

# Synthesis of functionalized fluorine-containing trimethylsilylcarbodiimides

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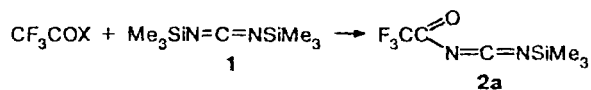
New functionalized polyfluorinated carbodiimides  $R_FN=C=NSiMe_3$  were prepared by the reactions of bis(trimethylsilyl)carbodiimide with electrophilic reagents. The structures of the resulting compounds were confirmed by  $^1H$ ,  $^{13}C$ ,  $^{29}Si$ ,  $^{14}N$ ,  $^{15}N$ , and  $^{17}O$  NMR spectroscopy.

**Key words:** polyfluorinated carbodiimides, substitution and addition reactions.

Fluorine-containing carbodiimides as promising precursors of azacyclic and acyclic compounds are rather poorly studied. Progress in the chemistry of these compounds is in part hampered by the absence of general procedures for the preparation of carbodiimides containing functional groups. Only methods for the synthesis of perfluoroalkyl-, alkyl(aryl)carbodiimides,<sup>1,2</sup> bis(perfluoroalkyl)carbodiimides,<sup>3,4</sup> and bis(chlorotrifluoroalkyl)carbodiimides<sup>5</sup> were reported in the literature.

With the aim of preparing functionally substituted carbodiimides, we studied the reactions of fluorine-containing electrophilic reagents with bis(trimethylsilyl)carbodiimide (**1**). Previously,<sup>6</sup> carbodiimide **1** was used for synthesizing *N*-cyanoimines from cyclic ketones in the presence of strong Lewis acids. The reaction of carbodiimide **1** with thionyl chloride to form unstable cyanosulfinylamine was also reported.<sup>7</sup> Both examples are characterized by the transfer of the reaction center to form the cyano group.

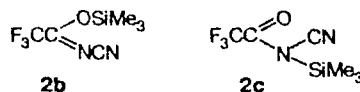
The reactions of carbodiimide **1** with trifluoroacetic anhydride as well as with trifluoroacetyl chloride<sup>8</sup> at low temperature ( $-30\text{ }^{\circ}C$ ) afforded *N*-trifluoroacetyl-*N'*-trimethylsilylcarbodiimide (**2a**). The structure of **2a** was interpreted<sup>8</sup> based on the data of IR and  $^1H$  and  $^{19}F$  NMR spectroscopy and mass spectrometry. The possibility of the formation of alternative structures **2b,c** was not considered.



X = Cl, OC(O)CF<sub>3</sub>

The data of  $^1H$ ,  $^{13}C$ ,  $^{19}F$ , and  $^{29}Si$  NMR (Table 1) and IR spectroscopy did not allow us to unambiguously establish the structure of the resulting compound, namely,

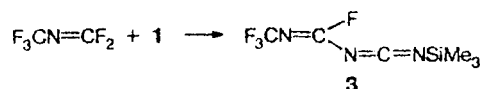
to elucidate whether **2a** or its possible isomers **2b** and **2c** were formed. The structure was conclusively established from the analysis of the  $^{17}O$ ,  $^{14}N$ , and  $^{15}N$  NMR spectra. Thus the chemical shift of the signal in the  $^{17}O$  NMR spectrum ( $\delta -422$ ) is observed in the region typical of the carbonyl group, which makes it possible to exclude structure **2b**. In addition, when polarization is transferred from the protons in the  $^1H-C-Si-^{15}N$  system, a  $^{15}N$  signal is observed at  $\delta -272.0$ , which proves the presence of the Si-N bond in the compound under study. Two signals in the  $^{14}N$  NMR spectrum are characterized by chemical shifts  $\delta -272.92$  and *ca.*  $-285$  relative to  $MeNO_2$  (the second signal exists as a quadrupole broadening), which excludes structure **2c**, because these signals cannot be assigned to signals for the N atom of the cyano group, which are typically observed in the region from  $-90$  to  $-140$  ppm.<sup>9</sup>



At the same time, carbodiimide structure **2a** corresponds to all the spectral characteristics. According to the published data,<sup>9</sup> the chemical shifts of the signals of the N nuclei for carbodiimides are in the region from  $\delta -270$  to  $-300$ , which agrees with the experimental values. The rather long duration of quadrupole relaxation of the  $^{14}N$  nuclei in the  $C=^{14}N-SiMe_3$  system allows the detection of a rather narrow signal in the  $^{14}N$  NMR spectrum ( $\Delta\nu_{1/2} = 16$  Hz) and the manifestation of spin-spin coupling with the two adjacent nuclei. Thus the signal for the  $^{13}C=N-SiMe_3$  fragment in the  $^{13}C$  NMR spectrum is observed as a broadened triplet (1 : 1 : 1) with the spin-spin coupling constant of 32.5 Hz, while the  $^{29}Si$  signal is noticeably broadened

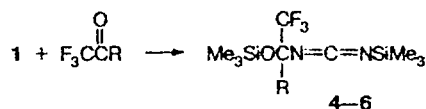
( $\Delta\nu_{1/2} = 4.6$  Hz). In this case, neither additional splitting nor broadening of the  $^{13}\text{C}$  signal of the carbonyl group is observed.

The reaction of carbodiimide **1** with perfluoro-*N*-methylmethanimine also afforded a product of replacement of one  $\text{Me}_3\text{Si}$  group. Judging from the spectral data, this product is carbodiimide **3** as a mixture of *syn* and *anti* isomers in a ratio of  $\sim 1 : 1$ .



Perfluoroisobutene and methyl perfluoromethacrylate did not react with carbodiimide **1** even on heating.

The reactions of carbodiimide **1** with polyfluorinated carbonyl compounds proceeded with addition with retention of the carbodiimide fragment. The reactions with hexafluoroacetone and chloropentafluoroacetone proceeded under mild conditions. The reaction with methyl trifluoropyruvate occurred only on heating to 70 °C.



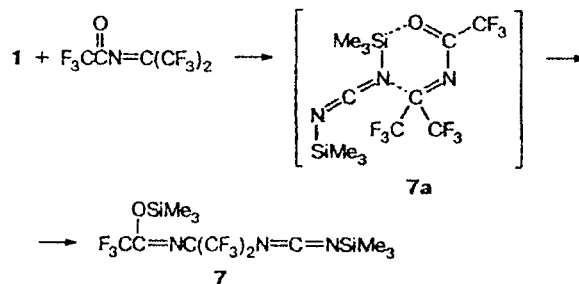
R =  $\text{CF}_3$  (**4**);  $\text{CF}_2\text{Cl}$  (**5**);  $\text{COOMe}$  (**6**)

The  $^1\text{H}$  NMR spectra of carbodiimides **2–6** have similar characteristics. The  $^{13}\text{C}$  chemical shifts of the carbodiimide fragment are also observed in the same region (see Table 1). The chemical shifts of the  $^{29}\text{Si}$  nuclei at the N atom are somewhat different. Thus the  $^{29}\text{Si}(\text{N})$  nuclei in compounds **2** and **3** are deshielded to a

somewhat greater extent than the  $^{29}\text{Si}(\text{N})$  nuclei in compounds **4** and **6** due to the acceptor effect of the carbonyl and azomethine groups.

The reaction of carbodiimide **1** with perfluoroheptanal in the cold afforded a glassy oligomeric product.

Unlike the reactions with fluorinated ketones and aldehydes, addition of carbodiimide **1** to trifluoronitrosomethane did not occur even at 100 °C. Hexafluoroacetone of *N*-benzoylimine also did not add carbodiimide **1** on heating up to 130 °C. Further heating afforded unidentified products. More electrophilic hexafluoroacetone of *N*-trifluoroacetylamine smoothly reacted with carbodiimide **1** even at room temperature to form carbodiimide **7**. The imidate structure of compound **7** is confirmed by the value of the  $^{29}\text{Si}$  chemical shift ( $\delta$  30.5) typical of the *O*-trimethylsilyl group in the imidate residue.<sup>10</sup> The results obtained are evidence in favor of the realization of six-center transition state **7a**, unlike the above-considered examples in which only the four-center transition state can exist.



Compounds **2–7** are rather stable on storage and heating. Their spectra remain unchanged for at least several months. The nucleophilic properties of these compounds are substantially reduced. Carbodiimide **4**

Table 1. Data of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{29}\text{Si}$  spectroscopy for compounds **2–7** (in  $\text{CDCl}_3$ )

Compound	NMR, $\delta$ (J/Hz)			
	$^1\text{H}$	$^{19}\text{F}$	$^{29}\text{Si}$	$^{13}\text{C}$
<b>2a</b>	0.41 (s, Me)	-1.5 (s, $\text{CF}_3$ )	13.0 (s, Si-N)	116.2 (q, $\text{CF}_3$ , $J = 283.1$ ); 163.0 (q, C(O), $J = 35.0$ ); 124.4 (t, $=\text{C}$ , $J_{\text{NC}} = 32.5$ ); -0.8 (s, Me)
<b>3*</b>	0.43 (s, Me)	-24.6 (d, $\text{CF}_3$ , $J = 13.0$ ); -60.7 (q, CF, $J = 13.0$ ); -22.9 (d, $\text{CF}_3$ , $J = 12.0$ ); -58.8 (q, CF, $J = 12.0$ )	14.4 (s, Si-N)	123.0 (d.q, $\text{CF}_3$ , $J = 243.3$ , $J = 35.7$ ); 121.3 (d.q, $\text{CF}_3$ , $J = 250.4$ , $J = 5.4$ ); 153.1 (d.q, CF, $J = 305.5$ , $J = 10.7$ ); 152.0 (d.q, CF, $J = 249.9$ , $J = 9.8$ ); 121.7 (m, $=\text{C}$ ); 122.2 (m, $=\text{C}$ ); -1.1 (m, Me)
<b>4</b>	0.26 (br.s, Me); 0.28 (br.s, Me)	3.0 (s, $\text{CF}_3$ )	7.3 (s, Si-N); 23.2 (s, Si-O)	-0.44 (m, Me); -0.41 (m, Me); 121.6 (q, $\text{CF}_3$ , $J = 292.1$ ); 85.1 (sept, $\text{C}(\text{CF}_3)_2$ , $J = 31.9$ ); 125.2 (br.s, $=\text{C}$ )
<b>5</b>	0.27 (br.s, Me); 0.29 (br.s, Me)	-0.7 (t, 3 F, $\text{CF}_3$ , $J = 10.7$ ); -12.7 (q, 2 F, $\text{CF}_2$ , $J = 11.0$ )	—	—
<b>6</b>	3.85 (s, 3 H, Me); 0.21 (s, 9 H, Me); 0.29 (s, 9 H, Me)	3.7 (s, $\text{CF}_3$ )	6.3 (s, Si-N); 20.8 (s, Si-O)	0.7 (s, Me); 0.1 (s, Me); 52.8 (s, OMe); 122.2 (q, $\text{CF}_3$ , $J = 286.5$ ); 85.9 (q, $\text{C}-\text{CF}_3$ , $J = 30.5$ ); 127.5 (br.s, $=\text{C}$ ); 166.7 (s, $\text{C}=\text{O}$ )
<b>7</b>	0.26 (s, 9 H, Me); 0.37 (s, 9 H, Me)	3.8 (s, 6 F, 2 $\text{CF}_3$ ); -0.3 (s, 3 F, $\text{CF}_3$ )	7.2 (s, Si-N); 30.5 (s, Si-O)	-0.1 (s, Me); -1.8 (s, Me); 122.4 (q, 2 $\text{CF}_3$ , $J = 265.7$ ); 77.1 (sept, $\text{C}(\text{CF}_3)_2$ , $J = 29.0$ ); 117.1 (q, $\text{CF}_3$ , $J = 275.4$ ); 126.2 (br.s, $=\text{C}$ ); 148.2 (m, $\text{C}-\text{O}$ )

\* Signals of both isomers in the  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra are given.

**Table 2.** Physicochemical characteristics and the data of elemental analysis for the synthesized compounds

Com- pound	B.p. /°C (p /Torr)	$n_D^{20}$	Found ( % ) Calculated			Molecular formula
			C	H	N	
2a	80 (15)	1.408	34.35 34.29	4.10 4.29	13.51 13.33	C <sub>6</sub> H <sub>9</sub> F <sub>3</sub> N <sub>2</sub> OSi
3	95 (20)	1.418	31.51 31.72	3.87 3.96	18.60 18.50	C <sub>6</sub> H <sub>9</sub> F <sub>4</sub> N <sub>3</sub> Si
4	88 (17)	1.386	34.15 34.09	5.10 5.11	7.89 7.95	C <sub>10</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> OSi <sub>2</sub>
5	92 (9)	1.410	32.40 32.56	4.80 4.88	15.16 15.20	C <sub>10</sub> H <sub>18</sub> ClF <sub>3</sub> N <sub>2</sub> OSi <sub>2</sub>
6	121 (19)	1.417	40.54 40.49	7.13 7.05	9.30 9.35	C <sub>11</sub> H <sub>21</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> Si <sub>2</sub>
7	108 (13)	1.384	32.39 32.21	4.10 4.03	9.33 9.40	C <sub>12</sub> H <sub>18</sub> F <sub>9</sub> N <sub>3</sub> OSi <sub>2</sub>

did not add the second hexafluoroacetone molecule even on heating.

Therefore, the substitution and addition reactions of bis(trimethylsilyl)carbodiimide **1** substantially extend the possibilities of the synthesis of fluorine-containing carbodiimides containing various functional groups.

### Experimental

The <sup>1</sup>H NMR spectra were recorded on a Bruker AC-300 spectrometer (300 MHz). The <sup>19</sup>F, <sup>29</sup>Si, and <sup>13</sup>C NMR spectra were obtained on a Bruker WP-200 SY spectrometer (188.31, 39.76, and 50.31 MHz, respectively). The <sup>13</sup>C, <sup>14</sup>N, <sup>15</sup>N, and <sup>17</sup>O NMR spectra of compound **2** were measured on a Bruker AM-300 spectrometer (75.47, 21.69, 50.69, and 40.69 MHz, respectively). The chemical shifts (δ) are given relative to the external standards: Me<sub>4</sub>Si (<sup>1</sup>H, <sup>29</sup>Si, and <sup>13</sup>C), CF<sub>3</sub>COOH (<sup>19</sup>F), H<sub>2</sub>O (<sup>17</sup>O), and MeNO<sub>2</sub> (<sup>14</sup>N and <sup>15</sup>N). The IR spectra were obtained on a UR-20 spectrometer in thin layers. The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectral data are given in Table 1. The physicochemical characteristics and the data of elemental analysis are listed in Table 2.

**N-Trifluoroacetyl-N'-trimethylsilylcarbodiimide (2).** A solution of trifluoroacetic anhydride (3.4 g, 0.016 mol) in dry ether (1 mL) was added to a solution of carbodiimide **1** <sup>11</sup> (3.0 g, 0.016 mol) in dry ether (3 mL) at -55 °C. Then the reaction mixture was warmed to -20 °C over 1 h and fractionated *in vacuo*. Carbodiimide **2** was obtained in a yield of 0.5 g (15%). IR, ν/cm<sup>-1</sup>: 1714 (C=O); 2217 (N=C=N); 2960 (C-H). <sup>14</sup>N NMR, δ: -272.92 (s, C=N=C); ~ -285.0 (br.g, N-Si). <sup>15</sup>N NMR, δ: -272.0 (s, C=N-Si). <sup>17</sup>O NMR, δ: 422 (br.s, C=O).

**N-(Tetrafluoro-2-azaprop-1-enyl)-N'-trimethylsilylcarbodiimide (3).** Carbodiimide **1** (12.2 g, 65 mmol) was slowly added to perfluoro-N-methylmethanimine<sup>12</sup> (7.5 g, 65 mmol) at -78 °C. Then the reaction mixture was warmed to -20 °C over 1 h. Fractionation *in vacuo* afforded carbodiimide **3** in a yield of 6.5 g (43%).

**N-(2-Trimethylsilyloxyperfluoropropan-2-yl)-N'-trimethylsilylcarbodiimide (4).** Hexafluoroacetone (5.1 g, 31 mmol) was slowly added to carbodiimide **1** (5.0 g, 26 mmol) at -78 °C. Then the mixture was stirred, warmed to -20 °C over 1 h, and distilled *in vacuo*. Carbodiimide **4** was obtained in a yield of 7.6 g (80 %). IR, ν/cm<sup>-1</sup>: 2201 (N=C=N); 2965 (C-H).

**N-(1-Chloropentafluoro-2-trimethylsilyloxypropan-2-yl)-N'-trimethylsilylcarbodiimide (5).** Chloropentafluoroacetone (2.3 g, 12 mmol) was slowly added to carbodiimide **1** (2.1 g, 11 mmol) at -78 °C. Then the mixture was stirred, warmed to -20 °C over 1 h, and distilled *in vacuo*. Carbodiimide **5** was obtained in a yield of 2.9 g (70%). IR, ν/cm<sup>-1</sup>: 1680 (C=O); 2210 (N=C=N); 2960 (C-H).

**N-(2,2,2-Trifluoro-1-methoxycarbonyl-1-trimethylsilyloxyethyl)-N'-trimethylsilylcarbodiimide (6).** Carbodiimide **1** (2.6 g, 14 mmol) was added to methyl trifluoropyruvate<sup>13</sup> (2.2 g, 14 mmol) at -30 °C. The reaction mixture was warmed to 20 °C over 1 h and then heated at 70 °C for 2 h in a sealed tube. The mixture was cooled and distilled *in vacuo*. Carbodiimide **6** was obtained in a yield of 3 g (62%). IR, ν/cm<sup>-1</sup>: 2205 (N=C=N); 2960 (C-H).

**N-[1,1-Bis(trifluoromethyl)trifluoro-3-trimethylsilyloxy-2-azabut-2-enyl]-N'-trimethylsilylcarbodiimide (7).** Carbodiimide **1** (0.71 g, 3.8 mmol) was added to hexafluoroacetone N-trifluoroacetylamine (1 g, 3.8 mmol) at -78 °C. The reaction mixture was warmed to 20 °C. After 12 h, the mixture was distilled *in vacuo*. Carbodiimide **7** was obtained in a yield of 0.9 g (32%).

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