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# Synthesis, Structural Studies and Desilylation Reactions of Some N-2-(Trimethylsilyl)ethyl-N-nitrosocarbamates

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**Synthesis, Structural Studies and Desilylation  
Reactions of Some N-2-(Trimethylsilyl)ethyl-N-  
nitrosocarbamates**

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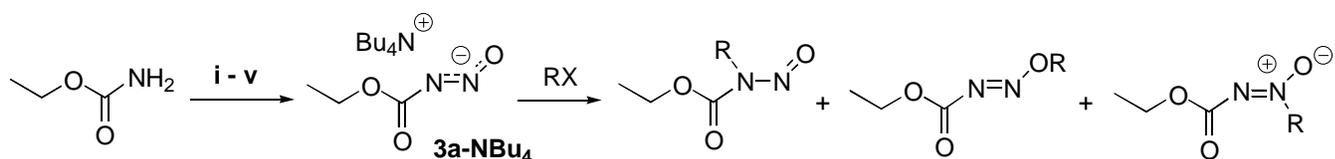
**Abstract:** The present report describes the preparation and characterization of several N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates, designed as precursors to thermally unstable secondary N-nitrosocarbamate anions *via* fluoride-assisted cleavage. X-ray structural studies demonstrate that the core N-nitrosocarbamate moiety has a nearly planar geometry, with an *s-E* orientation at the N – N bond. DFT calculations (*B3LYP/6-31+G(d)*) reproduce accurately the structural features of the title compounds and detailed conformational analysis at the same level of theory addresses the long-standing issue of preferred geometries for three classes of related structures: N-nitrosocarbamates, N-nitrosoureas and N-nitrosoamides. Desilylation studies demonstrate that both the solvent and the fluoride concentration influence the rate of the process.

**Keywords:** N-nitrosocarbamates, X-ray structures, 2-(trimethylsilyl)ethyl group, desilylation, DFT calculations

## Introduction

The work reported in this article is a reflection of our continuing efforts to generate and study secondary N-nitrosocarbamates, a class of thermally unstable and chemically labile structures.<sup>1</sup> The only known example of a secondary N-nitrosocarbamate, N-nitrosourethane, was prepared more than a 100 years ago from urethane, in a sequence of nitration followed by partial reduction, and conversion to the silver salt.<sup>2</sup> Its chemistry was recently revisited, the authors using primarily the organic-soluble tetrabutylammonium salt (Scheme 1).<sup>1</sup>

### Scheme 1

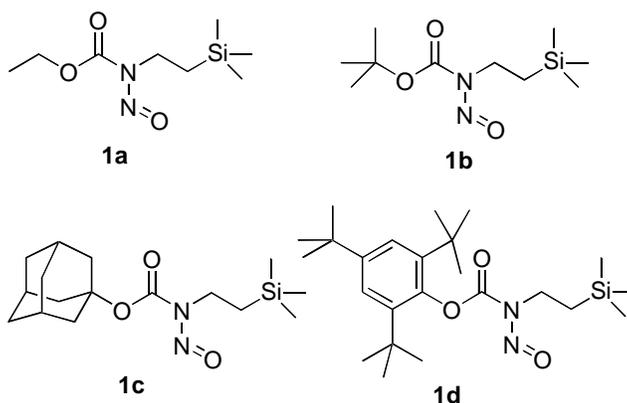


i: KNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>; ii: NH<sub>3</sub>-gas; iii: Zn/AcOH; iv: AgNO<sub>3</sub>; v: Bu<sub>4</sub>NBr  
R = Me, Et, *i*-Pr, benzyl

The experimental studies and gas-phase calculations led to the conclusion that the N-nitrosourethane anion is a typical ambident nucleophile, yielding products of both N-alkylation and O-alkylation, and the ratio of N- to O-alkylated product depends, as expected, on the steric demand of the alkyl halide. Smaller and less branched alkyl groups lead primarily to N-alkylation, while the O-alkylated product becomes predominant with the use of more sterically hindered substrates. In addition, the theoretical analysis and kinetic measurements demonstrated that the N-nitrosourethane anion and its O-alkylated derivatives undergo thermal decomposition in a concerted fashion, through a four-membered cyclic TS.

Certain questions, however, were not addressed, such as the potential influence of the size of the carbamate alkyl (or aryl) group on the thermal stability of the resultant N-

nitrosocarbamate anions and their O-alkylated derivatives. In addition, varying the size of the carbamate alkyl (aryl) group would be expected to influence the regioselectivity in their alkylation reactions. Hence, our goal has been to prepare and study other secondary N-nitrosocarbamates, with varying size of the carbamate alkyl (aryl) group, in an attempt to prepare exceptionally stable structures, suitable for isolation and solid-state studies. The initial efforts were focused on adaptation of the synthetic strategy used in the preparation of N-nitrosourethane salts. Such attempts have proved futile, prompting us to design and implement a new methodology, based on the fluoride-assisted cleavage of a 2-(trimethylsilyl)ethyl group (TMSE) incorporated into thermally and chemically stable N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates. The TMSE group has been used in the past as a protecting group for alcohols and carboxylic acids<sup>3</sup>, thiols<sup>4,5</sup> and phosphates.<sup>6</sup> In a recent article Bottaro et al. described its use as a removable moiety at a nitrogen center, in the generation of the dinitroamide anion.<sup>7</sup>



**Figure 1.** Four N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates with a gradually increasing size of the carbamate ester group.

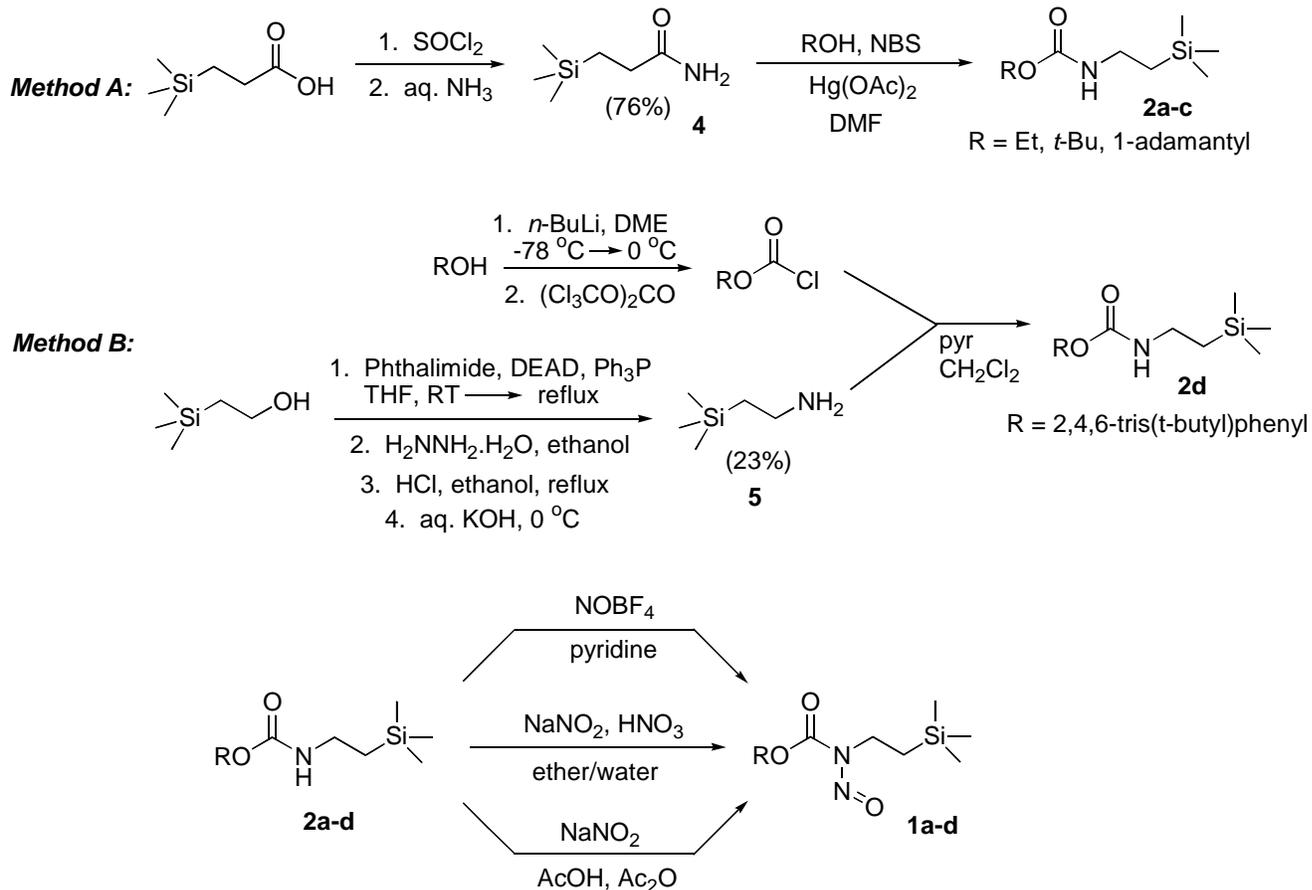
The present report outlines the details of our synthetic work leading to the preparation of four N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates (**1a-d**, Figure 1) and the current results from desilylation experiments. This article also reports the first crystal structures of N-

nitrosocarbamates, compounds **1c** and **1d**, and compares those with results from gas-phase DFT calculations (*B3LYP/6-31+G(d)*).

## Results and Discussion

*A. Synthesis.* The preparation of carbamates **1a-d** is outlined in Scheme 2. The corresponding alcohol (for compounds **1a-c**) or 2,4,6-tris(*t*-butyl)phenol (for compound **1d**) is converted to an N-2-(trimethylsilyl)ethylcarbamate (**2a-d**), by means of one of two general methods (*A* and *B*). *Method A* utilizes a Hoffmann-type rearrangement reaction of 3-(trimethylsilyl)propanamide (**4**)<sup>8</sup> with the corresponding alcohol, in the presence of NBS and Hg(OAc)<sub>2</sub>.<sup>9</sup> The reaction works very well for preparation of the ethyl carbamate (**2a**), but the yields drop significantly for the *t*-butyl (**2b**) and 1-adamnyl (**2c**) carbamates, and no reaction is observed in an attempt to generate the 2,4,6-tris(*t*-butyl)phenyl carbamate (**2d**). The latter was prepared using an alternative approach (*Method B*) that includes deprotonation of the starting phenol followed by reaction with triphosgene, leading to the generation of 2,4,6-tris(*t*-butyl)phenyl chloroformate.<sup>10</sup> Reaction of the chloroformate with 2-(trimethylsilyl)ethanamine (**5**) affords the carbamate **2d**. Compound **5** was prepared according to a patented procedure utilizing 2-(trimethylsilyl)ethanol, which is converted, in a Mitsunobu reaction, to N-2-(trimethylsilyl)ethylphthalimide.<sup>11</sup> The phthalimide, upon reaction with hydrazine hydrate followed by acidification, yields 2-(trimethylsilyl)ethanamine hydrochloride. In strongly basic conditions the hydrochloride is converted to the free amine **5**.

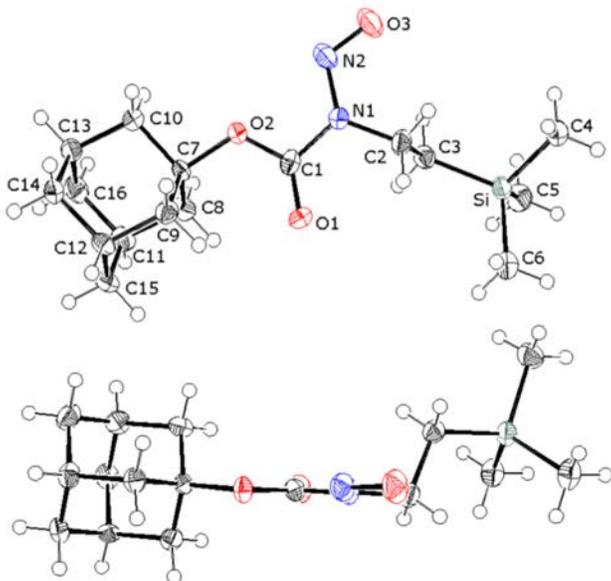
## Scheme 2



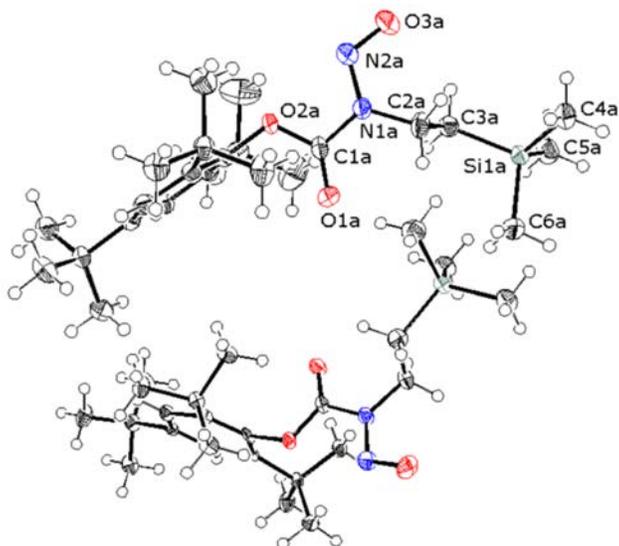
Nitrosation reactions were carried out utilizing three different approaches. Nitrosation in a two-phase (water – ether) system was carried out, with the nitrosating agent generated in the aqueous layer, upon reaction of  $\text{NaNO}_2$  with  $\text{HNO}_3$ .<sup>12</sup> The method gives satisfactory results for carbamates **2a-b**, but the yield is significantly reduced in the case of **2c** and only traces of nitrosated product are observed in the reaction of **2d**. Better yields for carbamates **2a-c** (but not **2d**) were observed when the nitrosation was performed in anhydrous conditions, with  $\text{NOBF}_4$  as a nitrosating agent and the presence of pyridine base.<sup>13</sup> The difficulties in nitrosation of **2d** have to be attributed to the steric effect (hindrance) of the two *ortho*-positioned *t*-butyl groups of the aromatic ring. Successful nitrosation of **2d** was eventually achieved following a modified

version of the method of Overberger and Anselm, which employs  $\text{NaNO}_2$  in a mixture of acetic acid and acetic anhydride.<sup>14</sup>

**B. Structural Studies.** X-ray crystallographic analysis was conducted on compounds **1c** and **1d**, providing the first reported crystal structures of N-nitrosocarbamates (Figures 2 and 3). The asymmetric unit in the unit cell of **1d** contains two unique molecules and the only major difference between them is the value of one of the dihedral angles in the TMSE group. Experimental and theoretical data on selected bond lengths, angles and torsional angles are shown in Table 1, together with structural parameters for N-methyl-N-nitroso-*p*-nitrobenzamide (**MNNB**) and N-methyl-N-nitrosoourea (**MNU**).<sup>15</sup> Bond lengths in **1c** and **1d** are more comparable to those in the N-nitrosoamide **MNNB**, particularly the N=O and C=O bonds. The deviations are slightly greater between **1c-d** and **MNU**. The C=O bond is longer in **MNU**, while the N – N bond is  $\sim 0.04$  Å shorter.



**Figure 2.** Two orientations of the X-ray structure of 1-adamantyl N-nitroso-N-(2-trimethylsilyl)ethyl carbamate (**1c**). The thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are given arbitrary radii.



**Figure 3.** X-ray structure of 2,4,6-tris(*t*-butyl)phenyl *N*-nitroso-*N*-(2-trimethylsilyl)ethylcarbamate (**1d**). The asymmetric unit contains two unique molecules. The thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are given arbitrary radii.

The *N*-nitrosocarbamate sub-structure in **1c** and **1d**, O–C(=O)–N–N=O, is very nearly planar, with a slightly greater twist around the C(1) – N(1) bond in the case of **1c**. The overall distortion from planarity is larger than the observed in **MNU**, but less than that of the *N*-nitrosoamide **MNNB**, particularly the N(2) – N(1) – C(1) – O(1) dihedral angle. The 2-(trimethylsilyl)ethyl group in both **1c** and **1d** adopts an *anti* conformation. The values for the dihedral angle C(4) – Si – C(3) – C(2) demonstrate that in the case of **1c** and one of the unique molecules in the unit cell of **1d** there is a nearly ideal *gauche* positioning of the C(2)H<sub>2</sub>-group relative to the methyl groups at the silicon center. The second unique structure for **1d** exhibits an almost 18° deviation from the *gauche*-orientation.

As evident from Table 1, the theoretically derived structural data are in very close agreement with the experimental parameters. The reported results are from gas-phase *DFT* studies at the *B3LYP/6-31+G(d)* level of theory.<sup>16-18</sup>

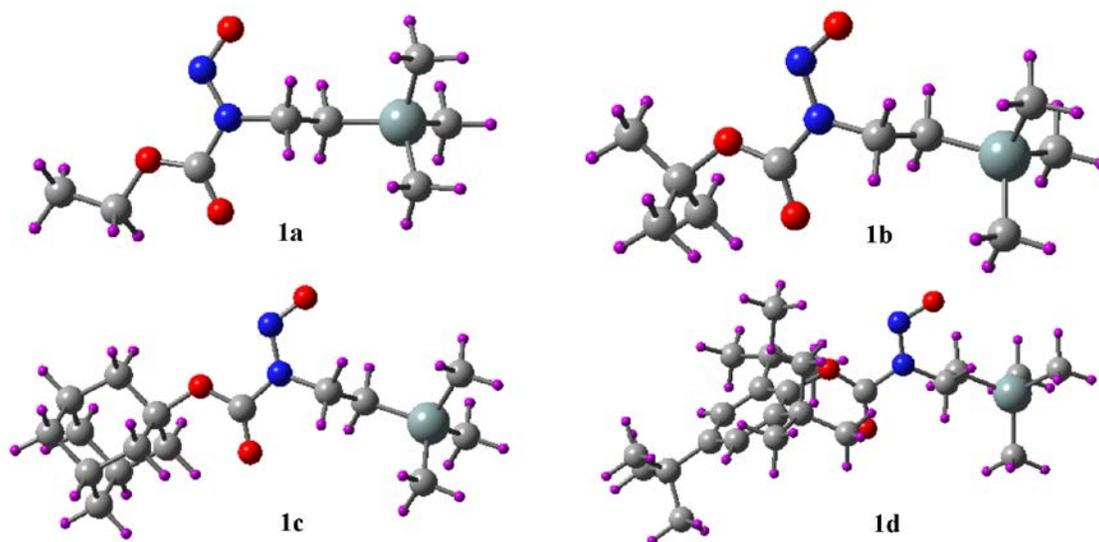
**Table 1.** Selected experimental (**bold characters**) and theoretical bond lengths (Å) and angles (deg) for N-nitrosocarbamates **1a** – **1d**, N-methyl-N-nitroso-*p*-nitrobenzamide (**MNNB**) and N-methyl-N-nitrosourea (**MNU**). Theoretical data from global minimum structures optimized at the *B3LYP/6-31+G(d)* level.

Bond lengths and angles <sup>a</sup>	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b> <sup>b</sup>	<b>MNNB</b> <sup>c</sup>	<b>MNU</b> <sup>c</sup>
O(1) – C(1)	- 1.216	- 1.217	<b>1.200(4)</b> 1.217	<b>1.203(5), 1.197(5)</b> 1.210	<b>1.204(5)</b> 1.219	<b>1.215(2)</b> 1.220
N(1) – N(2)	- 1.369	- 1.366	<b>1.360(4)</b> 1.370	<b>1.374(5), 1.359(5)</b> 1.369	<b>1.352(5)</b> 1.369	<b>1.326(2)</b> 1.353
N(1) – C(1)	- 1.412	- 1.418	<b>1.417(4)</b> 1.419	<b>1.410(4), 1.405(6)</b> 1.413	<b>1.405(6)</b> 1.416	<b>1.431(2)</b> 1.431
O(3) – N(2)	- 1.218	- 1.220	<b>1.220(3)</b> 1.220	<b>1.231(4), 1.222(6)</b> 1.218	<b>1.218(4)</b> 1.216	<b>1.231(2)</b> 1.220
O(2) – C(1)	- 1.333	- 1.328	<b>1.323(4)</b> 1.328	<b>1.331(5), 1.342(4)</b> 1.345	- -	- -
Si – C(3)	- 1.912	- 1.911	<b>1.880(3)</b> 1.911	<b>1.872(5), 1.886(4)</b> 1.912	- -	- -
N(2) – N(1) – C(1)	- 118.0	- 118.3	<b>118.3(2)</b> 118.3	<b>117.1(3), 117.4(3)</b> 118.2	<b>116.9(4)</b> 117.8	<b>116.6(2)</b> 117.1
O(3) – N(2) – N(1)	- 114.0	- 114.1	<b>113.2(2)</b> 114.1	<b>112.6(4), 113.0(4)</b> 114.0	<b>113.8(4)</b> 113.8	<b>114.4(2)</b> 116.3
C(1)–N(1)–N(2)–O(3)	- -178.0	- -178.0	<b>-177.2(3)</b> -177.4	<b>-176.6(3), -176.8(5)</b> -178.4	<b>-176.8</b> -173.3	<b>-177.7</b> 180.0
N(2)–N(1)–C(1)–O(1)	- 178.4	- 178.1	<b>173.4(3)</b> 175.8	<b>177.3(3), 176.7(5)</b> 179.2	<b>165.4</b> 162.5	<b>178.5</b> 180.0
C(4)–Si–C(3)–C(2)	- -59.0	- -60.2	<b>-56.7(3)</b> -62.9	<b>-76.7(3), -56.3(4)</b> -59.5	- -	- -

<sup>a</sup> Atom labels in accordance with the crystallographic designation for compounds **1c-d**. <sup>b</sup> X-ray data given for each of the two unique molecules in the asymmetric unit of **1d**. <sup>c</sup> X-ray data from Ref. 15.

All optimized minima structures, except for those of carbamate **1d**, were further validated by frequency calculations at the same level of theory and they had sets of only positive second derivatives. Values of Gibbs free energy differences were obtained after frequency calculations.

The computed values for bond lengths are usually within  $\pm 0.01$  Å of the experimental ones and the differences between theoretical and experimental values for angles and dihedral angles are usually within  $\pm 3^\circ$ . In general, DFT tends to slightly exaggerate the planarity of the core structures for both the carbamates **1c-d** and **MNU**. The global minimum structures for the four N-nitrosocarbamates **1a-d** are shown in Figure 4.



**Figure 4.** Optimized global minima structures of compounds **1a-d**. Data from *B3LYP/6-31+G(d)* calculations.

C. Conformational Analysis. Calculations demonstrate that each of the compounds **1a-d** has a set of rotamers with respect to both the C(1) – N(1) bond (*s-trans* and *s-cis*) and the N(1) – N(2) bond (*s-E* and *s-Z*). Table 2 lists the relative Gibbs free energies and the Boltzmann statistical contributions for the rotamers of structures **1a-c**, **MNU** and **MNNB**. In each case the corresponding (*s-E*, *s-trans*) isomer is the global minimum, and in the cases of **1c**, **1d**, **MNU** and **MNNB** these are in agreement with the *X-ray* crystal structures. Nakayama and Kikuchi reached similar conclusions in their recent theoretical studies of several N-nitroso compounds.<sup>19</sup> In almost all of the studied cases the (*s-E*, *s-cis*) isomer is the lowest energy local minimum. One

exception is **MNU**, in whose case the lowest energy local minimum is the (*s-Z*, *s-trans*) structure. The latter is most likely due to stabilizing hydrogen bonding realized between the NH<sub>2</sub> and NO groups in **MNU**, which has been suggested earlier based on NMR and IR studies.<sup>20</sup> In the cases of **MNNB** and **MNU** calculations could not locate a minimum structure corresponding to the (*s-Z*, *s-cis*) isomer, which appears to be due to steric repulsion.

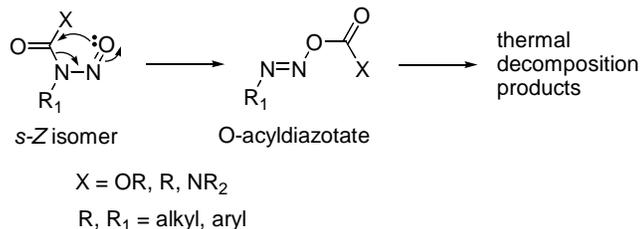
**Table 2.** Relative *Gibbs* free energies of conformers of N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates **1a** – **1c**, N-methyl-N-nitroso-*p*-nitrobenzamide (**MNNB**) and N-methyl-N-nitrosourea (**MNU**), with respect to rotation around the N(1) – N(2) bond (*s-E* and *s-Z*) and the C(1) – N(1) bond (*s-cis* and *s-trans*).<sup>a</sup> Data from *B3LYP/6-31+G(d)* geometry optimizations and frequency calculations. Boltzmann contributions (%) at 298 K given in parentheses.

	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>MNNB</b>	<b>MNU</b>
<i>s-E</i> , <i>s-trans</i>	0.0 (89.9)	0.0 (99.5)	0.0 (97.2)	0.0 (100)	0.0 (99.9)
<i>s-E</i> , <i>s-cis</i>	+1.3 (10.1)	+3.2 (0.5)	+2.1 (2.8)	+6.0 (~ 0)	+9.2 (~ 0)
<i>s-Z</i> , <i>s-trans</i>	+5.5 (~ 0)	+6.2 (~ 0)	+5.8 (~ 0)	+6.3 (~ 0)	+3.9 (0.1)
<i>s-Z</i> , <i>s-cis</i>	+6.7 (~ 0)	+7.7 (~ 0)	+6.0 (~ 0)	<sup>b</sup>	<sup>b</sup>

<sup>a</sup> Atom labels in accordance with the crystallographic designation for compound **1c**. <sup>b</sup> Minimum structure was not located.

The currently available experimental and theoretical data provide valuable information towards resolving the issue of thermal stability of N-nitroso compounds, which in turn bears relation to the relative stability of the *s-E* and *s-Z* conformations. In the *s-Z* conformation there is spatial proximity of the nitroso group oxygen center to the carbonyl carbon, and an intramolecular reaction becomes possible, leading to decomposition (Scheme 3).<sup>21,22</sup> No such reaction is feasible starting with the *s-E* isomer. Thus, it seems that greater relative stability of the *s-E* isomer is a pre-requisite for thermal stability of the corresponding N-nitroso compound.

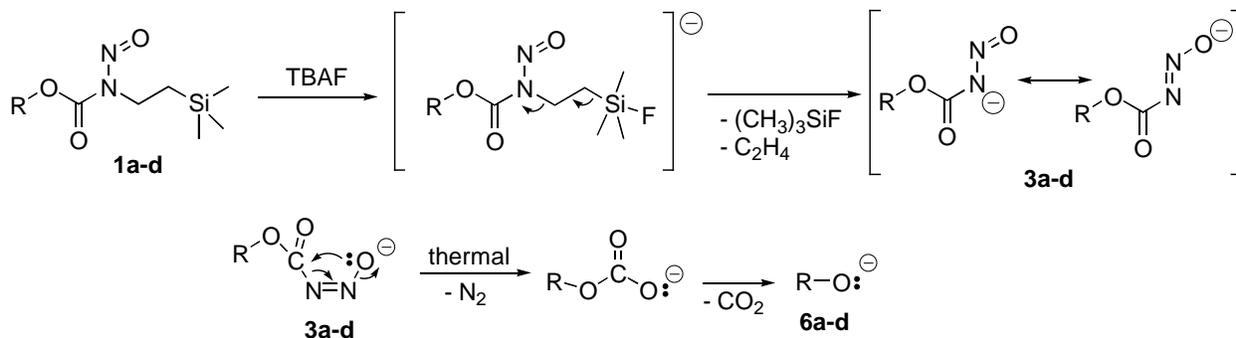
### Scheme 3



Our results and other recent studies are in agreement that the *s-E* isomer is indeed the predominant form in the solid state and in the gas phase.<sup>15,19,23</sup> However, it should be noted that the NMR and IR studies of Snyder and Stock were interpreted in favor of the *s-Z* isomers of several N-alkyl- and N,N'-dialkyl-N-nitrosoureas being exclusively present in solution.<sup>20</sup>

D. Desilylation studies. The use of the TMSE group as a temporary protecting group at a nitrogen center was reported recently in the successful preparation of the dinitroamide anion from N-2-(trimethylsilyl)ethyl-N,N-dinitroamine.<sup>7</sup> The dinitroamide anion is a resonance-stabilized species with a delocalized negative charge and reduced basicity. Thus, not surprisingly, relatively mild deprotection conditions were employed for the cleavage reaction.

### Scheme 4



Secondary N-nitrosocarbamate anions are also characterized by resonance stabilization and charge delocalization.<sup>1</sup> It has been estimated, for example, that N-nitrosourethane is more acidic than acetic acid.<sup>24</sup> Hence, cleavage of the TMSE group, according to Scheme 4, would be expected to occur readily. One significant obstacle arises from the fact that structures **3a-d** have been demonstrated (in the case of **3a**)<sup>1</sup> or are anticipated to be thermally unstable, thus making it a challenge to find the appropriate conditions for desilylation that would be sufficiently mild not to trigger further decomposition of **3a-d** to the corresponding alkoxide (phenoxide) anion **6a-d**.

Our current results are based on studies conducted in DMF or acetonitrile as solvents, with Bu<sub>4</sub>NF·3H<sub>2</sub>O as a fluoride source. Experiments were performed using compounds **1a**, with available independent literature data for comparison<sup>1</sup>, and **1d**, whose decomposition was particularly easy to follow by NMR, giving distinct peaks in the aromatic region. All experiments were performed on an NMR scale, in deuterated solvents, so that the progress of reaction and product composition could be monitored directly. Results from the desilylation experiments are shown in Table 3.

*a/ Role of the solvent and temperature.* The studied reactions showed clear dependence on the nature of the solvent, with the rates being consistently higher in DMF. Thus, in the case of **1a** desilylation is complete in 0.5 h even at -15 °C, while in acetonitrile complete desilylation of **1a** requires 16 h even at +10 °C. The desilylation reaction is slower in the case of **1d**, and the solvent has an even more pronounced effect. Compound **1d** is practically stable in acetonitrile at +10 °C and only traces of decomposition products were detected after 24 h and 5-fold excess of Bu<sub>4</sub>NF.

**Table 3.** Experimental conditions and product composition data for desilylation reactions of carbamates **1a** and **1d**.

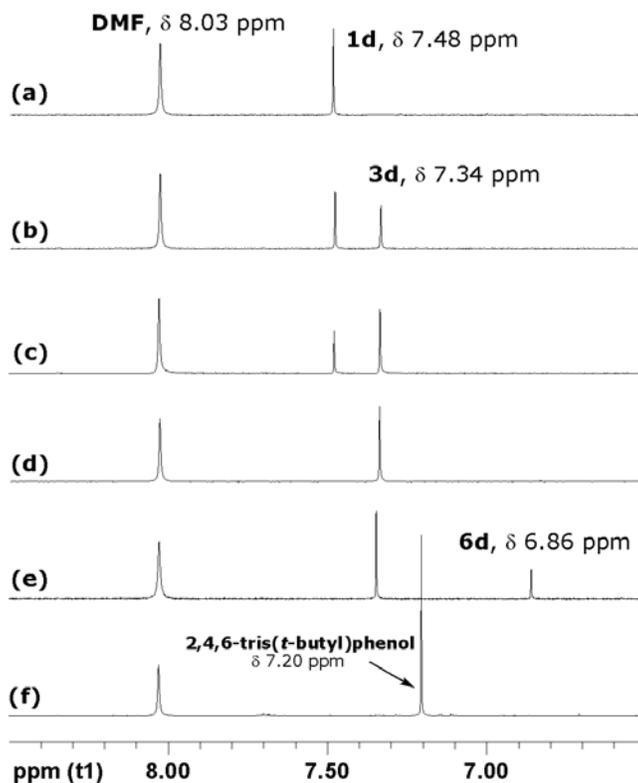
Carbamate	solvent	Temperature [°C]	Bu <sub>4</sub> NF.3H <sub>2</sub> O [# equivalents]	Time	Anion <b>3</b> (%)	Anion <b>6</b> (%)
<b>1a</b>	DMF	-15	3	30 min	29	71 <sup>a</sup>
	DMF	-15	5	30 min	31	69
	DMF	+5	1	24 h	29 <sup>b</sup>	57
	DMF	+10	5	10 min	19	81
	CH <sub>3</sub> CN	+5	5	22 h	35	65
	CH <sub>3</sub> CN	+10	5	16 h	41	59
	<b>1d</b>	DMF	+10	3	48 h	72 <sup>c</sup>
DMF		+5	5	23 h	98 <sup>e</sup>	0
CH <sub>3</sub> CN		+10	5	24 h	0 <sup>f</sup>	< 1

<sup>a</sup> Structure validated by comparison with authentic sample of **6a-NMe<sub>4</sub>** in DMF-*d*<sub>7</sub>. <sup>b</sup> Reaction not complete after 24 h, with 14% residual carbamate **1a** present in the mixture. <sup>c</sup> Reaction not complete after 48 h, with 13% residual carbamate **1d** present in the mixture. <sup>d</sup> Structure validated by comparison with a sample of **6d-Li** in DMF-*d*<sub>7</sub>. <sup>e</sup> 2% residual carbamate **1d**. <sup>f</sup> 98% residual carbamate **1d**.

*b/ Amount of Bu<sub>4</sub>NF.3H<sub>2</sub>O.* As Table 3 indicates, the process required some excess of the tetrabutylammonium salt in order to be conducted to completion. In the case of **1a** and 1 equivalent of Bu<sub>4</sub>NF.3H<sub>2</sub>O, the reaction mixture after 24 h at 5 °C showed 14% of unreacted carbamate and the desilylation of **1d** with 3 equiv. Bu<sub>4</sub>NF.3H<sub>2</sub>O at +10 °C was not complete even after 48 h. Typical runs were conducted with 3 to 5-fold excess of Bu<sub>4</sub>NF.3H<sub>2</sub>O. We anticipate that the relative amounts of fluoride and rates of desilylation are influenced by the fact that the used fluoride source is a trihydrate. It has been shown, both spectroscopically and theoretically, that the fluoride anion forms hydrate clusters with varying number of water molecules.<sup>25-27</sup> This is certain to affect the anion's reactivity and decelerate the desilylation process.

*c/ Product composition.* The immediate product of desilylation in each case is the corresponding N-nitrosocarbamate anion **3**. However, in most runs, particularly of carbamate **1a**, anion **6** was observed as well, in varying quantities. In the case of **1a** the product structures, **3a** and **6a**, were validated by comparison with the available in literature spectral data in

acetonitrile solvent.<sup>1</sup> In DMF, the NMR pattern of the product mixtures is similar, and we have assigned the quartet at  $\delta$  4.14 and the triplet at  $\delta$  1.23 to the anion **3a**, while the quartet at  $\delta$  3.50 and triplet at  $\delta$  1.06 were assigned to **6a**, after comparison with the spectrum of an independently prepared sample of **6a-NMe<sub>4</sub>** in DMF-*d*<sub>7</sub>. The maximum amount of **3a** in the studied cases, determined by integration of NMR signals, was about 40%, but in most runs it was lower and not significantly affected by temperature or the nature of the solvent. The desilylation of **1d** on the other hand occurs with predominant and in some cases exclusive formation of the desired product **3d**, whose signal for the aromatic H-atoms appears at  $\delta$  7.34 ppm in deuterated DMF (Figure 5a-d).

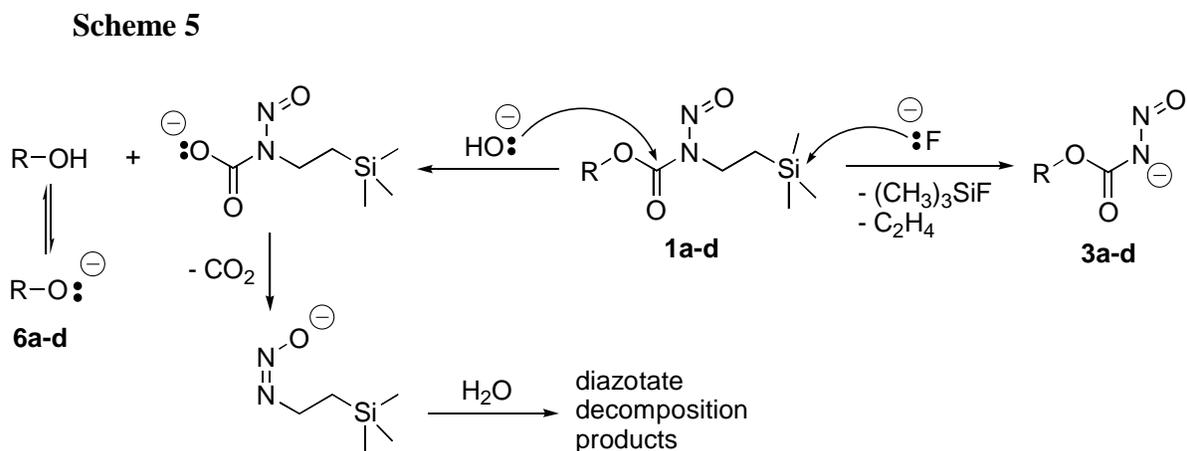


**Figure 5.** (a) Carbamate **1d** in DMF-*d*<sub>7</sub>; (b) – (d) Carbamate **1d** with 5 equivalents of Bu<sub>4</sub>NF<sub>3</sub>·3H<sub>2</sub>O in DMF-*d*<sub>7</sub>: (b) 1 hour at +5 °C; (c) 3 hours at +5 °C; (d) 23 hours at +5 °C; (e) Anion **3d** after 3 hours at +45 °C; (f) Anion **3d** after 5 days at ambient temperature. All spectra referenced to the solvent (DMF-*d*<sub>7</sub>,  $\delta$  8.03 ppm).

As Figure 5e demonstrates, subjection of **3d** to elevated temperature leads to its decomposition. The product of decomposition has a signal for the aromatic protons at  $\delta$  6.86 ppm, and was identified as the aryloxide anion **6d**. For comparison, we prepared the lithium salt of 2,4,6-tris(*t*-butyl)phenol by deprotonation with *n*-BuLi. The resultant **6d** – **Li** has a signal in the aromatic region at  $\delta$  6.90 ppm, in DMF-*d*<sub>7</sub>. Anion **6d**, in the presence of water in the reaction mixture, is eventually protonated and after several days at ambient temperature the sole product is 2,4,6-tris(*t*-butyl)phenol, whose signal in the aromatic region is at  $\delta$  7.20 ppm (Figure 5f).

The high percentage of ethoxide **6a** in the product mixtures from desilylation of **1a** cannot be entirely accounted for by a process of secondary decomposition of the anion **3a**, particularly at temperatures below 0 °C, since it would correspond to a much lower thermal stability of **3a** than established in earlier studies. An alternative explanation can be offered based on the hypothesis that the major portion of ethoxide is formed *via* parallel reaction of decomposition of **1a**. Previous studies have shown that tetrabutylammonium fluoride solutions are strongly basic and the presence of water leads to the generation of hydroxide anions.<sup>28-30</sup> At the same time N-nitrosocarbamates are known to be hydrolytically labile in such conditions.<sup>31-33</sup> To verify the hypothesis, we conducted a trial experiment with ethyl N-butyl-N-nitrosocarbamate<sup>33-37</sup>, which is a close structural analog of **1a** but lacks a silicon center. An NMR sample of it in DMF-*d*<sub>7</sub> was added to 5 equivalents of Bu<sub>4</sub>NF·3H<sub>2</sub>O at 5 °C. The spectrum after 30 min indicated complete decomposition of the starting material with the almost exclusive formation of **6a**, which in this case could occur only *via* basic hydrolysis of the starting N-nitrosocarbamate. Hence we are proposing a two-pathway decomposition for carbamates **1a-d** in

the presence of  $\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$ , as reflected in Scheme 5. The significant differences in product composition between **1a** and **1d** are due to the presence of the bulky and branched *t*-butyl groups in **1d** (See Figures 3 and 4), which render the carbonyl group virtually inaccessible, thus slowing down considerably the rate of basic hydrolysis.



## Conclusions

Our efforts to date have led to the formulation and implementation of a new synthetic strategy aimed at the preparation and isolation of secondary N-nitrosocarbamates *via* desilylation of chemically and thermally stable tertiary N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates.

The current article presents the first solid-state structural studies of N-nitrosocarbamates. X-ray data have demonstrated that both of the studied target structures exist as *s-E* conformers in the solid state, with a nearly planar N-nitrosocarbamate moiety. Further, DFT calculations demonstrate that the *s-E* orientation at the N – N bond is the preferred arrangement in the gas phase as well, for N-nitrosocarbamates, N-nitrosoureas and N-nitrosoamides.

Desilylation studies demonstrate that the process depends on several factors: temperature, solvent and concentration of fluoride anion. The current methodology, employing

Bu<sub>4</sub>NF·3H<sub>2</sub>O, seems to be most effective in cases of structures with large and branched carbamate groups, whose steric hindrance effectively suppresses the competing process of basic hydrolysis of the N-nitrosocarbamate, the latter leading directly to the anions **6** rather than **3**. Use of anhydrous fluoride ion sources, such as tetrabutylammonium triphenyldifluorosilicate (TBAT)<sup>28,30</sup> or CsF/CsOH mixtures<sup>38</sup> may prove advantageous in optimizing the yields of the N-nitrosocarbamate anions **3**.

## Experimental

<sup>1</sup>H and <sup>13</sup>C spectra of intermediate and target compounds were recorded at 300 MHz and 75 MHz respectively and referenced to the solvent (CDCl<sub>3</sub>: 7.27 ppm and 77.0 ppm; D<sub>2</sub>O: 4.76 ppm; acetonitrile-*d*<sub>3</sub>: 1.93 ppm; DMF-*d*<sub>7</sub>: 8.03 ppm). X-ray structures were obtained using an *Oxford Diffraction Xcalibur3* diffractometer with graphite monochromatic Cu K<sub>α</sub> radiation. Structure solution and refinement was performed using the SHELXTL 6.10 software package.<sup>39</sup> All calculations were performed utilizing the *Gaussian03-Linda/GaussView* software package<sup>40</sup> on a *Linux*-operated cluster (*QuantumCube QS4-2400C* by Parallel Quantum Solutions, Fayetteville, AR). Constant temperature desilylation reactions were conducted using the *Isotemp 1016S* circulating bath. Elemental analysis was provided by Atlantic Microlab, Norcross, GA. HRMS data was provided by the Mass Spectrometry and Proteomics facility at the Ohio State University. Nitrosonium tetrafluoroborate was purchased from the *Lancaster* chemical company. 3-(Trimethylsilyl)propanamide (**4**)<sup>8</sup> and 2,4,6-tris(*t*-butyl)phenyl chloroformate<sup>10</sup> were synthesized, following previously reported procedures. 2-(Trimethylsilyl)ethanamine (**5**) was prepared according to a published patent work.<sup>11</sup> The <sup>1</sup>H NMR data for compounds **4** and **5**, and precursors to them, are reported in this article, as they were previously unavailable.

**X-ray crystallography of 1-adamantyl N-2-trimethylsilylethyl-N-nitrosocarbamate (1c).** A crystal (yellow plate) of **1c** (C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>Si) having approximate dimensions 0.324 x 0.206 x 0.083 mm was mounted on a glass fiber. The preliminary set of cell constants was calculated from reflections harvested from 5 sets of 15 frames, merged to 139 peaks that were used to derive the initial orientation matrix. Data acquisition was conducted at 150 K using the phi and omega scans technique. Final cell constants were determined based on the full data set, leading to a triclinic cell (*P*  $\bar{1}$ ) with these dimensions: a = 6.6116 (13) Å, b = 9.8970 (18) Å, c = 13.958 (2) Å,  $\alpha = 75.660 (14)^\circ$ ,  $\beta = 84.856 (14)^\circ$ ,  $\gamma = 89.407 (14)^\circ$ , V = 881.3 (3) Å<sup>3</sup>. For Z = 2 and F.W. = 324.49, the calculated density is 1.223 g/cm<sup>3</sup>. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were assigned based on geometry. The final structure has values for the unweighted agreement factor R1 = 0.0459 based on 1300 strong reflections ( $I > 4\sigma$ ) and R1 = 0.0489 based on all data.

**X-ray crystallography of 2,4,6-tris(*t*-butyl)phenyl N-2-trimethylsilylethyl-N-nitrosocarbamate (1d).** A crystal (yellow needle) of **1d** (C<sub>24</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub>Si) having approximate dimensions 0.358 x 0.079 x 0.072 mm was mounted on a glass fiber. The preliminary set of cell constants was calculated from reflections harvested from 5 sets of 15 frames, merged to 155 peaks that were used to derive the initial orientation matrix. Data acquisition was conducted at 100 K using the phi and omega scans technique. Final cell constants were determined based on the full data set, leading to an orthorhombic cell (*Pbca*) with these dimensions: a = 11.3845 (11) Å, b = 20.5755 (18) Å, c = 45.454 (4) Å,  $\alpha = 90.00^\circ$ ,  $\beta = 90.00^\circ$ ,  $\gamma = 90.00^\circ$ , V = 10647.2 (17) Å<sup>3</sup>. For Z = 16 and F.W. = 434.67, the calculated density is 1.075 g/cm<sup>3</sup>. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were assigned based on geometry. The final

structure has values for the unweighted agreement factor  $R1 = 0.0917$  based on 7208 strong reflections ( $I > 4\sigma$ ) and  $R1 = 0.1193$  based on all data.

**Fluoride-assisted desilylation of ethyl N-2-(trimethylsilyl)ethyl-N-nitrosocarbamate (1a) and 2,4,6-tris(*t*-butyl)phenyl N-2-(trimethylsilyl)ethyl-N-nitrosocarbamate (1d). General Procedure.** In a typical run 0.020 mol of carbamate **1**, dissolved in 0.7 mL of the appropriate deuterated solvent (acetonitrile- $d_3$  or DMF- $d_7$ ), was added to  $\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$  (0.020 – 0.10 mol, 1 – 5 equivalents) at  $-15\text{ }^\circ\text{C}$  (ice – acetone bath). The resultant solution was transferred into an NMR tube and kept at the appropriate temperature until disappearance of the signals of the starting material. NMR measurements were conducted at regular time intervals. The change in quantity of reactant/product was monitored *via* integration of the NMR signals relative to the multiplet of  $\text{Bu}_4\text{N}^+$  centered at  $\delta$  1.76 ppm.

**Ethyl N-nitrosocarbamate, tetrabutylammonium salt (3a-Bu<sub>4</sub>N).**  $^1\text{H}$  NMR (DMF- $d_7$ , anion only)  $\delta$  4.14 (q,  $J = 7.1$  Hz, 2H), 1.23 (t,  $J = 7.1$  Hz, 3H);  $^1\text{H}$  NMR (acetonitrile- $d_3$ , anion only)  $\delta$  4.09 (q,  $J = 7.1$  Hz, 2H), 1.21 (t,  $J = 7.1$  Hz, 3H).<sup>1</sup>

**2,4,6-Tris(*t*-butyl)phenyl N-nitrosocarbamate, tetrabutylammonium salt (3d-Bu<sub>4</sub>N).**  $^1\text{H}$  NMR (DMF- $d_7$ , anion only)  $\delta$  7.34 (s, 2H), 1.43 (s, 18H), 1.31 (s, 9H).

**3-(Trimethylsilyl)propanamide (4).**<sup>8</sup> A) *3-(trimethylsilyl)propanoyl chloride*:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.80 – 2.87 (m, 2H), 0.91 – 0.97 (m, 2H), 0.03 (s, 9H); B) *3-(Trimethylsilyl)propanamide*:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.61 (broad s, 2H), 2.17 – 2.24 (m, 2H), 0.80 – 0.87 (m, 2H), 0.02 (s, 9H).

**2-(Trimethylsilyl)ethanamine (6).**<sup>8,11</sup> A) *N-2-(trimethylsilyl)ethylphthalimide*:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.82 – 7.85 (m, 2H), 7.68 – 7.71 (m, 2H), 3.69 – 3.75 (m, 2H), 0.99 – 1.05 (m, 2H),

0.07 (s, 9H). *B*) 2-(Trimethylsilyl)ethanamine hydrochloride:  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  2.94 – 3.01 (m, 2H), 0.84 – 0.91 (m, 2H), -0.03 (s, 9H). *C*) 2-(Trimethylsilyl)ethanamine:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.71 – 2.78 (m, 2H), 2.10 (broad s, 2H), 0.73 – 0.80 (m, 2H), - 0.01 (s, 9H).

**Preparation of N-2-(trimethylsilyl)ethylcarbamates. General procedure (Method A).** To a stirred solution of 3-(trimethylsilyl)propanamide (3.40 mmol) and mercuric acetate (4.60 mmol) in anhydrous N,N-dimethylformamide (10 mL), was added a solution of the corresponding alcohol (102.50 mmol) in anhydrous N,N-dimethylformamide (3 mL), at ambient temperature and under nitrogen. This was followed by addition of a solution of NBS (4.50 mol) in N,N-dimethylformamide (2 mL). The reaction was stirred for 12 hr at room temperature. The solvents were removed at reduced pressure and methylene chloride (50 mL) was added to the residual solid. The organic extract was washed with water (5 x 25 mL), dried ( $\text{MgSO}_4$ ) and the solvent was removed under reduced pressure. The resultant residue was passed through a short silica gel filter (hexane: ethyl acetate = 3:1) and the solvents were removed under reduced pressure to give the desired carbamate. Further purification *via* column chromatography (hexane: ethyl acetate = 3:1) led to isolated products that were > 95% pure by NMR.

**Ethyl N-2-trimethylsilylethylcarbamate (2a).** (*Method A*) Yield: 85%. Colorless liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.69 (bs, 1H), 4.10 (q,  $J = 7.0$  Hz, 2H), 3.18 – 3.24 (m, 2H), 1.24 (t,  $J = 7.0$  Hz, 3H), 0.77 – 0.83 (m, 2H), 0.01 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  156.5, 60.6, 37.4, 18.2, 14.6, -1.7; HRMS (FAB $^+$ )  $m/z$  Calcd. for  $\text{C}_8\text{H}_{19}\text{NO}_2\text{Si}$  [ $\text{M}+\text{Na}$ ] $^+$  212.1083, found 212.1076.

***t*-Butyl N-2-trimethylsilylethylcarbamate (2b).** (*Method A*) Yield: 36%. Colorless liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.80 (bs, 1H), 3.10 – 3.19 (m, 2H), 1.41 (s, 9H), 0.81 – 0.87 (m, 2H), 0.04 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.7, 79.0, 37.0, 28.4, 18.1, -1.7; HRMS (FAB $^+$ )  $m/z$  Calcd.

for C<sub>10</sub>H<sub>24</sub>NO<sub>2</sub>Si [M+Na]<sup>+</sup> 240.1396, found 240.1396. Anal. Calcd. for C<sub>10</sub>H<sub>23</sub>NO<sub>2</sub>Si: C, 55.25; H, 10.66; N, 6.44. Found: C, 55.50; H, 10.54; N, 6.14.

**1-Adamantyl N-2-trimethylsilylethylcarbamate (2c).** (*Method A*) Yield: 50%.

White solid: mp 92 – 94 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.42 (bs, 1H), 3.12 – 3.20 (m, 2H), 2.17 (m, 3H), 2.10 (m, 6H), 1.65 (m, 6H), 0.75 – 0.82 (m, 2H), 0.02 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.4, 41.7, 37.0, 36.2, 30.8, 18.2, 11.2, -1.7; HRMS (FAB<sup>+</sup>) *m/z* Calcd. for C<sub>16</sub>H<sub>30</sub>NO<sub>2</sub>Si [M+Na]<sup>+</sup> 318.1865, found 318.1876; Anal. Calcd. for C<sub>16</sub>H<sub>29</sub>NO<sub>2</sub>Si: C, 65.03; H, 9.89; N, 4.74. Found: C, 65.24; H, 9.93; N, 4.58.

**2,4,6-Tris(*t*-butyl)phenyl N-2-trimethylsilylethylcarbamate (2d).** (*Method B*) A

solution of 2-(trimethylsilyl)ethanamine (0.22 g, 1.85 mmol) and pyridine (0.15 g, 1.85 mmol, 0.15 mL) in dichloromethane (5 mL) was added dropwise over 15 min period to a solution of 2,4,6-tris(*t*-butyl)phenyl chloroformate (0.60 g, 1.85 mmol) in dichloromethane (5 mL) at 0 °C (ice – water), followed by stirring at ambient temperature for 12 h. The mixture was washed with water, the organic layer was separated, dried (MgSO<sub>4</sub>) and the solvent removed. The resultant residue was passed through a short silica gel filter and the product eluted with methylene chloride. The solvent was removed to yield the product as a white solid (0.34 g, 45%). Further purification *via* recrystallization from hexane, to yield white needles: mp 157 – 159 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (s, 2H), 4.99 (bs, 1H, NH), 3.28 – 3.36 (m, 2H), 1.37 (s, 18H), 1.32 (s, 9H), 0.88 – 0.94 (m, 2H), 0.06 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.2, 146.7, 145.7, 141.9, 123.1, 37.8, 35.6, 34.8, 31.52, 31.47, 18.4, -1.6; Anal. Calcd. for C<sub>24</sub>H<sub>43</sub>NO<sub>2</sub>Si: C, 71.05; H, 10.68; N, 3.45. Found: C, 71.23; H, 10.90; N, 3.45.

**Preparation of N-2-trimethylsilylethyl-N-nitrosocarbamates. General Procedure (*Aqueous method*).** To a solution of the corresponding alkyl N-2-(trimethylsilyl)ethylcarbamate

**2a-c** (1.25 mmol) in ether (2 mL) was added a solution of sodium nitrite (11.21 mmol) in ether (2 mL). Without stirring or cooling, nitric acid (1.5 mL, 35%) was added directly to the lower layer over one hour. The organic layer was separated, washed with water, then washed four times with saturated sodium bicarbonate, dried (MgSO<sub>4</sub>) and the solvent removed to afford the corresponding alkyl N-nitroso- N-2-(trimethylsilyl)ethylcarbamate **1a-c**. Further purification by column chromatography (silica gel, hexane : CH<sub>2</sub>Cl<sub>2</sub> = 2 : 1) led to isolated products that were > 95% pure by NMR.

**Preparation of N-2-trimethylsilylethyl-N-nitrosocarbamates. General procedure (Anhydrous method).** To a stirred solution of the corresponding alkyl N-2-(trimethylsilyl)ethylcarbamate **2a-c** (5.00 mmol) and anhydrous pyridine (10.00 mmol) in anhydrous acetonitrile (2.5 mL) at -20 °C, was added in one portion solid NOBF<sub>4</sub> (10.00 mmol). The solution was stirred at 0°C under nitrogen for a period of 1 – 2 h and the progress of the reaction was followed by thin layer chromatography (hexane : CH<sub>2</sub>Cl<sub>2</sub> = 2:1), the product exhibiting a rapidly moving yellow spot. The solvent was removed and the resultant mixture was passed through a short silica gel filter (hexane : CH<sub>2</sub>Cl<sub>2</sub> = 2:1). Removal of the solvents at reduced pressure gave the product **1a-c** that were > 95% pure by NMR.

**Ethyl N-2-trimethylsilylethyl-N-nitrosocarbamate (1a).** Yield: 72 % by the aqueous method, 78 % by the anhydrous method. Yellow liquid: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.53 (q, J = 7.3 Hz, 2H), 3.70 – 3.77 (m, 2H), 1.45 (t, J = 7.3 Hz, 3H), 0.65 – 0.72 (m, 2H), 0.03 (s, 9H); <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>) δ 4.43 (q, J = 7.0 Hz, 2H), 3.67 – 3.73 (m, 2H), 1.38 (t, J = 7.0 Hz, 3H), 0.63 – 0.68 (m, 2H), – 0.01 (s, 9H); <sup>1</sup>H NMR (DMF-*d*<sub>7</sub>) δ 4.54 (q, J = 7.2 Hz, 2H), 3.75 – 3.81 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H), 0.67 – 0.73 (m, 2H), 0.05 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.7, 64.2, 37.6, 15.4, 14.2, -2.0; HRMS (FAB<sup>+</sup>) *m/z* Calcd. for C<sub>8</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>Si [M+Na]<sup>+</sup> 241.0984,

found 241.0981. Anal. Calcd. for C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Si: C, 44.01; H, 8.31; N, 12.83. Found: C, 44.34; H, 8.38; N, 12.63.

***t*-Butyl N-2-trimethylsilylethyl-N-nitrosocarbamate (1b).** Yield: 69 % by the aqueous method. Yellow liquid: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.68 – 3.74 (m, 2H), 1.65 (s, 9H), 0.66 – 0.72 (m, 2H), 0.04 (s, 9H); <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>) δ 3.65 – 3.72 (m, 2H), 1.60 (s, 9H), 0.63 – 0.69 (m, 2H), 0.01 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 152.0, 85.0, 37.4, 28.0, 15.5, -2.0; HRMS (FAB<sup>+</sup>) *m/z* Calcd. for C<sub>10</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>Si [M+Na]<sup>+</sup> 269.1297, found 269.1301.

**1-Adamantyl N-2-trimethylsilylethyl-N-nitrosocarbamate (1c).** Yield: 30 % by the aqueous method, 81 % by the anhydrous method. Yellow solid, recrystallized from petroleum ether at -25 °C, to yield yellow plates: mp 98 – 99 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.67 – 3.73 (m, 2H), 2.29 (m, 9H), 1.72 (m, 6H), 0.66 – 0.72 (m, 2H), 0.04 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 151.4, 85.0, 41.3, 37.4, 36.0, 31.0, 15.5, -1.9. Anal. Calcd. for C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>Si: C, 59.22; H, 8.70; N, 8.63. Found: C, 59.03; H, 8.73; N, 8.45.

**2,4,6-Tris(*t*-butyl)phenyl N-2-trimethylsilylethyl-N-nitrosocarbamate (1d).** Carbamate **2d** (0.23 g, 0.57 mmol) was dissolved in a mixture of acetic acid (3.0 mL) and acetic anhydride (4.5 mL). The resultant solution was cooled to 5 °C (ice-water) and NaNO<sub>2</sub> (0.83 g, 12.06 mmol) was added in small portions, over 2-hour period, while keeping the temperature below 10 °C. Upon complete addition, the resultant mixture was stirred for additional 12 h at ambient temperature. The solvents were removed at reduced pressure and the residue was portioned between water and ether. The ether extract was stirred for 10 min with saturated aq. NaHCO<sub>3</sub>, the organic layer was separated, dried (MgSO<sub>4</sub>) and the solvent removed at reduced pressure. The resultant yellow oil was flash chromatographed on a short silica gel column (hexane : methylene chloride = 5 : 1). The yellow colored, highly mobile fraction was collected

and the solvent removed, leaving 0.21 g (84%) of the product as a yellow oil, which slowly solidified. Recrystallized from methanol at  $-30\text{ }^{\circ}\text{C}$  to yield yellow needles: mp  $62 - 64\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.41 (s, 2H), 3.84 – 3.89 (m, 2H), 1.39 (s, 18H), 1.37 (s, 9H), 0.74 – 0.78 (m, 2H), 0.07 (s, 9H);  $^1\text{H}$  NMR (acetonitrile- $d_3$ )  $\delta$  7.43 (s, 2H), 3.79 – 3.85 (m, 2H), 0.68 – 0.74 (m, 2H), 0.02 (s, 9H);  $^1\text{H}$  NMR ( $\text{DMF-}d_7$ )  $\delta$  7.48 (s, 2H), 3.89 – 3.95 (m, 2H), 0.72 – 0.78 (m, 2H), 0.07 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  153.5, 148.0, 145.4, 141.4, 123.5, 37.9, 35.6, 34.9, 31.51, 31.48, 15.4, -2.0. Anal. Calcd. for  $\text{C}_{24}\text{H}_{42}\text{N}_2\text{O}_3\text{Si}$ : C, 66.31; H, 9.74; N, 6.44. Found: C, 66.09; H, 9.77; N, 6.46.

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**Supporting Information Available.** Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers **CCDC 258576** and **258577**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

Energies and thermodynamic parameters of optimized minimum structures of compounds **1a-d**, **MNU** and **MNNB** are summarized in Table S1. Images of <sup>1</sup>H NMR spectra of compounds **1b** and **2a** are shown in Figure S1.

## References

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