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β,β'-Functionalized *N,N*-Divinyl-*N*-trimethylsilyloxyamines *via* Silylation of β-Substituted Aliphatic Nitro Compounds. The Investigation of the Mechanism of the Process Using Selective Trapping Reagents.

Sema L. Ioffe*, Il'ya M. Lyapkalo, Alexander A. Tishkov, Vitaliy M. Danilenko, Yuri A. Strelenko and Vladimir A. Tartakovsky.

N. D. Zelinsky Institute of Organic Chemistry of Russian Academy of Sciences
117913, Leninsky prosp. 47, Moscow, Russia, Fax: +7 095 135-53-28.

Abstract: Hitherto unknown *N,N*-divinyl-*N*-trimethylsilyloxyamines of the general formula $[XC(R)=CH]_2NOSiMe_3$ (X = CO_2Me, CN, 5-methyloxycarbonylisoxazolin-3-yl; R = H, Me, $CH(Me)CO_2Me$) were obtained with moderate to good yields by silylation of nitro compounds $XCH(R)CH_2NO_2$ with *N,O*-bis(trimethylsilyl)acetamide. The mechanism of this reaction was studied by the example of silylation of methyl-3-nitropropionate using selective trapping reagents. Trimethylsilyl ester of the starting *aci*-nitro compound and methyl 2-nitroso acrylate were intercepted as consecutive intermediates. Thus, the silylation of β-functionalized nitro compounds could be presented as a convenient route to practically unknown β-substituted nitroso-alkenes XC(R)=CHNO which behave as active 1,3-heterodienes towards ethyl vinyl ether used as trapping reagent. © 1997 Elsevier Science Ltd.

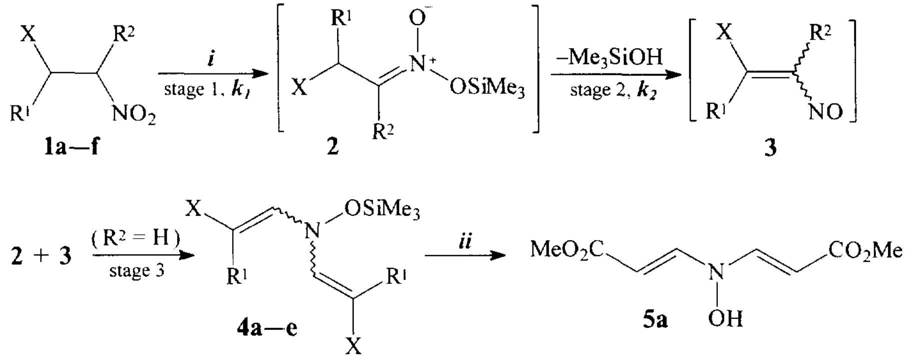
The importance of aliphatic nitro compounds (ANC) in organic synthesis has considerably increased since the development of silylation with subsequent involvement of the resultant trialkylsilyl esters of nitronic acids (abbreviated as silylnitronates) into the reaction of 1,3-dipolar cycloaddition[1] or employment of silylnitronates as modified substrates for highly stereoselective nitro-aldol condensation (Henry reaction)[2], suitable Nef[2], Mannich[3], and Michael[4] reactions in non-polar aprotic media, as well as for profound transformations of nitro group and carbon chain in ANC[2].

For the last 20 years the silylation of ANC was an object of rather detailed studies. However, the silylation of ANC containing the nitro group and functional substituent bound with different atoms of carbon chain was examined rather superficially despite the fact that such ANC undergo unusual transformations under the silylation conditions[5].

Considering this, the main purpose of the present research was a careful study of silylation of β-functionalized ANC of the general formula **1** (see Scheme 1) with *N,O*-bis(trimethylsilyl)acetamide (BSA). Our work was carried out within the framework of a large series of studies devoted to the activation of the β-C—H bonds in ANC. Nitro compounds of type **1** are readily available and have already found wide application as *C*-1 and/or *C*-2 nucleophiles in the synthesis of polyfunctional compounds and as the starting materials for the formation of the five-membered rings[6].

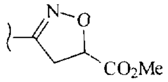
Synthesis of β,β′-Functionalized N,N-Divinyl-N-trimethylsilyloxyamines

We have found that ANC of the type **1** can be transformed with good to moderate yields into hitherto unknown *N*,*N*-divinyl-*N*-trimethylsilyloxyamines (abbreviated as siloxyamines) **4a—e** on treatment with BSA at 20 °C (Scheme 1).



Scheme 1. *i:* BSA (excess), 3 h, 20 °C, mol. ratio **1** : BSA = 1 : 3; *ii:* MeOH

Table 1. Synthesis of *N*,*N*-divinyl-*N*-trimethylsilyloxyamines **4**

Product	X	R^1	R^2	Yield (%)
4a	CO_2Me	H	H	32
4b	CN	H	H	29
4c	CO_2Me	Me	H	47
4d	CO_2Me	$CH(Me)CO_2Me$	H	72
4e		H	H	56
4f	CO_2Me	H	Me	0

The structures of **4a—e** were confirmed by microanalyses and NMR data. That of **4a** was additionally proven by desilylating **4a** with MeOH at 20 °C which resulted in *N*,*N*-bis[(2-methyloxycarbonyl)ethenyl]-hydroxylamine **5a**.

All structural fragments of **4a—e** were identified by NMR data (see Experimental).

The formation of **4** is a highly stereoselective process. All compounds **4** except **4d** were isolated as single stereoisomers. The coupling constants of vinyl protons $^3J_{H,H}$ = 13—13.5 Hz are in agreement with the *E*-configuration of C=C bond for **4a,b,e**[7]. The *Z*-configuration of both trisubstituted vinyl fragments in siloxyamines **4c,d** was confirmed by the vicinal coupling constants of vinyl protons with ^{13}C according to well-known rule: *trans*-$^3J(^1H,^{13}C)$ > *cis*-$^3J(^1H,^{13}C)$ (see Experimental[8]). According to the NMR data, compound **4d** was isolated as a 1 : 1.2 mixture of two stereoisomers (*meso-* and *d,l*-forms).

It is necessary to note that hydroxylamine **5a** showed high configurational stability in solutions. In contrast, the close analogue of **5a**, *N*-[2-(methyloxycarbonyl)-ethenyl]-*N*-phenyl hydroxylamine, exists in tautomeric equilibrium with corresponding nitrone[9].

The Trapping of the Intermediates

The conversion of compounds **1** into the products **4** is a very complicated process. It includes a series of sequential and parallel reactions. The most probable mechanism is presented in Scheme 1.

The key intermediates in this process are silylnitronates **2** and their fragmentation products -- conjugated nitroso-alkenes **3** (see Scheme 1). The participation of these intermediates in the process was confirmed by the example of the transformation **1a** → **4a** carried out using selective trapping agents.

Our choice of trapping agents was based upon following considerations:

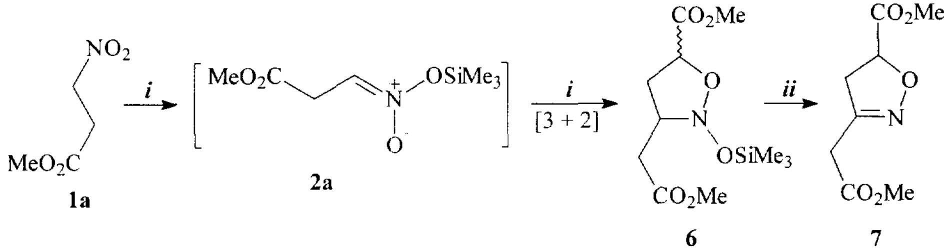
A. Silylnitronates **2** readily react with mono-substituted electrophilic alkenes as typical 1,3-dipoles giving rise to the products of concerted [3 + 2]-cycloaddition[1].

B. Conjugated nitroso-alkenes, with few exceptions, are very reactive but unstable compounds[10]. In particular, they react easily *in situ* with nucleophilic alkenes (trialkylsilyl- or alkyl vinyl ethers, enamines) mainly as 1,3-heterodienes to give [4 + 2]-cycloaddition products, 5,6-dihydro-4*H*-1,2-oxazines, with moderate to high yields[10,11].

C. We have observed recently that the simplest silylnitronates do not react with nucleophilic alkenes such as ethyl vinyl ether.

The above arguments predetermined a choice of methyl acrylate and ethyl vinyl ether as a selective trapping agents for silylnitronate **2a** and for nitroso-alkene **3a**, respectively (see Scheme 1).

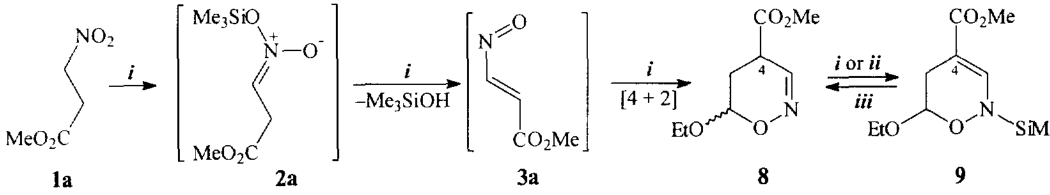
Intermediate **2a**, formed from **1a**, was trapped as a [3 + 2]-cycloaddition product, *N*-(trimethylsilyloxy)isoxazolidine **6**, (83% yield, a 2.5 : 1 mixture of two diastereomers) using a large excess of methyl acrylate under the conditions described above (see Scheme 1). The structure of cycloadduct **6** was determined by NMR as well as by its transformation into the stable isoxazoline **7** (50% yield) according to standard procedure[1a] (Scheme 2).



Scheme 2. *i:* BSA, $CH_2{=}CHCO_2Me$; *ii:* gaseous HCl/PhH

Thus, these results confirm unambiguously the participation of silylnitronates **2** as intermediates in the formation of **4**[12].

When ethyl vinyl ether was used instead of methyl acrylate under the same conditions, 2-trimethylsilyl-4-methyloxycarbonyl-6-ethyloxy-5,6-dihydro-2*H*-1,2-oxazine **9** was isolated as the main product (61% yield, Scheme 3). The reaction was carried out using diluted solution of **1a** in the presence of a large excess of ethyl vinyl ether. Under these conditions a low stationary concentration of **3a** was produced, and therefore side reactions (e.g., polymerization) of the reactive nitroso-alkene were suppressed[10].

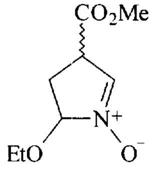


Scheme 3. *i:* BSA, $CH_2{=}CHOEt$; *ii:* treatment of **8** with BSA; *iii:* MeOH.

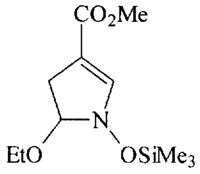
Oxazine **9**, when treated with MeOH, gives 4-methyloxycarbonyl-6-ethyloxy-5,6-dihydro-4*H*-1,2-oxazine **8** almost quantitatively as a 2 : 1 mixture of two stereoisomers. Obviously, oxazine **8** is an initial product of [4 + 2]-cycloaddition of methyl 2-nitroso acrylate (**3a**) to ethyl vinyl ether, since it was shown independently that the mixture of stereoisomers of **8** transforms into oxazine **9** under the influence of BSA.

Discussion of the Structures of the Oxazines 8 and 9

It was necessary to obtain an evidence for the structures of **8** and **9**, because it is known, that nitroso-alkenes can react according to [4 + 2]- as well as [3 + 2]-cycloaddition route[10]. In the latter case, the structural isomers of **8** and **9**, the cyclic nitrone "**8a**" and *N*-trimethylsilyloxy-pyrroline "**9a**", could be produced instead.



"**8a**"



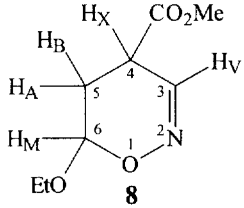
"**9a**"

The choice between structures **8** and "**8a**" was based upon the ^{14}N and ^{15}N NMR data. Namely, the ^{14}N NMR-spectrum for "**8a**" could be expected to contain a detectable signal in the area of −45 — −110 ppm (e.g., see[13]). For the real product **8** no signals are observed in the ^{14}N NMR-spectrum (^{14}N-signals of oximino-fragments at 27 °C, as a rule, can not be detected due to strong broadening). At the same time, the ^{15}N NMR-spectrum of **8** contains two signals (corresponding to the two stereoisomers): −18.5 ppm (^2J = 18.7 Hz) and −21.0 ppm (^2J = 20.0 Hz); these values are typical for nitrogen atoms of oximino groups (e.g., see ^{15}N NMR data for isoxazoline **7** in Experimental).

It is possible to make a choice between the isomeric structures of oxazine **9** and pyrroline "**9a**" using ^{29}Si NMR data. The ^{29}Si NMR-spectrum of the real product **9** exhibits a signal at 14.62 ppm, while in "**9a**" the signal of ^{29}Si-atom, bound with an oxygen atom, should be in the downfield area (e.g., see ^{29}Si NMR data of **4a**—**e** in Experimental).

All structural fragments of **8** and **9** were confirmed by NMR data. Furthermore, satisfactory microanalyses data for **8** were obtained.

The coupling constants $J_{H,H}$ for 1,2-oxazine cycle of compound **8** are presented in Table 2. The configurations of stereoisomers **8** can be deduced from the comparative analysis of vicinal coupling constants for H_A, H_B, H_X, and H_M (taking into account the data for the major and minor stereoisomer of 6-ethyloxy-4-azido-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine[14] and for a series of other 6-alkyloxy- and 6-silyloxy-5,6-dihydro-4*H*-1,2-oxazines[15]).



8

Table 2. The H,H-coupling constants (*J*/Hz) of **8**.

	J_{AX}	J_{BX}	J_{AM}	J_{BM}	J_{AB}	J_{BV}	J_{XV}	J_{VM}
trans-**8** (major)	12.1	7.3	2.7	2.7	13.3	1.8	1.8	1.8
cis-**8** (minor)	8.3	2.0	2.5	2.8	13.5	2.0	3.9	2.0

As a rule, pseudo-equatorial location of H_X predetermines smaller coupling constants J_{AX} and J_{BX} compared to the corresponding values when pseudo-axial orientation of H_X takes place. Therefore, the CO_2Me-group is pseudo-axial in the minor stereoisomer of **8** and pseudo-equatorial in the major stereoisomer (see Table 1).

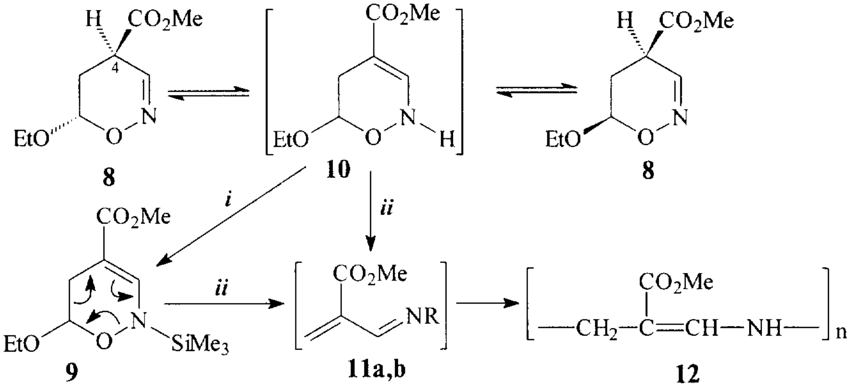
Small values of J_{AM} and J_{BM} unambiguously indicate the pseudo-axial orientation for EtO-substituents in both stereoisomers of **8**. The preference of the pseudo-axial orientation for 6-RO-substituents in 5,6-dihydro-4*H*-1,2-oxazines was discussed earlier in terms of anomeric effect typical for many other types of organic oxygen-contained compounds[16].

Thus, the major stereoisomer of **8** has *trans*-, and the minor one has *cis*-configuration of substituents.

1,2-Oxazines **8** and **9** are thermally unstable and decompose upon distillation *in vacuo* (see Experimental). In our opinion, this instability is due to irreversible concerted [4 + 2]-fragmentation leading to ethyl formate and 1-aza-1,3-butadienes **11a** or **11b**. For oxazine **8** such process could occur *via* reversible transformation into 4-methyloxycarbonyl-6-ethyloxy-5,6-dihydro-2*H*-1,2-oxazine **10** (Scheme 4) by the 1,3-*C*,*N*-migration of the proton at C(4), facilitated by the electron-withdrawing CO_2Me-group (Scheme 4). Earlier T. L. Gilchrist and co-workers suggested transient formation of 2*H*-tautomers followed by fragmentation as the most probable route for the thermolysis of 5,6-dihydro-4*H*-1,2-oxazines[17].

The concentration of 2*H*-tautomer **10** is too small for direct observation by ^1H NMR. However, it is possible to fix this tautomer as *N*-trimethylsilyl derivative **9** on treatment of **8** with BSA (Scheme 4).

The detection of ethyl formate by GLC as a thermolysis product of 1,2-oxazines **8** and **9**, as well as the formation of polymer **12** (31% yield, microanalyses data) as a result of the thermolysis of **8** could be considered as indirect evidences of the thermolysis pathway presented in Scheme 4.



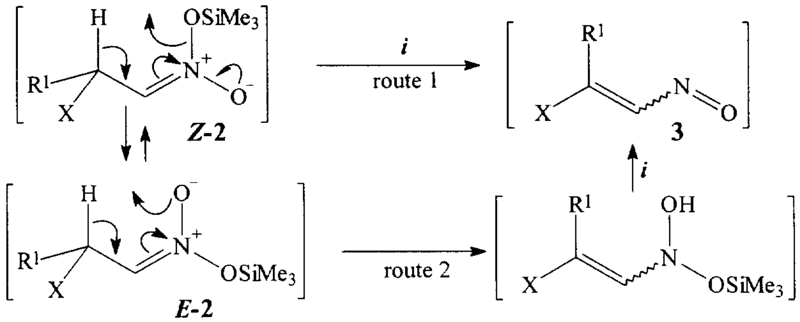
Scheme 4. *i*: BSA; *ii*: heating at 80—90 °C *in vacuo* (elimination of HCO_2Et); **11a**: R = H; **11b**: R = $SiMe_3$.

Discussion of the Mechanism

The results thus obtained confirm unambiguously the intermediate formation of methyl 2-nitroso acrylate **3a** from **1a**. This is the most important argument in support of the mechanism of the formation of the siloxyamines **4** (see Scheme 1).

The formation of the silylnitronates **2** by silylation of β-functionalized ANC **1** occurring on treatment with BSA (Scheme 1, stage 1) does not require any special comments. But the mechanism of subsequent fragmentation of **2** followed by the formation of nitroso-alkenes **3** (Scheme 1, stage 2) should be considered in detail.

The most probable ways for the fragmentation of **2** are shown in Scheme 5. The fragmentation can occur either as intramolecular concerted elimination of Me_3SiOH from *Z*-conformers of **2** (route 1) or as 1,4-*C*,*O*-migration of the proton in *E*-conformers of **2** followed by fast elimination of Me_3SiOH (route 2). The available data do not allow for us to define the real way of the **2** → **3** transformation: on the one hand, *E*-conformers of stable silylnitronates derived from primary nitro alkanes predominate in equilibrium mixture[18]; on the other hand, route 1 (Scheme 5) is also quite probable because *Z*-conformers of silylnitronates can be trapped in 1,3-dipolar cycloaddition reactions[18a].



Scheme 5. *i:* elimination of Me_3SiOH.

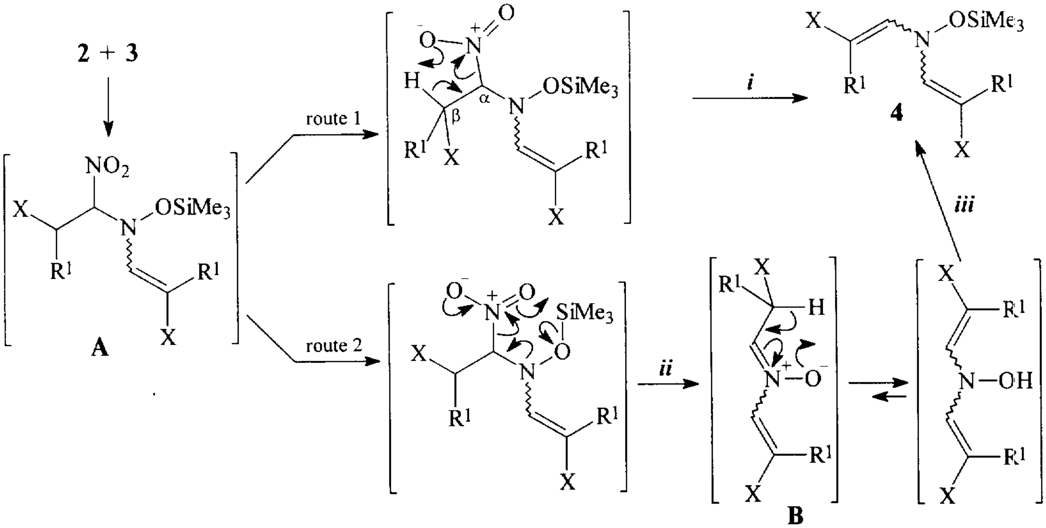
It is worth noting that unfunctionalized silylnitronates are stable under the conditions presented in Scheme 1[1a].

The chemistry of nitroso-alkenes is quite developed[10,11,15], however representatives containing electron-withdrawing substituents at β-carbon atom are unknown[20].

Perhaps, the considered transformation **1** → **[2]** → **[3]** → **...** is not the only example of the generation of conjugated nitroso-alkenes as intermediates in the silylation of ANC. There is a high probability that other "strange" reactions of nitro compounds containing electron-withdrawing substituents at β- or γ-carbon atoms also include nitroso-alkenes as intermediates[5].

Clearly, silylnitronates derived from the β-substituted ANC **1** can be considered as possible sources of new β-functionalized nitroso-alkenes.

The key step for the synthesis of the siloxyamines **4** is a rapid interaction of two intermediates **2** and **3** (Scheme 1) as a result of nucleophilic addition of silylnitronates **2** to the N=O-groups of alkenes **3**. This leads to the generation of intermediate **A** (Scheme 6). The latter can eliminate nitrous acid (route 1) or trimethylsilyl nitrite (route 2) to give, respectively, final product **4** or nitrone **B** that also transforms *via* isomerization followed by silylation into product **4**.



Scheme 6. *i:* elimination of HNO_2; *ii:* elimination of Me_3SiONO; *iii:* BSA.

So far, there is no direct evidence for the formation of siloxyamines **4** upon interaction of **2** and **3** but we have indirect evidence in support of the possibility of this process. Thus, it was shown that silylnitronates derived from primary nitroalkanes react rapidly with electrophilic nitroso arenes under very mild conditions to give nitrones[22]. The transformation of nitrones into vinyl trimethylsilyloxyamines is known[23]. Moreover, some β-functionalized ANC can easily eliminate nitrous acid (see[21] for comparison with Scheme 6, route 1)

In the synthesis of **4** (Scheme 1) silylnitronates **2** behave as the precursors of nitroso-alkenes **3** (stage 2) and as the trapping agents for **3** (stage 3). According to this, low stationary concentration of **3** and high concentration of **2** in the course of the reaction is preferred for the formation of siloxyamines **4**. These conditions are close to optimum for the interception of the reactive nitroso-alkenes[10].

If our suggestion about quick interaction of **2** with **3** is correct, the yields of products should depend ultimately on the ratio between the rate of formation of silylnitronates **2** and that of their fragmentation under the reaction conditions: the higher is the rate of formation and the lower is the rate of fragmentation into instable nitroso-alkenes **3** ($\mathbf{k_1} >> \mathbf{k_2}$), the higher is the probability of interaction of **2** with **3**. The yields of the products **4** presented in Table 1 are as a whole in agreement with such consideration.

Hence, the introduction of alkyl substituents at β-carbon atom (as in the case of **2c,d**) or the decrease of electronegativity of X (as with **2e**) leads, probably, to decrease of $\mathbf{k_2}$ but do not affect $\mathbf{k_1}$ essentially. As a result, the concentrations of **2c,d** and **2e**[12] are higher compared to those of **2a,b** and therefore, the yields of **4c,d,e** are higher compared to those of **4a,b** (Table 1).

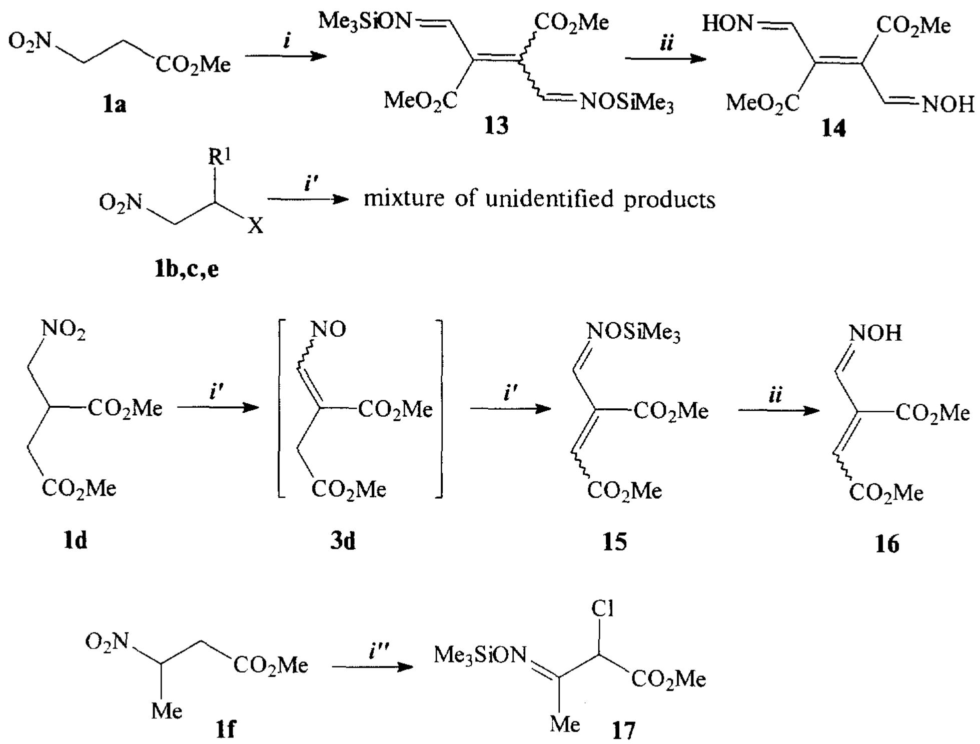
It is known that for secondary ANC the silylation proceeds much slower than for primary ones[1]. In accordance with this fact, the introduction of methyl substituent at α-carbon atom as with **2f** strongly decreases $\mathbf{k_1}$ but should not affect $\mathbf{k_2}$ essentially. Probably, it results in dramatic decrease of the concentration of the intermediate **2f** under the reaction conditions and thus suppresses the formation of the corresponding siloxyamine. Therefore, the silylation of **1f** gives a mixture of unidentified products (apparently due to the polymerization of the corresponding nitroso-alkene, Table 1).

It is necessary to note the importance not only of the stereoelectronic features of starting ANC **1**, but also of the type of the silylating reagent employed for the successful realisation of the transformation **1** → **4**.

In particular, the silylation of **1a—f** using a mixture of Me_3SiCl/Et_3N did not lead to the products **4a—f** (Scheme 7).

At present, the mechanism of the formation of the products **13**, **15**, and **17** as well as dramatic dependence of the results obtained on the structure of ANC **1** are not clear.

It is known that the rearrangement of nitroso-alkenes into α,β-unsaturated oximes can be accelerated by bases[24]. Therefore, one may assume that the conversion of nitroso-alkene **3d** into α,β-unsaturated oxime trimethylsilyl ester **15** should be facilitated by the employment of Et_3N as a base. The investigation of the mechanisms of the reactions given in Scheme 7 (in particular, the role of intermediates 3) will be the subject of our further research.



Scheme 7. *i:* Me_3SiCl/Et_3N in CH_2Cl_2 (**13**, *E* : *Z* = 1.3 : 1, 25% yield); *i':* Me_3SiCl/Et_3N in PhH (**15**, two stereoisomers ~ 2 : 1, 80% yield); *i'':* Me_3SiCl/Et_3N in MeCN (**17**, 39% yield). *ii:* MeOH (**14**, 50% overall yield; **16**, 60% yield, two stereoisomers ~ 2 : 1).

The structures of all new compounds shown in Scheme 7 are confirmed by NMR data. For compounds **14, 16** and **17** the satisfactory microanalyses data have been obtained. The *E*-isomer of **14** was transformed into the known 1,2-dicyano dimethyl fumarate[25].

EXPERIMENTAL

NMR spectra were recorded on «Bruker AM-300» instrument. Chemical shifts were measured relative to internal reference (δ = 0 ppm) TMS (^1H, ^{13}C and ^{29}Si) and external references (δ = 0 ppm): $MeNO_2$ (^{14}N and ^{15}N) and H_2O (^{17}O). The INEPT and SPT pulse sequences were used for ^{29}Si and ^{15}N signal observation[26]. The assignment of ^{13}C and ^1H signals was made by two-dimensioned C—H and H—H correlation spectroscopy, by selective proton decoupling, by DEPT 135° and by GATED method as well as SPT pulse sequences.

All experiments were carried out in the atmosphere of dry argon using dry solvents.

Starting ANC **1a**[27], **1b**[28], **1c**[29], **1e**[30] were obtained by known methods.

Dimethyl 2-nitromethyl-3-methyl succinate (1d) (by analogy with **1c**[29]). To the solution of *i*-Pr_2NH (2.57 g, 25.4 mmol) in THF—HMPTA (60 ml, vol. 5 : 1) at −35 °C the solution of *n*-BuLi in hexane (16.4 ml, 25.3 mmol) was added. The mixture was stirred at −35 °C for 10 min and, additionally, at −76 °C for 20 min. Then ANC **1a** (1.2 ml, 11,2 mmol) was rapidly added, the solution was stirred at −76 °C for 1 h. To mixture was added 2-iodo methyl propionate (2.4 g, 11.2 mmol); during 4 h the temperature of the mixture was allowed to raise to −25 °C. Further to the solution AcOH (4 ml, 11.2 mmol) at −25 °C and in 5 min H_2O (10 ml) were added. The temperature of solution was raised to 20 °C. Water (100 ml) simultaneously with Et_2O (70 ml) was added to the solution. The organic layer was separated and water solution was extracted with Et_2O (3 × 50 ml). The combined organic phases were washed with aqueous $NaHCO_3$, then H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was distilled at 88—89 °C (0.1 Torr) to provide 1.57 g (64% yield) of **1d**, a colourless liquid (≈ 1 : 1 mixture of two diastereomers); NMR ($CDCl_3$): δ (^1H) 1.21 and 1.23 (d, 3 H, Me, ^3J = 7.2 Hz), 3.02 and 3.60 (m, 2 H, CH + C<u>H</u>Me), 3.68, 3.70, 3.71 (s, 6 H, OMe), 4.83 (m, 2 H, CH_2NO_2); δ (^{13}C) 14.11 and 14.27 (Me), 39.50, 39.58. 45.55 and 45.61 (CH and <u>C</u>HMe), 52.42 and 52.67 (OMe), 73.89 (CH_2NO_2), 171.74, 171.90, 173.98 and 174.33 (C=O); δ (^{14}N) 1.1 ($\Delta\nu_{1/2}$ 220 Hz). Anal. Calcd for $C_8H_{13}NO_6$: C, 43.84; H, 5.94. Found: C, 43.94; H, 6.00.

Methyl 3-nitrobutanoate (1f). Ethyl-3-nitrobutanoate (6.9 g, 43 mmol) was refluxed for 48 h in MeOH (13.73 g, 0.43 mol), containing H_2SO_4 (0.15 ml). The mixture was evaporated *in vacuo* and the residue was distilled at 101—103 °C (12 Torr) to give 5 g (79% yield) of **1f**, a colourless liquid; NMR ($CDCl_3$): δ (^1H) 1.63 (d, 3 H, Me, ^3J = 6.9 Hz), 2.87 (dd, 1 H, CH_2, ^2J = 17.6 Hz, ^3J = 4.2 Hz), 3.13 (dd, 1 H, CH_2, ^3J = 9.2 Hz), 3.66 (s, 3 H, OMe), 4.97 (m, 1 H, $CHNO_2$); δ (^{13}C) 19.50 (Me), 38.43 (CH_2), 52.51 (OMe), 79.90 ($CHNO_2$), 170.74 (C=O); δ (^{14}N) 13.3 ($\Delta\nu_{1/2}$ 85 Hz). Anal. Calcd for $C_5H_9NO_4$: C, 40.82; H, 6.12; N, 9.52. Found: C, 40.65; H 6.20; N 9.38. Ethyl-3-nitrobutanoate was obtained from ethyl-3-hydroximino butanoate[31] *via* oxidation by Emmons' method[32] (54% yield).

***N,N*-Divinyl-*N*-trimethylsilyloxyamines (4a—e)**. To compounds **1** (0.1 mol) was added BSA (60.9 g, 0.3 mol) at 0 °C. The mixture was stirred for 3 h. The temperature of the mixture was allowed to raise to 20 °C. Further the resultant homogeneous mixture was allowed to stand for 10 h at 20 °C and evaporated *in vacuo*. For isolation of **4a** the residue was distilled at 120—140 °C (0.02 Torr) and oil obtained was crystallized by washing with hexane. For isolation of **4b** the residue was recrystallized with CCl_4. The products **4c—e** were isolated as yellowish oils by extraction of residues with petroleum ether followed by filtration and evaporation of filtrates *in vacuo*.

Spectroscopic, analytical data and physical constants for **4a—e**:

4a: m.p. 101—106 °C (hexane); NMR ($CDCl_3$): δ (^1H) 0.31 (s, 9 H, $SiMe_3$), 3.73 (s, 6 H, OMe), 5.33 (d, 2 H, CH, ^3J = 13.0 Hz), 7.81 (d, 2 H, CHN); δ (^{13}C) −0.16 ($SiMe_3$), 51.22 (OMe), 95.80 (CH, d, ^1J = 166.3 Hz), 144.38 (CHN, d, ^1J = 174.5 Hz), 167.72 (C=O, m, ^2J = 1.2 Hz, ^3J = 3.9 Hz, ^3J = 4.8 Hz); δ (^{15}N) −205.0; δ (^{29}Si) 36.45; δ (^{17}O) 121 (br. s, OMe and N—O), 317 (br. s, C=O); MS (E.I.) *m/z*: 273 ($M^{\cdot+}$), 258 $(M - Me)^+$, 214 $(M - Me - CO_2)^+$. Anal. Calcd for $C_{11}H_{19}NO_5Si$: C, 48.35; H, 6.96; N, 5.13; Si, 10.26. Found: C, 48.58; H, 7.07; N, 5.16; Si, 9.02.

4b: m.p. 84—95 °C (CCl_4), NMR (CD_3CN): δ (^1H) 0.28 (s , 9 H, $SiMe_3$), 4.85 (d, 2 H, CH, ^3J = 13.4 Hz), 7.29 (d, 2 H, CHN); δ (^{13}C) −0.43 ($SiMe_3$), 74.64 (CH, d, ^1J = 176.3 Hz), 118.68 (CN), 147.43 (CHN); δ (^{15}N) −198.85; δ (^{29}Si) 39.12; δ (^{17}O) 120 (broad). Anal. Calcd for $C_9H_{13}N_3OSi$: C, 52.17; H, 6.28; N, 20.29. Found: C, 51.96; H, 6.13; N, 20.34.

4c: oil, NMR (CD_3CN): δ (^1H) 0.25 (s, 9 H, $SiMe_3$), 1.97 (d, 6 H, Me, ^4J = 1.2 Hz), 3.67 (s, 6 H, OMe), 7.40 (q, 2 H, CHN); δ (^{13}C) −0.91 ($SiMe_3$), 12.65 (Me, d, ^3J = 6.5 Hz), 52.02 (OMe), 105.42 (C=), 141.33 (CHN, d, ^1J = 176.4 Hz), 169.55 (C=O, d, ^3J = 9.1 Hz); δ (^{15}N) −214.27 (d, ^2J = 5.7 Hz). Anal. Calcd for $C_{13}H_{23}NO_5Si$: C, 54.71; H, 8.12; N, 4.91. Found: C, 54.52; H, 8.29; N, 4.73.

4d: oil, (≈ 1 : 1.2 mixture of two diastereomers), NMR (CD_3CN): δ (^1H) 0.276 and 0.278 (s, 9 H, $SiMe_3$), 1.33 (d, 6 H, Me, ^3J = 7.6 Hz), 1.35 (d, 6 H, Me, ^3J = 7.5 Hz), 3.59, 3.60, 3.65, 3.651 (s, 12 H, OMe), 4.01 and 4.06 (q, 2 H, C<u>H</u>Me), 7.36 and 7.40 (s, 2 H, CHN); δ (^{13}C) −0.81 ($SiMe_3$), 16.52 and 16.88 (Me), 37.45 (two signals) (CH, m, ^1J = 125 Hz, ^2J = 4.4 Hz, ^3J = 6.6 Hz), 52.13 (two signals), 52.24, and 52.27 (all OMe, q, ^1J = 147 Hz), 113.10 and 113.20

(C=), 142.39 and 142.66 (CHN), 167.73 (C=O, d, ^3J = 7.8 Hz), 167.78 (C=O, d, ^3J = 7.8 Hz), 174.18 and 174.21 (CH$\underline{\mathrm{C}}$=O); δ (^{29}Si) 35.90 (major), 36.04 (minor); δ (^{15}N) −216.9 (d, ^2J = 5.3 Hz), −217.7 (d, ^2J = 4.8 Hz); M.S. (E.I.), *m/z* 414 (M − MeOH)$^{\cdot +}$, 386 (M − Me − CO$_2$)$^+$, 356 (M OSiMe$_3$)$^+$. Anal. Calcd for $C_{19}H_{31}NO_9Si$: C, 51.24; H, 6.97. Found: C, 51.21; H, 6.96.

4e: oil, NMR (CDCl$_3$): δ (^{1}H) 0.20 (s, 9 H, SiMe$_3$), 3.32 (m, 2 H, CH$_2$), 3.34 (m, 2 H, CH$_2$), 3.80 (s, 6 H, OMe), 5.05 (dd, 2 H, CH—O, ^3J = 7.3 Hz, ^3J = 10.3 Hz), 5.90 (d, 2 H, ^3J = 13.5 Hz), 6.70 (d, 2 H, CHN); δ (^{13}C) −0.33 (SiMe$_3$), 40.57 (CH$_2$), 52.77 (OMe), 77.35 (CH—O), 95.23 (CH), 137.47 (CHN), 154.99 (C=N), 170.79 (C=O); δ (^{29}Si) 35.29. Anal. Calcd for $C_{17}H_{25}N_3O_7Si$: N, 10.22. Found: N, 10.67.

***N,N*-Bis[(2-methyloxycarbonyl)ethenyl]-hydroxylamine (5a).** Product **4a** (0.41 g, 1.5 mmol) was stirred in MeOH (10 ml) for 10 min. The resultant mixture was concentrated *in vacuo* to 3 ml, the precipitate was filtered off to give **5a** (0.2 g, 69% yield), m.p. 113—115 °C, NMR ((CD$_3$)$_2$SO): δ (^{1}H) 3.62 (s, 6 H, OMe), 5.29 (d, 2 H, CH, ^3J = 13.1 Hz), 8.00 (d, 2 H, CHN), 10.82 (br. s, 1 H, OH); δ (^{13}C) 50.74 (OMe), 93.17 (CH), 144.98 (CHN), 167.13 (C=O). Anal. Calcd for $C_8H_{11}NO_5$: C, 47.76; H, 5.47; N, 6.97. Found: C, 48.05; H, 5.57; N, 7.07.

2-Trimethylsilyloxy-3-(methyloxycarbonylmethyl)-5-methyloxycarbonyl isoxazolidine (6). To dry methyl acrylate (24.90 g, 290 mmol) were added consecutively BSA (7.68 g, 38 mmol) and methyl-3-nitropropionate **1a** (1.06 g, 8 mmol). The mixture was kept with occasional stirring for 72 h at 17 °C. After evaporation of volatile products *in vacuo* isoxazolidine **6** was obtained as yellow oil (1.92 g, 83% yield, 2.5 : 1 mixture of two stereoisomers). NMR (CDCl$_3$): major stereoisomer, δ (^{1}H) 0.17 (s, 9 H, SiMe$_3$). 2.60 (m, 4 H, CH$_2$ + CH$_2$C=O), 3.70 (s, 3 H, OMe), 3.75 (m, 1 H, CH—N), 3.77 (s, 3 H, OMe), 4.90 (m, 1 H CH—O); δ ^{13}C −0.6 (SiMe$_3$), 33.7 and 34.0 (CH$_2$ and $\underline{\mathrm{C}}$H$_2$C=O), 51.3 (OMe), 51.8 (OMe), 67.2 (CH—N), 77.3 (CH—O), 170.48 (C=O), 170.8 (C=O); δ (^{29}Si) 25.26; minor stereoisomer, δ (^{1}H) 0.18 (s, 9 H, SiMe$_3$), 2.60 (m, 4 H, CH$_2$ + CH$_2$C=O), 3.68 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.75 (m, 1 H, CH—N), 4.90 (m, 1 H CH—O); δ ^{13}C −0.7 (SiMe$_3$), 34.1 and 37.3 (CH$_2$ and $\underline{\mathrm{C}}$H$_2$C=O), 51.1 (OMe), 51.9 (OMe), 69.8 (CH—N), 76.2 (CH—O), 170.49 (C=O), 170.6 (C=O); δ (^{29}Si) 24.86.

3-(Methyloxycarbonylmethyl)-5-methyloxycarbonyl isoxazoline (7). Dry HCl was passed through the solution of isoxazolidine **6** (1.80 g, 6.2 mmol) in benzene (15 ml) at 10—15 °C for 0.5 h. The resultant mixture was evaporated *in vacuo*, and the residue was distilled at 100—102 °C (0.1 Torr) to provide 0.67 g (50% yield) of **7**, a yellowish liquid, n^{20}_D 1.4760. NMR (CDCl$_3$): δ (^{1}H) 3.35 (m, 2 H, CH$_2$), 3.50 (s, 2 H, CH$_2$C=O), 3.75 (s, 3 H, OMe), 3.80 (s, 3 H, OMe); 5.05 (dd, 1 H, CH—O); δ (^{13}C) 32.6 (CH$_2$), 40.7 ($\underline{\mathrm{C}}$H$_2$C=O), 52.4 (OMe), 52.7 (OMe), 77.8 (CH—O), 152.9 (C=N), 168.8 (C=O), 170.7 (C=O); δ (^{15}N) −16.9. Anal. Calcd for $C_8H_{11}NO_5$: C, 47.76; H, 5.51; N, 6.96. Found: C, 47.66; H, 5.40; N, 6.98.

2-Trimethylsilyl-4-methyloxycarbonyl-6-ethyloxy-5,6-dihydro-2*H*-oxazine (9). To dry ethyl vinyl ether (15.42 g, 214 mmol) were added consecutively BSA (9.14 g, 45 mmol) and methyl-3-nitropropionate **1a** (2.10 g, 15 mmol) at 5 °C. The mixture was kept with occasional stirring for 96 h at 20 °C. After evaporation of volatile products *in vacuo* oxazine **9** was obtained as yellow oil (2.37 g, 61% yield). Product **9** contains **4a** (4%) as a by-product. The yield of **9** was determined by NMR with internal standard. NMR (CDCl$_3$): δ (^{1}H) 0.32 (s, 9 H, SiMe$_3$), 1.25 (t, 3 H, Me), 2.45 (ddd, 1 H, CH$_2$, ^2J = 15.9 Hz, ^3J = 4.5 Hz, ^4J = 0.9 Hz), 2.63 (ddd, 1 H, CH$_2$, ^3J = 3.8 Hz, ^4J = 1.1 Hz), 3.66 (m, 1 H, OCH$_2$), 3.67 (s, 3H, OMe), 3.93 (m, 1H, OCH$_2$), 4.89 (ddd, 1 H, CH—O, ^5J = 0.8 Hz), 7.58 (ddd, 1 H, CH); δ (^{13}C) −1.7 (SiMe$_3$), 15.1 (Me), 28.6 (CH$_2$), 50.7 (OMe), 64.9 (OCH$_2$), 90.0 (C=), 99.3 (CH—O), 140.1 (=CHN), 167.9 (C=O); δ (^{29}Si) 14.62; δ (^{15}N) −211.5.

4-Methyloxycarbonyl-6-ethyloxy-5,6-dihydro-4*H*-oxazine (8). To MeOH (5 ml) was added the solution of oxazine **9** (1.40 g, 5.4 mmol) in CH$_2$Cl$_2$ (2 ml) at 0 °C. The mixture was kept with occasional stirring for 24 h at 20 °C and evaporated *in vacuo*. The product **8** (0.97 g, 96% yield, 2 : 1 mixture of two stereoisomers) was isolated as yellowish oil by extraction of the residue with pentane (3 × 10 ml) followed by filtration and evaporation of filtrate *in vacuo*. NMR ($CDCl_3$, for the H,H-coupling constants see Table 2): major stereoisomer, δ (^1H) 1.20 (t, 3 H, Me, ^3J = 7.0 Hz), 2.11 (ddd, 1 H, H_A), 2.21 (dddd, 1 H, H_B), 3.43 (ddd, 1 H, H_X); 3.61 (m, 1 H, OCH_2), 3.77 (s, 3 H, OMe), 3.85 (m, 1 H, OCH_2), 5.14 (m, 1 H, H_M), 7.46 (ddd, 1 H, H_V); δ (^{13}C) 15.0 (Me), 25.1 (C^5), 33.3 (C^4), 52.6 (OMe), 63.8 (OCH_2), 95.3 (C^6), 146.2 (C^3), 170.5 (C=O); δ (^{15}N) −18.5 (d, J = 18.7 Hz); minor stereoisomer, δ (^1H) 1.12 (t, 3 H, Me, ^3J = 7.1 Hz), 2.10 (ddd, 1 H, H_A), 2.56 (dddd, 1 H, H_B), 2.99 (ddd, 1 H, H_X), 3.62 (m, 1 H, OCH_2), 3.74 (s, 3 H, OMe); 3.83 (m, 1 H, OCH_2); 5.14 (m, 1 H, H_M); 7.56 (ddd, 1 H, H_V); δ (^{13}C) 14.8 (Me), 25.5 (C^5), 32.8 (C^4), 52.3 (OMe), 63.1 (OCH_2), 94.8 (C^6), 147.2 (C^3), 170.4 (C=O), δ (^{15}N) −21.0 (d, J = 20.0 Hz). Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.49; H, 6.87; N, 7.25.

The silylation of oxazine 8 using BSA. To oxazine **8** (0.08 g, 0.43 mmol) was added BSA (1.00 g, 4.9 mmol) at 20 °C. The mixture was kept with occasional stirring for 96 h at 20 °C and evaporated *in vacuo*. The residue was identified by ^1H-NMR ($CDCl_3$) as the oxazine **9** (0.106 g, 96% yield) by comparison with the known sample of **9**.

The thermolysis of 9. 1,2-Oxazine **9** (1.54 g, 5.9 mmol) was heated for 0.5 h up to 90 °C (1 Torr). When the thermolysis was completed, the liquid from cooled trap was diluted with toluene (0.5 ml) and identified as ethyl formate in the solution by GLC.

The thermolysis of 8. Oxazine **8** (0.85 g, 4.5 mmol) was heated for 0.5 h up to 90 °C (1 Torr). After the dilution of the residue with Et_2O (10 ml) the resultant yellowish precipitate was filtered off and identified by microanalyses as the polymer **12** (0.16 g, 31% yield). The most probable structure of this polymer: $[-CH_2-C(CO_2Me)=CH-NH-]_n$. Anal. Calcd for $C_5H_7NO_2$: C, 53.09; H, 6.24; N, 12.38. Found: C, 53.25; H, 6.17; N, 12.20.

When the thermolysis was completed, the liquid from cooled trap was diluted with toluene (0.5 ml) and identified as ethyl formate in the solution by GLC.

2,3-Bis(trimethylsilyloximinomethyl)but-2*E,Z*-en-1,4-dicarboxylic acid dimethyl ester (13). To the solution of compound **1a** (2.4 g, 20.0 mmol) in dry CH_2Cl_2 (20 ml) the mixture of Et_3N (12.11 g, 120.1 mmol) and Me_3SiCl (13.2 g, 120.1 mmol) was added. The resultant mixture was stirred for 2 h and evaporated *in vacuo*. The residue was diluted with CCl_4 (50 ml), filtered and evaporated *in vacuo* to provide **13** (0.94 g, 25% yield, E/Z = 1.3 : 1). NMR ($CDCl_3$): δ (^1H) 0.11 (s, 18 H, $SiMe_3$), 0.12 (s, 18 H, $SiMe_3$), 3.57 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 7.87 (s, 2 H, CH), 8.01 (s, 2 H, CH); δ (^{13}C) −2.0 ($SiMe_3$), −1.8 ($SiMe_3$), 51.5 (OMe), 51.6 (OMe), 131.5 (dd, C=, ^2J = 2.8 Hz, ^3J = 7.8 Hz), 131.8 (dd, C=, ^2J = 3.5 Hz, ^3J = 6.7 Hz), 148.7 (d, CH, ^1J = 175.0 Hz); 149.1 (d, CH, ^1J = 175.0 Hz), 164.0 (C=O), 164.2 (C=O); δ (^{15}N) 13.1 (d, ^2J = 2.4 Hz), 14.9 (d, ^2J = 2.1 Hz); δ (^{29}Si) 29.07 and 29.29; δ (^{17}O) (CD_3CN, 70 °C) 130 (br, OMe and N—O), 350 (br, C=O).

Dimethyl 2,3-bis(hydroximinomethyl) fumarate (14). Product **13** (0.94 g, 2.5 mmol) was dissolved in MeOH, filtered through silica gel and evaporated *in vacuo*. The residue was purified by chromatography (column, silpearl, Et_2O) to provide **14** (0.29 g, 50% overall yield), m.p. 189—190 °C. NMR ($(CD_3)_2SO$): δ (^1H) 3.80 (s, 6 H, OMe), 7.90 (s, 2 H, CH), 12.25 (br. s, 2 H, OH); δ (^{13}C) 52.7 (OMe); 131.4 (C=, dd, ^2J = 2.8 Hz, ^3J = 8.1 Hz), 144.3 (CH, dd, ^1J = 171.6 Hz, ^3J = 9.8 Hz), 164.0 (C=O); δ (^{15}N) 11.5 (d, ^2J = 1.4 Hz).

Dimethyl 1,2-dicyano fumarate. To the solution of product **14** (0.29 g, 1.26 mmol) and pyridine (0.56 g, 7 mmol) in dioxane (5 ml) trifluoroacetic anhydride (1.19 g, 3.8 mmol) was added at 0—10 °C. The mixture was stirred at 20 °C for 4 h and allowed to stand overnight. Ice (15 g) was added to the mixture. The resultant precipitate was filtered off and purified by sublimation at 120—130 °C (0.5 Torr) to give 1,2-dicyano dimethyl fumarate (0.14 g, 56% yield), m.p. 176—177.5 °C (lit.[25] m.p. 176—178 °C). NMR ($CDCl_3$): δ (^{13}C) 55.07 (OMe), 111.13 (CN), 125.76 (C=), 158.0 (C=O).

2-(Trimethylsilyloximinomethyl)but-2*E*,*Z*-en-1,4-dicarboxylic acid dimethyl ester (15). To the mixture of Me$_3$SiCl (4.34 g, 40 mmol) and Et$_3$N (4.04 g, 40 mmol) was added the solution of compound **1d** (1.1 g, 5 mmol) in benzene (10 ml) for 10 min at 0 °C. The mixture was stirred for 1 h at 20 °C. After the filtration of the resultant mixture the precipitate of [Et$_3$NH]Cl was washed with benzene. Evaporation of the combined filtrates *in vacuo* gives rise to product **15** (1.09 g, 80% yield, 2 : 1 mixture of two stereoisomers). NMR (CD$_3$CN): major stereoisomer δ (^{1}H) 0.20 (s, 9 H, SiMe$_3$), 2.06 (s, 3 H, Me), 3.73 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 8.20 (s, 1 H, CH); δ (^{13}C) −0.91 (SiMe$_3$), 14.87 (Me), 52.59 (OMe), 52.99 (OMe), 133.80 (=$\underline{\mathrm{C}}$—Me), 135.92 (C=), 150.89 (CH, d, ^1J = 172.5 Hz), 167.39 (C=O), 167.78 (C=O); δ (^{29}Si) 28.80; δ (^{15}N) 11.41 (d, ^2J = 3.1 Hz); minor stereoisomer δ (^{1}H) 0.18 (s, 9 H, SiMe$_3$), 1.98 (s, 3 H, Me), 3.77 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 8.49 (s, 1 H, CH); δ (^{13}C) −0.91 (SiMe$_3$), 17.68 (Me), 52.68 (OMe), 52.99 (OMe), 134.01 (=$\underline{\mathrm{C}}$—Me), 136.42 (C=), 151.67 (CH, d, ^1J = 177 Hz), 167.26 (C=O), 167.64 (C=O); δ (^{29}Si) 28.38; δ (^{15}N) 6.96 (d, ^2J = 3.0 Hz).

2-Hydroximinomethylbut-2-en-1,4-dicarboxylic acid dimethyl ester (16). The solution of **15** (0.27 g, 1 mmol) in MeOH (3 ml) was kept for 2 h at 40—50 °C and evaporated *in vacuo* to provide oxime **16** (0.2 g, 60% yield, 2 : 1 mixture of two stereoisomers). The stereoisomers of **16** were separated by chromatography (silica gel, ether—hexane 1 : 1). Major stereoisomer, m.p. 113—113.5 °C, NMR (CDCl$_3$): δ (^{1}H) 2.09 (s, 3 H, Me), 3.72 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 8.17 (s, 1 H, CH), 11.09 (s, 1 H, OH); δ (^{13}C) 14.28 (Me), 52.28 (OMe), 52.70 (OMe), 131.62 (=$\underline{\mathrm{C}}$—Me), 137.18 (C=), 146.32 (CH), 167.27 (C=O), 167.48 (C=O). Anal. Calcd for $C_6H_{11}NO_5$: C, 47.76; H, 5.47; N, 6.97. Found: C, 47,97; H, 5.68; N, 7.47. Minor stereoisomer, m.p. 93—94 °C, NMR (CDCl$_3$): δ (^{1}H) 1.96 (s, 3 H, Me), 3.78 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 8.51 (s, 1 H, CH), 10.84 (s, 1 H, OH); δ (^{13}C) 17.66 (Me), 52.40 (OMe), 52.66 (OMe), 131.23 (=$\underline{\mathrm{C}}$—Me), 137.74 (C=), 147.06 (CH), 167.20 (C=O), 167.52 (C=O).

Methyl 2-chloro-3-trimethylsilyloximino butanoate (17). To the solution of compound **1f** (2.35g, 16.0 mmol) in acetonitrile (15 ml) the mixture of Et$_3$N (4.85 g, 48.0 mmol) and Me$_3$SiCl (5.23 g, 48.0 mmol) was added for 10 min at 20 °C. The mixture was stirred for 9 h at 20 °C and evaporated *in vacuo*. The residue was diluted with CCl$_4$, filtered and evaporated *in vacuo*. The product **17** (1.90 g, 50% yield) was isolated by extraction of the resultant residue with pentane (3 × 10 ml) followed by filtration and evaporation of filtrate *in vacuo*; b.p. 55—57 °C (0.02 Torr), NMR (CDCl$_3$): δ (^{1}H) 0.21 (s, 9 H, SiMe$_3$), 1.98 (s, 3 H, Me), 3.80 (s, 3 H, OMe), 5.04 (s, 1 H, CH); δ (^{13}C) −0.81 (SiMe$_3$); 10.83 (Me, qd, ^1J = 130.2 Hz, ^3J = 3.2 Hz), 53.3 (OMe, q, ^1J = 148.1 Hz), 59.1 (CH, dq, ^1J = 154.4 Hz, ^3J = 2.9 Hz), 156.6 (C=N, quint, ^2J = ^3J = 6.7 Hz), 167.1 (C=O, dq, ^2J = 5.3 Hz, ^2J = 4.2 Hz); δ (^{15}N) −12.7; δ (^{29}Si) 27.1; δ (^{17}O) (50 °C) 139 (OMe); 188 (N—O); 360 (C=O); MS (E.I.), *m/z* 239 and 237 ($M^{\cdot+}$, 1 : 3 ratio). Anal. Calcd for $C_8H_{16}NO_3SiCl$: C, 40.42; H, 6.74; N, 5.89; Cl, 14.95; Si, 11.79. Found: C, 41.21; H, 6.82; N, 6.17; Cl, 14.28; Si, 11.13.

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References and Notes

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