REACTION OF HEXAMETHYLDISILAZANE WITH PHENYL ISOCYANATE AND PHENYL THIOISOCYANATE

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Abstract

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REACTION OF HEXAMETHYLDISILAZANE WITH PHENYL ISOCYANATE AND PHENYL THIOISOCYANATE

Recently several papers have appeared in the literature devoted to the study of the interaction of alkylsilazanes with organic isocyanates ([1–5]). The authors established that, in the reaction of the indicated compounds, cleavage of the silicon–nitrogen bond and migration of the trialkylsilyl group to the nitrogen atom of the isocyanate group occur, with formation of a trialkylsilyl-substituted urea. On treatment of phenyl isocyanate with NN′-bis(trimethylsilyl)-N′-phenylurea (or in the interaction of one mole of hexamethyldisilazane with two moles of phenyl isocyanate) ([1,5]), NN′-diphenyl-N′-trimethylsilylurea and trimethylsilyl isocyanate are formed. In all these works, the reaction between alkylsilazanes and isocyanates was carried out at a temperature not exceeding 30°.

As our further investigations have shown, if the reaction of hexamethyldisilazane with phenyl isocyanate is carried out at elevated temperature, then even with an equimolar ratio of the starting components, instead of the expected trialkylsilylurea, two new reaction products are obtained in quantitative yield: trimethylsilyl isocyanate and N-phenyltrimethylsilylamine.

$$[(CH_3)_3Si]_2NH + XCNC_6H_5 \xrightarrow{120^\circ} (CH_3)_3SiNCX + (CH_3)_3SiNHC_6H_5, \quad (I)$$

where $X = O, S$.

Heating NN′-bis-(trimethylsilyl)-N′-phenylurea also leads to formation of trimethylsilyl isocyanate and N′-phenyltrimethylsilylamine. Evidently, the reaction between hexamethyldisilazane and phenyl isocyanate proceeds through the stage of formation of a trialkylsilyl-substituted urea, which should be regarded as an intermediate product of the reaction formed in the first stage of interaction of the alkylsilazane and the organic isocyanate:

$$[(CH_3)_3Si]_2NH + XCNC_6H_5 \xrightarrow{30^\circ} (CH_3)_3Si\underset{H}{\overset{X}{N}}CNC_6H_5{}_{Si(CH_3)_3} \xrightarrow{120^\circ}$$

$$\longrightarrow (CH_3)_3SiNCX + (CH_3)_3SiNHC_6H_5, \quad (II)$$

where $X = O, S$.

The reactivity of hexamethyldisilazane in the reaction with phenyl thioisocyanate is different from that with phenyl isocyanate. The interaction of hexamethyldisilazane with phenyl thioisocyanate proceeds considerably more slowly. If NN′-bis-(trimethylsilyl)-N′-phenylurea is formed according to equation (I) in quantitative yield, then under the same conditions the yield of NN′-bis-(trimethylsilyl)-N′-phenylthiourea is 5–7%. The reaction of hexamethyldisilazane with a twofold amount of phenyl thioisocyanate does not lead to the formation of trialkylsilyl thioisocyanate and the corresponding silylamine (which occurs in the interaction of one mole of hexamethyldisilazane with two moles of phenyl isocyanate), but contributes to an increase in the yield of NN′-bis-(trimethylsilyl)-N′-phenylthiourea to 70%.

At a temperature of 120° hexamethyldisilazane and phenyl thioisocyanate in equimolar ratios react according to equation (I), i.e., they form, in quantitative yield, trimethylsilyl thioisocyanate and N-phenyl-

trimethylsilylamine. Trimethylsilyl thioisocyanate and N-phenyltrimethylsilylamine were also isolated on heating NN′-bis-(trimethylsilyl)-N′-phenylthiourea according to equation (II). Evidently, the mechanism of the reaction of hexamethyldisilazane and phenyl thioisocyanate at 120° is the same as in the interaction of hexamethyldisilazane and phenyl isocyanate.

Thus, as a result of the investigation it was established that, in the interaction of hexamethyldisilazane with phenyl isocyanate (-thioisocyanate) at elevated temperature, trimethylsilyl isocyanate (-thioisocyanate) and the corresponding silylamine are formed. Trimethylsilyl isocyanate (-thioisocyanate) and silylamine are also formed on heating trialkylsilylurea (-thiourea).

Experimental Part

1. Interaction of hexamethyldisilazane and phenyl isocyanate at a temperature of 120°. In a three-necked flask fitted with a stirrer, thermometer, dropping funnel, and reflux condenser, 16.55 g of hexamethyldisilazane was placed, heating was begun, and then 12.2 g of phenyl isocyanate was added dropwise. The reaction mass was heated to 120°, which was maintained for 10 h. By distillation on a column, 10.8 g (91.4%) of trimethylsilyl isocyanate was obtained, with b.p. 91–92°/760 mm; d_4^{20} 0.8660; n_D^{20} 1.396; MR_D found 31.92, calculated 31.92.

Found, %: C 41.2; H 7.7; Si 24.9; N 11.8
C_4H_9SiNO. Calculated, %: C 41.77; H 7.82; Si 24.34; N 12.17

Molecular weight found 117; calculated 115.1. In addition to trimethylsilyl isocyanate, 15.4 g (91.2%) of N-phenyltrimethylsilylamine was isolated, with b.p. 205–206°/760 mm; d_4^{20} 0.938; n_D^{20} 1.5201; MR_D found 53.4; calculated 52.91.

Found, %: C 65.1; H 9.21; Si 17.2; N 8.6
$C_9H_{15}SiN$. Calculated, %: C 65.45; H 9.09; Si 16.98; N 8.48

2. Formation of trimethylsilyl isocyanate and N-phenyltrimethylsilylamine on heating NN′-bis-(trimethylsilyl)-N′-phenylurea. NN′-bis-(trimethylsilyl)-N′-phenylurea was obtained by us according to the known procedure ([1,5]). 8 g of NN′-bis-(trimethylsilyl)-N′-phenylurea was heated at 120° for 10 h. By distillation on a column, 3 g (91%) of trimethylsilyl isocyanate was obtained, with b.p. 91°; d_4^{20} 0.8690; n_D^{20} 1.369; MR_D found 32.03; calculated 31.92.

Found, %: C 41.5; H 7.85; Si 24.5; N 12.3
C_4H_9SiNO. Calculated, %: C 41.77; H 7.82; Si 24.34; N 12.17

Molecular weight found 118; calculated 115.1. In addition, 4.3 g (91.2%) of N-phenyltrimethylsilylamine was isolated, with b.p. 206°/760 mm.

Found, %: C 65.2; H 9.0; Si 16.58; N 8.6
$C_9H_{15}SiN$. Calculated, %: C 65.45; H 9.09; Si 16.98; N 8.48

3. Interaction of hexamethyldisilazane and phenyl thioisocyanate at a temperature of 30°*. In a three-necked flask fitted with a stirrer, dropping funnel, thermometer, and reflux condenser, hexamethyldisilazane was placed, and at 30° phenyl thioisocyanate was added dropwise to it with vigorous stirring. The reaction mass was kept at this temperature for 10 h. From 17.54 g of hexamethyldisilazane and 14.7 g of phenyl thioisocyanate (equimolecular ratio of the components), 2.4 g (7.4%) of NN′-bis-(trimethylsilyl)-N′-phenylthiourea was obtained, with m.p. 100–101°.

Found, %: C 52.2; H 7.94; Si 19.0; S 11.0
$C_{13}H_{24}Si_2N_2S$. Calculated, %: C 52.7; H 8.11; Si 18.92; S 10.81

* In the experiment, irrespective of the ratio of the components, a small amount of NN′-diphenylthiourea was isolated.

Molecular weight found 300; calculated 296. From 11.9 g of hexamethyldisilazane and 20 g of phenyl thioisocyanate (component ratio 1 : 2), the excess phenyl thioisocyanate that had not entered into the reaction was isolated, and 18 g (82.3%) of NN′-bis(trimethylsilyl)-N′-phenylthiourea, m.p. 100–101°, was obtained.

Found, %: C 52.6; H 7.92; Si 19.12; S 10.6
$C_{13}H_{24}Si_2N_2S$. Calculated, %: C 52.7; H 8.11; Si 18.92; S 10.81

Molecular weight found 290; calculated 296.

4. Interaction of hexamethyldisilazane with phenyl thioisocyanate at a temperature of 120°. Under conditions analogous to experiment 1, from 24.2 g of hexamethyldisilazane and 20.13 g of phenyl thioisocyanate, 18.1 g (92.3%) of trimethylsilyl thioisocyanate was obtained, b.p. 143°/760 mm; d_4^{20} 0.930; n_D^{20} 1.4820; MR_D found 40.15; calculated 40.46.

Found, %: C 36.45; H 6.85; Si 21.22; N 10.35; S 24.3
C_4H_9SiNS. Calculated, %: C 36.64; H 6.87; Si 21.37; N 10.69; S 24.43

Molecular weight found 129; calculated 131. Also isolated was 21.5 g (87.3%) of N-phenyltrimethylsilylamine, b.p. 206°/760 mm.

Found, %: C 65.1; H 9.11; Si 16.6; N 8.4
$C_9H_{15}SiN$. Calculated, %: C 65.45; H 9.09; Si 16.98; N 8.48

5. Formation of trimethylsilyl thioisocyanate and N-phenyltrimethylsilylamine upon heating NN′-bis(trimethylsilyl)-N′-phenylthiourea. 15.35 g of NN′-bis(trimethylsilyl)-N′-phenylthiourea was heated at 120° for 10 h. Distillation on a column gave 6 g (88.3%) of trimethylsilyl thioisocyanate, b.p. 143°; d_4^{20} 0.931; n_D^{20} 1.4820; MR_D found 40.15; calculated 40.46.

Found, %: C 36.28; H 6.7; Si 21.5; N 10.92; S 24.65
C_4H_9SiNS. Calculated: C 36.64; H 6.87; Si 21.37; N 10.69; S 24.43

Molecular weight found 130; calculated 131. In addition, 7 g (81.7%) of N-phenyltrimethylsilylamine was isolated, b.p. 205–206°/760 mm.

Found, %: C 65.71; H 9.15; Si 17.11; N 8.64
$C_9H_{15}SiN$. Calculated: C 65.45; H 9.09; Si 16.98; N 8.48

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