Reaction of *N*-alkyl-*N*´-(trimethylsilyl)carbodiimides with nitrating agents. The synthesis of *N*-(*tert*-butyl)-*N*´-nitrocarbodiimide

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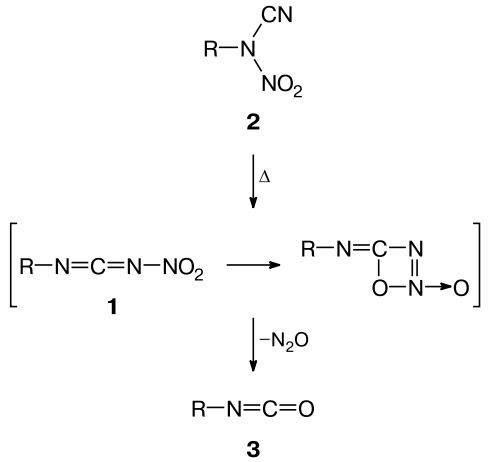
Reaction of *N*-Alk-*N*´-(trimethylsilyl)carbodiimides (Alk = Me, Bu^t) with nitrating agents (N_2O_5, $(NO_2)_2SiF_6$) affords alkyl(nitro)cyanamides and *N*-alkyl-*N*´-nitrocarbodiimides. The product ratio depends on the reaction conditions. *N*-(*tert*-butyl)-*N*´-nitrocarbodiimide can be obtained in almost pure form. This compound is stable at temperatures below 10 °C. Its structure was confirmed by ^{1}H, ^{13}C, and ^{14}N NMR. The reaction of *N*-(*tert*-butyl)-*N*´-nitrocarbodiimide with amines provides a new route to *N*-alkyl(aryl)-substituted *N*´-(*tert*-butyl)-*N*´´-nitroguanidines.

Key words: *N*-(trimethylsilyl)carbodiimides, *N*-nitrocarbodiimides, nitrocyanamides, nitroguanidines, substitutive nitration of N—$SiMe_3$ group.

N-Nitrocarbodiimides **1** are of interest as precursors in the synthesis of substituted nitroguanidines and *N*-nitroisoureas. Earlier, it was assumed that *N*-nitrocarbodiimides are formed as intermediates of the thermal rearrangement of substituted nitrocyanamides **2** (NCA);[1] however, it was impossible to isolate them under severe reaction conditions. The tentative mechanism of this rearrangement and the subsequent decomposition of *N*-nitrocarbodiimides into the corresponding isocyanates **3** is shown in Scheme 1 (see Ref. 1).

Scheme 1



Besides, alkyl(nitro)cyanamides can be obtained by alkylation of nitrocyanamide silver salts,[1,2] by the reaction of alkylnitramines with cyanogen bromide or by nitration of alkylcyanamides.[2]

Recently, we have reported that substitutive nitration of *N,N*´-bis(trimethylsilyl)carbodiimide affords *N*-nitro-*N*´-(trimethylsilyl)carbodiimide, the first representative of *N*-nitrocarbodiimides. This compound appeared to be stable at 0 °C; however, it slowly decomposed at room temperature with the formation of trimethylsilylisocyanate.[3]

In this work, we studied the possibility to synthesize *N*-alkyl-*N*´-nitrocarbodiimides **1** and their potential in organic synthesis.

Results and Discussion

As earlier,[3] *N*-alkyl-*N*´-nitrocarbodiimides were synthesized using one of the mildest nitration methods, *viz.*, substitutive nitration of compounds with the N—$SiMe_3$ bond.[4,5] The starting compounds were trimethylsilylated carbodiimides **4a**,**b**. Compound **4a** (R = Bu^t) can be obtained in almost pure form. Freshly distilled compound **4b** (R = Me) is also a carbodiimide; however, it slowly forms an equilibrium mixture containing 62% of *N*-methyl-*N*-trimethylsilylcyanamide on storage.[6]

It was found that nitration of trimethylsilylated carbodiimides **4a**,**b** by $(NO_2)_2SiF_6$ or N_2O_5 results in a mixture of the corresponding nitrocarbodiimides **1a**,**b** and cyanamides **2a**,**b** (Scheme 2 and Table 1). Independent experiments showed that these products do not undergo interconversion under the reaction conditions.

The nitration was carried out by mixing reactants at −30 °C; then, the temperature was raised to 0 °C, and the reaction mixture was analyzed by ^{1}H NMR spectroscopy. The product ratio depends on the nitrating agent, sol-

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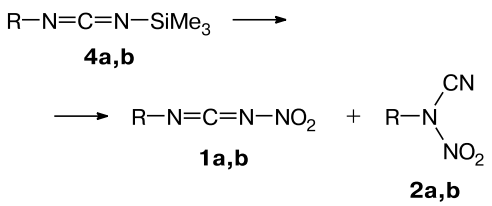
Table 1. Synthesis of *N*-alkyl-*N*´-nitrocarbodiimides **1a**,**b** and alkyl(nitro)cyanamides **2a**,**b**

Run	Starting carbodiimide[a] (mmol)	Nitrating agent (mmol)	Solvent	Product	Yield (%)[b]	**1** : **2** product ratio
1	**4a** (2.6)	$(NO_2)_2SiF_6$ (1.3)	CH_3CN	**1a**	91	24 : 1
				2a	3	
2	**4a** (2.6)	$(NO_2)_2SiF_6$ (1.3)	CH_2Cl_2	**1a**	48	1 : 1
				2a	48	
3	**4a** (2.6)	N_2O_5 (2.6)	CH_3CN	**1a**	64	2.1 : 1
				2a	31	
4	**4a** (2.6)	N_2O_5 (2.6)	CH_2Cl_2	**1a**	60	1.6 : 1
					38	
5	**4a** (22.8)[c]	$(NO_2)_2SiF_6$ (11.4)	CH_2Cl_2	**1a**	38	0.64 : 1
				2a	60 (58)	
6	**4b** (6.0)	N_2O_5 (6.0)	CH_2Cl_2	**2b**	63	—
7	**4b** (6.0)	$(NO_2)_2SiF_6$ (3.0)	CH_2Cl_2	**2b**	68 (45)	—
8	**4b** (6.0)	$(NO_2)_2SiF_6$ (3.0)	CH_3CN	**1b**	52	4 : 1
				2b	13	

[a] Concentrations of **4a**,**b** were 0.5 mol L^{-1}, except run *5*.
[b] The yield according to ^1H NMR data obtained using an internal quantitative reference. The yield of isolated product is given in parentheses.
[c] The concentration of **4a** was 2 mol L^{-1}.

vent, and concentration. In particular, the reaction in a weakly polar solvent (CH_2Cl_2) using N_2O_5 as nitrating agent (see Table 1, runs *4* and *6*) favors the formation of nitrocyanamides, whereas the process in a polar solvent (CH_3CN) with $(NO_2)_2SiF_6$ as nitrating agent (see Table 1, runs *1* and *8*) results in nitrocarbodiimides as major products. An increase in the reactant concentrations causes the proportion of nitrocyanamides to increase (see Table 1, run *5*).

Scheme 2



R = Bu^t(**a**), Me (**b**)

Reactants and conditions: $(NO_2)_2SiF_6$ or N_2O_5, −30→0 °C.

Nitration of trimethylsilylated carbodiimide **4a** (R = Bu^t) in CH_3CN using $(NO_2)_2SiF_6$ as nitrating agent gives compound **1a** in almost pure form (see Table 1, run *1*). In the case of carbodiimide **4b**, the reaction conducted under identical conditions yielded compounds **1b** and **2b** in a 4 : 1 ratio (see Table 1, run *8*).

Noteworthy is that nitration of trimethylsilylated carbodiimide **4b** (R = Me) in CH_2Cl_2 with N_2O_5 as nitrating agent affords pure compound **2b** (see Table 1, run *6*). The reaction of carbodiimide **4a** (R = Bu^t) performed under identical conditions led to **1a** and **2a** in a 1.6 : 1 ratio (see Table 1, run *4*).

The isomeric compounds **1** and **2** were also studied theoretically (Table 2). Geometry optimization and harmonic vibrational frequency calculations were carried out within the framework of the density functional theory (DFT) with the B3LYP hybrid potential and the 6-311++G(2df,2p) basis set using the Gaussian 09 program.[7] The calculated frequencies of all the structures optimized in the gas phase were checked for the absence of imaginary frequencies.

According to the total energy calculations, the carbodiimide structures **1** and the nitrocyanamide structures **2** differ insignificantly. The thermodynamically more stable

Table 2. Results of DFT calculations for pairs of isomers **1** and **2**

Compounds **1**, **2**	R	$-E'$ [a]	$-E''$ [b]	E [c] /kcal mol^{-1}
		a.u.		
a	Bu^t	510.538224	510.544728	4.1
b	Me	392.640573	392.638993	−1.0

[a] $E' = E_{tot}$ + ZPE is the total energy of nitrocyanamide **2** calculated with inclusion of zero-point vibrational energy correction (in atomic units).
[b] $E'' = E_{tot}$ + ZPE is the total energy for nitrocarbodiimide **1** calculated with inclusion of zero-point vibrational energy correction (in atomic units).
[c] $E = E' - E''$is the total energy difference between pairs of isomers **1** and **2**.

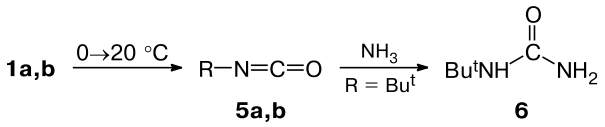
species were **1a** for R = Bu^t and **2b** for R = Me. These results are in agreement with the experimental product ratios. At the same time, the effect of the reaction conditions on the ratio of the products containing the same alkyl substituent suggests that the reaction is kinetically controlled just like the substitutive nitration reactions of trimethylsilylated carbodiimides we have studied previously.[3,8]

The structure of compound **1a** was confirmed by ^{13}C and ^{14}N NMR spectra. In the ^{14}N NMR spectrum, the signal of the nitro group ($\delta_N = -17$) is in the region characteristic of the (C=N—NO_2) fragment. This signal is significantly different from that of the nitro group in the ^{14}N NMR spectra of nitrocyanamides, where it undergoes an upfield shift by 20—40 ppm [8] (*cf.* $\delta_N = -41$ for **2a**).

In the ^{13}C NMR spectrum of compound **1a**, the signal of the carbon atom ($\delta_C = 117.5$) is in the range characteristic of the (=C=) fragment.[1] As to cyanamides, the signal of the carbon atom of the C≡N group undergoes an upfield shift to the region of δ 100—110 (see Ref. 1; *cf.* $\delta_C = 104.2$ ppm for **2a**).

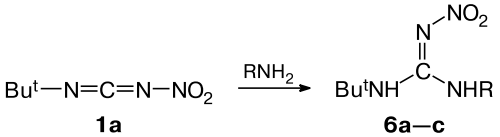
The structure of **1a** was also confirmed by the reactions with participation of this compound. At room temperature, this nitrocarbodiimide undergoes quantitative conversion to *tert*-butylisocyanate **5a** (Scheme 3) within 30 min. The tentative mechanism of this reaction is shown in Scheme 1. The progress of the reaction was monitored by ^1H NMR spectroscopy. The signal of **1a** ($\delta_H = 1.56$) gradually decreased and a signal of isocyanate **5a** ($\delta_H = 1.34$) developed simultaneously. The structure of **5a** was confirmed by the reaction with ammonia which afforded the expected compound, *N*-(*tert*-butyl)urea **6**.

Scheme 3



Reactions of nitrocarbodiimide **1a** with ammonia, *tert*-butylamine, and aniline result in the corresponding nitroguanidines in high yields (Scheme 4). These reactions also confirm the structure of this compound.

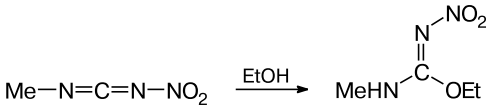
Scheme 4



6	R	Yield (%)
a	H	85
b	Bu	86
c	Ph	50

Compound **1b** is somewhat less stable than **1a**. Since it was not isolated in pure form, *viz.*, a mixture of **1b** and **2b** was obtained, it is of no concern as the starting compound for organic synthesis. The structure of **1b** was confirmed only by its reactions. Raising the temperature of the reaction mixture from 0 to 20 °C causes this nitrocarbodiimide to undergo a quantitative conversion to methylisocyanate **5b** (see Scheme 3). The reaction of compound **1b** with EtOH affords ethyl-*N*-methyl-*N*′-nitroimidocarbamate **7** (Scheme 5).

Scheme 5



Summing up, our study of the nitration of *N*-Alk-*N*′-(trimethylsilyl)carbodiimides (Alk = Me, Bu^t) by N_2O_5 or $(NO_2)_2SiF_6$ led to a novel method for the synthesis of alkyl(nitro)cyanamides and *N*-alkyl-*N*′-nitrocarbodiimides. *N*-(*tert*-Butyl)-*N*′-nitrocarbodiimide is the first representative of *N*-alkyl-*N*′-nitrocarbodiimides. Although this compound is unstable at room temperature, it can be used for the *in situ* synthesis of hardly accessible *N*,*N*′-substituted *N*′′-nitroguanidines.

Experimental

^1H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM 300 spectrometer operating at 300.13, 75.47, and 21.69 MHz, respectively. Chemical shifts are given relative to $SiMe_4$ (^1H, ^{13}C) or CH_3NO_2 (^{14}N, external reference, the upfield chemical shifts are negative). IR spectra were recorded on a Bruker ALPHA-T spectrometer. The reactions were monitored by TLC (Merck 60 F254). All reactions were carried out in anhydrous solvents under argon atmosphere. Silylated carbodiimides **4a,b** were obtained following a known procedure.[6]

Synthesis of *N*-alkyl-*N*′-nitrocarbodiimides 1a,b and alkyl(nitro)cyanamides 2a,b (general procedure). To a suspension of a nitrating agent (N_2O_5 or $(NO_2)_2SiF_6$), a solution of silylated carbodiimide (**4a** or **4b**) was added dropwise on stirring at −30 °C, the reaction mixture was maintained until complete dissolution of the suspension (about 20 min for $(NO_2)_2SiF_6$), the cooling bath was removed, and the temperature was allowed to raise to 0 °C over a period of 20 min. The reaction mixture was analyzed by ^1H NMR spectroscopy (see Table 1).

***N*-(*tert*-Butyl)-*N*′-nitrocarbodiimide (1a)** was obtained from silylated carbodiimide **4a** and $(NO_2)_2SiF_6$ (see Table 1, run *1*) following the general procedure. The solvent was evaporated *in vacuo* (1 Torr) at a bath temperature of at most 0 °C. The residue represented a white crystalline substance, which began to decompose above 10 °C. IR (deposition in a cryostat at −195 °C), ν/cm^{-1}: 1270, 1530 (NO_2); 2260—2290 (N=C=N). ^1H NMR (CD_2Cl_2, δ): 1.56 (s, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2, −70 °C,

δ): 29.3 (C(<u>C</u>H$_3$)$_3$); 62.3 (<u>C</u>(CH$_3$)$_3$); 117.5 (br.s, CN). ^{14}N NMR (CD$_2$Cl$_2$, −70 °C, δ): −17 (NO$_2$, $\nu_{1/2}$ = 25 Hz).

***tert*-Butyl(nitro)cyanamide (2a).** Cyanamide **2a** was obtained from silylated carbodiimide **4a** and $(NO_2)_2SiF_6$ (see Table 1, run *5*) following the general procedure. The solvent was removed *in vacuo*, the residue was dissolved in a minimum amount of pentane, cooled to −70 °C, and crystals precipitated were filtered off. Cyanamide **2a** (1.89 g, 58%) was obtained, m.p. 36—38 °C. Found (%): C, 42.10; H, 6.24; N, 29.03. $C_5H_9N_3O_2$. Calculated (%): C, 41.95; H, 6.34; N, 29.36. IR (KBr), ν/cm^{-1}: 1300, 1620 (NO$_2$); 2250 (CN). ^{1}H NMR (CD$_2$Cl$_2$, δ): 1.63 (s, 9 H, C(<u>C</u>H$_3$)$_3$). ^{13}C NMR (acetone-d$_6$, δ): 26.1 (C(<u>C</u>H$_3$)$_3$); 67.0 (<u>C</u>(CH$_3$)$_3$); 104.2 (CN). ^{14}N NMR (CD$_2$Cl$_2$, δ): −41 (NO$_2$, $\nu_{1/2}$ = 15 Hz).

Methyl(nitro)cyanamide (2b). Cyanamide **2b** was obtained following the general procedure (see Table 1, run *7*), the solvent was removed *in vacuo*, and the residue was distilled. Cyanamide **2b** (0.27 g, 45%) was obtained, b.p. 88—89 °C (13 Torr). Found (%): C, 23.83; H, 3.11; N, 41.29. $C_2H_3N_3O_2$. Calculated (%): C, 23.77; H, 2.99; N, 41.58. IR (KBr), ν/cm^{-1}: 1300, 1620 (NO$_2$); 2250 (CN). ^{1}H NMR (CD$_2$Cl$_2$, δ): 3.63 (s, 3 H, CH$_3$).

Ethyl-*N*-methyl-*N*´-nitroimidocarbamate (7) (reaction of *N*-methyl-*N*´-nitrocarbodiimide 1b with EtOH). To a suspension of $(NO_2)_2SiF_6$ (0.8 g, 0.34 mmol) in anhydrous MeCN (5 mL), a solution of freshly distilled carbodiimide **4b** (0.87 g, 0.68 mmol) in anhydrous MeCN (10 mL) was added dropwise over a period of 40 min on stirring at −30 °C. The reaction mixture was stirred at −25 °C until complete dissolution of nitronium salt (20 min) and the solvent was removed *in vacuo* at the same temperature. The residual compound **1b** was cooled to −40 °C, anhydrous EtOH (5 mL) was added, and the reaction mass was allowed to stay at −10 °C for 16 h. Then, the solvent was evaporated *in vacuo*, the residue was extracted with AcOEt (10 mL), the solvent was removed *in vacuo*, and the residue was recrystallized from a hexane—AcOEt mixture. Nitroimidocarbamate **7** (0.46 g, 46%) was obtained, m.p. 95—96 °C. Found (%): C, 32.44; H, 6.05; N, 28.70. $C_4H_9N_3O_3$. Calculated (%): C, 32.64; H, 6.18; N, 28.56. IR (KBr), ν/cm^{-1}: 1250, 1359, 1460, 1548, 1635. ^{1}H NMR (CD$_2$Cl$_2$, δ): 1.36 (t, 3 H, CH$_3$, *J* = 7.1 Hz); 2.97 (s, 3 H, NCH$_3$); 4.35 (q, 2 H, CH$_2$, *J* = 7.1 Hz).

The synthesis of substituted *N*-(*tert*-butyl)-*N*´-nitroguanidines 6 (general procedure). A solution of *N*-(*tert*-butyl)-*N*´-nitrocarbodiimide (**1a**) prepared following the general procedure (see Table 1, run *1*) was evaporated by one third when maintaining the temperature at most at 0 °C, cooled to −30 °C, and a solution of the equimolar amount of amine in 2 mL of MeCN (or excess gaseous ammonia) was added dropwise on stirring. The cooling bath was removed, the temperature was allowed to raise to 20 °C, the solvent was removed *in vacuo*, and the solid residue was recrystallized.

***N*-(*tert*-Butyl)-*N*´-nitroguanidine (6a).** Yield 85%, m.p. 201—202 °C (from H$_2$O; *cf.* 199—201 °C from Ref. 9). Compound **6a** was found to be identical to the authentic sample in its IR spectrum. ^{1}H NMR (acetone-d$_6$, δ): 1.43 (s, 9 H, C(CH$_3$)$_3$); 6.72 (br.s, 1 H, N<u>H</u>—Bu^t); 7.49 (br.s, 2 H, NH$_2$). ^{13}C NMR (acetone-d$_6$, δ): 29.5 (C(<u>C</u>H$_3$)$_3$); 52.8 (<u>C</u>(CH$_3$)$_3$); 160.1 (<u>C</u>=NNO$_2$). ^{14}N NMR (acetone-d$_6$, δ): −12 (NO$_2$, $\nu_{1/2}$ = 23 Hz); −275 (<u>N</u>H—Bu^t, $\nu_{1/2}$ = 350 Hz); −305 (NH$_2$, $\nu_{1/2}$ = 320 Hz).

***N,N*´-Di-*tert*-butyl-*N*´´-nitroguanidine (6b).** Yield 86%, m.p. 96—98 °C (from EtOH—H$_2$O). Found (%): C, 49.79; H, 9.43; N, 26.13. $C_9H_{20}N_4O_2$. Calculated (%): C, 49.98; H, 9.32; N, 25.92. ^{1}H NMR (acetone-d$_6$, δ): 1.48 (s, 18 H, C(CH$_3$)$_3$); 7.18 (br.s, 2 H, N<u>H</u>—Bu^t); ^{13}C NMR (acetone-d$_6$, δ): 29.8 (C(<u>C</u>H$_3$)$_3$); 53.2 (<u>C</u>(CH$_3$)$_3$); 157.6 (<u>C</u>=NNO$_2$). ^{14}N NMR (acetone-d$_6$, δ): −14 (NO$_2$, $\nu_{1/2}$ = 23 Hz); −270 (NH, $\nu_{1/2}$ = 500 Hz).

***N*-(*tert*-Butyl)-*N*´´-nitro-*N*´-phenylguanidine (6c).** The yield was 50%, m.p. 116—118 °C (from EtOH—H$_2$O mixture). Found (%): C, 55.99; H, 6.90; N, 23.97. $C_{11}H_{16}N_4O_2$. Calculated (%): C, 55.92; H, 6.83; N, 23.71. ^{1}H NMR (acetone-d$_6$, δ, *J*/Hz): 1.44 (s, 9 H, C(CH$_3$)$_3$); 5.93 (br.s, 1 H, N<u>H</u>—Bu^t); 7.33 (t, 1 H, H(4´), *J* = 7.3); 7.39 (d, 2 H, H(2´), H(6´), *J* = 7.3); 7.47 (t, 2 H, H(5´), H(3´), *J* = 7.3); 10.38 (br.s, 1 H, N<u>H</u>—Ph). ^{13}C NMR (acetone-d$_6$, δ): 29.4 (C(<u>C</u>H$_3$)$_3$); 53.9 (<u>C</u>(CH$_3$)$_3$); 126.4, 130,8 (C(2´), C(3´), C(5´), C(6´)); 128.0 (C(4´)); 136.6 (C(1´)); 157.4 (<u>C</u>=NNO$_2$). ^{14}N NMR (acetone-d$_6$, δ): −14 (NO$_2$, $\nu_{1/2}$ = 30 Hz); −273 (NH, $\nu_{1/2}$ = 650 Hz).

Thermal decomposition of *N*-(*tert*-butyl)-*N*´-nitrocarbodiimide (1a). A solution of **1a** (5 mL) prepared following the general procedure (see Table 1, run *1*) was evaporated by one third when maintaining the temperature at most at 0 °C, then kept at 20 °C for 30 min, and *tert*-butylisocyanate **5a** (δ = 1.34) was identified by comparing its ^{1}H NMR spectrum with that of the authentic sample.[10] Ammonia was bubbled through the solution, the solvent was evaporated *in vacuo*, and crystals were washed with hexane. *N*-(*tert*-butyl)urea **6** (259 mg, 86%) was obtained, m.p. 181—183 °C (from Et$_2$O; *cf.* 182—184 °C from Ref. 10), no m.p. depression when mixed with the authentic sample; identical to the authentic sample in its IR spectrum.

Thermal decomposition of *N*-methyl-*N*´-nitrocarbodiimide (1b). A solution **1b** prepared following the general procedure (see Table 1, run *8*) was heated to 20 °C and methylisocyanate (δ = 3.00) was identified by comparing its ^{1}H NMR spectrum with that of the authentic sample.[11]

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