

## New aspects of isocyanate synthesis with the use of *O*-silylurethanes

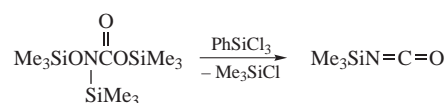
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**Silyl group at the nitrogen atom in the *O*-silylurethanes drastically affects the thermolysis processes and allows one to simplify the synthesis of methyl- and trimethylsilyl isocyanates.**

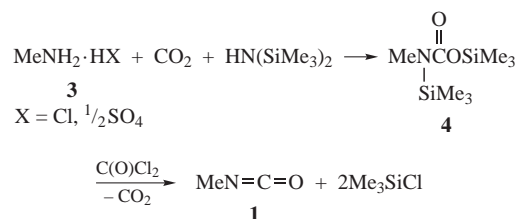


Organic and organosilicon isocyanates are widely used in the preparation of pharmaceuticals, herbicides, ureas and as raw material in basic organic synthesis.<sup>1–8</sup> Employment of so-called ‘organosilicon synthesis’<sup>3–5</sup> for their production can not only change the physical state of the starting reagents but, most importantly, create the prerequisites for formation of labile intermediates due to  $\beta$ -decomposition, with these intermediates releasing the target products<sup>9</sup> at a controlled rate. Valuable methyl isocyanate **1**<sup>10</sup> and trimethylsilyloxyl isocyanate **2**<sup>11</sup> were produced just by this method. In the first case, despite the absence of high pressure and temperatures, much siloxane bottoms is formed in the process. In the second case, because of close boiling points of target trimethylsilyloxyl isocyanate **2** and secondary hexamethyl disiloxane, there is a need for a stage of *O*-silylurethane transsilylation with triethylchlorosilane. Apparently, it seems reasonable to find alternative methods for the synthesis of these isocyanates depriving formation of large amounts of by-products with fewer process stages.

We have found (Scheme 1) that the use of amine salts **3** in *N*-silyloxycarbonylation reaction can simplify the process (previously,<sup>10</sup> free amine MeNH<sub>2</sub> was applied). In this process, the intermediate *N,O*-bis(trimethylsilyl)urethane **4** was formed, which allows one to obtain methyl isocyanate **1** *via* phosgenation at low temperatures (15–20 °C) and atmospheric pressure (Table 1).<sup>†</sup>

Note that the resulting trimethylchlorosilane can be recycled by transformation into the original hexamethyldisilazane by treatment with ammonia. This makes the process nearly waste-free.

In an effort to improve the synthesis of trimethylsilyloxyl isocyanate **2** by reducing the number of stages and lowering the temperature, thermolysis of *N,O,O'*-tris(trimethylsilyl)carbaminoic derivative **5** in the presence of phenyltrichlorosilane was carried out (Scheme 2).<sup>‡</sup> Compound **5** in the known<sup>11</sup> process is decomposed with triethylchlorosilane.



**Scheme 1**

**Table 1** Methyl isocyanate production on phosgenation of compound **4** at 15–20 °C.

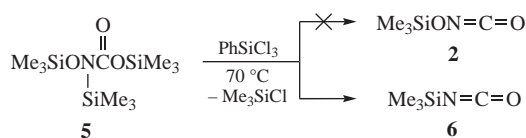
Entry	<i>O</i> -silyl-urethane <b>4</b> /g	C(O)Cl <sub>2</sub> /g	<i>t</i> <sup>a</sup> /h	Yield/g (%)	GC purity of <b>1</b> (%)
1	84.5	39	1	12.2 (56)	98.7
2	81.7	71	2	10.3 (48)	98.8
3	84.5	39 <sup>b</sup>	1	21.7 (99)	99.0
4	147.3	73 <sup>b</sup>	1	37.5 (98)	99.4
5	147.3	73 <sup>b</sup>	2	36.8 (96)	99.4

<sup>a</sup>The time is specified not taking into account the exposure. <sup>b</sup>Still bottom was phosgenated for the second time.

<sup>†</sup> IR spectra were recorded on a Specord 75IR instrument. GC analysis was performed on a Shimadzu G-8A instrument (stainless steel column 1.5 m × 3 mm; SE-30 on Chromaton N-AW; carrier gas, helium). GC-MS spectra were obtained on a Finnigan MAT 95 XL instrument [GC: capillary column Varian VF-5ms; length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm; carrier gas, helium; injector temperature, 270 °C, initial temperature of the thermostat 30 °C (5 min), then heating rate of 15 K min<sup>-1</sup> to 300 °C; MS: ionization energy, 70 eV, source temperature, 230 °C, scanning within the range of 10–800 Da at the rate of 1 s per decade in mass, resolution *R* = 1000]. The sample was syringed through the needle without purging. The integral values of the peak areas were determined without adjustment to the ionization efficiency. Reference mass spectra presented in interpretations are included in NIST/EPA/NIH 11 database.

*Phosgenation of trimethylsilyl N-methyl-N-trimethylsilylcarbamate 4.* Compound **4** (84.5 g, 38.6 mol) was placed in a flask equipped with a thermometer, bubbler and total refluxing head; phosgene was bubbled at such a rate that the temperature in the bottom was within the range of 10–20 °C. After phosgene flowing was over, the mixture was heated to 50 °C and kept at this temperature until carbon dioxide release ceased (1–2 h), then technical grade isocyanate (a mixture of methyl isocyanate with trimethylchlorosilane) was distilled. Final 12.2 g (56%) of methyl isocyanate **1**, bp 37.7 °C, *n*<sub>D</sub><sup>20</sup> = 1.3630, were extracted by rectification.

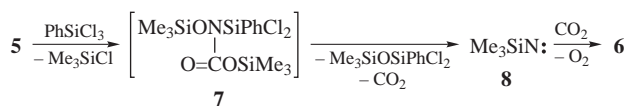
In the same way 21.7 g (99%) of methyl isocyanate **1**, bp 37.7 °C, *n*<sub>D</sub><sup>20</sup> = 1.3630, were extracted from compound **4** (84.5 g, 38.6 mol), but with repeated phosgenation of still bottoms after cooling.



Scheme 2

However, it turned out that moving from  $\text{Et}_3\text{SiCl}$  to  $\text{PhSiCl}_3$  changes the direction of the reaction. The reaction was accompanied by the violent release of carbon dioxide and did not afford the target **2**. According to chromatography-mass spectrometry data, another organosilicon isocyanate, trimethylsilyl isocyanate **6** was unexpectedly found in thermolysis products (see Scheme 2). In addition,  $(\text{Me}_3\text{Si})_2\text{O}$ ,  $\text{Me}_3\text{SiOSiCl}_2\text{Ph}$ ,  $\text{Me}_3\text{SiOSi}(\text{OSiMe}_3)\text{ClPh}$ , and  $\text{PhSi}(\text{OSiMe}_3)_3$  were also produced and characterized.

We can assume that after transsilylation of carbamate **5** with  $\text{PhSiCl}_3$ , partial desilylation of intermediate **7** occurs giving highly reactive trimethylsilylnitrene **8** and carbon dioxide (Scheme 3). Reasoning on this, we should expect the formation of oxygen along with carbon dioxide. However, monitoring of gas released allowed us to qualitatively identify the presence of carbon dioxide only.



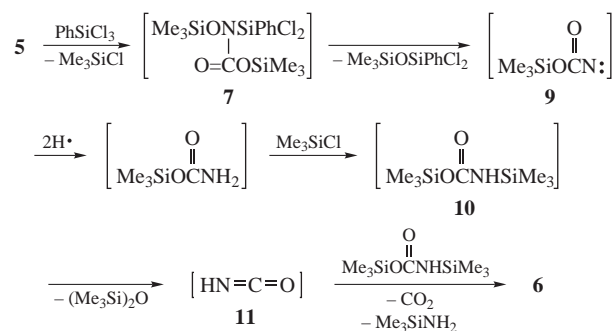
Scheme 3

Apparently, after transsilylation of initial *O*-silylurethane **5** with  $\text{PhSiCl}_3$ , an intermediate **7** is generated. Then the formation of (trimethylsilyloxycarbonyl)nitrene **9** and its conversion into *N,O*-bis(trimethylsilyl)carbamate **10** occur. The latter gives isocyanic acid **11**, whose silylation, finally, produces trimethylsilyl isocyanate **6** (Scheme 4).

In conclusion, we found a promising version for the production of methyl isocyanate. Our findings in the study of trimethylsilyloxyl isocyanate synthesis can be of fundamental and practical interest.

The work was performed within the framework of the governmental task no. 1984 ‘New polymeric materials based on organic silicon compounds modified with carbon-containing fillers and metal oxides’.

‡ *Thermolysis of trimethylsilyl N-trimethylsilyl-N-(trimethylsilyloxy)carbamate 5*. Compound **5** (10 g, 0.034 mol) was added under stirring to phenyltrichlorosilane (10.50 g, 0.05 mol), then additional amount of phenyltrichlorosilane (10.50 g, 0.05 mol) was added. The reaction mass was heated with the total refluxing head to  $70^\circ\text{C}$ , distilling 13.2 g of volatile products. Final redistillation afforded 10.90 g (99%) of trimethylchlorosilane, bp  $56.8\text{--}57.0^\circ\text{C}$ ,  $n_D^{20} = 1.3890$  (lit., bp  $57.7^\circ\text{C}$ ,<sup>12</sup>  $n_D^{20} = 1.3895$ <sup>13</sup>) and 2.30 g (60%) of trimethylsilyl isocyanate **6**, bp  $90\text{--}91^\circ\text{C}$ ,  $n_D^{20} = 1.3948$  (lit.,<sup>14</sup> bp  $91^\circ\text{C}$ ,  $n_D^{20} = 1.3950$ ). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2275 ( $\text{N}=\text{C}=\text{O}$ ). MS,  $m/z$ : 115  $[\text{M}-\text{H}]^+$  (calc. for  $\text{C}_4\text{H}_9\text{NOSi}$ ,  $m/z$ : 115.2059).



Scheme 4

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