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Abstract

Full Text

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On the Reaction of Silazanes with Organic Isocyanates

Reactions of organic isocyanates with silazanes until recently remained unknown. Only in 1963 did Wannagat and co-workers [(1)] obtain a substituted urea from hexamethyldisilazane and phenyl isocyanate, the formation of which the authors explain by migration of a hydrogen atom from the silazane nitrogen to the nitrogen atom of the isocyanate group.

Our investigations showed that, upon the action of phenyl isocyanate on alkylsilazanes containing, at the nitrogen atom, hydrogen or a radical, the reaction proceeds by a different mechanism: cleavage of the Si—N= bond occurs, with migration not of hydrogen from the nitrogen atom in the alkylsilazane, but of a trialkylsilyl group to the nitrogen of the isocyanate group and formation of the corresponding urea derivatives.

Fig. 1. IR spectrum of $(CH_3)_3SiNCO$

Upon the action of hexamethyldisilazane on phenyl isocyanate, the reaction proceeds according to the scheme:

$$[(CH_3)_3Si]_2NH + OCNC_6H_5 \rightarrow (CH_3)_3SiNCONC_6H_5. \qquad (1)$$

$$H \quad Si(CH_3)_3$$

N-Methylhexamethyldisilazane and N-diethyltrimethylsilylamine react with phenyl isocyanate according to analogous schemes:

$$[(CH_3)_3Si]_2NCH_3 + OCNC_6H_5 \rightarrow (CH_3)_3SiNCONC_6H_5, \qquad (2)$$

$$CH_3 \quad Si(CH_3)_3$$

IR spectra

Figure 2: IR spectra

$$(C_2H_5)_2NSi(CH_3)_3 + OCNC_6H_5 \rightarrow (C_2H_5)_2NCONC_6H_5. \qquad (3)$$

$$Si(CH_3)_3$$

Trialkylsilyl-substituted ureas not containing the =N–H bond interact with phenyl isocyanate in the same way as alkylsilazanes, i.e., with cleavage of the Si–N= bond and migration of the trimethylsilyl group to the nitrogen of the isocyanate group:

$$(CH_3)_3SiNCONC_6H_5 + OCNC_6H_5 \rightarrow C_6H_5NCO - N - CONC_6H_5. \qquad (4)$$

$$CH_3 \quad Si(CH_3)_3 \quad Si(CH_3)_3 \quad CH_3 \quad Si(CH_3)_3$$

Hexamethyldisilazane and phenyl isocyanate in a ratio of 1 : 2 form trimethylsilyl isocyanate and N,N′-diphenyl-N′-trimethylsilylurea. The same results were obtained in the reaction of phenyl isocyanate with N,N′-bis(trimethylsilyl)-N′-phenylurea. Obviously, in this case the second molecule of phenyl isocyanate reacts with the N,N′-bis(trimethylsilyl)-N′-phenylurea formed according to equation (1), according to scheme (5):

$$(CH_3)_3SiNCONC_6H_5 + OCNC_6H_5 \rightarrow C_6H_5NCONC_6H_5 + (CH_3)_3SiNCO. \qquad (5)$$

$$H \quad Si(CH_3)_3 \quad H \quad Si(CH_3)_3$$

It should be noted that trimethylsilyl isocyanate, under the conditions indicated in the experimental part, reacts neither with N,N′-bis(trimethylsilyl)-N′-phenylurea, nor with N,N′-diphenyl-N′-trimethylsilylurea, nor with hexamethyldisilazane.

In the IR spectrum of the trimethylsilyl isocyanate obtained there are bands of the isocyanate group (2280 cm^{-1}) and of the trimethylsilyl group (851 cm^{-1}) (Fig. 1, 2, 3). (The IR spectra of liquid samples were recorded in a thin layer between potassium bromide plates, and the solid samples—in pellets with potassium bromide.)

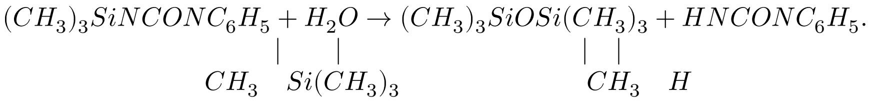
Fig. 2. IR spectra: $[(CH_3)_3Si]_2NH$ (1), $C_6H_5NHCONSi(CH_3)_3C_6H_5$ (2), $[(CH_3)_3Si]_2NCH_3$ (3), and $C_6H_5NSi(CH_3)_3CONCH_3CONSi(CH_3)_3C_6H_5$ (4)

In the IR spectra of all the remaining products of the reaction of alkylsilazanes with phenyl isocyanate, the bands of the isocyanate group near 2265 cm^{-1} are absent, and intense bands are observed in the region 1500-1700 cm^{-1}, which are amide bands I and II (^{2}).

In the spectra of trimethylsilyl isocyanate and of the product of the reaction of alkylsilylamine with phenyl isocyanate, the band of the nitrogen-silicon group is absent; in silylamines it is observed in the interval 800-900 cm^{-1}. The disappearance of this band is explained by the fact that the corresponding vibration in the silylurea or isocyanate is no longer characteristic and is not observed in the same region of the spectrum.

In the spectra of the products of the reaction of alkylsilazanes with isocyanates, intense bands in the region 700-1000 cm^{-1}, whose correlation would be doubtful, are absent. This confirms that in the present case the silazane bond is cleaved and silyl derivatives of urea are also formed, containing not more than one silyl group at nitrogen.

Hydrolysis of all the products obtained according to equations (1)–(5), for proof of their structure, was carried out according to the scheme:



$$(CH_3)_3Si\underset{\substack{|\\ CH_3}}{N}CO\underset{\substack{|\\ Si(CH_3)_3}}{N}C_6H_5 + H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_3 + H\underset{\substack{|\\ CH_3}}{N}CO\underset{\substack{|\\ H}}{N}C_6H_5.$$

As a result, the corresponding urea derivatives were obtained. In the IR spectra of all the hydrolysis products (except phenylurea) there are—

distinct bands of secondary amides are observed, and the sufficiently characteristic signs (⁀4) of the presence of primary amides are absent.

It has been established that, in the interaction of phenyl isocyanate with alkylsilazanes, cleavage of the bond $\equiv$ Si $-$ N $=$ occurs, with migration of the trimethylsilyl group to the nitrogen of the isocyanate group and formation of the corresponding substituted ureas. In the interaction of phenyl isocyanate with a trialkylsilyl-substituted urea containing hydrogen at the nitrogen atom, trialkylsilyl isocyanate and a silyl-substituted urea are formed. Trimethylsilyl isocyanate does not react with alkylsilazane or with trimethylsilyl-substituted urea.

Fig. 3. IR spectra: $(CH_3)_3SiN(C_2H_5)_2$ (1) and $(C_2H_5)_2NCONC_6H_5CONSi(CH_3)_3C_6H_5$ (2).

Fig. 3. IR spectra: $(CH_3)_3SiN(C_2H_5)_2$ (1) and $(C_2H_5)_2NCONC_6H_5CONSi(CH_3)_3C_6H_5$ (2).

Figure 3: Fig. 3. IR spectra: $(CH_3)_3SiN(C_2H_5)_2$ (1) and $(C_2H_5)_2NCONC_6H_5CONSi(CH_3)_3C_6H_5$ (2).

Experimental Part*

1. **N,N′-bis-(trimethylsilyl)-N′-phenylurea.** Into a three-necked flask equipped with a stirrer, dropping funnel, thermometer, and reflux condenser was placed a solution of 16 g of hexamethyldisilazane (II), and to it, with vigorous stirring, a solution of 10 g of phenyl isocyanate (I) was added dropwise. The mixture was kept at 30° for 3 hours. After treatment of the reaction mass, 25.2 g (98%) of crystalline product was obtained. M.p. 68–70°.

Found, %: C 55.6; H 8.6; Si 19.6; N 9.8

$C_{13}H_{24}Si_2N_2O$. Calculated, %: C 55.66; H 8.62; Si 20.03; N 9.98

Mol. wt. found 278, calculated 280.5.
Hydrolysis of the product gives $[(CH_3)_3Si]_2O$ and phenylurea. M.p. 146° (literature data 146°).

Found, %: C 61.7; H 6.12

$C_7H_8N_2O$. Calculated, %: C 61.75; H 5.92

2. **N-phenyl-N′-phenyltrimethylsilylurea.** Under analogous conditions, a solution of 10 g of I was introduced into a solution of 6.77 g of II. On distillation, 4.3 g of trimethylsilyl isocyanate was isolated. B.p. 91° (760 mm); d_4^{20} 0.867; n_D^{20} 1.396; MR_D found 31.92; calculated 31.92.

Found, %: C 41.21; H 7.8; Si 24.24; N 12.15

C_4H_9SiNO. Calculated, %: C 41.77; H 7.82; Si 24.34; N 12.17

Mol. wt. found 117; calculated 115.1.
Hydrolysis of trimethylsilyl isocyanate in an acidic medium leads to hexamethyldisiloxane. B.p. 99° (760 mm); d_4^{20} 0.7637; n_D^{20} 1.3750; MR_D found 48.68; calculated 48.65. From the still pot, 11.1 g (98.5%) of N,N′-diphenyl-N′-trimethylsilylurea was isolated. M.p. 68–69°.

Found, %: C 68.01; H 7.1; Si 10.0; N 9.8

$C_{16}H_{20}SiN_2O$. Calculated, %: C 67.56; H 7.09; Si 9.87; N 9.85

Mol. wt. found 282; calculated 284.4.

* Experiments 1, 3, 5 were carried out with a ratio of starting components of 1:1; experiments 2, 4, 6—with a component ratio of 1:2. In experiments 1, 3-6 the starting components were dissolved in 15 ml of petroleum ether, in experiment 2—in 15 ml of sulfur ether. Experiments 1, 2-4 were also carried out at −70° (ˆ1); identical results were obtained.

Upon hydrolysis, N,N′-diphenylurea was obtained. M.p. 236° (literature data 239°).

Found, %: C 73.24; H 5.8
$C_{13}H_{12}N_2O$. Calculated, %: C 73.59; H 5.66

3. **N-trimethylsilylmethyl-N′-trimethylsilylphenylurea.** Under analogous conditions, from 10 g of I and 12 g of N-methylhexamethyldisilazane (III), 19.8 g (88.9%) of a liquid product was obtained.

Found, %: C 57.57; H 8.85; Si 18.6; N 9.51
$C_{14}H_{26}Si_2N_2O$. Calculated, %: C 56.89; H 8.81; Si 19.01; N 9.48

Molecular weight found 294.5; calculated 295.5.
Upon hydrolysis, N-methyl-N′-phenylurea was obtained. M.p. 142-143°.

Found, %: C 64.51; H 6.6
$C_8H_{10}N_2O$. Calculated, %: C 64.04; H 6.67

4. **N,N′-bis(trimethylsilylphenyl)-N′-methyldiurea.** From 12 g of I and 8.8 g of III, 20.9 g (99%) of a crystalline product was obtained. M.p. 88-89°.

Found, %: C 61.1; H 7.8; Si 13.7; N 9.94
$C_{21}H_{31}Si_2N_3O_2$. Calculated, %: C 60.82; H 7.77; Si 13.6; N 10.13

Molecular weight found 418, calculated 414.67.
Upon hydrolysis, N,N′-diphenyl-N′-methyldiurea was obtained. M.p. 95-96°.

Found, %: C 67.0; H 5.8
$C_{15}H_{15}N_3O_2$. Calculated, %: C 66.9; H 5.73

5. **N-diethyl-N′-phenyltrimethylsilylurea.** From 11.9 g of I and 14.5 g of N-diethyltrimethylsilylamine (IV), 26.0 g (99%) of a liquid product was obtained.

Found, %: C 63.8; H 9.10; Si 10.2; N 10.41
$C_{14}H_{24}SiN_2O$. Calculated, %: C 63.58; H 9.15; Si 10.63; N 10.59

Molecular weight found 261, calculated 264.49.
Upon hydrolysis, N-diethyl-N′-phenylurea was obtained. M.p. 76°.

Found, %: C 68.11; H 8.4
$C_{11}H_{16}N_2O$. Calculated, %: C 68.83; H 8.33

6. **N-diethyl-N′-phenyl-N″-trimethylsilylphenyldiurea.** From 12 g of I and 7.3 g of IV, 19.1 g (99%) of product was obtained. M.p. 97-98°.

Found, %: C 66.0; H 7.54; Si 7.67; N 10.8
$C_{21}H_{29}SiN_3O_2$. Calculated, %: C 65.75; H 7.63; Si 7.33; N 10.95

Molecular weight found 387, calculated 383.6.
Hydrolysis of the product gives N-diethyl-N,N″-diphenyldiurea. M.p. 86°.

Found, %: C 69.44; H 6.74
$C_{18}H_{21}N_3O_2$. Calculated, %: C 69.42; H 6.79

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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