Reactions of *N*,*N*-bis(siloxy)enamines with trimethylsilyl cyanide: aliphatic nitro compounds as convenient precursors of 5-aminoisoxazoles

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A convenient procedure was developed for the synthesis of 5-aminoisoxazoles by the consecutive double silylation and cyanation of aliphatic nitro compounds.

N,*N*-Bis(siloxy)enamines (BENA) **1**,[1,2] double silylation products of available aliphatic nitro compounds, behave as β-C-electrophiles toward various C- and N-centred nucleophiles[3] (the anions of β-dicarbonyl and nitro compounds, silyl nitronates, primary or secondary amines, and silyl derivatives of *N*-nitroamines or azoles).

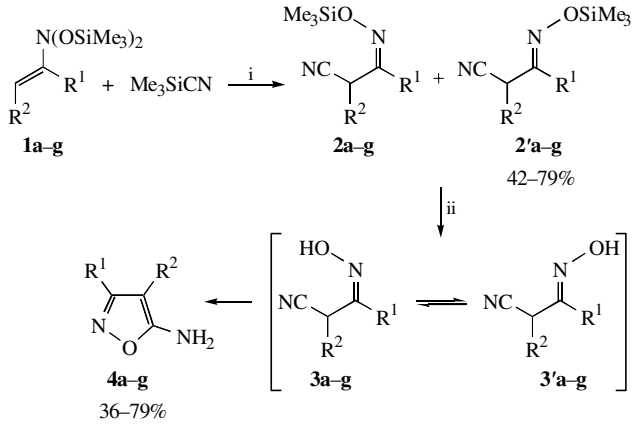
It was assumed[3,4] that conjugated nitrosoalkenes that resulted from BENA under the action of nucleophiles rather than BENA are actual intermediates in these reactions.

In this context, it is of interest to use the cyanide ion as a nucleophile in such reactions because the corresponding α-cyano oximes (or their silyl derivatives), the probable primary products of its C,C-cross-coupling reactions with BENA, were not described in the literature, although they might be usable in organic synthesis.

The aim of this work was to study the interaction of the cyanide ion with BENA **1**.

We found that BENA **1b** reacted with potassium cyanide in the presence of dibenzo-18-crown-6 afforded a difficult-to-separate mixture of unidentified products.

At the same time, trimethylsilyl cyanide (TMSCN) smoothly reacts with BENA **1** over a wide range of conditions to give previously unknown trimethylsilyl derivatives of cyanoximes **2**. It is likely that it is optimum to use solutions of equimolar amounts of reactants in CH_2Cl_2 in the presence of 10 mol% Et_3N (Scheme 1 and Table 1).† It is well known[6] that Et_3N catalysis is required for the C,C-cross-coupling of silyl nitronates with BENA. However, the reaction BENA + TMSCN can also be performed without Et_3N. In this case, the reaction occurs without a solvent at 20 °C for several days, and the yields of target products **2** are close to those given in Table 1.‡



Scheme 1 *Reagents and conditions*: i, CH_2Cl_2, Et_3N (cat.), 20–40 °C; ii, MeOH, Et_3N (cat.), 20 °C.

Scheme 2 illustrates a conceivable reaction mechanism. We believe that Et_3N, reacting with TMSCN, generates conjugated nitrosoalkene **A** from BENA **1**. This active intermediate further reacts with TMSCN to give a mixture of *syn*- and *anti*-isomers of the silyl derivatives of cyano-substituted oximes **2** and **2′** (see also Scheme 1). TMSCN may participate in this process in a tautomeric isonitrile form.[7]

It was previously noted[8] that the cyanide ion reacts with nitrosoalkenes **A** to form 5-aminoisoxazoles **4**. In the absence of Et_3N, intermediate **A** was generated with the use of TMSCN, however, at a much lower rate.

† *General procedure for the synthesis of silyl derivatives* **2a–e**.

All reactions with BENA were performed in specially dried solvents in a dry argon atmosphere.

Et_3N (0.5 mmol, 0.07 ml) and then BENA **1a–e** (5 mmol) were added to TMSCN[5] (5 mmol, 0.67 ml) in freshly distilled CH_2Cl_2 (7.5 ml) at 20 °C with intense stirring. After an induction period (from a few seconds to 45 min), the reaction mixture warmed up to boiling; it was allowed to stand for 1.5 h, volatile components were distilled at 40 °C/20 Torr, and the residue was fractionated in a vacuum to obtain silyl derivatives **2a–e** (the yields are given in Table 1).

NMR spectra were measured on a Bruker AM-300 spectrometer (operating frequency of 300.3 MHz for ^{1}H, 75.47 MHz for ^{13}C and 59.63 MHz for ^{29}Si, INEPT); TMS was used as an internal standard; $CDCl_3$ was a solvent, unless otherwise specified.

3-(Trimethylsilyloximino)propionitrile (**2a** + **2′a**; *E*/*Z* = 1:2.2): yield 49%, bp 35–36 °C/0.35 Torr. *E*: ^{1}H NMR, δ: 0.19 (s, 9H, $SiMe_3$), 3.28 (d, 2H, CH_2, ^3J 5.1 Hz), 7.41 (t, 1H, CH, ^3J 5.1 Hz); ^{13}C NMR, δ: –0.9 ($SiMe_3$), 19.0 (CH_2), 114.9 (CN), 143.8 (CH); ^{29}Si NMR, δ: 28.08. *Z*: ^{1}H NMR, δ: 0.19 (s, 9H, $SiMe_3$), 3.41 (d, 2H, CH_2, ^3J 4.4 Hz), 6.96 (t, 1H, CH, ^3J 4.4 Hz); ^{13}C NMR, δ: –0.9 ($SiMe_3$), 14.8 (CH_2), 115.6 (CN), 142.5 (CH); ^{29}Si NMR, δ: 28.72.

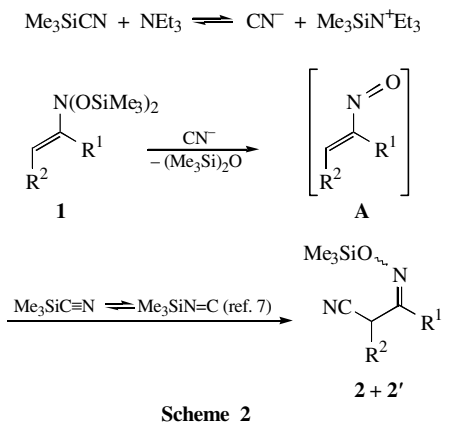
3-(Trimethylsilyloximino)butyronitrile (**2b** + **2′b**; *E*/*Z* = 1.2:1): yield 79%, bp 28–29 °C/0.35 Torr. *E*: ^{1}H NMR, δ: 0.19 (s, 9H, $SiMe_3$), 2.10 (s, 3H, Me), 3.38 (s, 2H, CH_2); ^{13}C NMR, δ: –0.8 ($SiMe_3$), 13.5 (Me), 24.7 (CH_2), 115.5 (CN), 151.6 (C=N); ^{29}Si NMR, δ: 26.65. *Z*: ^{1}H NMR, δ: 0.19 (s, 9H, $SiMe_3$), 1.98 (s, 3H, Me), 3.50 (s, 2H, CH_2); ^{13}C NMR, δ: –0.9 ($SiMe_3$), 17.8 (Me), 19.3 (CH_2), 115.6 (CN), 149.7 (C=N); ^{29}Si NMR, δ: 26.80.

2-Methyl-3-(trimethylsilyloximino)propionitrile (**2c** + **2′c**; *E*/*Z* = 4:3): yield 70%, bp 38 °C/0.4 Torr. *E*: ^{1}H NMR, δ: 0.20 (s, 9H, $SiMe_3$), 1.48 (d, 3H, Me, ^3J 7.3 Hz), 3.53 (m, 1H, C*H*Me), 7.41 (d, 1H, HC=N, ^3J 5.1 Hz); ^{13}C NMR, δ: –0.9 ($SiMe_3$), 16.4 (Me), 26.6 (*C*HMe), 118.7 (CN), 149.1 (C=N). *Z*: ^{1}H NMR, δ: 0.21 (s, 9H, $SiMe_3$), 1.43 (d, 3H, Me, ^3J 7.3 Hz), 4.23 (m, 1H, C*H*Me), 6.88 (d, 1H, HC=N, ^3J 5.2 Hz). ^{13}C NMR, δ: –0.9 ($SiMe_3$), 15.6 (Me), 21.7 (*C*HMe), 119.1 (CN), 148.3 (C=N).

Methyl 5-cyano-4-(trimethylsilyloxy)pentanoate (**2d** + **2′d**; *E*/*Z* = 1:3): yield 61%, bp 84–88 °C/0.20 Torr. *E*: ^{1}H NMR, δ: 0.12 (s, 9H, $SiMe_3$), 2.58, 2.69 (m, 4H, CH_2CH_2), 3.37 (s, 2H, CH_2), 3.62 (s, 3H, OMe); ^{13}C NMR: –1.0 ($SiMe_3$), 23.4 (CH_2CH_2NOSi), 23.8 (CH_2CN), 29.8 (CH_2CO_2), 51.7 (Me), 115.3 (CN), 154.0 (C=N), 172.7 (CO). *Z*: ^{1}H NMR, δ: 0.14 (s, 9H, $SiMe_3$), 2.58, 2.69 (m, 4H, CH_2CH_2), 3.44 (s, 2H, CH_2), 3.62 (s, 3H, OMe); ^{13}C NMR, δ: –0.9 ($SiMe_3$), 17.4 (CH_2CN), 28.6 (CH_2CH_2CNOSi), 29.6 (CH_2CO_2), 51.5 (Me), 115.3 (CN), 150.7 (C=N), 172.4 (CO).

3-Phenyl-3-(trimethylsilyloximino)propionitrile (**2e**): yield 72%, bp 92 °C/0.50 Torr. *E*: ^{1}H NMR, δ: 0.35 (s, 9H, $SiMe_3$), 3.87 (s, 2H, CH_2), 7.45, 7.70 (m, 5H, Ph); ^{13}C NMR: –0.6 ($SiMe_3$), 14.8 (CH_2), 115.3 (CN), 126.2, 128.7, 130.1, 133.5 (Ph), 150.9 (C=N).

‡ TMSCN (2 mmol, 0.27 ml) was added to freshly distilled enamine **1b** (2 mmol, 0.46 g) with stirring at room temperature, the reaction mixture was allowed to stand at 20 °C for 48 h, volatile components were distilled at 20 °C/0.1 Torr, and an aliquot portion of CH_2Cl_2 was added as an internal standard to the residue. The yield of mixture of **2b** + **2′b** was 82%, molar ratio **2b**:**2′b** ~ 1:1.2.



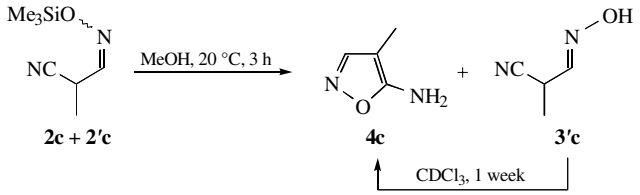
Scheme 2

The role of CH_2Cl_2 is reduced to the dissolution of reactants and to the control of reaction temperature by heat removal due to the boiling of the solvent.

According to NMR data, derivatives **2a–d** are mixtures of *Z*- and *E*-isomers (**2** and **2′**, respectively, in Scheme 1 and Table 1). Compounds **2e–g** were detected as individual isomers with the *Z*-configuration of CN and $OSiMe_3$ groups. It is likely that the *Z*/*E* ratios given in Table 1 are thermodynamic values because they remained unchanged after the vacuum distillation of these products. Note that compounds **2a–e** with > 90% purity (NMR data) can be isolated by fractionation (the synthesis of **2f**,**g** will be considered below).

The desilylation of derivatives **2a–g** by the action of methanol with Et_3N added afforded 5-aminoisoxazoles **4a–g** in place of corresponding free oximes **3a–g** (Scheme 1, Table 1).§

Evidently, only isomers **3**, in which CN and OH groups are close to each other, undergo cyclisation. The so-called mild methanolysis of oxime derivatives **2c** + **2′c** resulted in the formation of corresponding isoxazole **4c** only from isomer **2c**, whereas isomer **2′c** was converted into the *E*-isomer of oxime **3′c**. Isomer **3′c** in $CDCl_3$ was also very slowly isomerised to isoxazole **4c** in a spectrometer ampoule (Scheme 3). It is believed that the rate of this cyclisation corresponds to the rate of the equilibration **3c** ⇌ **3′c**.¶



Scheme 3

In contrast to the anions of aliphatic nitro compounds and silyl nitronates, TMSCN readily reacts with both terminal and internal BENA. All of these reactions are chemoselective; that is, the corresponding isonitrile derivatives were not detected.

Let us consider the reactions of TMSCN with BENA **1g**,**f**, containing a CO_2Alk group at the α-position, in more detail (Schemes 4 and 5).

Table 1 Product yields in the test reactions.

BENA	R^1	R^2	Yield of **2** + **2′** (%)	**2**:**2′**	Yield of **4** (%) on a BENA basis
1a	H	H	49	2.2:1	49
1b	Me	H	79	1:1.2	79
1c	H	Me	70	3:4	70
1d	$CH_2CH_2CO_2Me$	H	61	3:1	61
1e	Ph	H	72	only **2e**	72
1f	CO_2Et	H	42	only **2f**	36
1g	CO_2Me	Me	62[a]	obly **2g**	54

[a]With respect to an internal standard.

The cross-coupling of TMSCN with BENA **1f** is accompanied by a considerable contribution of the rearrangement of BENA **1f** into compound **5** (~15%).[13] For this reason, TMS derivative **2f** cannot be isolated from the reaction mixture (Scheme 5).††

The interaction of internal BENA **1g** with TMSCN is more complicated (Scheme 5). Under standard reaction conditions, only compound **6** was detected, which was transformed by desilylation into enoxime **7**, which is much more stable. However, the NMR monitoring allowed us to detect the initial formation of cyanoxime **2g**, which afforded aminoisoxazole **4g** as a result of rapid desilylation (Table 1). Compound **2g** in CH_2Cl_2 was gradually converted into silyl enoxime derivative **6** (Scheme 5). The reaction **2g** → **6** can include the consecutive

§ *General preparation procedure for aminooximes* **4a–e**.

Distilled compound **2** (3 mmol) was dissolved in methanol (5 ml), and Et_3N (0.1 ml) was added; after 24 h, the solvent was evaporated at 50 °C/20 Torr, and isoxazole **4** of > 90% purity (NMR data) was obtained.

5-Isoxazolamine **4a** (lit.[9]): yield 49%, mp 72–73 °C. ^{1}H NMR, δ: 4.9 (br. s, 2H, NH_2), 5.07 (d, 1H, $CHCNH_2$, ^3J 1.5 Hz), 7.91 (d, 1H, CHCN, ^3J 1.5 Hz); ^{13}C NMR, δ: 78.8 (CHCHC), 151.9 (C=N), 168.6 (CNH_2). Found (%): C, 42.82; H, 4.82; N, 33.21. Calc. for $C_3H_4N_2O$ (%): C, 42.86; H, 4.80; N, 33.32.

3-Methyl-5-isoxazolamine **4b** (lit.[10]): yield 79%, mp 82–84 °C. ^{1}H NMR, δ: 2.12 (s, 3H, Me), 4.5 (br. s, 2H, NH_2), 4.94 (s, 1H, CH); ^{13}C NMR, δ: 11.7 (Me), 80.6 (CH), 161.6 (C=N), 168.4 (CNH_2). Found (%): C, 48.94; H, 6.16; N, 28.63. Calc. for $C_4H_6N_2O$ (%): C, 48.97; H, 6.16; N, 28.55.

4-Methyl-5-isoxazolyloxazole **4c** (lit.[11]): yield 70%, oil. ^{1}H NMR, δ: 1.68 (s, 3H, Me), 4.7 (br. s, 2H, NH_2), 7.72 (s, 1H, CH); ^{13}C NMR, δ: 6.0 (Me), 87.4 (*C*Me), 153.2 (CH), 165.7 (CNH_2). Found (%): C, 49.20; H, 6.03; N, 28.31. Calc. for $C_4H_6N_2O$ (%): C, 48.97; H, 6.16; N, 28.55.

Methyl 3-(5-amino-3-isoxazolyl)propionate **4d**: yield 61%, mp 65–67 °C. ^{1}H NMR, δ: 2.64, 2.82 (t, 4H, CH_2CH_2, ^3J 7.4 Hz), 3.69 (s, 3H, Me), 4.7 (br. s, 2H, NH_2), 4.98 (s, 1H, CH); ^{13}C NMR, δ: 22.6 ($CH_2CH_2CO_2$), 29.1 (CH_2CO_2), 51.4 (Me), 83.7 (CH), 159.8 (C=N), 167.1 (CNH_2), 172.9 (CO). Found (%): C, 49.24; H, 5.86; N, 16.21. Calc. for $C_7H_{10}N_2O_3$ (%): C, 49.41; H, 5.92; N, 16.46.

3-Phenyl-5-isoxazolamine **4e** (lit.[12]): yield 72%, mp 104–108 °C. ^{1}H NMR, δ: 4.8 (br. s, 2H, NH_2), 5.41 (s, 3H, CH), 7.43 (m, 2H, Ph), 7.62 (m, 1H, Ph), 7.71 (m, 2H, Ph); ^{13}C NMR, δ: 78.26 (CH), 126.16, 126.79, 128.83, 129.87 (Ph), 163.94 (C=N), 169.25 (CNH_2). Found (%): C, 67.38; H, 5.18; N, 17.57. Calc. for $C_9H_8N_2O$ (%): C, 67.49; H, 5.03; N, 17.49.

¶ Distilled derivative **2c** (1 mmol, 0.17 g) was dissolved in methanol (1 ml); after 3 h, the mixture was evaporated at 20 °C/15 Torr. According to ^{1}H NMR data, the residue contained aminoisoxazole **4c** (67%) and *E*-2-methyl-3-oximinopropionitrile **3′c** (33%), ^{1}H NMR, δ: 1.49 (d, 3H, Me, ^3J 7.2 Hz), 3.53 (m, 1H, C*H*Me), 7.37 (d, 1H, CH=N, ^3J 5.9 Hz), 9.12 (br. s, 1H, OH). ^{13}C NMR, δ: 16.5 (Me), 26.6 (*C*HMe), 119.2 (CN), 145.2 (C=N). After a week, oxime **3′c** in an ampoule was completely converted into aminoisoxazole **4c**.

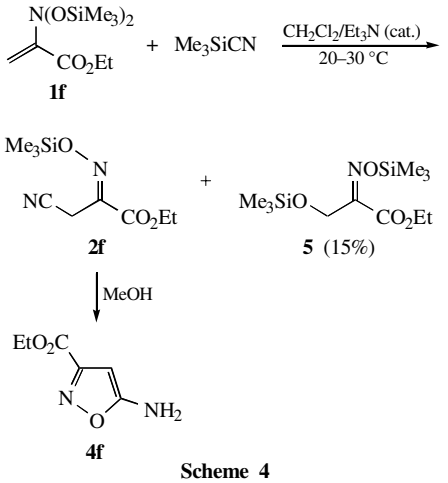
†† Et_3N (0.5 mmol, 0.7 ml) was added to TMSCN (5 mmol, 0.67 ml) in CH_2Cl_2 (7.5 ml) at 20 °C; next, a solution of BENA **1f** (5 mmol, 1.46 g) in CH_2Cl_2 (5 ml) was added for 5 min with intense stirring; the reaction mixture temperature was kept at 20–30 °C. The reaction exhibited an induction period. The mixture was allowed to stand for 1 h; volatile components were distilled at 40 °C/20 Torr, and the residue was fractionated at 70–80 °C/0.4 Torr. According to NMR data, the distillate contained compounds **2f** (42%, 0.48 g) and **5** (15%, 0.2 g).

E-*Ethyl 3-cyano-2-(trimethylsilyloximino)propionate* **2f**: ^{1}H NMR, δ: 0.29 (s, 9H, $SiMe_3$), 1.31 (t, 3H, Me, ^3J 7.4 Hz), 3.60 (s, 2H, CH_2CN), 4.29 (q, 2H, CH_2Me, ^3J 7.4 Hz). ^{13}C NMR, δ: –0.9 ($SiMe_3$), 13.8 (Me), 14.0 (CH_2CN), 62.4 (CH_2Me), 114.1 (CN), 145.9 (C=N), 161.8 (CO).

Ethyl 3-trimethylsiloxy-2-(trimethylsilyloximino)propionate **5** (lit.[2]): ^{1}H NMR, δ: 0.09 (s, 9H, CH_2OSiMe_3), 0.21 (s, 9H, $NOSiMe_3$), 1.29 (t, 3H, Me, ^3J 7.3 Hz), 4.25 (q, 2H, CH_2Me, ^3J 7.3 Hz), 4.52 (s, 2H, CH_2OSi). ^{13}C NMR, δ: –0.9 (CH_2OSiMe_3), –0.5 ($NOSiMe_3$), 14.1 (Me), 53.8 (CH_2C=N), 61.3 (CH_2Me), 156.5 (C=N), 163.4 (CO).

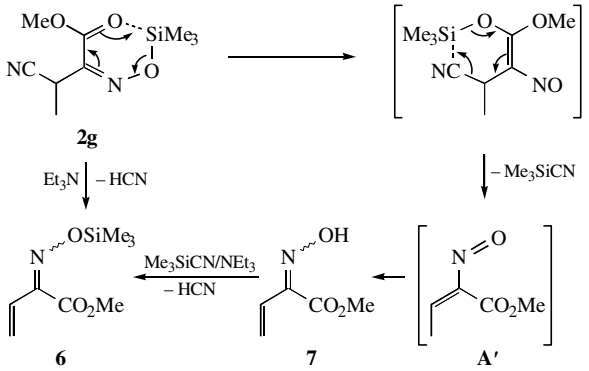
The distillate was dissolved in methanol (5 ml) with an additive of Et_3N (0.1 ml), the mixture was allowed to stand for 6 h at 20 °C and then evaporated at 50 °C/20 Torr. Oily crystals were obtained.

Ethyl 5-amino-3-isoxazolcarboxylate **4f**: (36%, 0.28 g), mp 96–98 °C (from CCl_4). ^{1}H NMR, (C_2D_5OD) δ: 1.40 (t, 3H, Me, ^3J 7.4 Hz), 4.37 (q, 2H, CH_2, ^3J 7.4 Hz), 5.23 (s, 2H, NH_2), 5.41 (s, 1H, CH). ^{13}C NMR, δ: 15.2 (Me), 63.1 (CH_2), 79.8 (CH), 158.5 (CN), 162.3 (CO), 174.0 (CNH_2). Found (%): C, 45.91; H, 5.07; N, 17.68. Calc. for $C_6H_8N_2O_3$ (%): C, 46.15; H, 5.16; N, 17.94.



Scheme 4

1,5-O,O migration of the Me_3Si group to the oxygen atom of the CO_2Me unit, the subsequent elimination of Me_3SiCN, the 1,5-CO proton shift[14] in resulting intermediate **A′** and, finally, the silylation of enoxime **7** with the use of Me_3SiCN/Et_3N. The direct elimination of HCN from oxime **2g** seems to be less probable, although it cannot be completely excluded (Scheme 5).



Scheme 5

Because of this, the general procedure used for the synthesis of isoxazoles **4a–e** was modified for preparing isoxazole **4g**.‡‡

The structures of compounds were supported by elemental analysis and NMR spectroscopy. The configuration of the oxyimino group in products **2a–d**, **2′a–d**, **3′c**, **6** and **7** was determined based on previously published rules,[2,15] as illustrated in Figure 1.

The configuration of the oxyimino group in products **2e–g**, which have only one stereoisomer, was found by comparing the chemical shifts of their characteristic fragments with the chemical shifts[16] of analogous fragments in isomers **2a–d** (Figure 1).

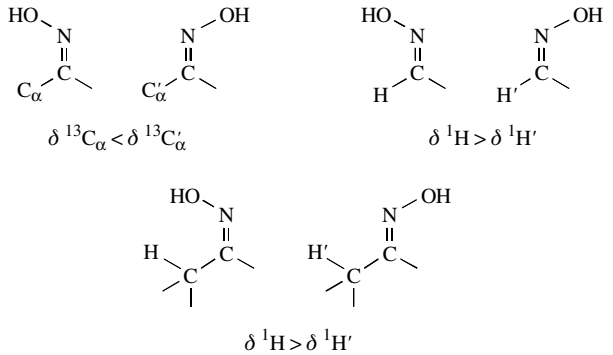


Figure 1

Thus, we proposed a convenient method for the synthesis of 5-aminoisoxazoles **4**, which may exhibit biological activity,[17] using the simplest aliphatic compounds as starting substrates.

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‡‡ BENA **1g** (5 mmol, 1.46 g) was added to a mixture of TMSCN (5 mmol, 0.67 ml) and Et_3N (0.5 mmol, 0.07 ml) for 10 min with intense stirring (the mixture warmed up in the course of adding BENA; however, the temperature was kept within a range of 30–40 °C). E-*Methyl 2-(trimethylsilyloximino)-3-cyanobutyrate* **2g** was detected by NMR spectroscopy (62% yield). ^{1}H NMR, δ: 0.31 (s, 9H, $SiMe_3$), 1.53 (d, 3H, CHMe, ^3J 7.4 Hz), 3.86 (s, 3H, OMe), 4.40 (q, 1H, CHMe, ^3J 7.4 Hz). ^{13}C NMR, δ: –0.9 ($SiMe_3$), 15.5 (Me), 22.1 (CH), 52.9 (OMe), 118.3 (CN), 150.2 (C=N), 162.2 (CO). After 10 min, methanol (5 ml) was added, and the mixture was allowed to stand for 6 h. Volatile components were distilled at 50 °C/20 Torr, and oily crystals were obtained.

Methyl 5-amino-4-methyl-3-isoxazolcarboxylate **4g**: yield 54%, 0.42 g; mp 112–114 °C (from CCl_4). ^{1}H NMR, δ: 1.92 (s, 3H, CMe), 3.76 (s, 3H, OMe), 5.26 (br. s, 2H, NH_2). ^{13}C NMR, δ: 6.2 (CMe), 52.7 (OMe), 89.2 (CMe), 156.2 (C=N), 162.6 (CO), 169.3 (CNH_2).

BSENA **1g** (2 mmol, 0.58 g) was added to a solution of TMSCN (2 mmol, 0.27 ml) and NEt_3 (0.5 mmol, 0.07 ml) in 3 ml of CH_2Cl_2 at 20 °C. The mixture was allowed to stand for 24 h and then distilled at 51 °C/0.9 Torr. The yield of enoxime **6** was 47% (0.19 g). Compound **6** is very unstable, and it completely decomposed at 20 °C in 1 h. Therefore, methanol (2 ml) was immediately added to the distillate, and the solution was chromatographed on silica gel (eluent: ethyl acetate–light petroleum, 1:1). R_f 0.68 (*Z*-isomer) or 0.44 (*E*-isomer). Compound **7**: *Z*: 13% (0.034 g), *E*: 28% (0.072 g).

Methyl 2-(trimethylsilyloximino)but-3-enoate (**6** + **6′**; *E*/*Z* = 7:4): *E*: ^{1}H NMR, δ: 0.25 (s, 9H, $SiMe_3$), 3.84 (s, 3H, OMe), 5.67 (dd, 1H, CH_2, ^3J 11.7 Hz, ^2J 2.1 Hz), 6.13 (dd, 1H, CH_2, ^3J 17.7 Hz, ^2J 2.1 Hz), 6.94 (dd, 1H, CH, ^3J 17.7 Hz, ^3J 11.7 Hz); ^{13}C NMR, δ: –0.8 ($SiMe_3$), 52.3 (OMe), 122.6 (CH_2), 128.8 (CH), 152.4 (C=N), 163.4 (CO). *Z*: ^{1}H NMR, δ: 0.25 (s, 9H, $SiMe_3$), 3.88 (s, 3H, OMe), 5.43 (d, 1H, CH_2, ^3J 17.7 Hz), 5.58 (d, 1H, CH_2, ^3J 11.2 Hz), 6.46 (dd, 1H, CH, ^3J 17.7 Hz, ^3J 11.2 Hz); ^{13}C NMR, δ: –0.9 ($SiMe_3$), 52.3 (OMe), 122.3 (CH_2), 125.4 (CH), 152.4 (C=N), 163.4 (CO).

Methyl 2-oximinobut-3-enoate (**7**, **7′**): *E*: ^{1}H NMR, δ: 3.84 (s, 3H, OMe), 5.78 (dd, 1H, CH_2, ^3J 11.8 Hz, ^2J 2.0 Hz), 6.38 (dd, 1H, CH_2, ^3J 17.7 Hz, ^2J 2.0 Hz), 6.82 (dd, 1H, CH, ^3J 17.7 Hz, ^3J 11.5 Hz), 10.1 (br. s, 1H, OH); ^{13}C NMR, δ: 52.6 (OMe), 121.8 (CH_2), 127.2 (CH), 146.5 (C=N), 163.1 (CO). *Z*: ^{1}H NMR, δ: 3.91 (s, 3H, OMe) 5.54 (d, 1H, CH_2, ^3J 17.7 Hz), 5.63 (d, 1H, CH_2, ^3J 11.2 Hz), 6.46 (dd, 1H, CH, ^3J 17.7 Hz, ^3J 11.2 Hz), 9.1 (br. s, 1H, OH); ^{13}C NMR, δ: 52.4 (OMe), 122.6 (CH_2), 128.3 (CH), 152.0 (C=N), 163.1 (CO).

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