Organic Chemistry

Trimethylsilyl derivatives of aliphatic nitro compounds in α,β-C,C-cross-coupling

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A new α,β-C,C-cross-coupling reaction of derivatives of aliphatic nitro compounds, silyl nitronates and *N,N*-bis(silyloxy)enamines, leading to β-nitro oximes was found. The scope and limitations of this reaction were studied, and a mechanism was proposed.

Key words: aliphatic nitro compounds, silyl nitronates, *N,N*-bis(silyloxy)enamines, nitroso alkenes.

The use of aliphatic nitro compounds (ANC) in the development of methods for the assembly of C—C bond presents considerable interest because the starting ANC are readily available and because the nitro group can be involved in subsequent transformations.[2—4]

We found that silyl nitronates **2**,[5] easily prepared by silylation of ANC **1**, and *N,N*-bis(silyloxy)enamines (BSENA) **3**,[6] formed from ANC of the type $MeCH(R_3)NO_2$, *viz.*, nitroethane (**1a**) or 2-nitropropane (**1b**), smoothly react with each other according to the α,β-C,C-cross-coupling pattern giving rise to silyl derivatives of β-nitroximes **4** and **5** (Scheme 1, Table 1).

Bis-derivatives **5** can arise only from primary ANC **1**. Their formation can be formally represented as the reaction of two BSENA **3** molecules with one silyl nitronate **2** molecule.

The corresponding oximes **6** and bis-oximes **7** can be synthesized by treatment of silyl derivatives **4** and **5** with NH_4F in methanol or AcOH in aqueous THF (Scheme 2).

Nitro compounds **1** were usually silylated by a one-pot procedure by adding them successively to the silylating reagent (Me_3SiCl—NEt_3) in acetonitrile. The different ratios of the rates of the first and the second silylation of ANC ensured the required ratio of silyl nitronates **2** and BSENA **3**. The removal of $Et_3N \cdot HCl$, excess silylating reagent, and the solvent induced a spontaneous exothermic reaction between compounds **2** and **3** (see Scheme 1). However, attempts to perform this process with BSENA **3** synthesized beforehand and purified by a special procedure[6] failed. Indeed, keeping a mixture of purified **2c** and **3b** for 24 h at ~20 °C did not result in the reaction; however, after the addition of 5 mol.% Et_3N, the C,C-cross-coupling reaction was completed over 1 h at 0 °C.

The role of Et_3N in the **2** + **3** reaction may include nucleophilic interaction with BSENA **3** according to

Table 1. Synthesis of silyl derivatives of β-nitroximes **4** and **5**

Compound	R^1	R^2	R^3	Yield (%)	
				4	**5**
4a, **5a**	Me	H	Me	29	20
4b, **5b**	Me	H	H	22	33
4c, **5c**	Et	H	Me	55	3
4d	Me	Me	Me	60	—
4e	$(CH_2)_2CO_2Me$	H	Me	43	—
4f	CO_2Me	H	Me	31	—

* For preliminary communication, see Ref. 1.

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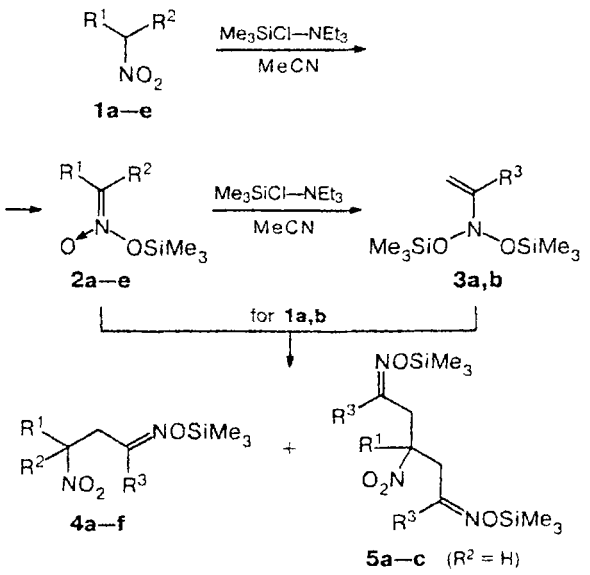
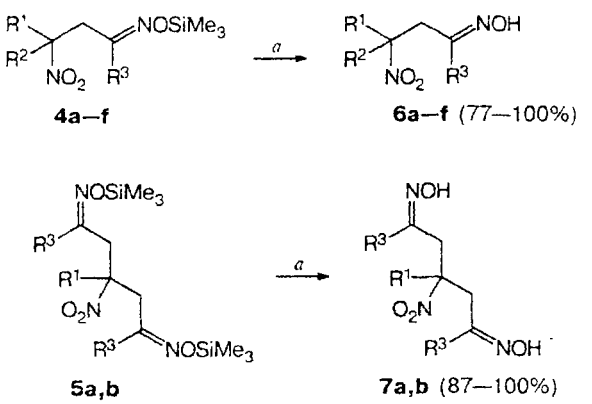
Scheme 1



1a, **2a**: R^1 = Me, R^2 = H; **1b**, **2b**: R^1 = Me, R^2 = Me; **1c**, **2c**: R^1 = Et, R^2 = H; **1d**, **2d**: R^1 = $(CH_2)_2CO_2Me$, R^2 = H; **1e**, **2e**: R^1 = CO_2Me, R^2 = H; **3a**,**3b**: R^3 = H, Me

Scheme 2

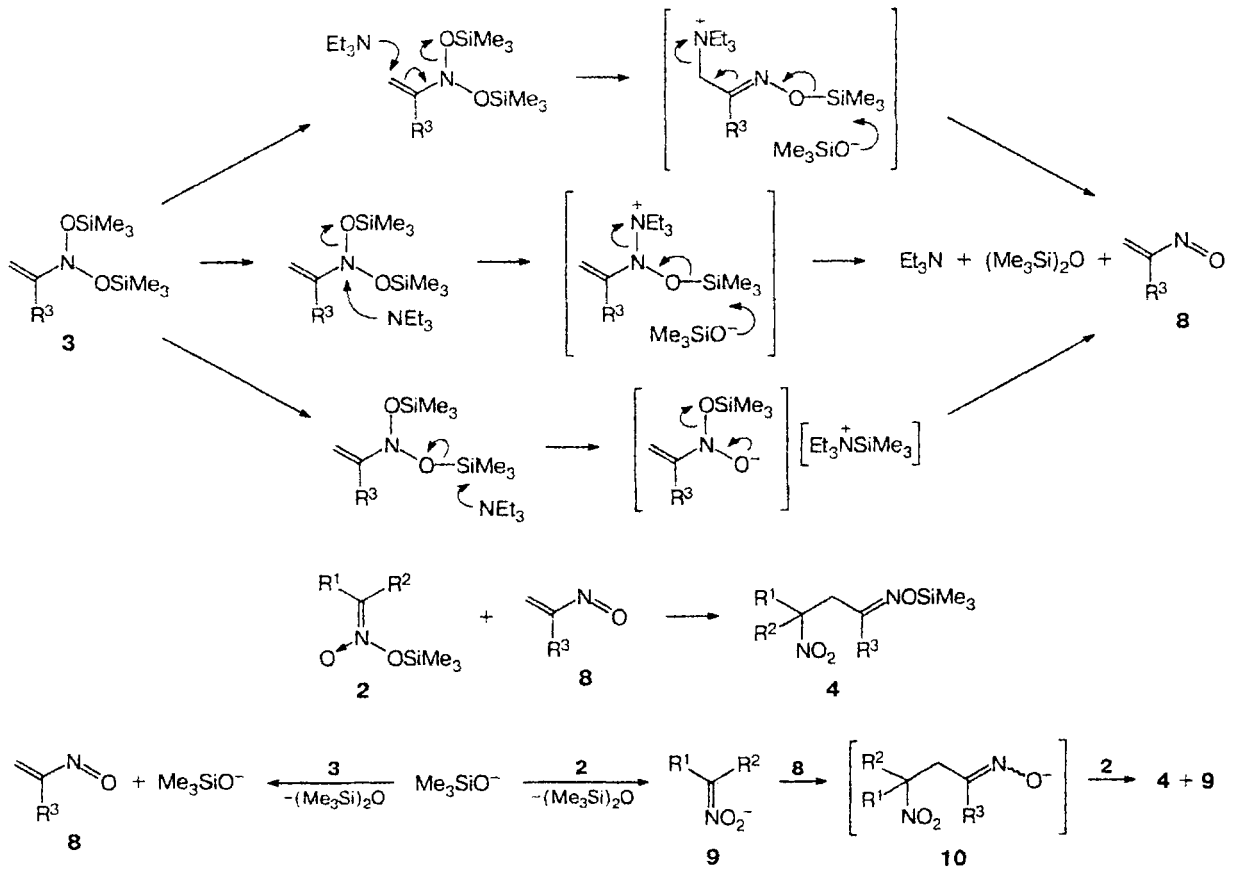


Reagents. *a*. NH_4F, MeOH or AcOH, $THF-H_2O$.

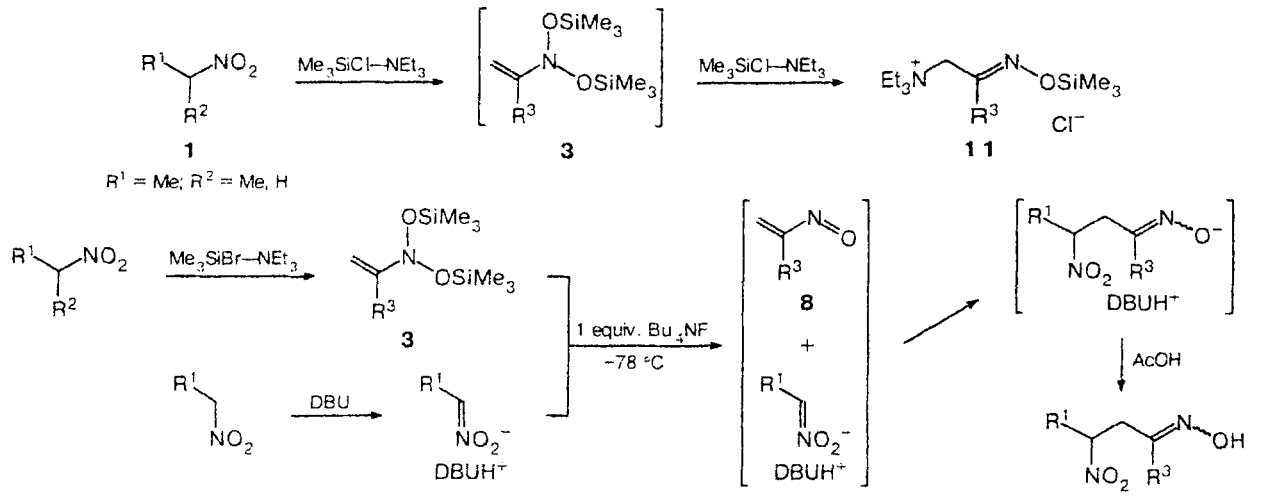
one of three pathways (Scheme 3) to give nitrosoalkenes **8** as reactive intermediates.

In this case, oxime derivatives **4** can be formed both upon the reaction of nitrosoalkenes **8** with silyl nitronates

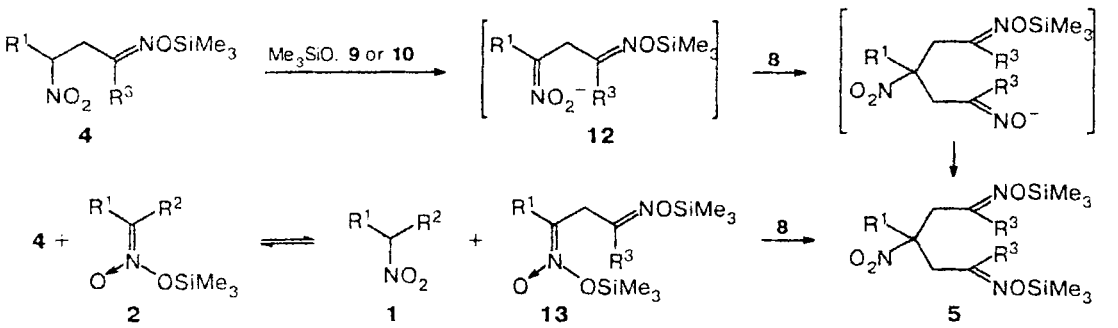
Scheme 3



Scheme 4



Scheme 5



2 and upon the transformation of silyl nitronate **2** into nitro carbanion **9**, able to react with nitrosoalkenes **8** to give anion **10**. This anion is converted into oxime **4** *via* the transfer of the Me_3Si^+ cation from silyl nitronate **2**, as shown in Scheme 3 (see also Refs. 7 and 8).

The trimethylsilyloxy anion, which can also arise in the reaction of Et_3N with BSENA, could also generate nitrosoalkene **8** according to a chain pattern; however, the reaction of these species with more electrophilic silyl nitronate **2** appears more favorable.

The participation of nitrosoalkanes **8** as reactive intermediates in the **2** + **3** C,C-cross-coupling is indicated by several facts. First, bases, including triethylamine, induce decomposition of BSENA **3**. Second, it is known that silylation of ANC **1** can give quaternary ammonium salts **11**,[6] which are evidently formed from the intermediate BSENA **3** (Scheme 4). Finally, recently we demonstrated[8] that the last step shown in Scheme 4 is actually possible because nitrosoalkenes **8** are smoothly trapped by nitronate anions generated from primary ANC.

It can be suggested that products **4** are deprotonated under reaction conditions to give anions **12**, which are converted into bis(oxime) derivatives **5** *via* the reaction with a second molecule of nitrosoalkene **8** followed by silylation (Scheme 5).

The possibility of reversible silylation of oximino derivatives **4** followed by the reaction of silyl nitronate **13** with nitrosoalkene **8** also cannot be ruled out (see Scheme 5). In any case, we detected the reversible reaction **4c** + **2c** ⇌ **1c** + **13c** by NMR spectroscopy after the addition of 5 mol.% Et_3N to a mixture of authentic samples of **4c** and **2c**. The **4c** : **2c** : **1c** : **13c** equilibrium ratio was 1.5 : 7.1 : 1.3 : 0.5. The presence of silyl nitronate **13c** was confirmed by comparison of the ^1H, ^{13}C, ^{29}Si, and ^{14}N NMR spectra of this mixture with the spectra of authentic **13c**, prepared by silylation of compound **4c** with chlorotrimethylsilane in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[9]

The structures of products **4**—**7** were established based on ^1H, ^{13}C, ^{14}N, and ^{29}Si NMR spectra and confirmed by the data of elemental analysis. The configuration of oximes was determined under the assumption that the chemical shifts δ_C of atoms adjacent to the C=NOH fragment and located in the *cis*-position with respect to the OH group are shifted upfield with respect to the δ_C values for similar atoms in the *trans*-position to the OH group.[10]

Thus, we found a novel reaction between mono- and bistrimethylsilyl derivatives of ANC, which can be formally classified as S_N2' substitution of the trimethylsilyloxy group in BSENA **3** on treatment with silyl nitronates **2**. This reaction is a new method for the construction of a C—C bond by virtue of aliphatic nitro derivatives.

Experimental

NMR spectra were recorded on a Bruker AM 300 spectrometer in $CDCl_3$ (unless another solvent is indicated in the corresponding procedure). Chemical shifts were referred to internal Me_4Si (^1H, ^{13}C, ^{29}Si) or external $MeNO_2$ (^{14}N, ^{15}N). For the NMR spectra of minor isomers, only some characteristic signals are given.

Cross-coupling reactions were carried out in anhydrous solvents under dry argon.

Nitro compound **1d** was prepared by a known procedure.[11] Silyl nitronate **2e** was synthesized by the Torssell method.[12] Acetonitrile and methylene chloride were distilled over P_2O_5. The other reagents ($EtNO_2$, $PrNO_2$, Pr^iNO_2, Et_3N, Me_3SiCl (Aldrich), and DBU (Fluka)) were distilled from CaH_2.

Synthesis of derivatives 4a,c,e and 5a,c (general procedure). Pr^iNO_2 (**1b**) (1.35 mL, 15 mmol) was added at 10 °C to a solution of NEt_3 (7.93 mL, 57 mmol) and Me_3SiCl (5.91 mL, 46.5 mmol) in MeCN (11 mL). The mixture was kept for 3 h at 10—15 °C and for 72 h at 22 °C. A solution of ANC **1a,c,d** (16.4 mmol) in MeCN (1.4 mL) was added at 10 °C and the mixture was kept for 24 h at 22 °C. Then the reaction mixture was diluted with benzene (12 mL) and filtered in an argon atmosphere and the precipitate was washed with benzene (12 mL). The combined filtrate was concentrated *in vacuo* (15 Torr). The residue was diluted with hexane (10 mL), and the resulting solution was filtered under argon and concentrated *in vacuo* (5 °C, 15 Torr). At the end of concentration, slight warming of the mixture is possible. The resulting mixture of compounds **2a,c,e** and **3a** was kept for 1 h at 15 °C, for 2 h at 45 °C, and for 24 h at 22 °C and evacuated, and the residue was distilled to give products **4a,c,e** and **5a,c**.

4-Nitropentan-2-one *O*-trimethylsilyloxime (4a). Yield 0.95 g (29%), b.p. 45—48 °C (0.25 Torr) (*cf.* Ref. 1).

4-Nitrohexan-2-one *O*-trimethylsilyloxime (4c). Yield 1.22 g (35%) (for the ratio **2c** : **3b** = 1.6 : 1.0, the yield of **4c** was 1.92 g (55%)), b.p. 60—61 °C (0.5 Torr) (*cf.* Ref. 1).

Methyl 4-nitro-6(*E*)-trimethylsilyloximinoheptanoate (4e). Yield 1.87 g (43%), b.p. 95—97 °C (0.25 Torr). Found (%): C, 45.28; H, 7.66; N, 10.03; Si, 9.80. $C_{11}H_{22}N_2O_5Si$. Calculated (%): C, 45.50; H, 7.64; N, 9.65; Si, 9.67. ^1H NMR, δ: 0.15 (s, 9 H, $SiMe_3$); 1.88 (s, 3 H, CH_3C=N); 2.15—2.25, 2.38—2.47 (both m, each 2 H, CH_2CH_2); 2.61 (dd, 1 H, CH_AH_B, ^2J = 16.8 Hz, ^3J = 4.4 Hz); 2.97 (dd, 1 H, CH_AH_B, ^2J = 16.8 Hz, ^3J = 8.9 Hz); 3.68 (s, 3 H, CO_2Me); 4.89—4.99 (m, 1 H, $CHNO_2$). ^{13}C NMR, δ: −1.2 ($SiMe_3$); 14.2 (CH_3C=N); 28.5, 29.6 (CH_2CH_2); 38.6 (CH_2C=N); 51.5 (CO_2CH_3); 83.0 ($CHNO_2$); 155.9 (C=N); 171.9 (C=O). ^{14}N NMR, δ: 10.1 ($\nu_{1/2}$ = 16.2 Hz).

A mixture of 4-ethyl-4-nitroheptane-2,6-dione *O,O*-bis(trimethylsilyl)dioximes (5c) (*E,E* : *E,Z* = 5 : 1; the mixture was prepared at **2c** : **3b** = 1.6 : 1.0). Yield 0.34 g (3%), b.p. 105—110 °C (bath temperature, 0.24 Torr). Found (%): C, 47.85; H, 8.79; N, 11.51; Si, 15.12. $C_{15}H_{33}N_3O_4Si_2$. Calculated (%): C, 47.97; H, 8.86; N, 11.19; Si, 14.95. ^1H NMR, δ, *E,E*-isomer: 0.17 (s, 18 H, $SiMe_3$); 0.87 (t, 3 H, CH_3CH_2, J = 7.4 Hz); 1.83 (s, 6 H, CH_3C=N); 2.10 (q, 2 H, CH_3CH_2, J = 7.4 Hz); 3.01 (d, 2 H, CH_AH_B, J = 16.4 Hz); 3.11 (d, 2 H, CH_AH_B, J = 16.4 Hz); *E,Z*-isomer: 0.93 (t, 3 H, CH_3CH_2, J = 7.4 Hz). ^{13}C NMR, δ, *E,E*-isomer: −0.7 ($SiMe_3$); 8.0 (CH_3CH_2); 15.4 (CH_3C=N); 30.6 (CH_3CH_2); 39.9 (CH_2C=N); 91.3 (CNO_2); 156.5 (C=N); *E,Z*-isomer: 8.5 (CH_3CH_2); 15.3 (CH_3C=N, *E*); 21.0 (CH_3C=N, *Z*); 30.0 (CH_3CH_2); 35.1 (CH_2C=N, *Z*); 41.1 (CH_2C=N, *E*); 91.4 (CNO_2). ^{29}Si NMR (INEPT), δ: 24.59 ($SiMe_3$, *E,E*). ^{14}N NMR, δ: 13.6 (NO_2, $\nu_{1/2}$ = 23.0, *E,E* and *E,Z*).

4-Methyl-4-nitroheptane-2,6-dione *O,O*-bis(trimethylsilyl)-(*E,E*)-dioxime (5a). Yield 2.17 g (20%), b.p. 100—102 °C (0.6 Torr), m.p. 24—30 °C. Found (%): C, 46.61; H, 8.65; N, 11.59; Si, 15.50. $C_{14}H_{31}N_3O_4Si_2$. Calculated (%): C, 46.50; H, 8.64; N, 11.62; Si, 15.53. ^1H NMR, δ: 0.16 (s, 18 H, $SiMe_3$); 1.67 (s, 3 H, CH_3CNO_2); 1.82 (s, 6 H, CH_3C=N); 2.92 (d, 2 H, CH_AH_B, J = 15.9 Hz); 3.02 (d, 2 H, CH_AH_B, J = 15.9 Hz). ^{13}C NMR, δ: −0.8 ($SiMe_3$); 15.3 (CH_3C=N); 23.6 (CH_3CNO_2); 44.2 (CH_2); 87.5 (CNO_2); 156.2 (C=N). ^{15}N NMR, δ: −15.8 (NO_2); 21.9 (C=N).

Synthesis of compounds 4b and 5b. A solution of $EtNO_2$ (5.53 mL, 0.074 mol) in MeCN (5 mL) was added at 10 °C to a solution of Et_3N (23.7 mL, 0.17 mol) and Me_3SiCl (19.8 mL, 0.16 mol) in MeCN (27 mL). The reaction mixture was kept for 72 h at −20 °C (**2a** : **3a** = 1.5 : 1.0, monitoring by ^1H NMR), diluted with benzene (30 mL), and filtered under argon, and the precipitate was washed with benzene (30 mL). The filtrate was concentrated *in vacuo* (15 Torr), the residue was diluted with hexane (20 mL), and the mixture was filtered (Ar). The filtrate was concentrated *in vacuo* (5 °C, 15 Torr). At the end of concentration, the mixture substantially warmed up. The reaction mixture was kept for 1 h at 40—50 °C and for 24 h at 20 °C and concentrated *in vacuo*, and the residue was distilled to give products **4b** and **5b**.

A mixture of 3-nitrobutanal (*E*)- and (*Z*)-*O*-trimethylsilyloximes (4b) (*E* : *Z* = 2 : 1). Yield 22%, b.p. 60—62 °C (0.6 Torr) (*cf.* Ref. 1).

A mixture of 3-methyl-3-nitropentanedial (*E,E*)- and (*E,Z*)-*O,O*-bis(trimethylsilyl)dioximes (5b) (*E,E* : *E,Z* = 4 : 1). Yield 33%, b.p. 114—115 °C (0.6 Torr) (*cf.* Ref. 1).

4-Methyl-4-nitropentan-2-one (*E*)-*O*-trimethylsilyloxime (4d). Pr^iNO_2 (3.30 mL, 37 mmol) was added in one portion at 10 °C to a solution of Et_3N (8.14 mL, 59 mmol) and Me_3SiCl (6.98 mL, 55 mmol) in MeCN (18 mL). The mixture was kept for 36 h at 15 °C (the ratio **2b** : **3b** = 1.1 : 1.0, monitoring by ^1H NMR). The reaction mixture was diluted with benzene (30 mL) and filtered (Ar), and the precipitate was washed with benzene (30 mL). The filtrate was concentrated *in vacuo* (15 Torr), and the residue was diluted with hexane (20 mL) and filtered (Ar). The filtrate was concentrated *in vacuo* (5 °C, 15 Torr). At the end of concentration, the mixture slightly warmed up. The reaction mixture was kept for 1 h at 40—50 °C and for 24 h at 20 °C and concentrated *in vacuo*, and the residue was distilled. Yield 2.45 g (60%), b.p. 62—64 °C (0.5 Torr) (*cf.* lit.[13]).

Methyl 2-nitro-4(*E*)-trimethylsilyloximinopentanoate (4f). Pr^iNO_2 (0.65 mL, 7.2 mmol) was added in one portion at 10 °C to a solution of Et_3N (2.33 mL, 16.6 mmol) and Me_3SiCl (2.03 mL, 15.8 mmol) in MeCN (3.6 mL). The mixture was kept for 3 h at 10—15 °C and for 72 h at 22 °C and silyl nitronate **2e** (2.06 g, 10.8 mmol) was added. The reaction mixture was diluted with benzene (5 mL) and filtered under argon, the precipitate was washed with benzene (5 mL), and the filtrate was concentrated *in vacuo* (15 Torr). The residue was diluted with hexane (10 mL), the mixture was filtered in an argon atmosphere, and the filtrate was concentrated *in vacuo* (5 °C, 15 Torr). The resulting mixture was kept for 1 h at 15 °C, for 4 h at 45 °C, and for 24 h at 22 °C and concentrated *in*

vacuo, and the residue was distilled to give 0.58 g (31%) of product **4f**, b.p. 68—72 °C (bath temperature, 0.08 Torr). Found (%): C, 41.50; H, 7.01; N, 10.50; Si, 10.64. $C_9H_{18}N_2O_5Si$. Calculated (%): C, 41.21; H, 6.92; N, 10.68; Si, 10.71. ^{1}H NMR, δ: 0.14 (s, 9 H, $SiMe_3$); 1.92 (s, 3 H, CH_3C=N); 3.06 (dd, 1 H, CH_AH_B, ^2J = 17.7 Hz, ^3J = 5.5 Hz); 3.23 (dd, 1 H, CH_AH_B, ^2J = 17.7 Hz, ^3J = 9.1 Hz); 3.84 (s, 3 H, CO_2Me); 5.64 (dd, 1 H, $CHNO_2$, ^3J = 9.1 Hz, ^3J = 5.5 Hz). ^{13}C NMR, δ: −1.1 ($SiMe_3$); 14.5 (CH_3C=N); 35.6 (CH_2); 53.5 (CO_2CH_3); 83.8 ($CHNO_2$); 155.4 (C=N); 164.9 (C=O). ^{29}Si NMR (INEPT), δ: 25.99 ($SiMe_3$). ^{14}N NMR, δ: −5.7 ($\nu_{1/2}$ = 11.5 Hz).

Trimethylsilyl 1-ethyl-3(*E*)-trimethylsilyloximino-*aci*-nitrobutanoate (13c). A solution of compound **4c** (232 mg, 1 mmol) in 0.4 mL of CH_2Cl_2 was added at 0 °C to a solution of DBU (0.15 mL, 1.01 mmol) in 1.3 mL of CH_2Cl_2. After 5 min, a solution of Me_3SiCl (0.13 mL, 1.05 mmol) in 1 mL of CH_2Cl_2 was added at 0 °C and the mixture was kept at this temperature for an additional 20 min. The volatile components were concentrated *in vacuo*, 4 mL of hexane was added to the residue, and the resulting solution was filtered in an argon atmosphere. Concentration of the filtrate gave 240 mg of an oil. According to NMR spectrum, this was a 3 : 1 mixture of **13c** and **4c**. The yield of product **13c** was 52%. ^{1}H NMR, δ: 0.18 (s, 9 H, C=NOSiMe_3); 0.32 (s, 9 H, C=N(O)OSiMe_3); 1.07 (t, 3 H, CH_3CH_2, ^3J = 7.5 Hz); 1.88 (s, 3 H, CH_3C=N); 2.35 (q, 2 H, CH_3CH_2, ^3J = 7.5 Hz); 3.29 (s, 2 H, CH_2). ^{13}C NMR, δ: −0.8 (NOSiMe_3); 0.2 (N(O)OSiMe_3); 9.5 (CH_2CH_3); 14.1 (CH_3C=N); 23.8 (CH_2CH_3); 36.5 (CH_2); 125.3 (C=N(O)OSiMe_3); 157.4 (C=NOSiMe_3). ^{29}Si NMR (INEPT), δ: 24.16, 24.58 (N(O)OSiMe_3, NOSiMe_3). ^{14}N NMR, δ: −90.9 (N(O)OSiMe_3 ($\nu_{1/2}$ = 36.7 Hz).

Desilylation of compounds 4a—c,f and 5b. Ammonium fluoride (4 mg, 0.11 mmol) was added to a solution of compounds **4a—c,f** or **5b** (2.1 mmol) in 2.5 mL of MeOH and the mixture was kept for 3 h at −20 °C. Concentration of the mixture *in vacuo* and crystallization of the residue gave oximes **6a—c,f** (or **7b**).

4-Nitropentan-2-one (*E*)-oxime (6a). Yield 301 mg (98%), m.p. 68—72 °C (hexane—ether, 1 : 5) (*cf.* Ref. 1).

4-Nitrohexan-2-one (*E*)-oxime (6c). Yield 330 mg (98%), m.p. 51—56 °C (hexane) (*cf.* Ref. 1).

4-Nitrobutanal oxime (6b) (*E* : *Z* = 1 : 1). Yield 277 mg (100%), oil. Found (%): C, 36.53; H, 6.34; N, 21.03. $C_4H_8N_2O_3$. Calculated (%): C, 36.36; H, 6.10; N, 21.20. ^{1}H NMR, δ: 1.55 (d, 3 H, CH_3); 1.57 (d, 3 H, CH_3); 2.60—3.10 (m, 4 H, 2 CH_2); 4.71—4.90 (m, 2 H, 2 $CHNO_2$); 6.80 (t, 1 H, HC=N, *Z*); 7.51 (t, 1 H, HC=N, *E*); 8.30—9.30 (br.s, 2 H, OH). ^{13}C NMR, δ: 19.1, 19.2 (CH_3, *E*, *Z*); 30.2 (CH_2, *Z*); 34.3 (CH_2, *E*); 79.9, 80.3 (CH, *E*, *Z*); 146.1, 146.5 (C=N, *E*, *Z*).

A mixture of methyl (*E*)- and (*Z*)-4-hydroximino-2-nitropentanoates (6f) (*E* : *Z* = 4 : 1, ^{1}H NMR data). Yield 397 mg (100%), oil. The NMR spectra were identical to those reported previously.[8]

A mixture of 3-methyl-3-nitropentanedial dioximes (7b) (*E*,*E* : *E*,*Z* : *Z*,*Z* = 5 : 8 : 1, ^{1}H NMR data). Yield 396 mg (100%), oil. The NMR spectra were identical to those reported previously.[1]

4-Nitro-4-methylpentan-2-one (*E*)-oxime (6d). A solution of compound **4d** (460 mg, 2 mmol) in MeOH (4 mL) was kept at 20 °C for 24 h and concentrated *in vacuo* and the residue was crystallized. Yield 270 mg (85%), m.p. 63—64 °C (hexane) (*cf.* Ref. 13).

Desilylation of oximes 4e and 5a. A solution of compound **4e** (3 mmol) or **5a** (1.5 mmol) in 2 mL of MeOH was added at 0 °C to an AcOH—THF—H_2O mixture (6 mL + 6 mL + 2 mL), and the mixture was kept for 30 min at 20 °C and concentrated *in vacuo* to give oxime **6e** or **7a**.

Methyl (*E*)-6-hydroximino-4-nitroheptanoate (6e). Yield 504 mg (77%), oil. The NMR spectra were identical to those reported previously.[8]

A mixture of 4-methyl-4-nitroheptan-2,6-dione dioximes (7a) (*E*,*E* : *E*,*Z* = 4 : 1, ^{1}H NMR data). Yield 283 mg (87%), m.p. 128—136 °C. Found (%): C, 44.02; H, 6.93; N, 19.11. $C_8H_{15}N_3O_4$. Calculated (%): C, 44.23; H, 6.96; N, 19.34. ^{1}H NMR (acetone-d_6), δ, *E*,*E*-isomer: 1.62 (s, 3 H, CH_3CNO_2); 1.80 (s, 6 H, CH_3C=N); 2.83 (d, 2 H, CH_AH_B, *J* = 15.4 Hz); 3.00 (d, 2 H, CH_AH_B, *J* = 15.4 Hz); 9.89 (s, 2 H, OH). ^{13}C NMR, δ, *E*,*E*-isomer: 14.9 (CH_3C=N); 22.7 (CH_3); 45.5 (CH_2); 89.0 (CNO_2); 152.4 (C=N); *E*,*Z*-isomer: 14.7 (CH_3C=N, *E*); 20.9 (CH_3C=N, *Z*); 22.4 (CH_3CNO_2); 38.8 (CH_2, *Z*); 46.1 (CH_2, *E*); 89.2 (CNO_2); 151.9, 152.3 (C=N, *E*, *Z*). ^{14}N NMR, δ: 17.4 (NO_2, *E*,*E* and *E*,*Z*).

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