Organic Chemistry

Chemistry of *N*,*N*-bis(silyloxy)enamines

4.* Study of the reactions of *N*,*N*-bis(silyloxy)enamines with 1,3-diones

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Smooth C,C-cross-coupling of *N*,*N*-bis(silyloxy)enamines with methyl malonates gives the corresponding methyl β-hydroxyiminoalkylmalonates.

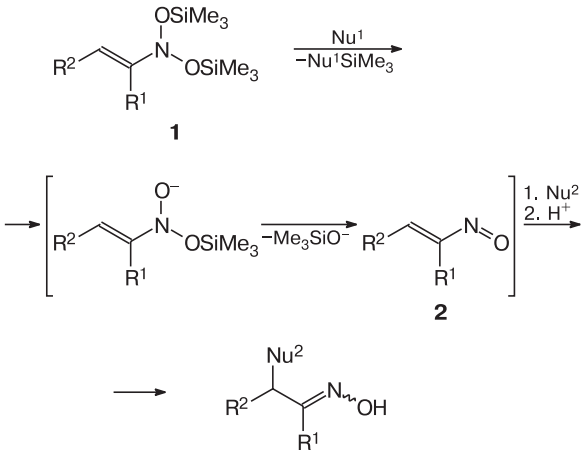
Key words: aliphatic nitro compounds; *N*,*N*-bis(silyloxy)enamines; nitrosoalkenes; methyl malonates; C,C-cross-coupling.

N,*N*-Bis(silyloxy)enamines **1** [2,3] (BENA) are new, convenient, and easily accessible reagents for organic synthesis.[4] Under the action of nucleophiles, they can serve as precursors of unstable conjugated nitrosoalkenes **2**, which made it possible to conduct a series of C,C-[5] and C,N-cross-coupling reactions[6—8] (Scheme 1).

Earlier, these reactions have been carried out only for anions of aliphatic nitro compounds[5] or silyl nitronates[9] as C-nucleophiles (Nu^2). It appeared reasonable to involve in the process other stabilized carbanions, *e.g.*, anions of 1,3-diones **3**.

It was found that C,C-cross-coupling of BENA **1a—e** with methyl malonates **3a—d** occurs smoothly, yielding oximes **6** (Scheme 2, Table 1). The structures of the compounds obtained were confirmed by ^1H and ^{13}C NMR and elemental analysis data. The configuration of the hydroxyimino group was determined from previously[5] noted characteristic signs; either individual isomers with *E*-configuration of the hydroxyimino group or a mixture of two stereoisomers were obtained, depending on the structure of the starting reagents.

Scheme 1



* For Part 3, see Ref. 1.

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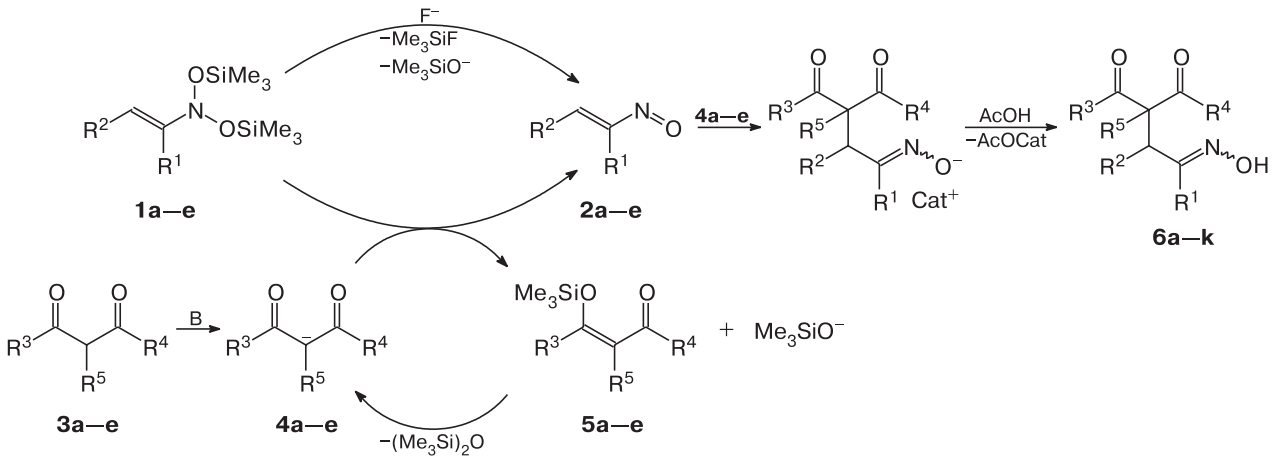
Scheme 2



B = NaH, DBU, or P-1; radicals R^1—R^5 are listed in Table 1

The reaction conditions were optimized for a model reaction **1a** + **3a** (R^1 = Me, R^2 = H, R^3 = R^4 = OMe, and R^5 = H) (Table 2). The corresponding carbanion **4a** was generated by deprotonation of methyl malonate **3a** with different bases such as NaH, DBU, *N-tert*-butyltris(1-pyrrolidinyl)phosphinimide (P-1)[10] (see Table 2, runs *1*—*4*), or by desilylation of ketene silyl acetal **5a** with fluoride anions (run *5*). Nitrosoalkene **2a** was generated from BENA **1a** using two known methods,[5] namely, by their reactions with fluoride anions at −78 °C or with carbanion **4a** at 0 °C. The Me_3SiO^- anion generated in the latter reaction (see Table 2, run *4*) recovers the starting carbanion **4a** through desilylation of silyl derivative **5a**, which is simultaneously formed in the reaction mixture.

As can be seen in Table 2, oxime **6a** is synthesized most simply, conveniently, and efficiently using DBU in Et_2O at 0 °C (run *4*). For this reason, oximes **6b**—**j** were mostly obtained under these conditions.

The reactions of methyl malonates **3a**—**d** with BENA **1a**—**e** are more general than analogous processes with α-nitro carbanions since both terminal and internal BENA can be involved in reaction **1** + **3** (see Table 1). It is of special note that neither side bishydroxyiminoalkylation of malonates **3a**—**d** nor reactions due to the ambident nature of intermediates **2a**—**e** and **4a**—**d** occurred under the conditions specified in Tables 1 and 2.

At the same time, the range of suitable β-dicarbonyl compounds proved to be limited. For example, 1,3-diketones (acetylacetone, dimedone, 2-benzoylcyclo-

Table 1. Synthesis of oximes **6a**—**k** from BENA **1a**—**e** and diones **3a**—**e**

BENA	R^1	R^2	Dione	R^3	R^4	R^5	Procedure[a]	Target oxime	Yield (%)
1a	Me	H	**3a**	OMe	OMe	H	*A*	**6a**	90
1b	H	H	**3a**	OMe	OMe	H	*A*	**6b**	55
1c	$MeO_2C(CH_2)_2$	H	**5a**	OMe	OMe	H	*B*	**6c**	70
1d	H	Me	**5a**	OMe	OMe	H	*B*	**6d**	59
1d	H	Me	**3a**	OMe	OMe	H	*C*	**6d**	59
1e	$(CH_2)_4$		**3a**	OMe	OMe	H	*A*	**6e**	33
1e	$(CH_2)_4$		**3a**	OMe	OMe	H	*C*	**6e**	47
1a	Me	H	**3b**	OMe	OMe	Bn	*A*	**6f**	74
1d	H	Me	**3b**	OMe	OMe	Bn	*A*	**6g**	46
1c	$MeO_2C(CH_2)_2$	H	**3b**	OMe	OMe	Bn	*A*	**6h**	54
1a	Me	H	**3c**	OMe	OMe	$MeO_2C(CH_2)_2$	*A*	**6i**	50
1a	Me	H	**3d**	OMe	OMe	NO_2	*A*[b]	**6j**	17
1a	Me	H	**3e**	Ph	OEt	H	*A*[c]	**6k**	38

[a] See Experimental.
[b] With Et_3N instead of DBU.
[c] Et_2O—DMF = 3 : 1.

Table 2. Optimization of the C,C-cross-coupling of BENA **1a** with methyl malonate **3a**

Run	Base (B)	Solvent	Ratio of **1a** : **3a** : B : Bu_4NF	*T*/°C	Yield[a] of oxime **6a** (%)
1	DBU	CH_2Cl_2	1 : 1.05 : 1 : 1	−78	53
2	P-1	CH_2Cl_2	1 : 1.2 : 1 : 1	−78	64
3	NaH	THF	1 : 1.05 : 1.1 : 2.1	−78	67
4	DBU	Et_2O	1 : 1.05 : 1 : 0	0	90
5	Bu_4NF [b]	CH_2Cl_2	1 : 1 [b] : 0 : 2.1 [c]	−78	81

[a] Yield of the isolated product.
[b] With ketene silyl acetal **5a** instead of methyl malonate **3a**.
[c] The total amount of Bu_4NF was 2.1 equiv. (one equivalent is required to generate anion **4a** from **5a**).

hexanone) react with BENA to give multi-component mixtures rather than the expected substituted oximes **6**. Most probably, this is attributed to polymerization of intermediate nitrosoalkenes **2a—e** under these conditions. However, the low nucleophilicities of the anions of the above diketones seem not to be the sole reason for this, though they are known[11] to linearly correlate with their basicity and are inversely proportional to the acidity of the corresponding conjugated acids (their $pK_a(BH^+)$ values are given in parentheses): $(RC(CO_2Me)_2)^-$ (11—12)[12] > $(CH(Ac)_2)^-$ (9)[12] >> >> $(O_2NC(CO_2Me)_2)^-$ (3.14).[13]

Weakly nucleophilic nitromalonate **3d** does enter into C,C-cross-coupling with BENA **1a** to give oxime **6j** in a low yield (see Table 1).

According to the literature data,[14] the anions of dicarbonyl compounds can react with α-halo oximes. Subsequent acid treatment of the reaction mixture affords oximes, which immediately undergo cyclization into *N*-hydroxypyrroles. This allowed one to suggest the formation of intermediate nitrosoalkenes.[14] However, the reaction of BENA **1a** with acetylacetone followed by acid treatment as described earlier[15] gave no corresponding 3-acetyl-1-hydroxy-2,5-dimethylpyrrole. Apparently, the known reactions of α-halo oximes with 1,3-diketonate anions proceed as S_N2-substitution for the halogen atom in the starting halo oximes rather than through the generation of nitrosoalkenes.

We attempted to reduce the probability of *O*-alkylation of the corresponding anions with BENA **1a** by coordination of the carbonyl groups of acetylacetone. However, using magnesium acetylacetonate bromide, we isolated only *N*,*C*-bis(silyloxy)propan-2-imine $Me_3SiOCH_2C(Me)=NOSiMe_3$, which is the product of the well known rearrangement of BENA **1a** under the action of acids.[6]

Cross-coupling of BENA **1** with the anions of β-oxo esters, which are intermediate in basicity between malonates and 1,3-diketones, provides the desirable outcome only in separate cases. Thus BENA **1a** reacts with ethyl benzoylacetate **3e** to give the target oxime **6k** in no higher than 38% yield (see Scheme 2). However, we failed to extend this reaction to other BENA (*e.g.*, compound **1c**) or involve ethyl acetoacetate in C,C-cross-coupling with BENA **1a**.

Hence, C,C-cross-coupling of BENA **1** with various malonates **3** (but not with β-oxo esters or especially with 1,3-diketones) can be used in organic synthesis to construct a carbon framework of some polyfunctional derivatives.

Experimental

^1H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 radio spectrometer in $CDCl_3$ with Me_4Si as the internal standard (^1H and ^{13}C) and $MeNO_2$ as the external standard (^{14}N). For minor isomers, selected characteristic NMR signals are given only.

N,*N*-Bis(silyloxy)enamines **1a—e**,[2] methyl malonates **3b**,[16] **3c**,[17] and **3d** [18] and ketene silyl acetal **5a** [19] were prepared according to the known procedures. The other reagents and solvents were commercial chemicals of reagent grade.

Cross-coupling was carried out in an atmosphere of dry argon; solvents were additionally dried and purified. The procedures for the synthesis of oximes **6a—k** are given in Table 1.

Cross-coupling of BENA 1a—e with methyl malonates 3a—d in the presence of DBU (general procedure *A*). 1,8-Diazabicyclo[5.4.0]undec-7-ene (1 mmol, 150 μL) was added at 0 °C to a solution of a malonate **3** (1 mmol) in 7 mL of Et_2O. A solution of a BENA (**1**) (1.1 mmol) in 3 mL of Et_2O was added dropwise over 20 min. The reaction mixture was kept at 0 °C for 2 h, and then solutions of AcOH (2 mmol, 0.11 mL) and NH_4F (1 mmol, 37 mg) in 2.5 mL of MeOH were added. After 20 min, the reaction mixture was poured into a system composed of water (20 mL) and Et_2O (40 mL). The organic phase was separated, and the aqueous layer was washed with Et_2O (3×10 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel.

Cross-coupling of BENA 1 with ketene silyl acetal 5a (general procedure *B*). A 0.6 *M* solution of Bu_4NF in THF (2.1 mmol, 3.5 mL) was added dropwise at −78 °C to a solution of acetal **5a** (1.05 mmol, 214 mg) in 7 mL of CH_2Cl_2. After 5 min, a solution of a BENA (**1**) (1 mmol) in 3 mL of CH_2Cl_2 was slowly added dropwise. The reaction mixture was kept at −78 °C for 10 min, and then AcOH (2 mmol, 0.11 mL) was added. The resulting solution was poured into a system composed of water (20 mL) and Et_2O (40 mL). The organic phase was separated, and the aqueous layer was washed with Et_2O (3×10 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel.

Cross-coupling of BENA 1 with a sodium salt of methyl malonate in the presence of Bu_4NF (general procedure *C*). Tetrahydrofuran (7 mL) and methyl malonate **3a** (1.05 mmol, 120 μL) were added successively to a ~60% suspension of NaH in mineral oil (the suspension was prewashed with THF (2×10 mL) and dried with NaH (1.1 mmol, 26 mg)). The

reaction mixture was kept at ~20 °C for 5 min and cooled to −78 °C, and a solution of a BENA (**1**) (1 mmol) in 3 mL of Et_2O was slowly added dropwise. Then a solution of Bu_4NF (2.1 mmol) in 3.5 mL of THF was added dropwise over 5 min while vigorously stirring the resulting mixture. After 10 min, AcOH (2 mmol, 0.11 mL) was added, and the reaction mixture was kept at −78 °C for an additional 5 min and poured into a system composed of water (20 mL) and Et_2O (40 mL). The organic phase was separated, and the aqueous layer was washed with Et_2O (3×10 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel.

Methyl (*E*)-2-(2-hydroxyiminopropyl)malonate (6a). Column chromatography in hexane—AcOEt (2 : 1) gave compound **6a** as an oil in 90% yield, R_f 0.36 (light petroleum—AcOEt, 1 : 1). Found (%): C, 47.00; H, 6.52; N, 7.18. $C_8H_{13}NO_5$. Calculated (%): C, 47.29; H, 6.45; N, 6.89. ^{1}H NMR, δ: 1.85 (s, 3 H, MeC=N); 2.76 (d, 2 H, CH_2, ^3J = 7.4 Hz); 3.68 (s, 6 H, 2 CO_2Me); 3.75 (t, 1 H, CH, ^3J = 7.4 Hz); 8.68 (s, 1 H, C=NOH). ^{13}C NMR, δ: 14.1 (MeC=N); 34.4 (CH_2); 48.2 (CH); 52.6 (OMe); 154.5 (C=N); 169.2 (C=O).

Mixture of methyl (*E*)- and (*Z*)-2-(2-hydroxyiminoethyl)malonates (6b) (*E* : *Z* = 1.3 : 1). Column chromatography in hexane—AcOEt (2 : 1) gave mixture **6b** as an oil in 55% yield, R_f 0.37 (light petroleum—AcOEt, 1 : 1). Found (%): C, 44.22; H, 5.86; N, 7.29. $C_7H_{11}NO_5$. Calculated (%): C, 44.45; H, 5.86; N, 7.40. ^{1}H NMR, δ: 2.80 (dd, 2 H, CH_2, *E*, ^3J = 5.0 Hz, ^3J = 7.0 Hz); 2.93 (dd, 2 H, CH_2, *Z*, ^3J = 5.2 Hz, ^3J = 7.0 Hz); 3.65 (t, H, CH, *E* + *Z*, ^3J = 7.0 Hz); 3.75 (s, 6 H, 2 CO_2Me, *E*); 3.76 (s, 6 H, 2 CO_2Me, *Z*); 6.82 (t, 1 H, CH=N, *Z*, ^3J = 5.2 Hz); 7.47 (t, 1 H, CH=N, *E*, ^3J = 5.0 Hz); 8.10—9.30 (br.s, NOH). ^{13}C NMR, δ: 24.5 (CH_2, *Z*); 28.7 (CH_2, *E*); 48.2 (CH, *Z*); 48.7 (CH, *E*); 52.8 (Me, *E* + *Z*); 147.9 (C=NOH, *E* + *Z*); 168.86 and 168.93 (C=O, *E* + *Z*).

Dimethyl 4-hydroxyimino-2-methoxycarbonylheptanedioate (6c). Column chromatography in hexane—AcOEt (2 : 1) gave compound **6c** as an oil in 70% yield, R_f 0.33 (light petroleum—AcOEt, 1 : 1). Found (%): C, 47.74; H, 6.22; N, 5.30. $C_{11}H_{17}NO_7$. Calculated (%): C, 48.00; H, 6.23; N, 5.09. ^{1}H NMR, δ: 2.50—2.60 (m, 4 H, CH_2CH_2); 2.79 (d, 2 H, CH_2CH, ^3J = 7.6 Hz); 3.63 (s, 3 H, CH_2CO_2Me); 3.67 (s, 6 H, 2 CHCO$_2$Me); 3.76 (t, 1 H, CH, ^3J = 7.6 Hz); 8.10—8.70 (br.s, NOH). ^{13}C NMR, δ: 24.1, 29.6, 33.1 (3 CH_2); 48.1 (CH); 51.8 (CH_2CO_2Me); 52.7 (CHCO$_2$Me); 156.3 (C=NOH); 169.2 (CHC=O); 173.1 (CH_2C=O).

Mixture of methyl (*E*)- and (*Z*)-2-[1-(2-hydroxyiminomethyl)ethyl]malonates (6d) (*E* : *Z* = 3.3 : 1). Column chromatography in hexane—AcOEt (3 : 1) gave mixture **6d** as an oil in 59% yield, R_f 0.41 (light petroleum—AcOEt, 3 : 1). Found (%): C, 47.24; H, 6.49; N, 7.07. $C_8H_{13}NO_5$. Calculated (%): C, 47.29; H, 6.45; N, 6.89. ^{1}H NMR, δ: 1.10 (d, 3 H, MeC=N, *E*, ^3J = 7.4 Hz); 1.11 (d, 3 H, MeC=N, *Z*, ^3J = 7.0 Hz); 3.00—3.18 (m, CH, *E* + *Z*); 3.50 (d, 1 H, CHC=O, *E*, ^3J = 8.0 Hz); 3.60 (d, 1 H, CHC=O, *Z*, ^3J = 6.9 Hz); 3.67 and 3.69 (both s, CO_2Me, *E* + *Z*); 6.75 (d, 1 H, CH=N, *Z*, ^3J = 5.9 Hz); 7.42 (d, 1 H, CH=N, *E*, ^3J = 5.1 Hz); 8.10—9.30 (br.s, NOH). ^{13}C NMR, δ: 14.8 (Me, *Z*); 15.7 (Me, *E*); 29.9 (CHCN, *Z*); 34.3 (CHCN, *E*); 52.58 (CO_2Me, *Z*); 52.61 (CO_2Me, *E*); 54.1 (CHC=O, *Z*); 55.1 (CHC=O, *E*); 152.3 (C=N); 168.2 and 168.31 (2 C=O, *E*); 168.35 and 168.38 (2 C=O, *Z*).

Methyl 2-(2-hydroxyiminocyclohexyl)malonate (6e). Column chromatography in hexane—AcOEt (3 : 1) gave compound **6e** in 47% yield, m.p. 79—83 °C, R_f 0.14 (light petroleum—AcOEt, 3 : 1). Found (%): C, 54.07; H, 7.09; N, 5.68. $C_{11}H_{17}NO_5$. Calculated (%): C, 54.31; H, 7.04; N, 5.76. ^{1}H NMR, δ: 1.32—1.65, 1.72—1.92, 2.95—3.09, 3.16—3.28 (all m, 3 H + 4 H + 1 H + 1 H, $(CH_2)_4$CH); 3.69 (s, 3 H, Me); 3.73 (s, 3 H, Me); 3.74 (d, 1 H, CH, ^3J = 10.3 Hz); 7.80—8.80 (br.s, NOH). ^{13}C NMR, δ: 24.3, 24.9, 25.8, 30.8 ($(CH_2)_4$); 42.2 (CHCN); 52.5 (CO_2Me); 52.6 (CO_2Me); 53.2 (CHC=O); 159.7 (C=N); 168.8 (C=O); 169.1 (C=O).

Methyl (*E*)-2-benzyl-2-(2-hydroxyiminopropyl)malonate (6f). Yield 74%, m.p. 81—82 °C (from toluene—light petroleum), R_f 0.22 (light petroleum—AcOEt, 1 : 1). Found (%): C, 61.33; H, 6.58; N, 4.69. $C_{11}H_{17}NO_5$. Calculated (%): C, 61.42; H, 6.53; N, 4.78. ^{1}H NMR, δ: 1.83 (s, 3 H, MeC=N); 2.69 (s, 2 H, CH_2C=N); 3.39 (s, 2 H, CH_2Ph); 3.70 (s, 6 H, 2 CO_2Me); 7.00—7.10 (m, 2 H, Ph); 7.15—7.32 (m, 3 H, Ph). ^{13}C NMR, δ: 14.8 (MeCN); 37.5 and 38.2 (2 CH_2); 52.7 (OMe); 57.3 (C(CO$_2$Me)$_2$); 127.0 (C_p); 129.9 and 128.3 (C_o and C_m); 136.1 (C_{ipso}); 154.2 (C=N); 171.1 (C=O).

Methyl (*E*)-2-benzyl-2-[1-(2-hydroxyiminomethyl)ethyl]malonate (6g). Column chromatography in hexane—AcOEt (2 : 1) gave compound **6g** in 46% yield, m.p. 82—83 °C, R_f 0.48 (light petroleum—AcOEt, 1 : 1). Found (%): C, 61.43; H, 6.74; N, 4.82. $C_{11}H_{17}NO_5$. Calculated (%): C, 61.42; H, 6.53; N, 4.78. ^{1}H NMR, δ: 1.20 (d, 3 H, MeCH, ^3J = 7.0 Hz); 3.04—3.16 (m, 1 H, CHC=N); 3.23 (d, 1 H, CH_2, ^3J = 7.7 Hz); 3.27 (d, 1 H, CH_2, ^3J = 3.3 Hz); 3.42—3.54 (m, 1 H, CHC=N); 3.68 (s, 3 H, CO_2Me); 3.69 (s, 3 H, CO_2Me); 7.09—7.32 (m, 5 H, Ph); 7.52 (d, 1 H, CH=N, ^3J = 6.6 Hz). ^{13}C NMR, δ: 14.1 (MeCH); 37.8 and 39.5 (CH and CH_2); 52.3 (OMe); 62.2 (C); 127.2 (C_p); 128.2 and 130.0 (C_o and C_m); 135.6 (C_{ipso}); 153.1 (C=N); 170.0 (C=O); 170.2 (C=O).

Dimethyl 2-benzyl-4-hydroxyimino-2-methoxycarbonylheptanedioate (6h). Column chromatography in hexane—AcOEt (3 : 1) gave compound **6h** as an oil in 54% yield, R_f 0.18 (light petroleum—AcOEt, 3 : 1). Found (%): C, 59.09; H, 6.57; N, 4.01. $C_{18}H_{23}NO_7$. Calculated (%): C, 59.17; H, 6.34; N, 3.83. ^{1}H NMR, δ: 2.42—2.60 (m, 2 H, CH_2CH_2); 2.69 (s, 2 H, CCH_2CN); 3.40 (s, 2 H, CH_2Ph); 3.61 (s, 3 H, CH_2CO_2Me); 3.65 (s, 6 H, 2 C(CO$_2$Me)$_2$); 6.92—7.04 (m, 2 H, H_m, Ph); 7.11—7.25 (m, 3 H, H_o and H_p, Ph). ^{13}C NMR, δ: 24.5, 29.7, 35.7 and 38.2 (all CH_2); 51.8 (CH_2COOMe); 52.7 (CH(COOMe)$_2$); 57.0 (C); 127.1 (C_p); 128.3 and 129.8 (C_o and C_m); 136.2 (C_{ipso}); 155.8 (C=N); 171.0 (CHCO); 172.9 (CH_2CO).

Dimethyl (*E*)-2-(2-hydroxyiminopropyl)-2-methoxycarbonylpentanedioate (6i). The residual ester **3c** was removed by evacuating the crude product at 90—100 °C (0.2 Torr). Column chromatography of the residue on silica gel in hexane—AcOEt (1 : 1) gave compound **6i** as an oil in 50% yield, R_f 0.36 (light petroleum—AcOEt, 1 : 1). Found (%): C, 49.51; H, 6.40; N, 4.55. $C_{12}H_{19}NO_7$. Calculated (%): C, 49.82; H, 6.62; N, 4.84. ^{1}H NMR, δ: 1.74 (s, 3 H, MeC=N); 2.19—2.28 (br.s, 4 H, CH_2CH_2); 2.76 (s, 2 H, CH_2C=N); 3.57 (s, 3 H, CH_2CO_2Me); 3.64 (s, 6 H, (CO$_2$Me)$_2$); 8.49—8.67 (br.s, 1 H, OH). ^{13}C NMR, δ: 14.4 (MeC=N); 27.7, 29.2, 38.7 (all CH_2); 51.6 (CH_2CO_2Me); 52.7 (2 CO_2Me); 55.5 (C(CO$_2$Me)$_2$); 153.4 (C=N); 171.0 (2 CO_2Me); 173.0 (CH_2CO_2Me).

Methyl (*E*)-2-(2-hydroxyiminopropyl)-2-nitromalonate (6j). Triethylamine (0.9 mmol, 125 μL) and a solution of BENA **1a** (1.1 mmol, 256 mg) in 3 mL of Et_2O were successively added at 20 °C to a solution of methyl nitromalonate **3d** (1 mmol, 177 mg) in 7 mL of Et_2O and 2 mL of DMF. The reaction mixture was kept for 24 h, and a solution of AcOH (2 mmol, 0.11 mL) and NH_4F (1 mmol, 37 mg) in 2.5 mL of MeOH was added. After 20 min, the reaction mixture was poured into a system composed of water (20 mL) and Et_2O (40 mL). The organic phase was separated, and the aqueous layer was washed with ether (3×10 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel in hexane—AcOEt (2 : 1) to give product **6j** (43 mg, 17%) as an oil, R_f 0.53 (light petroleum—AcOEt, 1 : 1). Found (%): C, 38.77; H, 4.80; N, 11.52. $C_8H_{12}N_2O_7$. Calculated (%): C, 38.71; H, 4.87; N, 11.29. ^{1}H NMR, δ: 1.94 (s, 3 H, MeC=N); 3.36 (s, 2 H, CH_2); 3.88 (s, 6 H, 2 CO_2Me); 7.70—8.30 (br.s, NOH). ^{13}C NMR, δ: 14.6 (Me); 39.2 (CH_2); 54.4 (OMe); 95.0 (C); 151.8 (C=N); 162.5 (C=O). ^{14}N NMR, δ: −11.3 (NO_2, $\Delta\nu_{1/2}$ = 150 Hz).

Mixture of ethyl (*E*)- and (*Z*)-2-benzoyl-4-hydroxyiminopentanoates (6k) (*E* : *Z* = 1.6 : 1) was obtained according to procedure *A* from benzoyl acetate and BENA **1a**. A mixture of Et_2O (6 mL) and DMF (2 mL) was used as a solvent for carbanion generation. Column chromatography in hexane—AcOEt (3 : 1) gave mixture **6k** as an oil in 38% yield, R_f 0.55 (light petroleum—AcOEt, 1 : 1). Found (%): C, 63.72; H, 6.44; N, 5.18. $C_{14}H_{17}NO_4$. Calculated (%): C, 63.87; H, 6.51; N, 5.32. ^{1}H NMR ($CDCl_3$, 60 °C), δ: 1.13 (t, 3 H, $OCH_2\underline{Me}$, *E*, ^3J = 7.4 Hz); 1.15 (t, 3 H, $OCH_2\underline{Me}$, *Z*, ^3J = 7.4 Hz); 1.89 (s, 3 H, MeC=N, *E* + *Z*); 2.82—2.99 (m, 2 H, CH_2C=N, *E* + *Z*); 4.05—4.18 (m, 2 H, $OC\underline{H}_2$Me, *E* + *Z*); 4.76 (t, 1 H, CH, *E*, ^3J = 6.8 Hz); 4.93 (t, 1 H, CH, *Z*, ^3J = 7.4 Hz); 7.38—7.60 (m, 3 H, Ph); 7.92—8.08 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 60 °C), δ: 13.9 and 14.3 ($OCH_2\underline{C}H_3$, *E* + *Z*, $\underline{Me}$C=N, *E*); 21.2 ($\underline{Me}$C=N, *Z*); 29.1 ($\underline{CH_2}$C=N, *Z*); 34.6 ($\underline{C}H_2$C=N, *E*); 50.7 (CH, *Z*); 50.8 (CH, *E*); 61.5 ($O\underline{C}H_2$Me, *E*); 61.6 ($O\underline{C}H_2$Me, *Z*); 128.6, 128.7, 128.78, 128.84 (C_o and C_m, Ph, *E* + *Z*); 133.1 and 133.5 (C_p, Ph, *E* + *Z*); 136.4 (C_{ipso}, *Z*); 136.7 (C_{ipso}, *E*); 156.3 (C=N, *E* + *Z*); 169.2 ($\underline{C}O_2$Et, *E*); 169.4 ($\underline{C}O_2$Et, *Z*); 194.8 (Ph$\underline{C}$=O, *E* + *Z*).

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