Silylation of *N,O*-Diacylhydroxylamines: NMR Spectra and Structure of the Products

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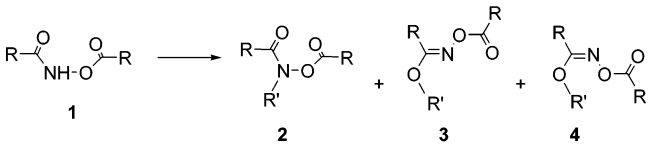
Received December 10, 2003

Silylation of *N,O*-diacylhydroxylamines with *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide produces only O-silylated products and no N-silylated derivative. Steric interactions of the substituents on the nitrogen atom with the O−N oxygen atom control the configuration on the C═N bond in the product: a *Z* isomer is formed almost exclusively from *N*-benzoylhydroxylamines, and a mixture of *E* and *Z* isomers is produced from *N*-acetyl derivatives. The relative stability of all isomers in various conformations was confirmed by calculations at the B3LYP/6-31G(d,p) level. The *tert*-butyldimethylsilyl derivatives have been fully characterized by their ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectra.

Introduction

Acyl derivatives of hydroxylamine presented specific structural problems.[1] In many cases, all possible isomers have not been always isolated and the structure of reported isomers is not always certain. One tool for solving similar problems is the silylation reaction. Silylation replaces the exchangeable NH and OH protons and introduces a new nucleus for NMR investigation. The silylation products can be identified even when the silylation is accompanied by isomerization.[2] In the course of the successive acylation of hydroxylamine, the *N,O*-diacylhydroxylamine **1** is the most common product



1 **2** **3** **4**

a: R = C_6H_5, R' = COC_6H_5
b: R = CH_3, R' = $COCH_3$
c: R = C_6H_5, R' = alkyl
d: R = XC_6H_4, R' = $SO_2C_6H_5$

and also the key intermediate.[3] Substitution of the last hydrogen atom may yield the three isomers **2**−**4**, only some of which were prepared and characterized. In 1875 Lossen described three isomers of tribenzoylhydroxylamine.[4,5] Structures of two of them, **2a** and **4a**, were later established,[3,6,7] but the preparation of **3a** could not be reproduced.[3, 6−8] Triacetylhydroxylamine was prepared at least twice without dealing with its structure.[9,10] Structure **2b** was established, but a small admixture of isomers in the liquid product was not excluded.[3] Alkylation of **1c** yielded only two isomers,[11,12] **2c** and one of the remaining two, **3c** or **4c**, with the configuration on the C═N bond not determined. Benzenesulfonylation of **1** yielded only one product, **3d** or **4d (**the configuration was not examined).[13]

The objective of the present paper is the synthesis and NMR spectral characterization of the *tert*-butyldimethylsilyl (TBDMS) derivatives of the *N,O*-diacylhydroxylamines **5** with the anticipated structures **6**−**8**. We assumed that certain isomers not accessible in other cases (**3** in particular) could be obtained and well characterized in this case. Some silyl derivatives could possibly be used for preparation of acyl derivative isomers not accessible in a direct way. The *tert*-butyldimethylsilyl derivatives were chosen instead of trimethylsilyl ones because of their higher stability. To evaluate the possible role of the nature of the substituents R and R′ and to facilitate the NMR identification,

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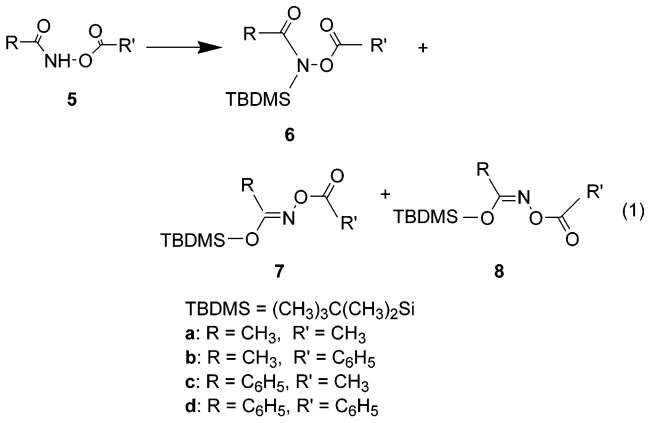
10.1021/om030684u CCC: $27.50
Publication on Web 04/01/2004

Table 1. Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) Measured in Concentrated Chloroform-*d* Solutions[a]

compd	isomer	R	R′	%	$\delta(^{15}N)$	$^1J(C{=}N,C\alpha)$	$\delta(^{13}C{=}N)$	$\delta(^{13}C\alpha)$	$\delta(^{29}Si)$	$^2J(Si,C{=}N)$	$^3J(SiOC(N)C\alpha)$	$^1J(C{=}O,C\alpha)$	$\delta(^{13}C{=}O)$	$\delta(^{13}C\alpha)$
7a	*E*	Me	Me	55	−64.2	51.7	166.36	14.83	25.97	3.5	1.8	58.9	167.22	18.68
8a	*Z*	Me	Me	45	−82.3	57.3	157.10	17.92	24.97	3.6	0.8	59.5	166.85	18.67
7b	*E*	Me	Ph	60	−65.3	52.2	167.74	15.35	26.66	3.4	1.8	76.8	162.80	128.73[b]
8b	*Z*	Me	Ph	40	−82.2	56.1	158.51	18.29	25.02	3.0	0.9	76.3	163.49	128.73[b]
8c	*Z*	Ph	Me	95	−76.3	72.3	155.38	130.63	26.85	3.9	1.2	59.5	167.25	19.16
7c	*E*	Ph	Me	5	−68.8	*c*	*c*	*c*	27.01	*c*	*c*	*c*	*c*	*c*
8d	*Z*	Ph	Ph	80	−74.0	71.7	158.09	131.12	27.12	3.4	0.9	76.4	163.85	128.93
7d	*E*	Ph	Ph	20	−70.0	65.8	164.43	129.91	27.72	3.3	1.8	75.2	163.09	128.67
10	*E*			65	−71.2[d]	53.0	163.94	14.29	24.96/22.18[e]	5.2/3.5[f]	−/2.1[g]			
11	*Z*			35	−84.3[h]	60.8	153.82	18.78	25.47/21.53[e]	4.6/4.1[f]	−/1.3[g]			

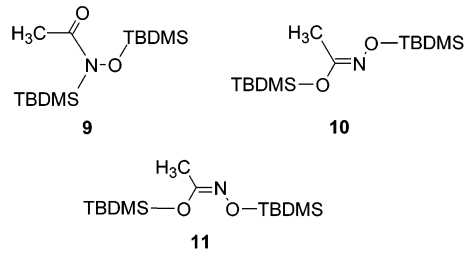
[a] Chemical shifts in δ scale relative to external CH_3NO_2 (^{15}N) or tetramethylsilane (^{13}C and ^{29}Si). Cα denotes either the methyl carbon (R, R′ = Me) or the C-1 carbon of the phenyl ring (R, R′ = Ph). Coupled nuclei are given in italics in the column heading. [b] One of the two lines is hidden under another line. [c] The line is either not observed or not assigned due to low S/N. [d] Coupling to CH_3 acetyl proton $^3J(^{15}N{-}^1H) = 1$ Hz. [e] Tentative assignment: the first value is the shift of silicon in the SiOC= fragment, and the second one is due to that in the SiON= fragment. [f] According to the tentative assignment the first value is the $^2J(Si,C{=}N)$ coupling in the SiOC= fragment, and the second value is $^3J(Si,C{=}N)$ coupling in the SiON=C fragment. [g] According to the tentative assignment there is no observable $^3J(Si,C)$ coupling in the fragment $SiOC(=N)CH_3$; the second value is $^4J(Si,C)$ coupling in the $SiON{=}CCH_3$ fragment. [h] Coupling to the CH_3 acetyl proton $^3J(^{15}N{-}^1H) = 3.1$ Hz.



(1)

all combinations of methyl and phenyl substituents (**5a**−**d**) were examined. We used direct silylation of **5** by *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA).

While NMR spectroscopy appears to be the only analytical method capable of identification of the above products in their mixtures, proof of their structure is a difficult task, due to a long heteronuclear link, CO−N−O−CO, between R and R′. This link interrupts any of the usually measured coupling pathways. This is especially true for the compounds with R or R′ = Ph which lack protons on the α-carbon atom (aromatic C-1 or C_{ipso} carbon). To facilitate comparison of NMR parameters, unpublished data on *tert*-butyldimethylsilylated acetohydroxamic acid (**10** and **11**) have also been included. The structures of these TBDMS derivatives



were assigned by the same experiments and arguments as those applied to their trimethylsilyl (TMS) analogues earlier.[14]

Results and Discussion

Products of the Silylation Reaction. We have not noticed any formation of the *N*-silyl derivative **6**. In all studied cases the silylation of **5** produced a mixture of *E* and *Z O*-silylated products **7** and **8** in different isomer ratios (Table 1). In line with general expectations, the isomer ratio is controlled by the *N*-acyl group, i.e., by the substituent R in **5**. The silylation of *N*-acetyl-*O*-acylhydroxylamines yields preferentially *E* isomers (**7a**,**b**), while the silylation of *N*-benzoyl-*O*-acylhydroxylamines produces preferentially *Z* isomers (**8c**,**d**). Varied amounts of silylating agent and different reaction times and temperatures did not produce significantly different ratios of the products. No NMR-observable isomerization was noticed in chloroform solutions over the course of 800 h at room temperature. Only in the case of *N*-acetyl-*O*-benzoylhydroxylamine products (**7b** and **8b**) did the isomer ratio change because of the faster decomposition of the *E* isomer into several products detected by ^{29}Si NMR (but not identified).

The *E*/*Z* isomer ratio (**7**/**8**) did not change when the product mixtures were stored in various solvents (chloroform, cyclohexane, deuteriobenzene, carbon tetrachloride, acetone, acetonitrile, tetrahydrofuran). Also, ^1H and ^{29}Si NMR spectra measured in deuteriochloroform solutions in the temperature range 223−323 K did not indicate any exchange. The compounds **7** and **8**, however, decomposed in dimethyl sulfoxide (at room temperature), producing the parent compounds **5**. The TBDMS derivatives of acetohydroximic acid (**10** and **11**) also decomposed in contrast to their TMS analogues, which changed the isomer ratio in this solvent.[15]

The described behavior is contrasted by the silylation of secondary amides, which gives much more varied products: e.g., acetanilides yield mixtures of *N*-silyl and *O*-silyl derivatives.[16−19] On the other hand, the sole

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formation of Si−O products was reported for the structurally close *N′*,*N′*-dimethylhydrazides of carboxylic acids[20−22] and proved for the silylation of hydroxamic acids,[14,23,24] in contrast to the originally proposed structure.[15,25]

The *E*/*Z* ratios of O-silylated isomers, i.e., **7**:**8**, found here can be compared to those established in silylated hydroxamic acids and *N′*,*N′*-dimethylhydrazides, which are controlled in a similar way. Ring-substituted benzhydroxamic acids produced solely *Z* isomers of disilyl derivatives,[23,24,26] while the aliphatic hydroxamic acids yielded mixtures of *E* and *Z* isomers.[14,27] Trimethylsilylation of aromatic *N′*,*N′*-dimethylhydrazides also leads only to the *Z* isomers, while in the case of the aliphatic derivative the *E* isomer is formed as well.[20−22]

Calculated Structures and Energies. The absence of *N*-silyl derivatives among our products may have both kinetic and thermodynamic origins: i.e., the low nucleophilicity of nitrogen or subsequent equilibration. The mobility of the silyl group bound on an amide nitrogen has already been noted.[16] Without speculating about the reaction mechanism, the calculations at the B3LYP/6-31G(d,p) level indicate that *N*-silyl derivatives are thermodynamically less stable than their *O*-silyl isomers (Table 2). The calculations were carried out on the slightly simplified compounds **6a′**, **7a′**, **8a′**, **6c′**, **7c′**, and **8c′**, which differ from their respective paradigms **6a**, **7a**, **8a**, **6c**, **7c**, and **8c** in that the *tert*-butyldimethylsilyl group has been replaced by the trimethylsilyl group. We examined, as far as possible, all probable conformations for each compound. The smallest difference between the minimum-energy conformer and the next higher conformer is 5.6 kJ mol^{-1} (**6a′**); thus, the conformer could represent only 10% of the population in the equilibrium mixture and contribute to its energy by 0.6 kJ mol^{-1}. In all other cases the energy difference is larger and so the minor isomer population is even lower. Obviously, it is not necessary to consider the contribution of these isomers. The optimum conformations are shown in Figure 1, and some conformers with a higher energy are mentioned in Table 2. The conformations of the *N*-silyl derivatives **6a′** and **6c′** are virtually the same (Figure 1) and can be compared to that of *N*,*O*-dibenzoylhydroxylamine (**5d**), as determined either in the crystal state[28] or in solution from the dipole moments.[29] The experimental and calculated structures are similar in the dihedral angle C−N−O−C, which is close to 90°, determining thus the shape of the whole molecule.

Table 2. B3LYP/6-31G(d,p) Total Electronic Energies E_e and Zero-Point Vibrational Energies of the Most Stable Conformers[a]

compd, conformation[b]	E_e (hartree)	ZPE (hartree)	ΔE_e (kJ/mol)	$\Delta E_{0\,K}$ (kJ/mol)
6a′	−845.759 729	0.216 922	14.1	14.4
6a′, sp (O−C−N−O)	−845.753 305	0.217 322	31.0	32.3
7a′	−845.765 117	0.216 825	0	0
7a′, ap (O−C−O−N)	−845.762 852	0.216 670	5.9	5.6
8a′	−845.764 905	0.217 204	0.6	1.5
8a′, sp (O−C−O−N)	−845.760 458	0.216 622	12.2	11.7
6c′	−1 037.497 37	0.270 293	22.6	22.5
6c′, sp (O−C−N−O)	−1 037.491 23	0.270 806	38.7	40.0
7c′	−1 037.502 28	0.270 288	9.7	9.6
7c′, ap (O−C−O−N)	−1 037.499 37	0.270 300	17.3	17.3
8c′	−1 037.505 98	0.270 319	0	0
8c′, sp (O−C−O−N)	−1 037.501 98	0.269 855	10.5	9.3

[a] Compounds **6a′**, **7a′**, **8a′**, **6c′**, **7c′**, and **8c′** were derived from compounds **6a**, **7a**, **8a**, **6c**, **7c**, and **8c**, respectively, through replacement of the TBDMS substituent by the TMS group. Relative electronic energies, ΔE_e, and relative energies at 0 K, $\Delta E_{0\,K}$, are given for each structure in relation to the most stable isomer of the given compound. [b] The lowest energy conformers have the structures shown in Figure 1; the second lowest energy conformers are specified as syn-periplanar (sp) or anti-periplanar (ap) for the moiety shown in parentheses.

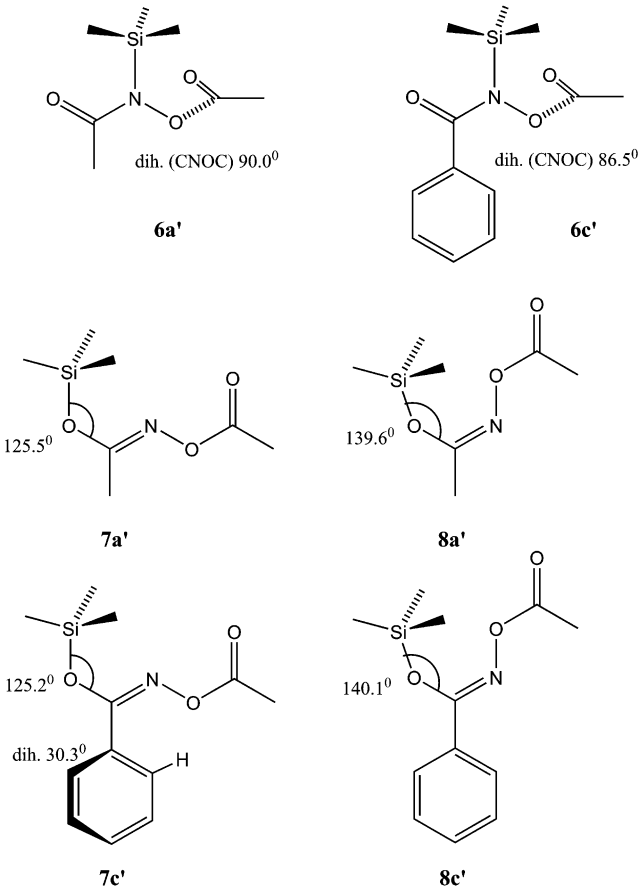

Figure 1. Structures and approximate conformations of the most stable conformers of the molecules **6a′**, **7a′**, **8a′**, **6c′**, **7c′**, and **8c′**.

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However, they differ in the conformations on the C−N bond which are opposite. The difference is evidently caused by the strong steric interaction of the trimethylsilyl group and would be certainly still greater in **6a** and **6c**, containing the bulkier *tert*-butyldimethylsilyl group. The geometries of **6a′** and **6c′** depicted in Figure 1 with an anti-periplanar arrangement on the C−N bond represent the most stable conformations of *N*-silyl derivatives. Additional minima were found by rotating the acyl substituent (acetyl and benzoyl, respectively) around the C−N bond to a syn-periplanar arrangement, which is associated with an increase of energy of about 18 kJ mol^{-1} in both cases. Steric interactions in these structures may be another cause of their lower stability compared to **7** and **8**, in addition to the weak N−Si bond. The energy differences 14 and 23 kJ mol^{-1} between isomers **6a′** and **7a′** and isomers **6c′** and **8c′**, respectively, conform to our experiments and represent the most important result of the calculations.

The *E* and *Z* *O*-silyl derivatives, **7a′** and **8a′**, can possess many conformations on the three single bonds C−O, N−O, and C−O, but the minimum-energy forms (Figure 1) are almost planar and differ distinctly in energy from the other conformers (Table 2). The energy difference between **7a′** and **8a′** is negligible and is in accord with the almost equal populations of **7a** and **8a**, as found experimentally in the silylation reaction. Equal energies of **7a′** and **8a′** were in fact unexpected: a rather strong steric interaction between the TMS group and the oxygen atom of the ester-like group is seen in **8a′**, as manifested by the widened C−O−Si bond angle (140°). Although this interaction is absent in **7a′**, the total energy is practically the same. The position of the silyl group appears somewhat strange; one would guess that rotation around the C−O bond is possible. However, the main reason for the increased energy of **7a′** is evidently the unnatural conformation around the C−O bond within the ester-like group, which differs from all known compounds with this grouping.[30] We made a great effort to find a better conformation of **7a′**, but every change resulted in either a steep rise of energy or no local energy minimum being found.

The energy relation is changed when the methyl group is replaced by phenyl to give **7c′** and **8c′**. In **7c′** there is a strong steric interaction between this phenyl group and the O atom. The phenyl ring is rotated out from the O−C−N plane (dihedral angle 30°), and the energy is raised by 10 kJ mol^{-1} against that of the isomer **8c′**. Even this relation is fully in accord with the experimentally found ratio of isomers in the silylation reaction; thermodynamic or kinetic control of this reaction would lead to the same results.

Conclusions

Silylation of *N*,*O*-diacylhydroxylamines does not yield N-silylated products, which would be thermodynamically less stable than the O-silylated isomers with *E* and *Z* hydroximic structures. The silylation reaction thus resembles benzenesulfonylation and differs from alkylation and acylation in which the *N*-isomers prevail. This difference may be attributed mainly to the weak Si−N bond. The relative stabilities of the *E* and *Z* isomers of RC(OTMS)═NOCOR′ are probably controlled sterically by the two steric interactions of the O−N oxygen atom: either with the substituent on the silicon atom (in the *Z* isomers) or with the substituent R (in the *E* isomers). In the case of a small substituent R (R = Me) the former interaction leads to a preference for the *E* isomer. For the more bulky substituents the latter interaction makes *Z* isomer favored, provided that the interaction brings about a sufficient increase in energy, as in the case of conjugation loss when R = Ph.

Experimental Section

Synthesis. The starting compounds **5a**,[10] **5b**,[31] **5c**,[32] and **5d**[8] were prepared according to the literature.

General Procedure for Silylation. All silylated derivatives were prepared by the same procedure. *N*-(*tert*-Butyldimethylsilyl)-*N*-methyltrifluoroacetamide (Aldrich, 1.2 equiv excess) was added to a solution of the parent *N*,*O*-diacylhydroxylamine in acetonitrile (0.1 g/1.5 mL). The mixture was stirred at 65 °C for 2.5 h. The excess of the silylating agent and acetonitrile were removed under reduced pressure (1.1 Pa, 65 °C). The overall yields of colorless-to-yellow syrupy products varied around 85%. The possibility of separating the isomers by HPLC was successfully tested on the mixture of **7b** and **8b**, the least stable product. No attempt was done to separate the isomers by distillation for possible decomposition or rearrangement.[13] Mixtures of isomers **7a** and **8a**, **7b** and **8b**, and **7c** and **8c** could be separated on the GC/MS system HP6890/HP5973 equipped with a DB-5MS column (30 m × 0.25 mm × 0.25 μm), using helium as a carrier gas. MS spectra of these isomers are given in the paragraphs for each individual compound. Isomers **7d** and **8d** decomposed in the GC system.

(*E*)- and (*Z*)-*tert*-Butyldimethylsilyl *N*-(Acetyloxy)acetoimidates (7a and 8a). Anal. Calcd for $C_{10}H_{21}O_3NSi$: C, 51.91; H, 9.15; N, 6.05. Found: C, 51.78; H, 9.24; N, 5.95.

7a. ^{1}H NMR ($CDCl_3$): 0.31 (s, 6H, CH_3−Si), 0.95 (s, 9H, CH_3-CSi), 2.01 (s, 3H, CH_3(R)), 2.15 (s, 3H, CH_3(R′)). MS (EI; *m*/*z* (%)): 174 (89) [M − $C_4H_9^+$]; 132 (32); 117 (82); 75 (100).

8a. ^{1}H NMR ($CDCl_3$): 0.27 (s, 6H, CH_3Si), 0.97 (s, 9H, CH_3-CSi), 2.01 (s, 3H, CH_3(R)), 2.14 (s, 3H CH_3(R′)). MS (EI; *m*/*z* (%)): 174 (16) [M − $C_4H_9^+$]; 132 (100); 117 (15); 75 (43).

(*E*)- and (*Z*)-*tert*-Butyldimethylsilyl *N*-(Benzoyloxy)-acetoimidates (7b and 8b). Anal. Calcd for $C_{15}H_{23}O_3NSi$: C, 61.40; H, 7.90; N, 4.77. Found: C, 60.49; H, 7.90; N, 4.72.

7b. ^{1}H NMR ($CDCl_3$): 0.39 (s, 6H, CH_3Si), 0.98 (s, 9H, CH_3-CSi), 2.12 (s, 3H, CH_3C═N), 7.46 (m, 2H, H-3/5), 7.57 (m, 1H, H-4), 8.05 (dd, 2H, H-2/6). MS (EI; *m*/*z* (%)): 236 (22) [M − $C_4H_9^+$]; 179 (31); 135 (10); 105 (100).

8b. ^{1}H NMR ($CDCl_3$): 0.26 (s, 6H, CH_3Si), 0.97 (s, 9H, CH_3-CSi), 2.12 (s, 3H, CH_3C═N), 7.46 (m, 2H, H-3/5), 7.57 (m, 1H, H-4), 8.07 (dd, 2H, H-2/6). MS (EI; *m*/*z* (%)): 236 (74) [M − $C_4H_9^+$]; 179 (95); 135 (27); 105 (100).

The two *E*/*Z* isomers could be separated by HPLC using an 86:14 cyclohexane−chloroform mixture (v/v) as a mobile phase and Nucleosil 100-5 NO_2 (Macherey-Nagel, Dûren, Germany) as a stationary phase in the analytical column (250 × 4 mm i.d.). UV detection at 254 nm and a flow rate of 0.5 mL/min were used. Under these conditions the **8b** isomer eluted first, while the **7b** isomer held tighter on the stationary phase. The resolution of the isomers was 7.4. The isomers were identified

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according to their CH_3Si proton lines in ^1H NMR spectra, measured in LC NMR.

(*E*)- and (*Z*)- *tert*-Butyldimethylsilyl *N*-(Acetyloxy)-benzoimidates (7c and 8c). Anal. Calcd for $C_{15}H_{23}O_3NSi$: C, 61.40; H, 7.90; N, 4.77. Found: C, 60.72; H, 7.95; N, 4.54.

7c. ^1H NMR ($CDCl_3$): 0.30 (s, 6H, CH_3Si), 1.02 (s, 9H, CH_3-CSi), 2.26 (s, 3H $CH_3C{=}O$), 7.39 (m, 2H, H-3/5), 7.46 (m, 1H, H-4), 7.86 (dd, 2H, H-2/6). MS (EI; *m*/*z* (%)): 236 (12) [M − $C_4H_9^+$]; 194 (100); 178 (14); 117 (49); 75 (60).

8c. ^1H NMR ($CDCl_3$): 0.41 (s, 6H, CH_3Si), 0.92 (s, 9H, CH_3-CSi), 2.30 (s, 3H, CH_3). MS (EI; *m*/*z* (%)): 236 (5) [M − $C_4H_9^+$]; 194 (25); 178 (24); 117 (49); 103 (87); 75 (100).

(*E*)- and (*Z*)-*tert*-Butyldimethylsilyl (Benzoyloxy)benzoimidates (7d and 8d). Anal. Calcd for $C_{20}H_{25}O_3NSi$: C, 67.57; H, 7.09; N, 3.94. Found: C, 65.71; H, 6.98; N, 3.79.

7d. ^1H NMR ($CDCl_3$): 7.38−7.52 (m, 5H, H-3/5, H-4 (R)), 7.60 (m, 1H, H-4 (R′)), 7.88 (dd, 2H, H-2/6 (R)), 8.11 (dd, 2H, H-2/6 (R′)).

8d. ^1H NMR ($CDCl_3$): 7.38−7.52 (m, 6H, H-3/5, H-4), 7.76 (dd, 2H, H-2/6 (R)), 7.94 (dd, 2H, H-2/6 (R′)).

(*E*)- and (*Z*)-*tert*-Butyldimethylsilyl *N*-(*tert*-Butyldimethylsilyloxy)acetoimidate (10 and 11). The parent acetohydroxamic acid was added directly into 1.5 equiv of *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (Aldrich) containing 1% of *tert*-butyldimethylsilyl chloride. The reaction mixture was held at 90 °C for 2 h. The excess of the silylating agent was removed under vacuum at 1.1 Pa and 65 °C, yielding 86% of the isomer mixture. Compounds **10** and **11** could not be separated using GC/MS, and therefore mass spectra are not given.

10. ^1H NMR ($CDCl_3$): 1.93 (s, 3H, CH_3), 0.93 (s, 9H, CH_3-CSi), 0.92 (s, 9H, CH_3CSi), 0.22 (s, 6H, CH_3Si), 0.12 (s, 6H, CH_3Si).

11. ^1H NMR ($CDCl_3$): 1.83 (s, 3H, CH_3), 0.94 (s, 9H, CH_3-CSi), 0.92 (s, 9H, CH_3CSi), 0.22 (s, 6H, CH_3Si), 0.14 (s, 6H, CH_3Si).

Computational Details. The theoretical studies employed the density functional method B3LYP[33,34] in conjunction with the Gaussian polarized double-ζ basis set 6-31G(d,p), as implemented in the Gaussian 98 suite of programs.[35] Trimethylsilyl derivatives (TMS, their structures being denoted by a slanted prime) were calculated instead of TBDMS derivatives, since they show qualitatively the same chemical reactivity but are more manageable for calculations. For each isomer **6′**−**8′**, all reasonable conformer structures were examined. No symmetry conditions were presumed. For all optimized structures, frequency analysis at the same level of theory was carried out in order to assign them as genuine minima. The calculated zero-point vibrational energies (ZPEs) were scaled by 0.96 for the determination of energies at 0 K.[34] The structures of the most stable conformers are shown in Figure 1, and their energies and energies of the conformers with the second lowest energy are listed in Table 2.

NMR Spectra and Structure Determination. The spectra were measured in dry $CDCl_3$ solutions (with 1% of hexamethyldisilane, HMDSS, as an internal reference) in two concentrations (approximately 1 M and 10 mM). ^1H, ^{13}C, ^{29}Si, and ^{15}N NMR measurements were performed on a Varian Inova-500 spectrometer (operating at 499.9 MHz for ^1H, at 125.7 MHz for ^{13}C, at 99.3 MHz for ^{29}Si, and at 50.7 MHz for ^{15}N NMR measurements) and a Mercury-Vx-300 spectrometer (operating at 299.9 MHz for ^1H, at 75.4 MHz for ^{13}C, at 59.6 MHz for ^{29}Si) using 5 mm switchable broad-band probes. LC NMR experiments were performed on the Inova-500 combined with a Varian ProStar HPLC chromatograph and an interchangeable flow cell with 60 μL active volume. In all cases the standard software was used. All of the spectra were recorded at 25 °C. The ^1H NMR spectra were measured using a spectral width of 8 kHz and acquisition time of 4 s; FID data were zero-filled to 128 K. The spectra were referenced to internal HMDSS (δ 0.040 relative to TMS). The ^{13}C NMR spectra were measured using a spectral width of 20−30 kHz. GARP decoupling was applied during both acquisition (1−2 s) and relaxation delay (2−5 s). Up to 3000 transients were accumulated. Zero filling to 128 K and a mild line broadening were used in data processing. The spectra were referenced to the line of the solvent (δ 76.99 relative to TMS). The $^{13}C-^{13}C$ couplings were determined by INADEQUATE experiments[36] performed on the samples of higher concentration. The $^{29}Si-^{13}C$ coupling constants were measured[37] by $^{29}Si-^{13}C$ HMQC using INEPT for ^{29}Si line enhancement in a dedicated ^{29}Si-{^1H,^{13}C} pulsed field gradient 5 mm probe (Nalorac). ^{15}N NMR spectra were measured using 90° excitation pulses, 60 s relaxation delay, and 2 s acquisition for the spectral width of 30 kHz. Usually, 100−500 transients yielded spectra with a sufficient *S*/*N* ratio. The spectra were referenced externally to the ^{15}N NMR line of nitromethane in 50% solution in the same deuterated solvent; no susceptibility correction was applied. The ^{29}Si NMR spectra, referenced to the line of hexamethyldisilane (HMDSS) at δ −19.79, were measured by the INEPT pulse sequence optimized for trimethylsilyl groups.[38]

All the NMR spectra recorded confirm the presence of two isomers in each silylation product. The ^{15}N chemical shifts unambiguously confirm the presence of isomers with a C=N double bond (i.e., they exclude the isomeric structure **6**). Assignments of the *E*/*Z* isomer structures are based on the direct $^1J(^{13}C-^{13}C)$ couplings between C=N carbon and α-carbon, ^{15}N chemical shift differences, ^{15}N-^1H couplings, ^{13}C chemical shifts of α and C=N carbons, and $^{29}Si-^{13}C$ couplings ($^2J(^{29}Si-O-^{13}C{=}N)$, $^3J(^{29}Si-O-C(N)-^{13}C$-1), $^5J(^{29}Si-O-C{=}N-O-^{13}C{=}O)$).

Acknowledgment. The financial support of the Grant Agency of the Academy of Science (Grant No. A4072005) is gratefully acknowledged. The Academy also supported the purchase of the NMR spectrometer. Partial support was provided also through a grant from the Grant Agency of the Czech Republic (Grant No. 203/03/1566).

Supporting Information Available: NMR data for diluted solutions and details of line assignment and *E*/*Z* isomer determination. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030684U

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