dry nitrogen atmosphere. Into a mixture of THF (20 mL) or diethyl ether (20 mL) and **4** (6.5 g (0.02 mol)), a mixture of alcohol and THF (20 mL) or diethyl ether (20 mL) was added dropwise at 0 °C. Triethylamine (2.0 g (0.02 mol)) was added as a catalyst before the reflux in some cases followed by filtration of white solids. Solvents were removed under reduced pressure. Alkoxyisocyanatosilanes (**15**, **17**, **20**, **21**, **22**, and **24**) were isolated by distillation under reduced pressure.

1,1,3,3-Tetraethoxy-1,3-diisocyanatodisiloxane (15). Yield: 3.0 g (45%). Bp 87.0—87.5 °C (2.5 Torr). IR 2980, 2290, 1100, 1090 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.26$ (t, 12H), 3.89 (q, 8H); ^{13}C NMR (22.6 MHz) $\delta = 18.0$ (s), 60.2 (s), 123.0 (s); ^{29}Si NMR (79.5 MHz) $\delta = -94.5$ (s); MS *m/z* 336 (M^+). Found: Si, 16.6%. Calcd for $C_{10}H_{20}N_2O_7Si_2$: Si, 16.7%.

Hexaethoxydisiloxane (17). Yield: 4.9 g (71%). Bp 115.5—116.2 °C (12.0 Torr). IR 2950, 2290, 1120, 1090 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.20$ (t, 18H), 3.76 (q, 12H); ^{13}C NMR $\delta = 18.2$ (s), 59.3 (s); ^{29}Si NMR (79.5 MHz) $\delta = -88.9$ ($\underline{Si}(OEt)_3O$); MS *m/z* 342 (M^+). Found: Si, 16.3%. Calcd for $C_{12}H_{30}O_7Si_2$: Si, 16.4%.

1,3-Diisocyanato-1,1,3,3-tetraisopropoxydisiloxane (20). Yield: 5.2 g (70%). Bp 89.0—89.5 °C (2.0 Torr). IR 2990, 2300, 1120, 1080 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.20$ (d, 24H), 4.21 (m, 4H); ^{13}C NMR (22.6 MHz) $\delta = 25.1$ (s), 67.3 (s), 123.0 (s); ^{29}Si NMR (79.5 MHz) $\delta = -97.6$ (s); MS *m/z* 371 (M^+). Found: Si, 14.4%. Calcd for $C_{14}H_{28}N_2O_7Si_2$: 14.3%.

Hexaisopropoxydisiloxane (21). Yield: 5.1 g (60%). Bp 96.0—96.5 °C (3.0 Torr). IR 2970, 2300, 1120, 1100, 1054 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.20$ (d, 36H), 4.27 (m, 6H); ^{13}C NMR (22.6 MHz) $\delta = 25.4$ (s), 65.8 (s); ^{29}Si NMR (79.5 MHz) $\delta = -92.0$ (s). MS *m/z* 367 (M^+-59). Found: Si, 13.2%. Calcd for $C_{18}H_{42}O_7Si_2$: Si, 13.2%.

1,3-Di-*t*-butoxy-1,1,3,3-tetraisocyanatodisiloxane (22). Yield: 4.0 g (73%). Bp 96.8—97.0 °C (1.0 Torr). IR 2980, 2310, 2290, 1110 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.37$ (s, 18H); ^{13}C NMR (22.6 MHz) $\delta = 31.2$ (s), 77.5 (s), 122.9 (s); ^{29}Si NMR (79.5 MHz) $\delta = -107.2$ (s). MS *m/z* 258 (M^+-15). Found: Si, 14.5%. Calcd for $C_{12}H_{18}N_4O_7Si_2$: Si, 14.5%.

1,1,3,3-Tetra-*t*-butoxy-1,3-diisocyanatodisiloxane (24). Yield: 1.5 g (28%). Bp 116—117 °C (2.0 Torr). IR 2980, 2290, 1110 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.37$ (s, 36H); ^{13}C NMR (22.6 MHz) $\delta = 31.3$ (s), 74.9 (s), 122.6 (s); ^{29}Si NMR (79.5 MHz) $\delta = -106.1$ (s). MS *m/z* 261 (M^+-15). Found: Si, 12.6%. Calcd for $C_{18}H_{36}N_2O_7Si_2$: Si, 12.5%.

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References

1) U. S. Patent 2932586 (1960); S. Endo, *Yosetsu*, **30**, 36 (1986).

2) G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 1241 (1947); J. Pump and V. Wannagat, *Mh. Chem.*, **93**, 352 (1962); J. Goubeau and D. Paulin, *Chem. Ber.*, **93**, 1111 (1960); V. P. Kozyukov, V. D. Sheludyakov, and V. F. Mironov, *Russ. Chem. Rev. Engl. Transl.*, **42**, 662 (1973).

3) I. Kijima and Y. Mori, Jpn. Kokai Tokkyo Koho Japan Patent 81-26895.

4) G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **62**, 761 (1940).

5) Y. Abe, T. Kanemaru, T. Yamazaki, Y. Nagao, and T. Misono, *Nippon Kagaku Kaishi*, **1991**, 1094; Y. Abe, T. Kanemaru, T. Yamazaki, Y. Nagao, and T. Misono, *Nippon Kagaku Kaishi*, **1992**, 649; Y. Abe, K. Motoyama, T. Kobayashi, T. Iwasaki, and T. Gunji, *Nippon Kagaku Kaishi*, **1996**, 969.

6) 1,1,3,5,5-Pentaisocyanato-1,3,5-trimethyltrisiloxane was isolated as a minor product. Bp: 167.0—168.0 °C (15 Torr). IR 2310, 1280, 1100 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 0.42$ (s, 6H), 0.49 (s, 3H); ^{13}C NMR (22.6 MHz) $\delta = -2.0$ (s), -0.4 (s), 123.1 (s); ^{29}Si NMR (79.5 MHz) $\delta = -61.4$ (s), -60.1 (s); MS *m/z* 356 (M^+-15). Found: Si, 22.5%. Calcd for $C_8H_9N_5O_7Si_3$: Si, 22.7%.

7) The compound **18** was synthesized by the hydrolysis of isopropoxytriisocyanatosilane in order to investigate the ^{13}C and ^{29}Si NMR spectral features according to the following procedure: Into a mixture of diethyl ether (250 mL) and triisocyanatoisopropoxysilane (22 g, 0.11 mol), a mixture of water (0.95 g, 0.053 mol), diethyl ether (30 mL), and THF (50 mL) was added slowly at 0 °C followed by stirring for 1 h and distillation under reduced pressure. Yield: 8.9 g (45%). Bp 111—112 °C (2.0 Torr). IR 2980, 2300, 1120, 1100, 1070 cm^{-1}; ^{1}H NMR (60.0 MHz) $\delta = 1.27$ (d, 12H), 4.34 (m, 2H); ^{13}C NMR (22.6 MHz) $\delta = 24.9$ (s), 68.9 (s), 122.8 (s); ^{29}Si NMR (79.5 MHz) $\delta = -103.1$ (s); MS *m/z* 343 (M^+-15). Found: Si, 15.9%. Calcd for $C_{10}H_{14}N_4O_7Si_2$: Si, 15.7%.