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New N-hydroxy carbamic acid trialkylsilyl derivatives: preparation and thermal reactions

M. Mörtl, D. Knausz *, Zs. Böcskei, Zs. Kolos, K. Újszászy, L. Szakács, P. Sohár

Department of General and Inorganic Chemistry, Eötvös Loránd University Budapest, PO Box 32., H-1518 Budapest 112, Hungary

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Abstract

New N-siloxy- or N-alkoxy-carbamic acid derivatives have been prepared. The crystal structure of N-siloxy-O-tert-butyl carbamate was determined. The thermal behaviour of these compounds was studied in the absence and in the presence of other reaction partners. The reaction products were identified by gas chromatography, gas chromatography–mass spectroscopy, IR spectroscopy and NMR. The experimental results can be explained by the formation of a radical-type transition state (carboxynitrene), detected by mass spectroscopy.

Keywords: Silicon; Nitrene; Trimethylsilyl; Mass spectroscopy; Crystal structure

1. Introduction

The thermal behaviour of trimethylsilyl carbamates has been studied earlier [1]. The decomposition of organosilylated hydroxylamine derivatives was investigated by Tsui et al. [2]. The N-trimethylsilyl-N-trimethylsiloxy-O-ethyl carbamate and related compounds were prepared and investigated as nitrene generators [3]. Some trapping products (with cyclohexane and diphenylacetylene) have also been prepared. The mass spectroscopy (MS) studies of the above compounds were carried out by Schwartz et al. [4]. In the case of N-trimethylsilyl-N-trimethylsiloxy-O-ethyl carbamate no nitrene cation was detected by electron impact (EI) mass spectroscopy (MS). Mironov et al. [5] prepared the N,O-bis-trimethylsilyl-N-trimethylsiloxy carbamate and Sheludyakov et al. [6] studied its thermal decomposition. Some addition products were obtained from the reaction between 2,3-dimethyl-1,3-butadiene and the silylnitrene formed during the decomposition [7]. We have prepared several alkoxy and siloxy carbamate derivatives in order to study whether they undergo α-deoxysilylation.

2. Experimental details

2.1. Preparation

All preparations were carried out under moisture free conditions.

The preparation of n-butyl-N-trimethylsilyl-N-trimethylsiloxy carbamate (general procedure for carbamic acid alkyl or aryl esters) (method 1) is as follows. The N-siloxy carbamates were prepared from the corresponding N-hydroxy-O-alkylcarbamates in two steps. A mixture of n-butyl-N-hydroxy carbamate and hexamethyl-disilazane (molar ratio, 1 : 1) was stirred at 70°C for 1 day. The n-butyl-N-trimethylsiloxy carbamate as product was distilled in vacuo. For the silylation of nitrogen, trimethylchlorosilane was used in the presence of triethylamine in CH_2Cl_2 solution. After 1 h reflux the solution was filtered off, the solvent was evaporated and the product was purified by vacuum distillation. In the case of N-siloxy-O-tert-butyl carbamate the second step does not take place, probably for steric reasons. The N,O-bis-trimethylsilyl-phenyl carbamate synthesized by this method decomposes during vacuum distillation with the elimination of $PhOSiMe_3$.

For the preparation of carbamic acid silyl esters the method described in [1] (method 2) was used. The

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* Corresponding author.

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N-benzyloxy-*O*-trimethylsilyl-carbamate cannot be silylated on the nitrogen either.

The *N*,*O*-bis-trimethylsilyl-*N*-trimethylsiloxy carbamate was prepared by the method of Mironov et al. [5]. Their method was modified as follows. After the silylation of hydroxyl-amine with hexamethyl-disilazane, carbon dioxide was led into the cooled mixture and the third silyl group was built in with chlorotrimethylsilane in the presence of triethylamine.

2.2. Spectroscopic methods

The mass spectra were recorded with a Kratos-AEI MS50 instrument electron impact (EI) (at 70 eV; chemical ionization (CI) with isobutane). The IR spectra were determined with a Zeiss Specord 75 spectrophotometer in 0.05 M CCl_4 solution. The NMR spectra were recorded by a Bruker WM-250 FT spectrometer in $CDCl_3$ solution containing tetramethylsilane as internal standard. The gas chromatography (GC) indices were determined with a Chrompack CP-9000 gas chromatograph equipped with CP-Sil5 CB (10 m × 0.25 mm × 0.12 μm) capillary column (carrier gas, He; flame ionization detector).

The physical and spectroscopic data are summarized in Table 1.

2.3. X-ray diffraction study

Crystals of **4** were prepared by cooling a concentrated solution of **4** in dicloromethane. One of these crystals (size, 0.4 × 0.3 × 0.15 mm) was mounted in a quartz capillary to avoid decomposition and evaporation.

Data collection for **4** was performed on a Rigaku RAXIS-II imaging plate area detector using graphite-monochromated Mo Kα radiation at 293 K. Data processing was carried out using the software supplied with the diffractometer.

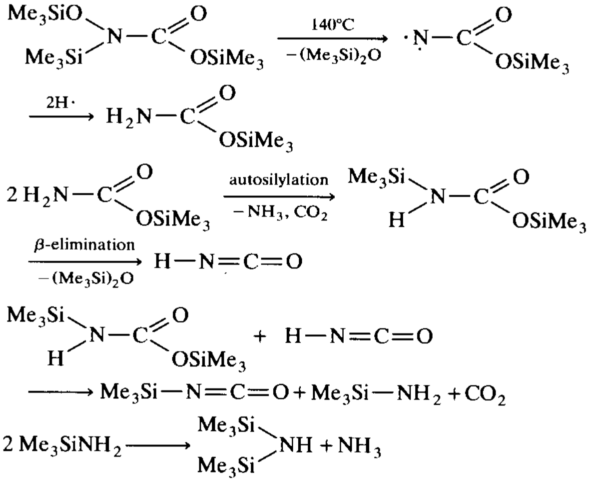
The crystal data were as follows: $C_8H_{19}O_3NSi$; $M = 205.33$; monoclinic; space group $P2_1/c$; $a = 6.6261(8)$, $b = 19.2960(27)$, $c = 9.7575(8)$ Å; $\beta = 94.757(3)°$; $V = 1243.3(2)$ Å^3; $Z = 4$; $D_c = 1.097$ g cm^{-3}; μ(Mα Kα) = 6.66 cm^{-1}; λ(Mo Kα) = 1.5418 Å. Intensities of 4527 reflections (2535 unique; $R_{sym} = 2.84\%$) were measured to $\theta_{max} = 26.3°$. Corrections for Lorentz polarization effects was applied.

Structure solution with direct methods and refinement with the full matrix least-squares method on F were carried out with the teXsan package [8]. Anisotropic thermal motion parameters for non-H atoms and isotropic thermal motion parameters for hydrogen atoms were refined. The refinement converged at $R = 0.053$ and $R_w = 0.037$ for 1387 ($I > 3.00\sigma(I)$) reflections.

3. Results

3.1. Self-decomposition

The thermal decomposition of *N*-trimethylsiloxy-*N*,*O*-bis-trimethylsilyl carbamate results in a reaction mixture of *N*,*O*-bis-trimethylsilyl carbamate, trimethylsilylisocyanates, hexamethyl-disilazane, hexamethyl-disiloxane and octamethyl-trisiloxane. These reaction products were identified by IR and GC–MS. The following reaction scheme may explain their formation:



During the formation of octamethyl-trisiloxane, $Me_2SiOSiMe_3$ seems likely to be an intermediate produced from $Me_3SiOSiMe_3$ by Me loss. The compounds **3**, **6** and **8** also decompose at 140°C with the elimination of hexamethyl-disiloxane. The other compounds **7** and **11** are stable, i.e. the β elimination of hexamethyl-disiloxane does not occur. The formation of alkoxysilane by α or β elimination from **5**, **7**, **11** and **12** does not take place, the only exception is $PhOSiMe_3$ mentioned above. This corresponds to the observation that the decomposition of *N*,*O*-bis(trimethylsilyl)hydroxyl amine is 200 times faster than one of the corresponding *O*-methyl derivatives [2].

3.2. Mass spectra

The CI was carried out at 300°C when the thermal decomposition of the sample becomes intensive. Hence the $m/z = 278$ quasi-molecular ion of **3** gradually disappears. However, both the $m/z = 163$ ion, which is the quasi-molecular ion of hexamethyldisiloxane, and the $m/z = 116$ ion relating to the $[M + H - 162]^+$ quasi-molecular ion of butyl-carboxy nitrene appears.

A process analogous to the above can also be observed in the case of **1**.

3.3. X-ray crystal and molecular structure of $SiMe_3$-$ONHCOO^tBu$

The crystalline structure of **4** was determined by single-crystal studies and is shown in Fig. 1. Fractional

Table 1
Physical and spectroscopic data for $R^1ON(R^2)C(O)OR^3$ compounds.

Compound	R^1	R^2	R^3	Yield (%)	Boiling point (°C) 12 mbar	GC index	IR ν(C=O) (cm^{-1})	MS (EI) I(%)		MS (CI) I(%)			method of preparation
								M^+	$(M-15)^+$	$(M+1)^+$	$(M+1-15)^+$	$(M+1-162)^+$	
1	$SiMe_3$	$SiMe_3$	$SiMe_3$	58	60	1290	1708, 1656	7	86	100	23	67 [a]	2
2	$SiMe_3$	H	n-Bu	84	65– 67	1294	1765, 1720	70	14	100	5	—	1
3	$SiMe_3$	$SiMe_3$	n-Bu	71	76– 78	1372	1727, 1680	10	67	100	8	76 [a]	1
4	$SiMe_3$	H	^{t}Bu	75	66– 68	1296	1761, 1717	0	78	50	7	—	1
5	$SiMe_3$	Me	$SiMe_3$	82	32– 35	1130	1720, 1683	2	79				2
6	$SiMe_3$	$SiEt_3$	Bu	67	116–118	1590	1760, 1720	8	72				1
7	Me	$SiMe_3$	$SiMe_3$	60	55– 58	1144	1717	31	28				2
8	$SiMe_3$	$SiEt_3$	$SiMe_3$	56	98–100	1502	1760, 1697	3	12				1
9	Bz	H	$SiMe_3$	70	120–122	1663	1702	26	17				2
10	Et	H	$SiMe_3$	32	42– 45	1082	1693	0.6	10				2
11	Et	$SiMe_3$	$SiMe_3$	55	89– 90	1189	1715	28	18				2
12	Me	Me	$SiMe_3$	85	39– 41	1058	1692	3	39				2

[a] 300°C

coordinates of non-hydrogen atoms are listed in Table 2 while relevant bond lengths and interesting torsion angles can be found in Tables 3 and 4.

The most interesting structural feature of **4** is thought to be the fact that the OHNCOO moiety is not planar; the OHNC and the NCOO planes form an angle of about 18°. This is attributed to a long-range interaction between the oxygen atoms O(2) and O(3). This feature is also shown by the torsion angle O2–C(1)–N(1)–O(3)(−20.1(5)°). The N(1)–C(1)–O(1)–C(2) angle is *anti*, while the C(1)–N(1)–O(3)–Si angle is *gauche*. It is worth noting that a weak intermolecular hydrogen bond is formed between N(1)–H(1) and O(2), although the geometry of it is far from ideal (N(1) · · · O(2), 2.944(3) Å; N(1)–H(1) · · · O(2), 126.1°).

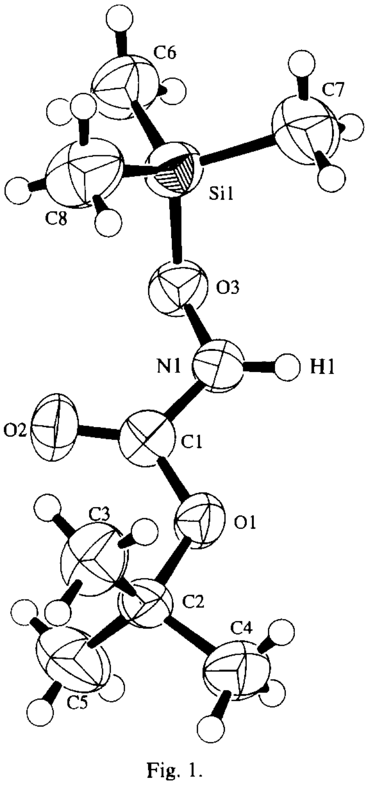


Fig. 1.

Table 2
Fractional coordinates and equivalent isotropic displacement parameters with estimated standard deviations in parentheses for **4**

Atom	x	y	z	B_{eq} ($Å^2$)
Si(1)	0.4519(2)	0.3906(5)	0.8180(1)	4.68(5)
O(1)	0.8854(4)	0.2071(1)	0.7666(2)	4.5(1)
O(2)	0.6721(4)	0.2245(1)	0.9356(2)	5.2(1)
O(3)	0.4540(4)	0.3091(1)	0.7602(2)	4.4(1)
N(1)	0.6517(5)	0.2868(1)	0.7350(3)	4.2(2)
C(1)	0.7298(6)	0.2370(2)	0.8231(4)	4.2(2)
C(2)	1.0249(6)	0.1602(2)	0.8461(3)	4.2(2)
C(3)	1.1277(8)	0.1993(3)	0.9687(5)	6.5(2)
C(4)	1.1710(7)	0.1448(3)	0.7428(5)	6.5(3)
C(5)	0.9160(9)	0.0954(3)	0.8835(7)	7.8(3)
C(6)	0.1791(6)	0.4052(3)	0.8327(5)	6.3(3)
C(7)	0.5517(9)	0.4500(2)	0.6903(6)	7.5(3)
C(8)	0.6052(9)	0.3975(3)	0.9856(5)	7.4(3)

Table 3
Selected bond lengths where the estimated standard deviations in the least significant figure are given in parentheses

Atom	Atom	Intramolecular distance (Å)
Si(1)	O(3)	1.670(2)
Si(1)	C(6)	1.847(4)
Si(1)	C(7)	1.855(4)
Si(1)	C(8)	1.857(4)
O(1)	C(1)	1.339(4)
O(1)	C(2)	1.468(4)
O(2)	C(1)	1.216(4)
O(3)	N(1)	1.420(3)
N(1)	C(1)	1.363(4)
C(2)	C(3)	1.525(5)
C(2)	C(4)	1.523(5)
C(2)	C(5)	1.504(5)

Table 4
Torsion of conformation angles where the sign is positive if, when looking from atom (2) to atom (3) a clockwise motion of atom (1) would superimpose it on atom (4)

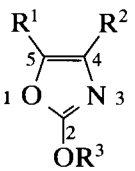
(1)	(2)	(3)	(4)	Angle (°)	(1)	(2)	(3)	(4)	Angle (°)
Si(1)	O(3)	N(1)	C(1)	111.5(3)	N(1)	O(3)	Si(1)	C(8)	−62.5(3)
O(1)	C(1)	N(1)	O(3)	162.7(3)	N(1)	C(1)	O(1)	C(2)	168.8(3)
O(2)	C(1)	O(1)	C(2)	−8.3(6)	C(1)	O(1)	C(2)	C(3)	−60.4(4)
O(2)	C(1)	N(1)	O(3)	−20.1(5)	C(1)	O(1)	C(2)	C(4)	−176.1(3)
N(1)	O(3)	Si(1)	C(6)	177.5(2)	C(1)	O(1)	C(2)	C(5)	66.2(4)
N(1)	O(3)	Si(1)	C(7)	59.4(3)					

Other structural data are much as expected. An additional refinement calculation with anisotropic N–H was carried out, whereby the hydrogen atom moved slightly out of the plane of the O(3)N(1)C(1) moiety. This seems to be significant since it is in accordance with previous theoretical results [9].

3.4. Decomposition in the presence of radical traps

We studied the decomposition of **1** and **3** in the presence of radical traps. The nitrene as a highly reactive species reacts with several radical traps, e.g. with cyclohexane, providing the corresponding *N*-cyclohexyl carbamate. The products were identified by GC–MS.

By the reaction of diphenyl-acetylene with **1** or **3** we obtained analogous products as in [2]. We stirred **3** with phenyl-acetylene at 140°C for 5 h. The product was distilled in vacuo and identified as 5-phenyl-2-butoxy-1,3-oxazole. By using phenylacetylene as a trapping agent we could observe only one of the two products possible in principle. Its structure was proved by ^{13}C NMR spectroscopy. We assigned the signals by DEPT measurement. On the basis of proton-coupled ^{13}C spectra we decided between the two possible structures. The ^{13}C signals corresponding to the C(5) and C(4) show a doublet and a double triplet splitting respectively. In the case of reversed addition a mutually interchanged multiplicity would be expected. Compound **1** reacts similarly.



13. R^1: H, R^2: Ph, R^3: $SiMe_3$
14. R^1: Ph, R^2: Ph, R^3: $SiMe_3$
15. R^1: Ph, R^2: Ph, R^3: Bu
16. R^1: H, R^2: Ph, R^3: Bu
17. R^1: H, R^2: p-tolyl, R^3: Bu

The reaction between *p*-tolyl acetylene and **3** also led to an oxazole derivative, i.e. the 1,3 dipolar addition is preferred to the insertion to a C–H bond while in the case of cyclohexene the addition and the insertion are competitive reaction routes [2]. The yield of the above reactions is strongly influenced by the temperature. Above 140°C the self-decomposition is preferred, giving gaseous products and tar. There was no reaction with hexachloro-propene and hexachloro-1,3-butadiene as trapping agent.

The physical and spectroscopic data for the oxazol-type additional products are in Table 5.

4. Conclusion

On the basis of our investigations we can conclude that the decomposition of **1**, **3**, **6** and **8** leads (if α

Table 5
Physical and spectroscopic data for oxazole compounds

	R^1	R^2	R^3	yield (%)	GC index	IR, ν (cm^{-1})	MS (EI) M$^+$	MS (EI) I (°)	^{13}C NMR shifts δ (ppm) C(2)	^{13}C NMR shifts δ (ppm) C(4)	^{13}C NMR shifts δ (ppm) C(5)	^1H NMR δ (ppm) C(5)–H
13 [a]	H	Ph	$SiMe_3$	—	1668	—	233	24	—	—	—	—
14 [a]	Ph	Ph	$SiMe_3$	—	2150	—	309	50	—	—	—	—
15	Ph	Ph	*n*-Bu	31	2212	1740, 1600	293	52	160.6	134.0	139.9	—
16	H	Ph	*n*-Bu	38	1710	1757, 1723, 1800, 1600	217	100	161.5	120.4	145.8	6.92 [b]
17	H	*p*-Tolyl	*n*-Bu	37	1742	1750, 1598	231	72	161.4	119.8	146.1	6.95 [c]

[a] **13** and **14** were identified by GC–MS.
[b] ^2J(C(4), H) = 15.8 Hz; ^3J(C(4), H) = 4.3 Hz; ^1J(C(5), H) = 192.8 Hz.
[c] ^2J(C(4), H) = 16.0 Hz; ^3J(C(4), H) = 4.5 Hz; ^1J(C(5), H) = 192.0 Hz.

elimination of hexamethyldisiloxane is possible) to a reactive intermediate (nitrene) radical which can be detected under appropriate circumstances (source temperature, 300°C; CI) by MS. β elimination was observed only for *N*-trimethylsilyl-*N*-trimethylsiloxy-*O*-phenyl carbamate; the other compounds are stable. This nitrene intermediate participates in further reactions in the presence of radical traps in two different ways.

(1) The nitrogen as a reaction centre can be inserted into a σ(C–H) bond.

(2) The nitrogen and the oxygen as a double reaction centre can be added to a π bond.

The latter cycloaddition is regiospecific. In the carboxynitrene radical the nitrogen is more negative than the oxygen; so during the cycloaddition the nitrogen will be connected to the carbon atom of acetylene with a lower electron density (bearing the hydrogen atom) and the oxygen atom to the carbon atom with a higher electron density (which differs from the structure assumed in [2]).

Acknowledgements

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Supplementary material

Crystal data, the details of the data collection as well as processing procedure, selected weighted least-squares planes etc. are available from Zs.B. upon request. The usual data items will be deposited at the Cambridge Crystallographic Data Centre.

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