Synthesis of *N*,*N*-bis(silyloxy)enamines with a functionalized double bond

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The general method for the double silylation of α- or β-functionalized aliphatic nitro compounds **1** leading to regio- and stereoselective formation of *N*,*N*-bis(silyloxy)enamines **3** with a functionalized double bond is elaborated. The configuration of obtained products is determined by NMR spectroscopy.

After the discovery of silyl nitronates in 1972,[1] the silylation of aliphatic nitro compounds has evolved into a separate field of chemistry. Depending on the nature of starting nitro substrate **1**, silylating reagent, and reaction conditions this process may afford either silyl nitronates **2**, *N*,*N*-bis(silyloxy)enamines (BENA) **3**,[2,3] or quaternary ammonium salts **4**[3] (Scheme 1).

Currently, from the silylation products shown in Scheme 1, BENA **3** are the most attractive substances from the standpoint of broadening the reactivity of aliphatic nitro compounds. Originally, BENA were described[2] as unstable species prone to decomposition upon concentration of their solutions as well as easily undergoing rearrangement into silyloxy oximes **6**. However, recently we demonstrated[3] that BENA **3** are stable and easy-to-handle compounds *provided that aqueous work-up is employed upon their isolation*. In addition, BENA turned out to be valuable reagents in C,C[4] and N,C[5] cross-coupling reactions. Since BENA are enamines containing the unusual fragment $N(OSiMe_3)_2$, investigation of the barrier to nitrogen lone-pair inversion is also of considerable interest.†

In this connection, it is important to have access to a wide range of structurally diverse BENA **3**. Previously unknown BENA with a functionalized double bond are especially interesting. Recently,[3] we introduced bromotrimethylsilane for the synthesis of BENA containing alkyl or functionalized alkyl substituents R^1 and R^2 (see Scheme 1). However, this method proved to be inapplicable for the preparation of BENA with a functionalized double bond. Thus, treatment of ethyl 2-nitropropionate **1a** with 2.2 equiv. of Me_3SiBr and 2.3 equiv. of NEt_3 in methylene dichloride at −30 °C gives rise to silyl nitronate **2a** and quaternary salt **4a** in the ratio 1:1, thereby suggesting that formation of salt **4a** (step 3) occurs faster than does conversion of **2a** to **3a** (step 2, Scheme 1). Salt **5a** (X = Br) can be isolated in 45% yield upon silylation of **1a** with an excess of silylating agent followed by methanolysis of **4a**.

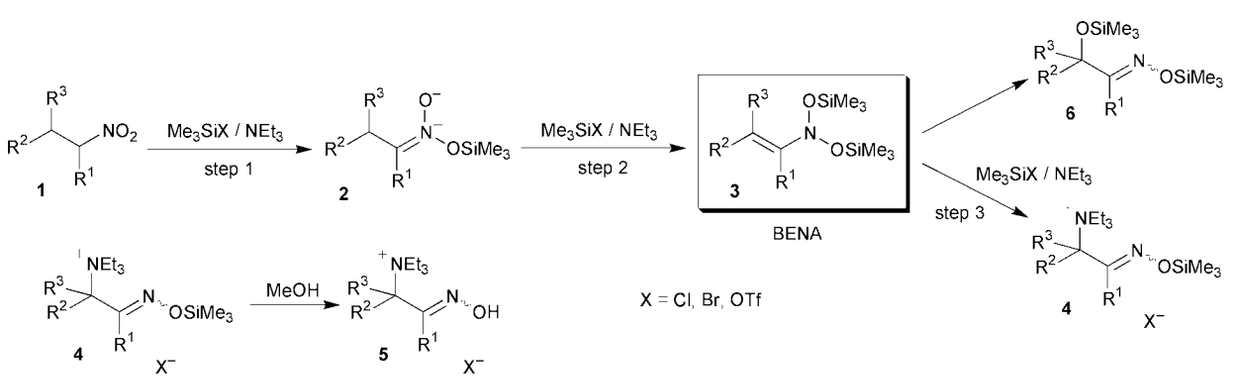
Results and discussion

Obviously, to retard step 3 and accelerate step 2 it is necessary to lower the reaction temperature along with application of a silylating reagent stronger than Me_3SiBr.‡[7] Employment of Me_3SiOTf for this purpose allowed us to develop a general method for the synthesis of BENA **3a**–**f** possessing a functionalized double bond (Scheme 2, Table 1).

Comparison of the conditions for silylation of **1a**–**g** with the conditions for the analogous process for unfunctionalized nitro alkanes[2] indicates that functionalization of the α or β carbon atom of the starting nitro substrate **1** does not lead to a dramatic change in the rate of its double silylation. Entry 7 in Table 1 demonstrates that under similar conditions BENA **3g** containing bulky substituents at silicon could be obtained when *t*-$BuMe_2SiOTf$ is used instead of Me_3SiOTf.

† Introduction of electron-withdrawing groups to nitrogen tends to increase the barrier of lone-pair inversion substantially. (For a review on dialkoxyamines see ref. 6.) Data on barriers of lone-pair inversion in BENA will be published in due course.

‡ Attempts to retard step 3 using $EtNPr^i_2$ instead of NEt_3 failed. In fact, no reaction was observed upon treatment of **2a** with Me_3SiBr–$EtNPr^i_2$ in $CDCl_3$ (60 °C; 1 h; NMR monitoring).



Scheme 1

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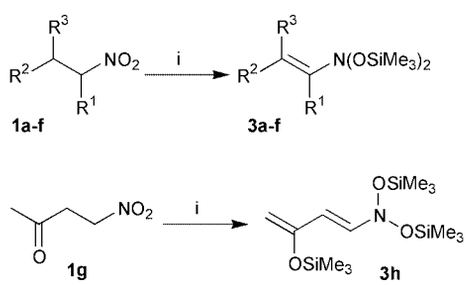
Table 1 Synthesis of BENA **3a**–**h** from nitro compounds **1a**–**g**

Entry	Nitro compound	R^1	R^2	R^3	Reaction conditions: Temp. (*T*/°C)	Reaction conditions: Time (*t*/h)	Product	Bp[a] (*T*/°C/mmHg)	Yield (%)
1	**1a**	CO_2Et	H	H	−75	5	**3a**	42–52/0.08[b]	94
2	**1b**	H	CO_2Me	H	−75	2.5	**3b**	54–58/0.05	87
3	**1c**	CO_2Me	Me	H	−50	4	**3c**	43–49/0.06[c]	92
4	**1d**	H	CO_2Me	Me	−75	5	**3d**	60–65/0.05	87
5	**1e**	H	CO_2Me	$PhC(O)CH_2$	−75	1.5	**3e**		71
6	**1f**	Me	CO_2Me	H	−30	3	**3f**	52–55/0.1	85
7	**1f**	Me	CO_2Me	H	0	3	**3g**[d]	90–95/0.1	75
8	**1g**	H	MeC(O)	H	−75	2	**3h**[e]	75–82/0.1	84

[a] Bp refers to bath temperature. [b] Distilled product contained 40% of **6a**. [C] Distilled product contained 10% of **6c**. [d] *t*-$BuMe_2Si$ group instead of Me_3Si in silylating agent as well as in resulting BENA. [e] $R^2 = CH_2=C(OSiMe_3)$, see Scheme 2.

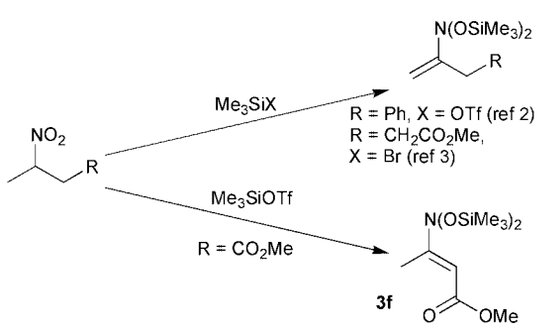
In some cases double silylation of the nitro group is accompanied by silylation of the functional group (*e.g.*, Entry 8, Table 1; Scheme 2, **3h**).



Scheme 2 *Reagents*: i, Me_3SiOTf, NEt_3, CH_2Cl_2.

We would like to point out that double silylation of nitro compounds **1a**–**g** is a highly regio- and stereoselective process furnishing BENA **3a**–**h** as single isomers.

Previously,[2,3] silylation of nitro compounds containing an α-methyl substituent afforded BENA with a terminal double bond, clearly indicating that steric effects prevail over electronic ones. Thus, the activating effect of a methoxycarbonylmethyl or even a phenyl group in the β-position is insufficient to override the kinetic preference for terminal C=C bond formation (Scheme 3, top). Nonetheless, the introduction of a strongly electron-withdrawing group (R = CO_2Me) makes the β-hydrogen acidic enough to completely reverse the regiochemical outcome to give BENA **3f** with an internal double bond (Scheme 3, bottom).



Scheme 3

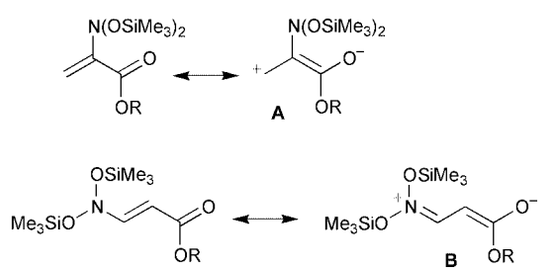
It should be noted that other possible side-reactions (*e.g.*, 1,3-N,C-elimination of Me_3SiOH from silyl nitronate **2b**[8] are suppressed under our suggested conditions for BENA synthesis.

In contrast to very moisture-sensitive silyl nitronates **2**, BENA **3a**–**h** need not be carefully protected from atmospheric moisture. Hexane solutions of BENA **3** can be stored for long periods of time at −30 to 0 °C.

Determination of the geometry of BENA 3a–h

The structures of BENA **3a**–**h** were confirmed by NMR spectroscopy and additionally for **3b**,**d**,**f**–**h** by microanalysis. The characteristic NMR data for **3a**–**h** as well as for the previously reported[3] **3i**–**k** are presented in Table 2.

Generally, the calculated chemical shifts are in satisfactory agreement with the observed ones. It is worth noting that a CO_2Me group significantly contributes to polarization of the BENA π-system, which is reflected in mesomeric structures **A** and **B** (Scheme 4).



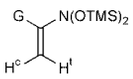
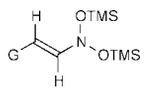
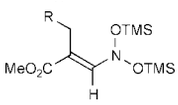
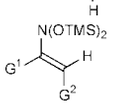
Scheme 4

We assigned the *E*-configuration to vicinally substituted BENA **3b**,**h** on the basis of the large value for $^3J_{H-H}$ coupling constant (13.4 and 13.1 Hz, respectively) typical for *trans* α,β-disubstituted alkenes.[10] For assignment of configuration of trisubstituted BENA **3** we applied the rule that $^3J(^{13}C_\alpha–H)$ (*E*) > $^3J(13C_\alpha–H)$ (*Z*) for the fragment H–C=C–C$^\alpha$. We have already used this rule to establish the configuration of functionalized enoximes.[11] It is general and gives unambiguous results by comparison of two isomers. But having only single isomers, we had to resort to measurement of coupling constants of the model terminal BENA **3a**,**j** and internal BENA **3b**,**k**, the configuration of which can be established independently by the $^3J_{H-H}$-value (see Table 2).

Inspection of Table 2 indicates that there is considerable difference in magnitudes of $^3J(^{13}C_\alpha–H)$ (*E*) and $^3J(^{13}C_\alpha–H)$ (*Z*) for model BENA **3a**,**b** containing a (m)ethoxycarbonyl group [G = CO_2Me(Et)] with $^3J(^{13}C_\alpha–H)$ (*Z*) being always less than 5 Hz and $^3J(^{13}C_\alpha–H)$ (*E*) being around 10 Hz. Comparison of these data with values of $^3J(^{13}C_\alpha–H)$ for BENA **3c**,**d**,**e** allows unambiguous assignment of their configuration as shown in Table 2.

However, if G = Me, such an approach could not confidently be used owing to the less pronounced difference between $^3J(^{13}C_\alpha–H)$ (*Z*) and $^3J(^{13}C_\alpha–H)$ (*E*) (4.2 and 8.5 Hz, respectively) in model BENA **3j**. The $^3J(^{13}C_\alpha–H)$ for BENA **3f** has an intermediate value of 6.2 Hz. Therefore, in this case the *E*-configuration was established on the basis of the observation of a nuclear Overhauser enhancement (NOE) between a trimethylsilyl group and the =CH proton.

Table 2 Selected NMR data of BENA **3a**–**k**

	BENA[a]		Chem. shifts, δ/ppm (calculated[b])		^3J Coupling constants/Hz[c]			
			$^{13}C^{\alpha}$	$^{13}C^{\beta}$	$^3J_{H-H}$	$^3J(H^Z\_^{13}C_\alpha)$	$^3J(H^E\_^{13}C_\alpha)$	Confign.
	G = H	**3i**[d]	148.6	102.3				
	G = Me	**3j**[d]	156.0 (159.2)	103.7 (94.3)		4.2	8.5	
	G = CO_2Et	**3a**	151.5 (154.6)	111.8 (109.3)		4.5	10.0	
	G = Me	**3k**[d]	143.4 (140.6)	117.3 (112.9)	13.5	4.5		*E*
	G = CO_2Me	**3b**	155.4 (155.6)	104.4 (108.3)	13.4	5.0		*E*
	G = CH_2=C(OTMS)	**3h**	142.8	116.6	13.1			*E*
	R = H	**3d**	149.2 (147.6)	120.9 (118.9)		4.5	6.0	*E*
	R = PhC(O)	**3e**	151.3	118.7		4.5	5.0	*E*
	G^1 = CO_2Me, G^2 = Me	**3c**	144.6 (146.6)	125.8 (119.9)			9.0	*E*
	G^1 = Me, G^2 = CO_2Me	**3f**[e]	165.3 or 167.3 (166.2)	105.0 (100.3)			6.2	*E*

[a] TMS = Me_3Si. [b] The increments of RO_2C +6.0 (for C^{α}), +7.0 (for C^{β}); of Me +10.6 (for C^{α}), −8.0 (for C^{β}) (see ref. 9); and of $N(OSiMe_3)_2$ +25.3 (for C^{α}) and −21.0 (for C^{β}) were calculated from NMR ^{13}C spectra of **3i** (see ref. 3). [c] The precision of coupling constant determination was ±0.25 Hz. [d] See ref. 3. [e] Configuration of **3g** was assigned by analogy with **3f**.

In summary, we have developed an efficient method for the regio- and stereoselective synthesis of BENA with a functionalized double bond. At present, a wide variety of terminal and internal BENA with or without functional groups are available. It allows us to open the way for extensive investigations of their chemical properties as well as of their characteristic dynamic processes.

Experimental

NMR spectra were recorded on a Bruker AM-300 instrument for samples in $CDCl_3$ unless otherwise indicated. Chemical shifts were measured relative to internal reference ($\delta = 0$) Me_4Si (^1H, ^{13}C and ^{29}Si) and external reference ($\delta = 0$) $MeNO_2$ (^{14}N). The INEPT pulse sequence was used for ^{29}Si signal observation. The values of ^1H–^{13}C coupling constants were determined using either gated proton-decoupling ^{13}C spectra or selective polarization transfer from one proton with simultaneous selective decoupling of another proton (SPT_CW).[12] *J*-Values are given in Hz.

Starting nitro compounds **1a**,[13] **1b**,[14] **1d**,[15] **1e**,[16] **1h**,[17] **1g**,[8] were obtained according to literature procedures. Nitro compound **1c** was prepared from methyl 2-bromobutyrate and $NaNO_2$ in DMF[13] (bp 82–84 °C/10 mmHg; lit.,[18] 77 °C/2.5 mmHg).

All reactions were performed in a dry argon atmosphere using methylene dichloride freshly distilled from CaH_2. Petroleum spirit refers to the fraction having a distillation range of 60–70 °C.

N,*N*-Bis(trimethylsiloxy)enamines 3a–f,h. General procedure

To a solution of nitro compound **1a**–**g** (1.5 mmol) in CH_2Cl_2 (1.5 mL) at −75 °C was added Et_3N (for **1a**–**f** 0.50 mL, 3.6 mmol; for **1g** 0.71 mL, 5.1 mmol) followed by dropwise addition of a solution of Me_3SiOTf (for **1a**–**f** 0.62 mL, 3.3 mmol; for **1g** 0.90 mL, 4.8 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred (time and temperature indicated in Table 1). For work-up, petroleum spirit (15 mL) was added dropwise to maintain a low temperature. MeOH (50 μL) was added and the mixture was stirred for an additional 10 min at the same temperature, then the mixture was poured into water (10 mL)–petroleum spirit (20 mL). The organic phase was washed successively with aq. $NaHSO_4 \cdot H_2O$ (60 mg in 20 mL), water (10 mL), and brine (2 × 10 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give BENA **3a**–**f**,**h** as clear, colorless oils.

N,*N*-Bis(*tert*-butyldimethylsiloxy)enamine 3g

To a solution of nitro compound **1f** (1.5 mmol) in CH_2Cl_2 (1.5 mL) at −75 °C was added Et_3N (0.50 mL, 3.6 mmol) followed by dropwise addition of a solution of *t*-$BuMe_2$-SiOTf (0.72 mL, 3.3 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 3 h at 0 °C. For work-up, a mixture of citric acid (200 mg) and Et_3N (0.84 mL) in CH_2Cl_2 (2 mL) was added rapidly and the whole was stirred for an additional 2 min at 0 °C. Then petroleum spirit (15 mL) was added and the mixture was poured into water (10 mL)–petroleum spirit (20 mL). The organic phase was washed successively with water (20 mL), saturated aq. $NaHCO_3$ (10 mL), water (10 mL), aq. $NaHSO_4 \cdot H_2O$ (800 mg in 80 mL), water (10 mL), and brine (2 × 10 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give BENA **3g** as a clear, colorless oil.

Compounds **3a**–**d**,**f**,**h** were pure according to ^1H, ^{13}C, and ^{29}Si NMR analysis. BENA **3e** contained ≈10% of unidentified impurity. Crude **3g** contained a trace amount of *t*-$BuMe_2SiOH$. NMR data for BENA **3a**–**h** are reported in Table 3.

Analytically pure samples of **3b**,**d**,**f**–**h** were obtained by vacuum distillation in a short-path apparatus (deviations of obtained microanalytical data from calculated ones were C ± 0.31, H ± 0.26, N ± 0.34, Si ± 0.31%).

Distillation of **3a** and **3c** afforded partially rearranged products: **3a** : **6a** = 60 : 40 and **3c** : **6c** = 90 : 10, respectively.

Authentic specimens of **6a** and **6c** were obtained from **3a** and **3c** by treatment with 5–10 mol% of CF_3SO_3H in CH_2Cl_2, with isolated yields of 25–27%.

Ethyl 3-trimethylsiloxy-2-(trimethylsiloxyimino)propionate 6a

Bp 45–55 °C/0.07 mmHg (Found: C, 45.43; H, 8.67; N, 4.55; Si, 19.50. Calc. for $C_{11}H_{25}NO_4Si_2$: C, 45.33; H, 8.64; N, 4.81; Si, 19.27%); δ_H 0.12 (9 H, s) and 0.26 (9 H, s) (two $OSiMe_3$), 1.34 (3 H, t, *J* 7.2, *Me*CH_2O), 4.31 (2 H, q, *J* 7.2, MeCH_2O), 4.57 (2 H, s, CH_2C=N); δ_C −0.8 and −0.5 (two $OSiMe_3$), 14.2 (*Me*CH_2O), 53.9 (CH_2C=N), 61.4 (MeCH_2O), 156.5 and 163.5 (C=O and C=N); δ_{Si} 21.11 and 29.59 ($NOSiMe_3$ and CH_2OSiMe_3).

Methyl 3-trimethylsiloxy-2-(trimethylsiloxyimino)butyrate 6c

Bp 34–44 °C/0.05 mmHg (Found: C, 45.39; H, 8.52; N, 4.50; Si, 19.61. Calc. for $C_{11}H_{25}NO_4Si_2$: C, 45.33; H, 8.64; N, 4.81; Si, 19.27%); two isomers around the C=N bond, *E* : *Z* =

Table 3 NMR data for BENA **3a–h**

BENA	^{1}H NMR, δ, J/Hz	^{13}C NMR, δ	^{29}Si NMR, δ
3a	0.24 (18 H, s, $SiMe_3$), 1.32 (3 H, t, J 6.7, *Me*CH_2), 4.24 (2 H, q, J 6.7, MeCH_2), 5.77 (1 H, s, CH_A-H_B=C), 5.81 (1 H, s, CH_AH_B=C)	0.1 ($SiMe_3$), 14.2 (*Me*CH_2), 60.9 (MeCH_2), 111.8 (CH_2=), 151.5 (*C*=CH_2), 162.9 (C=O)	26.23
3b	0.19 (18 H, s, $SiMe_3$), 3.66 (3 H, s, OMe), 5.47 (1 H, d, J 13.4, CHCO), 7.20 (1 H, d, J 13.4, CHN)	−0.1 ($SiMe_3$), 51.3 (OMe), 104.4 (CH=*C*HCO), 155.4 (*C*H=CHCO), 166.8 (C=O)	27.92
3c	0.18 (18 H, s, $SiMe_3$), 1.90 (3 H, d, J 7.3, *Me*CH), 3.78 (3 H, s, OMe), 6.24 (1 H, q, J 7.3, CH)	−0.3 ($SiMe_3$), 13.1 (*Me*CH), 51.2 (OMe), 125.8 (CH), 144.6 (*C*=CH), 164.1 (C=O)	24.82
3d	0.21 (18 H, s, $SiMe_3$), 1.94 (3 H, d, J 1.4, *Me*C=CH), 3.77 (3 H, s, OMe), 6.98 (1 H, q, J 1.4, CH)	−0.1 ($SiMe_3$), 12.2 (*Me*C=), 51.9 (OMe), 120.9 (*C*=CH), 149.2 (CH), 168.0 (C=O)	24.49
3e	0.19 (18 H, s, $SiMe_3$), 3.73 (3 H, s, OMe), 4.18 (2 H, s, CH_2), 7.27 (1 H, s, CH=C), 7.43–7.50 (2 H, m, *o*-CH), 7.53–7.61 (1 H, m, *p*-CH), 7.89–8.04 (2 H, m, *m*-CH)	0.0 ($SiMe_3$), 36.3 (CH_2), 51.9 (OMe), 118.7 (*C*=CH), 127.8 and 128.5 (*o*-CH and *m*-CH), 133.0 (*p*-CH), 136.5 (*C-ipso*), 151.3 (CHN), 167.0 (*C*O_2Me), 195.3 (Ph*C*=O)	25.68
3f	0.22 (18 H, s, $SiMe_3$), 2.27 (3 H, d, J 1, MeC), 3.70 (3 H, s, OMe), 5.79 (1 H, q, J 1, CH)	0.0 ($SiMe_3$), 13.7 (C*Me*), 51.0 (OMe), 105.0 (CH), 165.3 and 167.3 (C=O and C–N)	26.75
3g	0.17 (12 H, s, Si*Me*$_2$Bu^t), 0.90 (18 H, s, $SiMe_2$*Bu^t*), 2.26 (3 H, d, J 1, MeC), 3.68 (3 H, s, OMe), 5.79 (1 H, q, J 1, CH)	−4.1 (Si*Me*$_2$Bu^t), 13.6 (C*Me*), 18.0 (*C*Me_3), 25.9 (C*Me*$_3$), 51.1 (OMe), 105.8 (CH), 165.4 and 167.4 (C=O and C–N)	27.59
3h	0.22 [18 H, s, N($OSiMe_3$)$_2$], 0.23 (9 H, s, $COSiMe_3$), 4.31 (1 H, s, CH_AH_B=C), 4.33 (1 H, s, CH_AH_B=C), 5.82 (1 H, d, J 13.1, CHN), 6.42 (1 H, d, J 13.1, C*H*=CHN)	−0.2 [N($OSiMe_3$)$_2$ and $OSiMe_3$], 96.3 (CH_2), 116.6 (*C*H=CHN), 142.8 (CHN), 153.0 (*C*$OSiMe_3$)	19.00 ($COSiMe_3$), 24.31 [N($OSiMe_3$)$_2$]

2.8 : 1.§ *E*-isomer δ_H 0.09 (9 H, s) and 0.24 (9 H, s) (two $OSiMe_3$), 1.44 (3 H, d, J 6.6, *Me*CH), 3.81 (3 H, s, OMe), 5.23 (1 H, q, J 6.6, CH); *Z*-isomer δ_H 0.12 (9 H, s) and 0.19 (9 H, s) (two $OSiMe_3$), 1.41 (3 H, d, J 6.6, *Me*CH), 3.85 (3 H, s, OMe), 4.61 (1 H, q, J 6.6, CH); *E*-isomer δ_C −0.86 and −0.35 (two $OSiMe_3$), 20.9 (*Me*CH), 52.0 (OMe), 62.3 (CH), 161.2 (C=O), 163.6 (C=N); *Z*-isomer δ_C −0.93 and −0.16 (two $OSiMe_3$), 21.9 (*Me*CH), 51.6 (OMe), 67.4 (CH), 159.0 (C=O), 163.4 (C=N); *E*-isomer δ_{Si} 19.23 and 28.76 ($NOSiMe_3$ and $CHOSiMe_3$); *Z*-isomer δ_{Si} 19.49 and 27.77 ($NOSiMe_3$ and $CHOSiMe_3$).

Owing to difficulties in the isolation of salt **4a**, it was identified in the corresponding reaction mixture by ^{1}H NMR spectroscopy δ_H 0.34 (9 H, s, $OSiMe_3$), 1.38 (3 H, t, J 7.0, *Me*CH_2O), 1.48 (9 H, t, J 7.0, *Me*CH_2N), 3.58 (6 H, q, J 7.0, MeCH_2N), 4.37 (2 H, q, J 7.0, MeCH_2O), 4.45 (2 H, s, CH_2C=N).

N-[2-Ethoxycarbonyl-2-(hydroxyimino)ethyl]-*N*,*N*,*N*-triethylammonium bromide 5a

To a solution of **1a** (220.5 mg, 1.5 mmol) and Et_3N (0.69 mL, 5 mmol) at −70 °C was added a solution of Me_3SiBr (0.63 mL, 4.8 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at −70 °C (10 min), −30 °C (5 h), and room temperature (18 h), followed by addition of MeOH (5 mL). After stirring of the mixture for an additional 20 min at room temperature, the volatile components were evaporated *in vacuo* and the residue was dried (20 °C/0.2 mmHg). The resulting solid was washed with 50 mL of CH_2Cl_2 to give salt **5a** (210 mg, 45%); mp 136–138 °C; (decomp.) (Found: C, 42.76; H, 7.22, Br, 25.80; N, 9.41. Calc. for $C_{11}H_{23}BrN_2O_3$: C, 42.45; H, 7.45; Br, 25.67; N, 9.00%); δ_H (acetone-d_6–D_2O, 4 : 1) 1.28 (3 H, t, J 7.1, *Me*CH_2O), 1.40 (9 H, t, J 7.1, *Me*CH_2N), 3.44 (6 H, q, J 7.1, MeCH_2N), 4.31 (2 H, q, J 7.1, MeCH_2O), 4.40 (2 H, s, CH_2C=N); δ_C (acetone-d_6–D_2O, 4 : 1) 8.8 (*Me*CH_2N), 14.4 (*Me*CH_2O), 49.4 (*C*H_2C=N), 55.9 (MeCH_2N), 63.6 (MeCH_2O), 142.3 (C=N), 164.6 (C=O); $\delta_{^{14}N}$ (acetone-d_6–D_2O, 4 : 1) −313.6 ($\Delta\nu_{1/2}$ 57 Hz, $[NEt_3]^+$).

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§ Configuration of isomeric oximes was assigned by ^{13}C chemical-shift values of substituents adjacent to the C=NOH group; similar assignments are given in refs. 4*a–c* and 5*b*,*c*.

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