# Synthesis of *N*-nitro-*N´*-(trimethylsilyl)carbodiimide

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Nitration of *N,N´*-bis(trimethylsilyl)carbodiimide with $N_2O_5$ or $(NO_2)_2SiF_6$ afforded *N*-nitro-*N´*-(trimethylsilyl)carbodiimide, the first representative of *N*-nitrocarbodiimides. Its further nitration led to the release of $CO_2$, which is presumably formed in the course of *N,N´*-dinitrocarbodiimide decomposition. The reactions of *N*-nitro-*N´*-(trimethylsilyl)carbodiimide with nucleophiles take place both at the trimethylsilyl group (for example, with $NH_3$) to give nitrocyanamide salts and at the carbodiimide C atom (for example, with $Et_2NH$) to give the corresponding nitroguanidines.

**Key words:** *N*-(trimethylsilyl)carbodiimides, *N*-nitrocarbodiimides, *N*-nitrocyanamides, nitration of N—SiMe₃ group.

Earlier, we have found that nitrocyanamides **1** (R = MeOCO, $MeSO_2$) obtained by the nitration of the corresponding *N*-(trimethylsilyl)carbodiimides **2** undergo rapid conversion to the corresponding isocyanates **3** (Scheme 1).[1]

Later, it was shown[2] that alkylnitrocyanamides **1** obtained by the alkylation of nitrocyanamide Ag salt with alkyl halides also undergo ready conversion to the corresponding isocyanates. The mechanism of this process probably[2] includes rearrangement of alkylnitrocyanamides **1** to *N*-nitrocarbodiimides **4**, cyclization of the latter to cyclic intermediates **5** and their conversion to isocyanates **3** with liberation of $N_2O$ (see Scheme 1). Note that *N*-nitrocarbodiimides **4** were not isolated or spectrally detected.

In the present work, a task was set to study a possibility of the preparation of dinitrocyanamide (**1a**, R = $NO_2$) and *N,N´*-dinitrocarbodiimide (**4a**, R = $NO_2$). Dinitrocyanamide **1a** could have been of interest as a high-energy oxidant, while *N,N´*-dinitrocarbodiimide as a starting compound for the preparation of new classes of energetic compounds.

## Results and Discussion

Assuming that dinitrocyanamide **1a** and *N,N´*-dinitrocarbodiimide **4a** can be labile compounds, we have chosen for their preparation one of the mildest methods of nitration, namely, nitration of compounds containing an N—SiMe₃ group with nitronium salts. Substitutive nitration of this type of compounds have been studied earlier in a number of works.[3,4]

The nitration of *N*-(trimethylsilyl)carbodiimides **2**, as well as the alkylation of nitrocyanamide Ag salt (see Scheme 1) can *a priori* lead to both *N*-substituted nitrocyanamides **1** and *N*-nitrocarbodiimides **4**.

We carried out theoretical studies of isomers **1a**—**c** and **4a**—**c** (Table 1). The optimization of the geometry and the calculation of the harmonic vibrational frequencies were carried out by the Gaussian 09 program[5] using density functional theory (DFT) with the B3LYP hybrid potential and the 6-311++G(2df,2p) basis. The calculated frequencies of all the structures optimized in the gas phase were checked for the absence of imaginary frequencies.
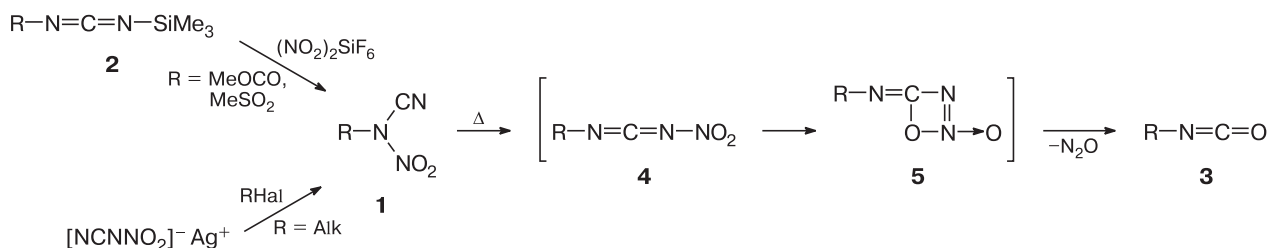
**Scheme 1**

**Table 1.** DFT calculation results for pairs of isomers **1** and **4**

| 1 and 4 | R | $-E'^a$ | $-E''^b$ | $\Delta E^c$ |
|---|---|---|---|---|
| | | a.u. | | /kcal mol$^{-1}$ |
| a | NO$_2$ | 557.858661 | 557.865068 | 4.0 |
| b | Me$_3$Si | 762.029115 | 762.038973 | 6.1 |
| c | MeSO$_2$ | 941.308137 | 941.317285 | 5.8 |

$^a$ $E' = E_{tot} + ZPE$ is a total energy of compound **1** including a zero point energy.
$^b$ $E'' = E_{tot} + ZPE$ is a total energy of compound **4** including a zero point energy.
$^c$ $\Delta E$ is a difference in the total energies for pairs of isomers **1** and **4**.

The calculations showed that the carbodiimide structures **4** are thermodynamically more stable than nitrocyanamide ones **1** (see Table 1). Therefore, nitrocyanamides **1** (see Scheme 1, R = MeCO$_2$, MeSO$_2$) obtained by us earlier[1] are kinetically controlled reaction products.

Bis(trimethylsilyl)carbodiimide (**6**) served as the starting compound in our studies (Scheme 2). It could have been expected that its nitration with one equivalent of nitrating agent, similarly to the nitration of *N*-(trimethylsilyl)carbodiimides **2** (see Scheme 1), would give *N*-(trimethylsilyl)nitrocyanamide (**1b**) as a primary reaction product. However, *N*-nitro-*N'*-(trimethylsilyl)carbodiimide **4b** was found to be the only nitration product (see Scheme 2). This result can be explained by the easiness of the migration of the SiMe$_3$ group in compound **1b** (*cf.* Refs 6 and 7). At the same time, the pathway in which carbodiimide **4b** is a primary product of nitration cannot be excluded either.
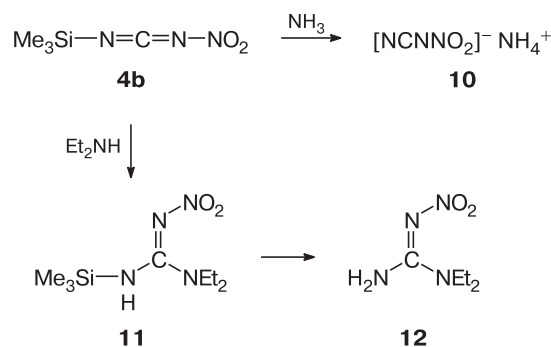
**Scheme 2**
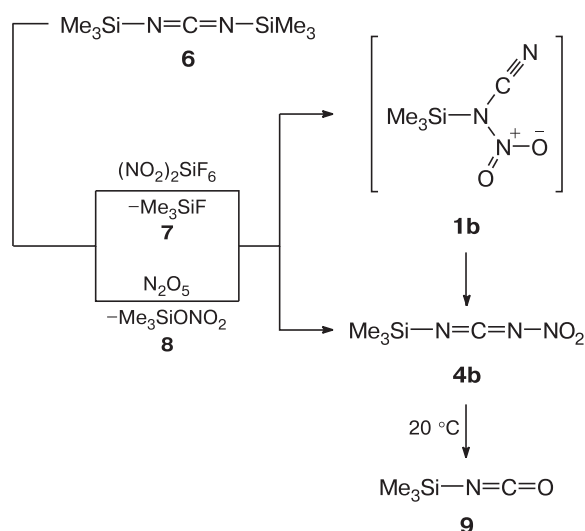


Nitration of carbodiimide **6** was carried out using (NO$_2$)$_2$SiF$_6$ or N$_2$O$_5$ in CH$_2$Cl$_2$ as a solvent. The reaction

progress was monitored by $^1$H NMR, gradually raising the temperature of the reaction mixtures from $-30$ to $0$ °C. The monitoring showed the disappearance of the signal for the starting carbodiimide **6** ($\delta_H = 0.15$) and the appearance of the signal for nitrocarbodiimide **4b** ($\delta_H = 0.50$). Fluorotrimethylsilane (**7**) ($\delta_H = 0.20$, d, $^3J_{F,H} = 7$ Hz) and trimethylsilyl nitrate (**8**) ($\delta_H = 0.41$) were the second observed reaction products in the nitration with nitronium hexafluorosilicate and nitric anhydride, respectively. No other products were observed in the reaction mixtures.

Nitrocarbodiimide **4b** was isolated in the individual state as a white crystalline compound, relatively stable at $0$ °C. At room temperature, it undergoes slow conversion to trimethylsilyl isocyanate (**9**) ($\delta_H = 0.24$) (see Scheme 2). At $20$ °C, this conversion reaches $95\%$ within $20$ h (monitoring by $^1$H NMR spectroscopy).

The structure of nitrocarbodiimide **4b** was confirmed by spectroscopic methods. In the $^{14}$N NMR spectrum, the signal for the nitro group ($\delta_N = -20$) was found in the region characteristic of the fragment (C=N—NO$_2$). In nitrocyanamide, the signal for this group is observed in the region $\delta_N$ $-40 \div -60$. In the $^{13}$C NMR spectra, the signal for the carbon atom ($\delta_C = 123.8$) is in the region characteristic of the carbodiimide fragment (=C=).[2] For cyanamides, the signal for the carbon atom of the nitrile group is observed in the region $\delta_C$ $100—110$ (see Refs 1 and 2).

Nucleophiles react with nitrocarbodiimide **4b** either at the Si atom, or at the C atom. Ammonia attacks the SiMe$_3$ group, resulting in the formation of the ammonium salt of nitrocyanamide (**10**). Conversely, diethylamine reacts only at the carbodiimide C atom, leading to the silylated nitroguanidine **11**, which after hydrolysis gives nitroguanidine **12** (Scheme 3).

**Scheme 3**



We suggested that nitration of silylated nitrocarbodiimide **4b** with N$_2$O$_5$, similarly to the nitration of *N*-(trimethylsilyl)carbodiimides **2** (see Scheme 1), can give dinitrocyanamide (**1a**) (Scheme 4). However, carrying out this reaction in both a polar solvent (MeCN) and a weakly polar one (CH$_2$Cl$_2$) already at $-30$ °C leads to

the liberation of $CO_2$ (75% yield), which was identified by the reaction with barite water. This result can be explained by the fact that the rearrangement of dinitrocyanamide (**1a**) to *N,N*´-dinitrocarbodiimide (**4a**) proceeds much readier than in the studied by us earlier nitrocyanamides **1** (R = MeOCO, MeSO$_2$, see Scheme 1), while dinitrocarbodiimide (**4a**) decomposes already at −30 °C, being converted initially to *N*-nitroisocyanate **13** and then to $CO_2$ following by the mechanism similar to that given in Scheme 1.

### Scheme 4
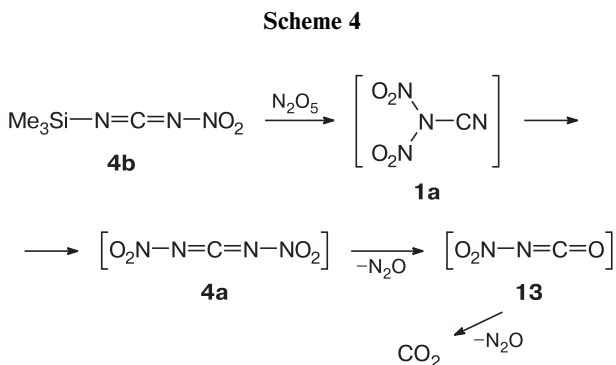


In conclusion, we synthesized *N*-nitro-*N*´-(trimethylsilyl)carbodiimide (**4b**), the first representative of a new class of nitro compounds, *N*-nitrocarbodiimides, and studied its reactions with nucleophiles. Attempted synthesis of *N,N*-dinitrocyanamide (**1a**) was unsuccessful. Presumably, this compound readily isomerizes to *N,N*´-dinitrocarbodiimide (**4a**), which decomposes with the formation of $CO_2$ and $N_2O$ already at −30 °C.

### Experimental

$^1$H, $^{13}$C, and $^{14}$N NMR spectra were recorded on a Bruker AM300 spectrometer (300.13, 75.47, and 21.69 MHz, respectively). Chemical shifts are given relative to SiMe$_4$ ($^1$H, $^{13}$C) or CH$_3$NO$_2$ ($^{14}$N, external standard, the high-field chemical shifts are negative). IR spectra were recorded on a Bruker ALPHA-T spectrometer. Reaction progress was monitored by TLC (Merck 60 F254). *N,N*´-Bis(trimethylsilyl)carbodiimide was obtained according to the known procedure.[8] Nitration reactions were carried out in anhydrous solvents under argon.

***N*-Nitro-*N*´-(trimethylsilyl)carbodiimide (4b).** Method *A*. A solution of *N,N*´-bis(trimethylsilyl)carbodiimide (**6**) (800 mg, 4.28 mmol) in CH$_2$Cl$_2$ (4 mL) was added to a suspension of (NO$_2$)$_2$SiF$_6$ (500 mg, 2.14 mmol) in CH$_2$Cl$_2$ (5 mL) with stirring at −30 °C. After a complete dissolution of (NO$_2$)$_2$SiF$_6$ (~20 min), the temperature was allowed to rise to 0 °C. The reaction mixture was analyzed by $^1$H NMR: a complete disappearance of the starting compound **6** ($\delta_H$ = 0.15) and the appearance of the signals for *N*-nitro-*N*´-(trimethylsilyl)carbodiimide (**4b**) ($\delta_H$ = 0.50) and trimethylfluorosilane ($\delta_H$ = 0.20, δ, $^3J_{F,H}$ = 7 Hz) were observed. The reaction mixture was concentrated *in vacuo*, keep-

ing temperature below 0 °C, a solid residue was evacuated (1 Torr) for 30 min at 0 °C (at temperatures above 10 °C, carbodiimide **4b** slowly undergoes conversion to trimethylsilyl isocyanate **9** ($\delta_H$ = 0.24), for details see below). The yield of carbodiimide **4b** was 3.47 mmol (81%), which was determined by $^1$H NMR using cyclohexane as an internal quantitative standard.

Method *B*. Similar experiment with N$_2$O$_5$ (462 mg, 4.28 mmol) led to carbodiimide **4b** in 73% yield. IR (CH$_2$Cl$_2$), ν/cm$^{-1}$: 2250, 2300—2380 (=C=); 1260—1280, 1545 (NO$_2$). $^1$H NMR (CD$_2$Cl$_2$), δ: 0.50 (s, Me$_3$Si). $^{13}$C NMR (−70 °C, CD$_2$Cl$_2$), δ: −1.59 ((Me$_3$Si); 123.8 (br, =C=). $^{14}$N NMR (0 °C, CD$_2$Cl$_2$), δ: −20.3 (NO$_2$, $\Delta\nu_{1/2}$ = 25 Hz).

**Thermal decomposition of *N*-nitro-*N*´-(trimethylsilyl)carbodiimide (4b).** A solution of carbodiimide **4b** (3.74 mmol) in CH$_2$Cl$_2$ (8 mL) was allowed to stand at 20 °C, regularly recording its $^1$H NMR spectra. After 20 h, carbodiimide **4b** converted to trimethylsilyl isocyanate (**9**) by 95%. Isocyanate **9** was found to be identical to the authentic sample[9] in its IR spectrum and $^1$H and $^{13}$C NMR spectra.[10]

**Reaction of *N*-nitro-*N*´-(trimethylsilyl)carbodiimide (4b) with ammonia.** Carbodiimide **4b** obtained by procedure *A* was dissolved in CH$_2$Cl$_2$ (10 mL), ammonia was passed through this solution at −20 °C. A precipitate was collected by filtration. The yield of the ammonium salt of nitrocyanamide **10** was 75% (determined by UV spectroscopy, $\lambda$ = 265 nm, $\varepsilon$ = 9000). The ammonium salt was converted to the potassium one upon treatment with an ethanolic solution of KOH, which was recrystallized from ethanol (m.p. 132—134 °C, Ref. 11: m.p. 135—136 °C). The potassium salt was found to be identical to an authentic sample[12] in its UV, IR, and $^{14}$N NMR spectra.

**Reaction of *N*-nitro-*N*´-(trimethylsilyl)carbodiimide (4b) with Et$_2$NH.** Diethylamine (0.28 g, 3.88 mmol) was added dropwise to a solution of carbodiimide **4b** (3.88 mmol) obtained by procedure *A* in CH$_2$Cl$_2$ (8 mL) at −50 °C with stirring. The temperature was allowed to rise to 0 °C over 15 min, the reaction mixture was maintained at this temperature for 1 h. The solvent was evaporated at reduced pressure, a solid residue was evacuated (1 Torr) for 1 h at 20 °C. The yield of *N,N*-diethyl-*N*´-trimethylsilyl-*N*´´-nitroguanidine (**11**) was 3.67 mmol (95%), which was determined by $^1$H NMR spectroscopy in CD$_2$Cl$_2$ using MeCN as an internal quantitative standard. $^1$H NMR (CD$_2$Cl$_2$), δ: 0.30 (s, 9 H, (CH$_3$)$_3$Si); 1.26 (t, 6 H, 2 C**H**$_3$CH$_2$, *J* = 7.0 Hz); 3.50 (q, 4 H, 2 CH$_3$C**H**$_2$, *J* = 7.0 Hz). The solid product was dissolved in CH$_2$Cl$_2$ (8 mL), H$_2$O (0.3 mL) was added and this mixture was stirred for 30 min. The solvent was evaporated at reduced pressure, the residue was dried *in vacuo* to obtain *N,N*-diethyl-*N*´´-nitroguanidine (**12**) (0.58 g, 93%), m.p. 83—88 °C, after recrystallization from water m.p. 93—95 °C (Ref. 13: 92—94 °C). The product was identical to the authentic sample in its IR and $^1$H NMR spectra.

**Reaction of *N*-nitro-*N*´-(trimethylsilyl)carbodiimide (4b) with N$_2$O$_5$. *A*.** A solution of carbodiimide **4b** in MeCN (2.5 mL) was added dropwise from a cooled dropping funnel to a suspension of N$_2$O$_5$ (0.46 g, 4.28 mmol) in MeCN (2.5 mL) at −30 °C. Evolution of a gas was observed. The reaction mixture was stirred for 20 min at −20 °C under argon, trapping a liberated gas with barite water. The yield of BaCO$_3$ was 0.63 g (75%). The reaction mixture recondensed into a trap cooled to −70 °C at a pressure of 1 Torr (bath temperature *T* ≤ 0 °C). The yield of trimethylsilyl nitrate in the condensate determined by $^1$H NMR was 3.85 mmol (90%).

**B.** Similar experiment was carried out using $CH_2Cl_2$ as a solvent. A 75% yield of $BaCO_3$ was reached by maintaining the reaction mixture for 1 h at $-10$ °C and 2 h at 0 °C.

## References

1. A. M. Churakov, S. L. Ioffe, B. N. Khasapov, V. A. Tartakovskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 577.
2. J. H. Boyer, T. Manimaran, L. T. Wolford, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2137.
3. H. Schultheiss, E. Fluck, *Z. Anorg. Allg. Chem.*, 1978, **445**, 20.
4. M. S. Pevzner, T. N. Kulibabina, S. L. Ioffe, I. A. Maslina, B. V. Gidaspov, V. A. Tartakovskii, *Khim. Geterotsikl. Soedin.*, 1979, 550 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1979].
5. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
6. S. L. Ioffe, L. M. Makarenkova, V. A. Tartakovsky, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23**, 433.
7 A. L. Blyumenfeld, A. S. Shashkov, S. L. Ioffe, O. B. Belkina, L. M. Makarenkova, V. A. Tartakovsky, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25**, 2368.
8. I. A. Vostokov, Yu. I. Dergunov, A. S. Gordetsov, *Zh. Obshch. Khim.*, 1977, **47**, 1769 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1977, **47**].
9. V. P. Kozyukov, E. K. Dobrovinskaya, V. F. Mironov, *Zh. Obshch. Khim.*, 1976, **46**, 1531 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1976, **46**].
10. M. J. Barany, R. P. Hammer, R. B. Merrifield, G. Barany, *J. Am. Chem. Soc.*, 2005, **127**, 508.
11. A. A. Astrat´ev, L. L. Kuznetsov, *Russ. J. Org. Chem.*, 2002, **38**, 1252 [*Zh. Org. Khim.*, 2002, **38**, 1308].
12. O. V. Anikin, M. S. Klenov, V. A. Tartakovsky, *Russ. Chem. Bull.*, 2012, **61**, 1638.
13. L. Fishbein, J. A. Gallaghan, *J. Am. Chem. Soc.*, 1954, **76**, 1877.