Silylation of bicyclic six-membered nitronates. Ring—chain tautomerism of intermediate *N*,*N*-bis(oxy)iminium cations*

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Silylation of bicyclic six-membered nitronates was studied as a possible route to conjugated enoximes with a distant carbonyl group. Apart from the target enoximes, this reaction yielded nitro compounds. The ratio of these two types of products and the configurations of their stereogenic centers depend on the nature and configurations of the starting nitronates and the silylation conditions. The results obtained were interpreted in terms of ring—chain tautomerism of intermediate *N*,*N*-bis(oxy)iminium cations.

Key words: nitro compounds, cyclic nitronates, cycloaddition, retroreactions, silylation.

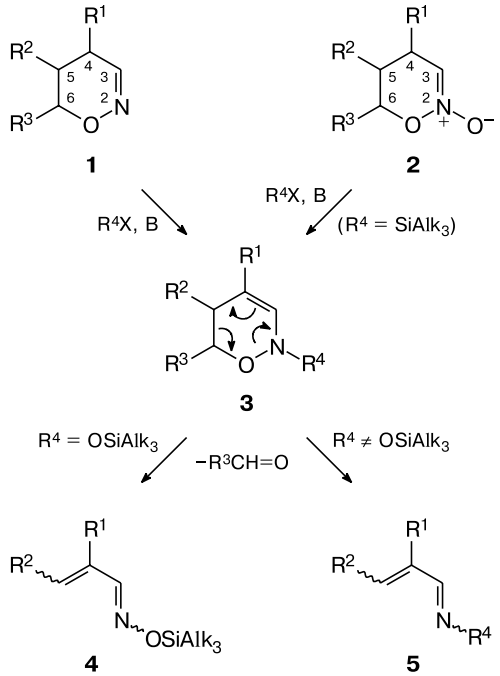
Reactions of 5,6-dihydro-4*H*-oxazines **1** and their *N*-oxides **2** with electrophilic agents in the presence of bases are known to lead to migration of the double bond in the heterocycle and the formation of 5,6-dihydro-2*H*-oxazines **3** (see Refs 1—4). The latter compounds can undergo fragmentation with loss of the C(6) atom to give conjugated enoximes **4** (see Ref. 4)** or enimines **5** (see Refs 1—3), respectively (Scheme 1). The presence of the *N*-OSiAlk$_3$ group in intermediate oxazines **3** sharply increases the fragmentation rate (*cf.* Refs 1—3 and 4).

The sequence of transformations for 5,6-dihydrooxazines, which is shown in Scheme 1, is employed in organic synthesis; however, the loss of the C(6) atom can sometimes be regarded as a drawback to this synthesis of enoximes. This drawback can be eliminated by starting from bicyclic 5,6-dihydro-4*H*-oxazines[1,6] or their *N*-oxides,[7] in which the C(6) atom is bound to the rest of the molecule by an additional chain of atoms.

In terms of this approach to the synthesis of enoximes, it was of interest to investigate silylation of bicyclic nitronates **6** since the fragmentation of the corresponding intermediates **7** allows one to obtain virtually unstudied α,β-unsaturated oximes with the distant carbonyl group from very accessible compounds (simplest nitroalkanes and derivatives of cyclic ketones) (Scheme 2).

However, the scope of this strategy has been illustrated hitherto with only one example.[7]

Scheme 1



R^4X = AlkX, AcX, Alk_3SiX; X = Hal, OTf
R^4 = Alk,[1] Ac,[2] Alk_3Si,[3] Alk_3SiO (see Ref. 4); B is a base.

* Dedicated to Academician O. M. Nefedov on the occasion of his 75th birthday.

** The known examples include fragmentation of the 5,6-dihydro-2*H*-oxazine anions generated from six-membered cyclic nitronates under the action of bases[5] *via* deprotonation of position 4 of the oxazine ring.

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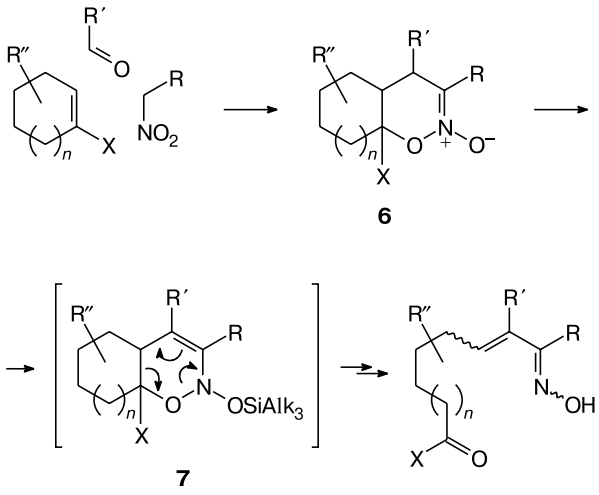
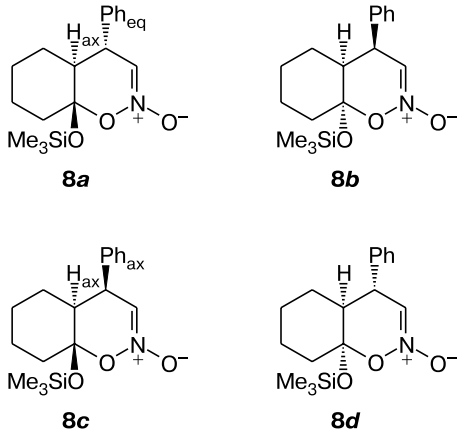
Scheme 2



X = AlkO, Alk_3SiO



Note. Hereafter, the letters ***a***, ***b***, ***c***, and ***d*** denote the corresponding configurations.

A mixture of diastereomeric nitronates **8*a*—*d*** prepared according to a known procedure[8] was converted into a mixture of silylated *E*- and *Z*-oximes **10** in 70% yield (with respect to β-nitrostyrene) (Scheme 3).

The goal of the present work was to study the factors that affect the stereoselectivity of new C=C double bonding in enoximes of the type **10*** and determine the scope of this approach to enoxime synthesis.

Results and Discussion

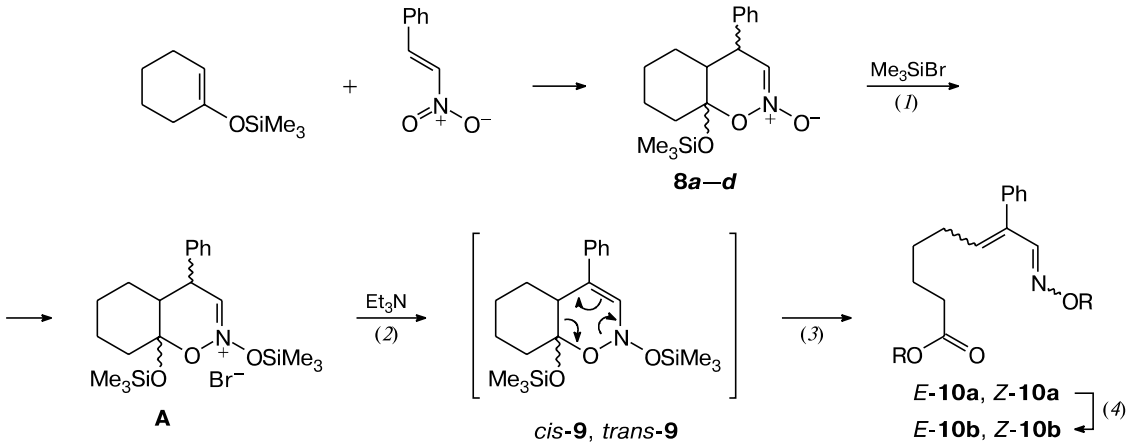
To investigate the stereochemistry of the silylation—fragmentation of bicyclic nitronates, we obtained each of the four stereoisomers **8*a*—*d*** in the individual state from β-nitrostyrene and 1-trimethylsilyloxycyclohexene with various promoting Lewis acids. Since the configurations of nitronates **8*a*,*c*,*d*** are already known,[8,9] the configuration of novel nitronate **8*b*** can be unambiguously determined.

Nitronates **8*a*—*d*** were silylated with a mixture of trimethylsilyl bromide and triethylamine at −30 °C (see Ref. 7). After the silylation was completed (monitoring by TLC), the reaction products were *in situ* desilylated with NH_4F in methanol and oximes **10b** were purified by column chromatography and analyzed by ^1H and ^{13}C NMR spectroscopy. The results obtained are given in Table 1. For their interpretation, it is expedient to discuss the mechanisms of silylation and fragmentation.

The most plausible way of the transformation **8** → **10b** is shown in Scheme 3 (also see Ref. 7). Earlier,[1] the fragmentation of oxazines **3** has been considered to be a concerted process. We will also analyze the stereochemi-

* The configuration of the C=N double bond is not discussed; according to the proposed synthesis of enoximes, it is assumed to be flexible and its isomerization is possible during both the course of the reaction and isolation of products.

Scheme 3



R = Me_3Si (**10a**), H (**10b**)

Table 1. Silylation of isomeric bicyclic nitronates **8*a*—*d***

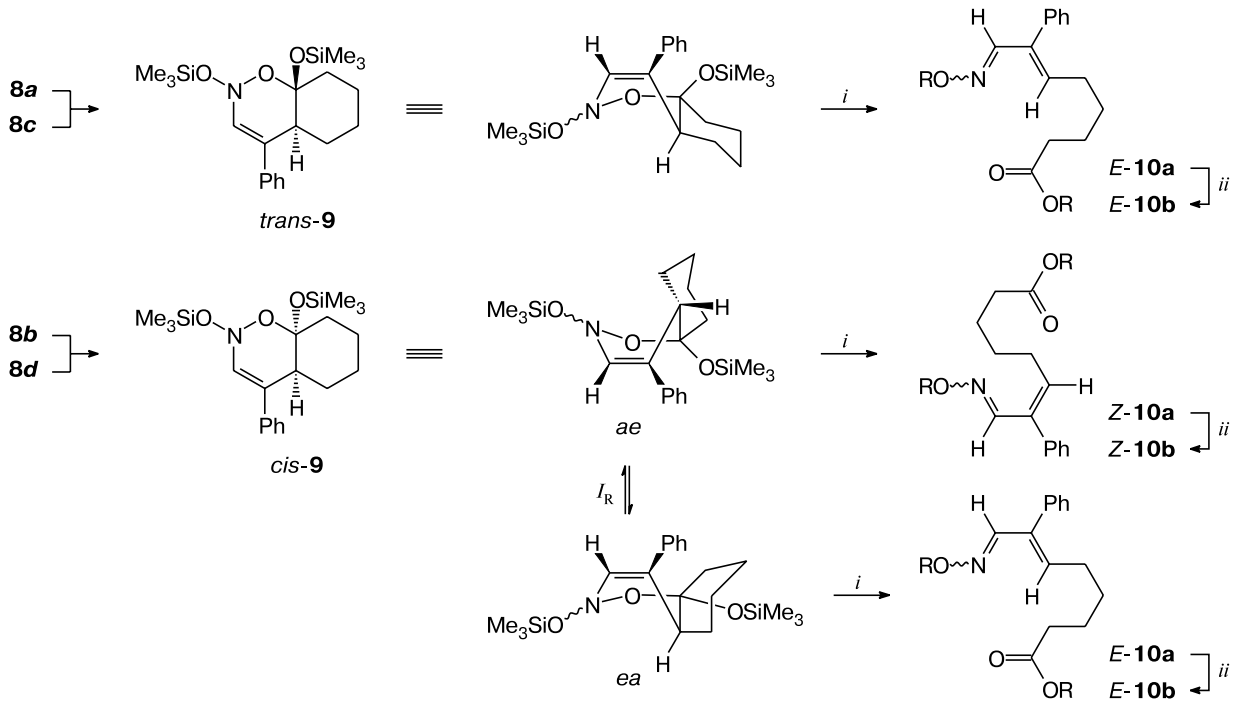
Nitronate	τ/h	Product	Yield (%)
8*a*	72	*E*-**10b** + *Z*-**10b** (1 : 10)	73
8*b*	72	*Z*-**10b**	82
8*c*	0.7	*E*-**10b**	88
8*d*	24	*Z*-**10b**	84

cal outcome of the silylation—fragmentation of nitronates **8*a*—*d*** in terms of concerted process.

The formation of cation **A** (see Scheme 3, step *1*) *via* reversible transfer of the Me_3Si group from trimethylsilyl bromide to the exocyclic O atom of nitronate **8** does not affect the relative configurations of the stereogenic centers C(4), C(5), and C(6); for this reason, four stereoisomers **8*a*—*d*** should yield the corresponding four diastereomeric cations **A**. Deprotonation of the C(4) atom in cations **A** makes the C(4) atom nonstereogenic; this can give rise to only two isomeric 5,6-dihydro-2*H*-oxazines, namely, *trans*-**9** and *cis*-**9** (step *2*), which differ in the type of joining the hetero- and carbocyclic rings. In the context of concerted fragmentation, it is the configurations and conformations of *trans*-**9** and *cis*-**9** that should be decisive for the configuration of the resulting C=C double bond (step *3*). Being sterically hindered, *trans*-**9** can exist as only one conformer (*ee*-joint of the rings) and its concerted fragmentation can give only the *E*-isomer of compound **10a** (Scheme 4). The other intermediate *cis*-**9** can exist as two *ea*- and *ae*-conformers, which leads to silylated *E*- and *Z*-isomeric oximes (*E*-**10a** and *Z*-**10a**, respectively) (see Scheme 4). Therefore, fragmentation of the isomer *trans*-**9** (see Scheme 3, step *3*) generated from isomeric nitronates **8*a*** and **8*c*** should yield, in the context of concerted fragmentation, the target enoxime with the *trans*-configuration (*E*-**10b**). At the same time, the fragmentation of the *cis*-joined oxazine *cis*-**9** (derived from nitronates **8*b*** and **8*d***) can *a priori* give a mixture of isomeric oximes *E*-**10b** and *Z*-**10b**; their ratio seems to depend on a number of thermodynamic and kinetic factors and thus is difficult to predict.

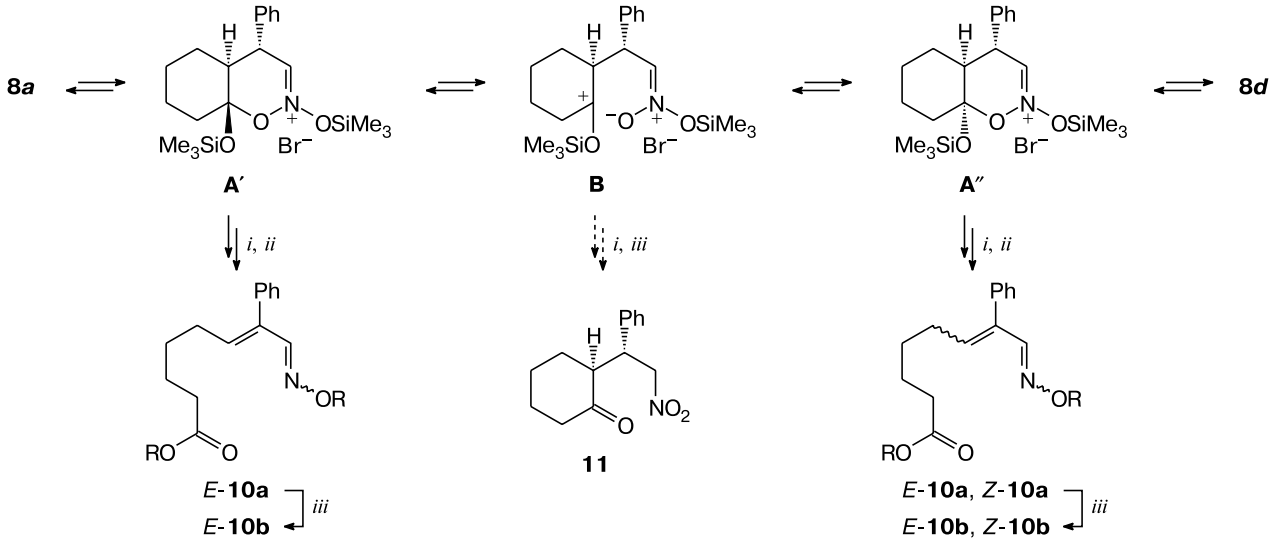
The outcomes of the silylation of nitronates **8*b*—*d*** (see Table 1) are consistent with our analysis given above. Indeed, the silylation of nitronate **8*c*** gave the expected *E*-isomer **10b**. The silylation of both nitronates **8*b*** and **8*d*** selectively yielded oxime *Z*-**10b**, which generally agrees with the mechanism shown in Scheme 4. However, the silylation of nitronate **8*a*** gave absolutely different results from that of nitronate **8*c***. Obviously, Scheme 4 does not reflect this process comprehensively. In terms of the concerted fragmentation of intermediate *trans*-**9**, the outcome of the silylation of nitronate **8*a*** can be explained by possible epimerization of intermediate cation **A** (see Scheme 3). Such a process including the epimerization **A′** ⇌ **A″** through open-chain tautomer **B** is shown in

Scheme 4



Note. i. retro-[4+2]. *ii.* Desilylation. I_R is the inversion of the heterocyclic ring.

Scheme 5



i. Deprotonation of cations **A´**, **A″**, and **B**. *ii*. Fragmentation of the intermediates *trans*-**9** and *cis*-**9**. *iii*. Desilylation (NH_4F in MeOH).

detail in Scheme 5 with the silylation of nitronate ***8a*** as an example.*

Note that sequential deprotonation and desilylation of the open-chain intermediate **B** could yield nitro ketone **11**, which was not detected in the real reaction mixture.

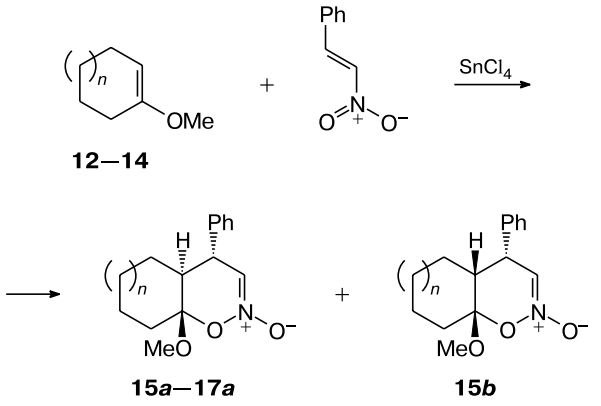
More convincing evidence for the epimerization of the cations of six-membered bicyclic nitronates was obtained in the silylation of 6-methoxy-4*H*-1,2-oxazine 2-oxides **15**—**17**** (Scheme 6).

The configurations of nitronates **15**—**17** determined from NMR data are given in Table 2.

Nitronates **15**—**17** were silylated with a Me_3SiBr—amine mixture with subsequent standard treatment with NH_4F in methanol (see Table 2).

Interpretation of the data obtained is represented in Scheme 7. The formation of enoximes **23** and **24** is due to deprotonation of the cyclic cationic tautomers **C´** or **C″**, while nitro compounds **25**—**27** form *via* deprotonation of the open-chain cationic tautomer **D** followed by desilylation of the resulting nitronates **20**—**22**.

Scheme 6



n = 1 (**12**, **15**), 2 (**13**, **16**), 3 (**14**, **17**)

It is worth noting that the contribution of the open-chain cationic tautomer **D** to the silylation of bicyclic nitronates **15**—**17** becomes more substantial than that in the silylation of nitronates **8**. Moreover, the silylation of nitronate ***17a*** gave nitro derivative ***27a*** as the sole reaction product we isolated (see Table 2, entry *9*).

In the series of nitronates **15**—**17**, the nitro compound : enoxime ratio in the reaction products characteristically increases with enlargement of the annulated carbocycle. This trend correlates well with the stability order of cyclic carbocations, which is determined from solvolysis of their precursors.[14] This correlation confirms that nitro compounds **25**—**27** can really form through deprotonation of the carbocyclic cation **D** stabilized by the methoxy group.

* The possibility of ring—chain tautomerism of silyl nitronates of functionalized nitro compounds in the presence of Lewis acids has been assumed earlier.[10,11] Epimerization of oxazines **1** and nitronates **2** has also been mentioned[12] but has not been studied in detail.

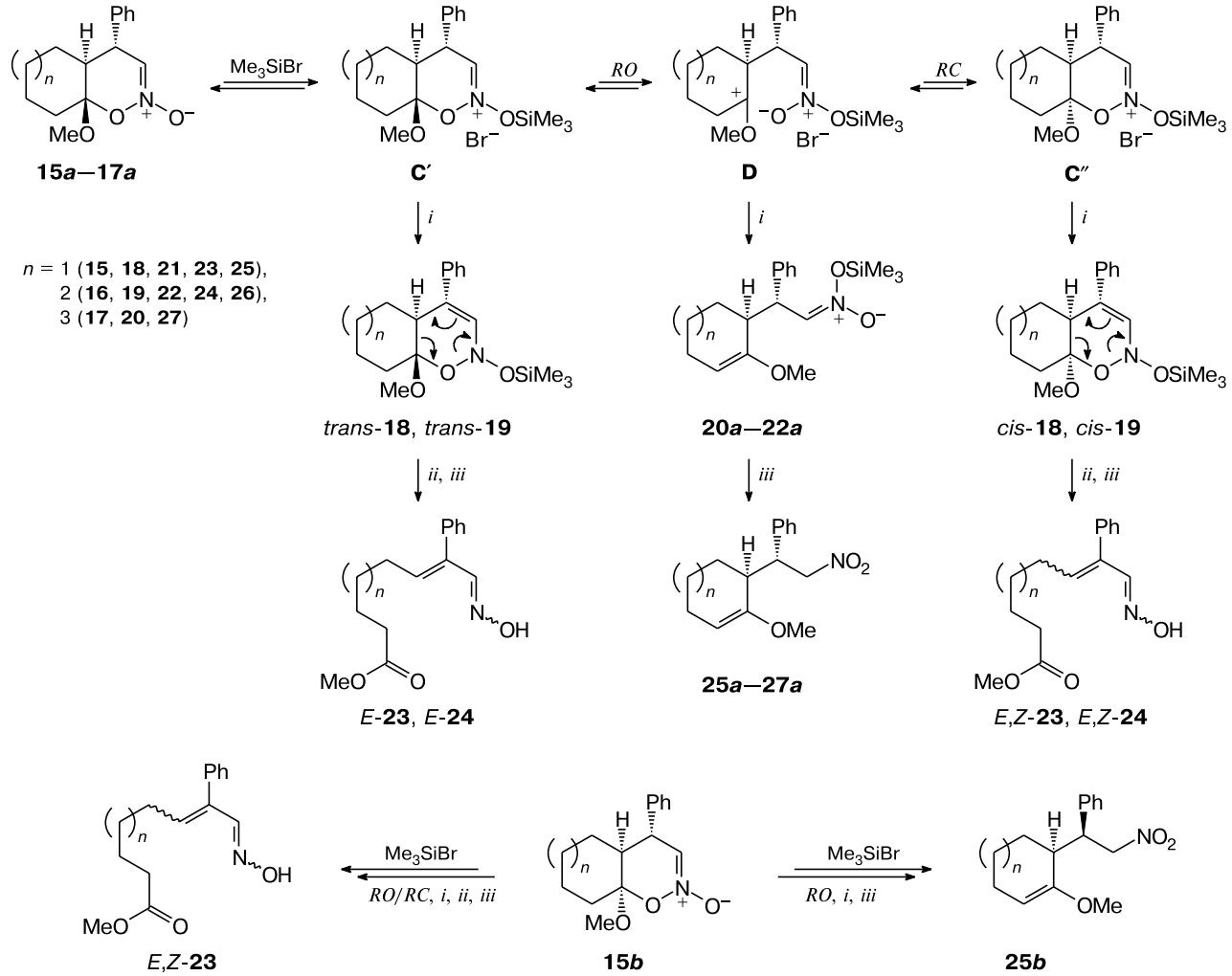
** The Me_3SiO group at the C(6) atom was replaced in nitronates **15**—**17** by the MeO group, which comparably stabilizes the cation,[13] for unambiguous interpretation of the results obtained. Indeed, when the starting nitronates contain the Me_3SiO group at the C(6) atom, nitro ketones of the type **11** can form both through "open-chain" cationic intermediates and as a result of desilylation of the starting nitronates (*e.g.*, see Ref. 8).

Table 2. Silylation of cyclic nitronates **15**—**17**

Entry	Nitronate	Silylation conditions			Enoxime	Yield (%)	Nitro compound	Yield (%)
		Base	τ/h	*T*/°C				
1	**15*a*** (*n* = 1)	Et_3N	96	−30	**23** *E*/*Z* ≈ 4.7 : 1	79	—	—
2	**15*b*/15*a*** (~2.5 : 1)	Et_3N	150	−30	**23** *E*/*Z* ≈ 0.47 : 1	94	—	—
3	**15*a***	Pr^i_2NEt	103	0	**23** *E*/*Z* ≈ 1 : 9	12*	**25*a***	76*
4	**15*a***	Pr^i_2NEt	114	20	**23** *E*/*Z* ≈ 1 : 6.7	17	**25*a***	73
5	**15*b*/15*a*** (~1.1 : 1)	Pr^i_2NEt	103	0	**23** *E*/*Z* ≈ 1 : 3	26**	**25*a*,*b*** ~1 : 1	47**
6	**15*b*/15*a*** (~1.1 : 1)	Pr^i_2NEt	114	20	**23** *E*/*Z* ≈ 1 : 2	16	**25*a*,*b*** ~0.6 : 1	68
7	**16*a*** (*n* = 2)	Et_3N	68	−30	**24** *E*/*Z* ≈ 1 : 1.75	65	**26*a***	27
8	**16*a***	Pr^i_2NEt	104	0	**24** *Z* only	6	**26*a***	88
9	**17*a*** (*n* = 3)	Et_3N	24	−30	—	—	**27*a***	93

* The yield with respect to the consumed compound **15*a*** (the conversion of **15*a*** was 74%). ** The yield with respect to the consumed mixture of **15*a*/15*b***. Apart from the reaction products, the unreacted isomer **15*a*** (28%) was recovered.

Scheme 7



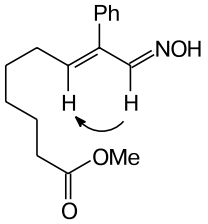
Note. *RO* is ring opening and *RC* is ring closure. *i*. Deprotonation of cations **C′**, **C″**, and **D**. *ii*. Fragmentation of intermediates **18** and **19**. *iii*. Desilylation (NH_4F in MeOH).

The formation of nitro derivatives **25—27** is promoted by sterically more hindered bases. For instance, the silylation of nitronate **15*a*** in the presence of ethyl(diisopropyl)amine (Hunig´s base) afforded nitro compound **25*a*** in 73% yield, while the silylation in the presence of triethylamine gave only a mixture of isomeric oximes *E*,*Z*-**23**. Replacement of triethylamine by sterically more hindered Hunig´s base in the silylation of nitronate **16*a*** also radically increased the yield of nitro compound **26*a*** (see Table 2, entries *3*, *4*, *7*, *8*). An increase in the size of the base molecule sharply lowers the silylation rate; that is why the reaction temperature should be substantially raised for the reaction to be completed over a reasonable period of time.

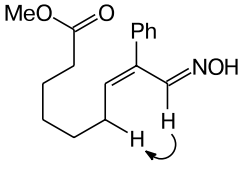
It should be emphasized that the formation of nitro compounds **25—27** is stereoselective. The silylation of nitronates **15*a*—17*a*** gave diastereomerically pure nitro compounds **25*a*—27*a***. Product **25*a*** was assigned the *erythro*-configuration (see below). The silylation of a mixture of isomeric nitronates **15*a*** and **15*b***, which differ in the configuration of the stereogenic center at the C(4) and C(5) atoms, gave a mixture of isomeric *erythro*-**25*a*** and *threo*-**25*b***. The ratio of the isomers **25*a*** : **25*b*** can depend not only on the **15*a*** : **15*b*** ratio but also on the relative deprotonation rates of the corresponding open-chain cationic intermediates **D**. A comparison of entries *5* and *6* (see Table 2) revealed that isomeric open-chain cationic intermediates **D** formed from nitronates **15*a*** and **15*b*** are probably deprotonated at different rates. The **25*a*** : **25*b*** ratio also depends on the silylation temperature. Taking into consideration the results under entry *5* (see Table 2), one can conclude that the silylation of nitronate **15*b*** in the presence of Hunig´s base occurs slightly more rapidly than the silylation of isomeric nitronate **15*a***.

The structures and purity of the compounds obtained were confirmed by NMR spectra and elemental analysis data.

The configurations of novel nitronates **15*a*—17*a*** and **15*b*** were taken to be the same as for nitronates **8*a*** and **8*b***, respectively, because of the similarity of their NMR spectra (characteristic signals for H(3) and H(4), see Experimental) and with consideration for the methods of their preparation.



E-**24**



Z-**24**

The configuration of the C=C double bond in oximino derivatives **10a** and **10b** has been completely confirmed earlier.[7] The configuration of the C=C double bond in isomeric oximes *E*- and *Z*-**23** was determined from their NMR spectra similar to those of standard oximes **10b**. The NOE technique was used to assign the configurations of conjugated oximes *E*- and *Z*-**24**. Irradiation at the frequency of the oximine proton (δ 7.81 for *E*-**24** and δ 8.26 for *Z*-**24**) gave rise to the responses of the vinylic proton in *E*-**24** (δ 5.95) and of the allylic proton in *Z*-**24** (δ 2.34). Nitro compounds **25*a*** and **25*b*** were assigned to the *erythro*- and *threo*-series, respectively, from close similarity of the signals (δ and *J* values) for their benzyl protons to those for *erythro*- and *threo*-1-(β-nitro-α-phenylethyl)cyclohexanones.[8,9]*

Thus, we interpreted the results of the silylation of bicyclic nitronates **8** and **15—17** in terms of ring—chain tautomerism of cationic silylation intermediates (see Scheme 7, transformation **C** ⇌ **D**). For more convincing confirmation of the tautomeric equilibrium, we attempted its direct detection.

Recently,[15] we have proposed a low-temperature NMR procedure for direct detection of cationic intermediates generated in the silylation of six-membered cyclic nitronates. Our purpose was to observe open-chain tautomeric cation **28** in the silylation of nitronate **17*a*** (Scheme 8). However, the low-temperature NMR spectra contained only one set of signals for one of the two stereoisomers of cyclic cationic tautomer **29**. In contrast, in the silylation of nitronate **30**, the open-chain cation of silyl nitronate **31** was detected only.**

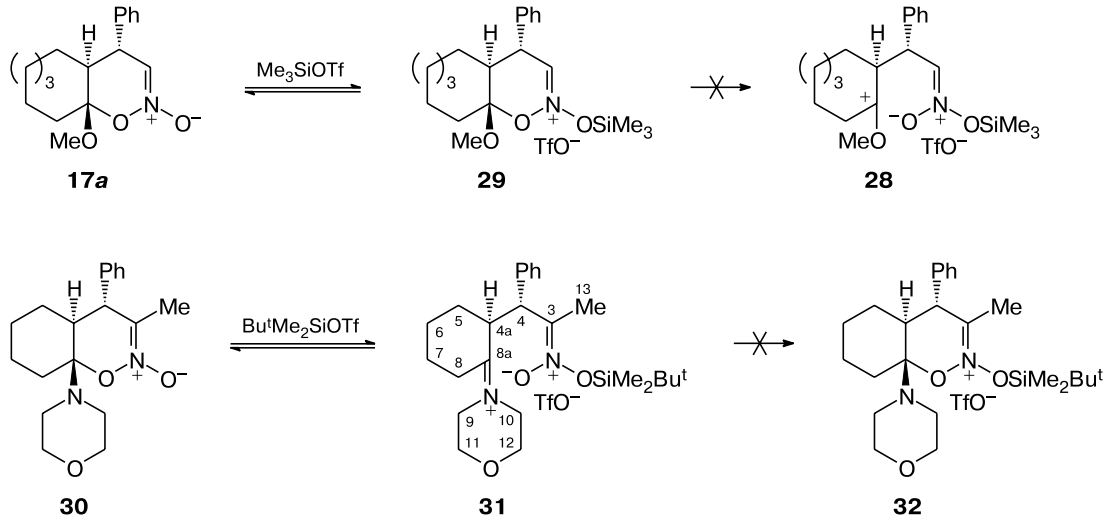
Thus, the silylation of bicyclic nitronates with silyl triflates gave both cyclic and open-chain cations; however, these forms were not in mobile tautomeric ring—chain equilibrium. For this reason, ring—chain tautomerism of cationic intermediates can be regarded so far only as a fairly justified hypothesis.

Hence, the silylation of annulated bicyclic six-membered nitronates in the presence of bases afforded a small series of conjugated enoximes with the distant carboxy group. Extension of this strategy to other objects can be hindered by a side process such as the formation of cyclic vinylic ethers containing a nitro fragment. The stereoselectivity of the generation of the new C=C double bond is determined by both the configurations of the starting

* For instance, for the *threo*-isomer of 1-(β-nitro-α-phenylethyl)cyclohexanone, the signals for the protons at the nitro group appear at δ 4.92 (dd, 1 H, J = 4.5 Hz, J = 12.5 Hz) and 4.64 (dd, 1 H, J = 9.7 Hz, J = 12.5 Hz), while for the *erythro*-isomer, the corresponding signal appears at δ 4.79 (d, 2 H, J = 7.5 Hz).

** Nitronate **30** has been kindly provided by A. V. Lesiv. Silylation of nitronate **30** in the presence of bases will be reported elsewhere.

Scheme 8



bicyclic nitronates and the contributions from tautomeric processes.

Experimental

All reactions were carried out in an atmosphere of dry argon. The reagents Et_3N (Acros), $EtPr^i_2N$ (Acros), $SnCl_4$ (Acros), and Me_3SiBr (Acros) and the solvents CH_2Cl_2, $CDCl_3$, and CD_2Cl_2 were distilled over CaH_2 under dry argon. NMR spectra were recorded on a Bruker AM-300 instrument (300 (^{1}H), 75 (^{13}C), and 59.6 MHz (^{29}Si)) at 30 °C in $CDCl_3$, unless otherwise specified; the NMR scale was calibrated against the residual signal of the solvent.[16] Chemical shifts are quoted in ppm (δ scale) and coupling constants are given in Hz. The INEPT technique was used in recording ^{29}Si spectra. Column chromatography was carried out on Silica gel 60 (Merck, 230—400 mesh). Thin-layer chromatography was carried out on Merck plates (silica gel 60 F_{254} on an aluminum sheet). Trimethylsilyl triflate,[17] β-nitrostyrene,[18] 1-(trimethylsilyloxy)cyclohexene,[19] 1-methoxycyclohexene,[20] 1-methoxycycloheptene,[20] 1,1-dimethoxycyclooctane,[20] and nitronates **8*a***,[8] **8*c***,[8] and **8*d*** were prepared as described earlier (see Refs 8, 9).

rel*-(4*S*,4a*S*,8a*R*)-4-Phenyl-8a-trimethylsilanyloxy-4a,5,6,7,8,8a-hexahydro-4*H*-benzo[*e*][1,2]oxazine 2-oxide (8*b*).** Tin tetrachloride (7.2 mmol, 0.84 mL) was added at −94 °C (cooling with acetone—liquid nitrogen) to a stirred solution of β-nitrostyrene (0.90 g, 6 mmol) and 1-(trimethylsilyloxy)cyclohexene (1.74 mL, 8.92 mmol) in CH_2Cl_2 (24 mL). The reaction mixture was kept at −94 °C for 5 min and poured into a vigorously stirred mixture of light petroleum (75 mL) and a saturated aqueous solution of $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous phase was washed with light petroleum (75 mL). The combined organic phases were successively washed with a saturated aqueous solution of $NaHCO_3$ and brine (2×30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Light petroleum (5 mL) was added to the resulting colorless oil. On cooling to −30 °C for 16 h, white crystals of nitronate **8*a (750 mg, 2.34 mmol, 39%) were filtered off, the mother liquor was concentrated *in vacuo*, and the residue was chromatographed on silica gel (AcOEt—hexane, 1 : 3) to give nitronate **8*b*** (0.74 g, 2.34 mmol, 39%) as a colorless oil contaminated with 8% nitronate **8*a*** (^{1}H NMR data).

Nitronate 8*b*, R_f 0.28 (AcOEt—hexane, 1 : 1). ^{1}H NMR (300.13 MHz), δ: 7.22—7.40 (m, 3 H, Ph); 7.15—7.22 (m, 2 H, Ph); 6.47 (d, 1 H, CH=N, J = 2.8 Hz); 4.41 (dd, 1 H, C<u>H</u>Ph, J = 2.8 Hz, J = 6.0 Hz); 2.34 (t, C<u>H</u>CHPh, J = 6.5 Hz); 2.21 (m, 1 H, CH_2); 1.87 (m, 2 H, CH_2); 0.90—1.80 (m, 5 H, CH_2); 0.27 (s, 9 H, $Si(CH_3)_3$). ^{13}C NMR, δ: 137.7, 128.7, 128.5, 127.4, 113.0, 105.2, 41.6, 40.7, 37.5, 24.8, 24.5, 22.8, 1.8. ^{29}Si NMR, δ: 16.6.

Silylation of nitronates 8*a*—*d* (general procedure). Triethylamine (2.6 mmol, 0.36 mL) and Me_3SiBr (2.3 mmol, 0.31 mL) were successively added at −30 °C (cooling with acetone—liquid nitrogen) to a stirred solution of nitronate **8** (320 mg, 1 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was kept in a freezing chamber at −30 °C for a time specified in Table 1. Methanol (2.5 mL) and 0.1 *M* NH_4F in MeOH (0.5 mL) were added. The resulting reaction mixture was kept at room temperature until silylated products disappeared completely (usually for 4—5 h; TLC monitoring in AcOEt—hexane, 1 : 1) and neutralized with trifluoroacetic acid (0.024 mL). Silica gel (1 g) was added and the resulting suspension was evaporated to dryness in a rotary evaporator. The solid residue was placed at the head of a column prepacked with silica gel (15 g) and eluted as normal with AcOEt—hexane (1 : 1). The products obtained and their yields are specified in Table 1.

6-(*E*)-8-Hydroxyimino-7-phenyloct-6-enoic acid (*E*-10b), R_f 0.20 (AcOEt—hexane, 1 : 1), m.p. 106—110 °C. Found (%): C, 67.62; H, 6.76; N, 5.49. $C_{14}H_{17}NO_3$. Calculated (%): C, 68.00; H, 6.93; N, 5.66. ^{1}H NMR, δ: 9.80 (br.s., 2 H, OH); 7.91 (s, 1 H, HC=N); 7.35 (m, 3 H, Ph); 7.12 (m, 2 H, Ph); 5.97 (t, 1 H, HC=C, ^3J = 7.5 Hz); 2.20 (t, 2 H, CH_2CO_2, ^3J = 7.2 Hz); 2.06 (dt, 2 H, CH_2C=C, $^3J \approx {}^3J \approx$ 7.4 Hz); 1.52 (tt, 2 H, CH_2, $^3J \approx {}^3J \approx$ 7.4 Hz); 1.42 (tt, 2 H, CH_2, $^3J \approx {}^3J \approx$ 7.2 Hz). ^{13}C NMR, δ: 178.9, 153.7, 140.3, 137.0, 135.4, 129.3, 128.4, 127.7, 33.7, 28.7, 28.6, 24.3.

6-(*Z*)-8-Hydroxyimino-7-phenyloct-6-enoic acid (*Z*-10b), R_f 0.18 (AcOEt—hexane, 1 : 1), m.p. 103—105 °C. Found (%): C, 67.99; H, 7.05; N, 5.83. $C_{14}H_{17}NO_3$. Calculated (%): C, 68.00; H, 6.93; N, 5.66. ^{1}H NMR, δ: 10.30 (br.s, 2 H, OH); 8.31 (s, 1 H, HC=N); 7.30 (m, 5 H, Ph); 5.93 (t, 1 H, HC=C, ^3J = 7.8 Hz); 2.37 (dt, 2 H, CH_2C=C, $^3J \approx {}^3J \approx$ 7.3 Hz); 2.33 (t, 2 H, CH_2CO_2, ^3J = 7.1 Hz); 1.66 (tt, 2 H, CH_2, $^3J \approx {}^3J \approx$ 7.4 Hz); 1.54 (tt, 2 H, CH_2, $^3J \approx {}^3J \approx$ 7.5 Hz). ^{13}C NMR, δ: 179.0, 147.9, 139.3, 138.9, 134.8, 128.6, 128.3, 127.6, 33.8, 29.0, 28.0, 24.4.

Synthesis of nitronates 15*a*,*b* and 16 (general procedure). Tin tetrachloride (12 mmol, 1.40 mL) was added at −78 °C (cooling with acetone—dry ice) to a stirred solution of β-nitrostyrene (1.50 g, 10 mmol) in CH_2Cl_2 (30 mL). The mixture was kept at this temperature for 5 min and then an appropriate vinylic ether (15 mmol) was added. The reaction mixture was kept at −78 °C for an additional 10 min and poured into a vigorously stirred mixture of AcOEt (90 mL) and a saturated aqueous solution of $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous phase was washed with AcOEt (2×50 mL). The combined organic phases were successively washed with a saturated aqueous solution of $NaHCO_3$ and brine (2×30 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a colorless oil, which crystallized as colorless crystals of the target product upon addition of ether (15 mL).

***rel*-(4*R*,4a*S*,8a*R*)-8a-Methoxy-4-phenyl-4a,5,6,7,8,8a-hexahydro-4*H*-benzo[*e*][1,2]oxazine 2-oxide (15*a*).** The yield was 69%, m.p. 134—135 °C (Et_2O), R_f 0.25 (AcOEt—hexane, 1 : 1). Found (%): C, 69.11; H, 7.55; N, 5.44. $C_{15}H_{19}NO_3$. Calculated (%): C, 68.94; H, 7.33; N, 5.36. ^{1}H NMR, δ: 7.22—7.35 (m, 3 H, Ph); 7.12—7.18 (m, 2 H, Ph); 6.30 (d, 1 H, CH=N, J = 3.0 Hz); 3.51 (dd, 1 H, C<u>H</u>Ph, J = 3.0 Hz, J = 11.0 Hz); 3.44 (s, 3 H, OCH_3); 2.20—2.28 (m, 1 H, C<u>H</u>CHPh); 1.80 (dt, 1 H, CH_2, J = 3.8 Hz, J = 11.4 Hz); 1.62—1.72 (m, 2 H, CH_2); 1.05—1.52 (m, 5 H, CH_2). ^{13}C NMR, δ: 138.6, 128.9, 128.5, 127.8, 115.6, 105.4, 49.1, 44.0, 43.2, 28.9, 25.7, 24.9, 22.1.

rel*-(4*R*,4a*R*,8a*R*)-8a-Methoxy-4-phenyl-4a,5,6,7,8,8a-hexahydro-4*H*-benzo[*e*][1,2]oxazine 2-oxide (15*b*).** The mother liquor from the crystallization of nitronate **15*a was concentrated *in vacuo* and cooled with ether (5 mL) to −30 °C. The resulting colorless crystals were filtered off. According to ^{1}H NMR data, the crystals were composed of nitronates **15*b*** and **15*a*** in the ratio from 2.5 : 1 to 1 : 1. The yield of nitronate **15*b*** was ~10% (^{1}H NMR data), R_f 0.25 (AcOEt—hexane, 1 : 1). Found (together with **15*a***) (%): C, 69.04; H, 7.57; N, 5.41. $C_{15}H_{19}NO_3$. Calculated (%): C, 68.94; H, 7.33; N, 5.36. ^{1}H NMR, δ: 7.22—7.35 (m, 3 H, Ph); 7.10—7.18 (m, 2 H, Ph); 6.44 (d, 1 H, CH=N, J = 2.8 Hz); 4.43 (dd, 1 H, C<u>H</u>Ph, J = 2.8 Hz, J = 6.4 Hz); 3.49 (s, 3 H, OCH_3); 2.36 (br.d, 1 H, C<u>H</u>CHPh, J = 13.4 Hz); 0.90—1.95 (m, 8 H, CH_2). ^{13}C NMR, δ: 137.4, 128.8, 128.4, 127.4, 113.5, 106.1, 49.2, 40.7, 39.7, 31.2, 24.9, 24.4, 22.2.

***rel*-(4*R*,4a*S*,9a*R*)-9a-Methoxy-4-phenyl-4,4a,5,6,7,8,9,9a-octahydrocyclohepta[*e*][1,2]oxazine 2-oxide (16*a*).** The yield was 75%, m.p. 152—153 °C (Et_2O), R_f 0.26 (AcOEt—hexane, 1 : 1). Found (%): C, 69.72; H, 7.84; N, 5.21. $C_{16}H_{21}NO_3$. Calculated (%): C, 69.79; H, 7.69; N, 5.09. ^{1}H NMR, δ: 7.22—7.36 (m, 3 H, Ph); 7.13—7.19 (m, 2 H, Ph); 6.24 (d, 1 H, CH=N, J = 3.0 Hz); 3.49 (dd, 1 H, C<u>H</u>Ph, J = 3.1 Hz, J = 11.2 Hz); 3.45 (s, 3 H, OCH_3); 2.07—2.20 (m, 1 H, C<u>H</u>CHPh); 2.00—1.82 (m, 2 H, CH_2); 1.56—1.74 (m, 4 H, CH_2); 1.04—1.53 (m, 4 H, CH_2). ^{13}C NMR, δ: 138.9, 129.0, 128.8, 127.9, 115.4, 109.0, 49.7, 47.3, 44.6, 32.4, 26.9, 26.2, 25.5, 20.0.

***rel*-(4*R*,4a*S*,10a*R*)-10a-Methoxy-4-phenyl-4a,5,6,7,8,9,10,10a-octahydro-4*H*-cycloocta[*e*][1,2]oxazine 2-oxide (17*a*).** Tin tetrachloride (2.08 g, 0.94 mL, 8 mmol) was added at −78 °C (cooling with acetone—dry ice) to a stirred solution of β-nitrostyrene (0.6 g, 4 mmol) and 1,1-dimethoxycyclooctane (1.03 g, 6 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was kept at −78 °C for 5 min and then $EtNPr^i_2$ (0.83 g, 1.06 mL, 6.4 mmol) was added. After the mixture was stirred at −78 °C for an additional 10 min, it was poured into a vigorously stirred mixture of AcOEt (40 mL) and a saturated aqueous solution of $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous phase was washed with AcOEt (2×20 mL). The combined organic phases were successively washed with a saturated aqueous solution of $NaHCO_3$ and brine (2×15 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel with AcOEt—hexane (1 : 1) as an eluent. The yield was 0.613 g (53%), m.p. 126—128 °C (Et_2O), R_f 0.33 (AcOEt—hexane, 1 : 1). Found (%): C, 70.77; H, 7.79; N, 5.03. $C_{17}H_{23}NO_3$. Calculated (%): C, 70.56; H, 8.01; N, 4.84. ^{1}H NMR, δ: 7.38—7.26 (m, 3 H, Ph); 7.19—7.25 (m, 2 H, Ph); 6.27 (d, 1 H, CH=N, J = 2.9 Hz); 3.51 (dd, 1 H, C<u>H</u>Ph, J = 2.9 Hz, J = 11.1 Hz); 3.46 (s, 3 H, OCH_3); 2.14—2.28 (m, 2 H, C<u>H</u>CHPh + CH_2); 1.94—2.06 (m, 1 H, CH_2); 1.21—1.83 (m, 10 H, CH_2). ^{13}C NMR, δ: 138.9, 129.0, 128.8, 127.8, 115.5, 109.3 (–), 49.7, 45.1, 40.8, 30.6, 28.4, 26.3, 26.2, 24.5, 21.0.

Silylation of nitronates 15*a*—17*a* and 15*b* (general procedure). A solution of a nitronate (1 equiv.) in CH_2Cl_2 (3 mL per millimole of the nitronate) was cooled to −30 °C. An appropriate amine (1.5 equiv., see Table 2) and Me_3SiBr (1.2 equiv.) were successively added with stirring and the reaction mixture was kept at −30 °C for a time specified in Table 2. Methanol (2.5 mL) and 0.1 *M* NH_4F in MeOH (0.5 mL) were added. The resulting mixture was kept at room temperature until silylated products disappeared completely (usually for 4—5 h; TLC monitoring). Silica gel (1 g) was added and the resulting suspension was evaporated to dryness. The solid residue was placed at the head of a column prepacked with silica gel (15 g) and eluted as normal with AcOEt—hexane (1 : 3). The yields of the products obtained are specified in Table 2.

Methyl 6-(*E*)-8-hydroxyimino-7-phenyloct-6-enoate (*E*-23), R_f 0.25 (AcOEt—hexane, 1 : 3). ^{1}H NMR, δ: 8.53 (br.s, 1 H, OH); 7.80 (s, 1 H, HC=N); 7.24—7.41 (m, 3 H, Ph); 7.08—7.16 (m, 2 H, Ph); 5.91 (t, 1 H, HC=C, J = 7.5 Hz); 3.63 (s, 3 H, OMe); 2.22 (t, 2 H, CH_2CO_2, J = 7.3 Hz); 2.06 (q, 2 H, CH_2C=C, J = 7.3 Hz); 1.54 (tt, 2 H, CH_2, $^3J \approx {}^3J \approx$ 7.4 Hz); 1.41 (tt, 2 H, CH_2, $^3J \approx {}^3J \approx$ 7.2 Hz). ^{13}C NMR, δ: 174.0, 153.4, 139.6, 137.1, 135.6, 129.2, 128.3, 127.6, 51.5, 33.8, 28.7, 28.6, 24.4.

Methyl 6-(*Z*)-8-hydroxyimino-7-phenyloct-6-enoate (*Z*-23), R_f 0.25 (AcOEt—hexane, 1 : 1). ^{1}H NMR, δ: 8.74 (br.s, 1 H, OH); 8.17 (s, 1 H, HC=N); 7.22—7.41 (m, 5 H, Ph); 5.88 (t, 1 H, HC=C, ^3J = 7.7 Hz); 3.67 (s, 3 H, OMe); 2.36 (q, 2 H, CH_2C=C, J = 7.4 Hz); 2.33 (t, 2 H, CH_2CO_2, ^3J = 7.2 Hz); 1.70 (tt, 2 H, CH_2, J = 7.4 Hz); 1.55 (tt, 2 H, CH_2, J = 7.2 Hz). ^{13}C NMR, δ: 174.0, 147.6, 138.4, 137.1, 135.0, 128.6, 128.1, 127.5, 51.5, 33.8, 29.1, 27.8, 24.4.

For the mixture of the isomers *E*-**23** and *Z*-**23**, found (%): C, 69.11; H, 7.48; N, 5.62; $C_{15}H_{19}NO_3$; calculated (%): C, 68.94; H, 7.33; N, 5.36.

Methyl 7-(*E*)-9-hydroxyimino-8-phenylnon-7-enoate (*E*-24), R_f 0.26 (AcOEt—hexane, 1 : 3). ^{1}H NMR, δ: 8.40 (br.s, 1 H, OH); 7.81 (s, 1 H, HC=N); 7.25—7.38 (m, 3 H, Ph); 7.10—7.18 (m, 2 H, Ph); 5.95 (t, 1 H, HC=C, ^3J = 7.7 Hz); 3.66 (s, 3 H, OMe); 2.22 (t, 2 H, CH_2CO_2, J = 7.3 Hz); 2.06 (q, 2 H, CH_2C=C, J = 7.3 Hz); 1.66 (tt, 2 H, CH_2, J = 7.5 Hz); 1.51 (tt, 2 H, CH_2, J = 7.1 Hz); 1.41 (tt, 2 H, CH_2, J = 6.7 Hz). ^{13}C NMR, δ: 174.0, 148.3, 140.1, 136.7, 135.6, 129.2, 128.6, 128.1, 51.5, 33.9, 29.2, 28.8, 28.6, 24.8.

Methyl 7-(*Z*)-9-hydroxyimino-8-phenylnon-7-enoate (*Z*-24), R_f 0.26 (AcOEt—hexane, 1 : 3). ^{1}H NMR, δ: 8.28 (br.s, 1 H, OH); 8.26 (s, 1 H, HC=N); 7.27—7.32 (m, 5 H, Ph); 5.92 (t, 1 H, HC=C, ^3J = 7.7 Hz); 3.67 (s, 3 H, OMe); 2.34 (q, 2 H, CH_2C=C, J = 7.4 Hz); 2.32 (t, 2 H, CH_2CO_2, ^3J = 7.3 Hz); 1.66 (tt, 2 H, CH_2, J = 7.5 Hz); 1.51 (tt, 2 H, CH_2, J = 7.1 Hz); 1.41 (tt, 2 H, CH_2, J = 6.7 Hz). ^{13}C NMR, δ: 174.0, 148.3, 139.5, 139.0, 134.5, 128.5, 128.0, 127.4, 51.5, 34.0, 29.1, 28.7, 28.0, 24.7.

For the mixture of *E*-**24** and *Z*-**24**, found (%): C, 69.99; H, 7.53; N, 5.41; $C_{16}H_{21}NO_3$; calculated (%): C, 69.79; H, 7.69; N, 5.09.

***erythro*-[1-(2-Methoxycyclohex-2-enyl)-2-nitroethyl]benzene (25*a*)**, R_f 0.55 (AcOEt—hexane, 1 : 1). Found (%): C, 69.20; H, 7.25; N, 5.19. $C_{15}H_{19}NO_3$. Calculated (%): C, 68.94; H, 7.33; N, 5.36. ^{1}H NMR, δ: 7.21—7.36 (m, 5 H, Ph); 4.83—4.90 (m, 1 H, C<u>H</u>=$COCH_3$); 4.67—4.77 (m, 2 H, CH_2NO_2); 3.75 (dt, 1 H, C<u>H</u>Ph, J = 6.0 Hz, J = 9.6 Hz); 3.52 (s, 3 H, OCH_3); 2.42—2.50 (m, 1 H, C<u>H</u>CHPh); 2.04—2.15 (m, 2 H, CH_2); 1.37—1.72 (m, 4 H, CH_2). ^{13}C NMR, δ: 155.2, 139.3, 128.7, 128.1, 127.9, 96.1, 80.0, 53.5, 47.2, 40.6, 25.6, 23.5, 18.3.

***threo*-[1-(2-Methoxycyclohex-2-enyl)-2-nitroethyl]benzene (25*b*)**, R_f 0.55 (AcOEt—hexane, 1 : 1). ^{1}H NMR, δ: 7.10—7.40 (m, 5 H, Ph); 4.95 (dd, 1 H, $CHNO_2$, J = 13.0 Hz, J = 10.7 Hz); 4.77 (t, 1 H, C<u>H</u>=$COCH_3$, J = 3.0 Hz); 4.66 (dd, 1 H, $CHNO_2$, J = 13.4 Hz, J = 4.7 Hz); 4.00 (dt, 1 H, C<u>H</u>Ph, J = 10.9 Hz, J = 3.8 Hz); 3.54 (s, 3 H, OCH_3); 2.66 (m, 1 H, C<u>H</u>CHPh); 1.97 (m, 1 H, CH_2); 1.86 (m, 1 H, CH_2); 1.55—1.64 (m, 1 H, CH_2); 1.25—1.40 (m, 3 H, CH_2). ^{13}C NMR, δ: 154.3, 138.3, 128.5, 128.2, 127.2, 97.4, 77.7, 53.9, 46.0, 41.8, 26.7, 23.6, 21.5.

For the mixture of **25*a*** and **25*b***, found (%): C, 68.63; H, 7.00; N, 5.55; $C_{15}H_{19}NO_3$; calculated (%): C, 68.94; H, 7.33; N, 5.36.

***E*-1-Methoxy-7-(2-nitro-1-phenylethyl)cycloheptene (26*a*)**, R_f 0.51 (AcOEt—hexane, 1 : 3), m.p. 111—112 °C. Found (%): C, 69.52; H, 7.54; N, 4.88. $C_{16}H_{21}NO_3$. Calculated (%): C, 69.79; H, 7.69; N, 5.09. ^{1}H NMR, δ: 7.21—7.38 (m, 5 H, Ph); 4.83—4.93 (m, 1 H, C<u>H</u>=$COCH_3$); 4.57—4.66 (m, 2 H, CH_2NO_2); 3.86—4.00 (m, 1 H, C<u>H</u>Ph); 3.47 (s, 3 H, OCH_3); 2.53—2.64 (m, 1 H, C<u>H</u>CHPh); 2.08—2.36 (m, 2 H, CH_2); 1.24—1.83 (m, 6 H, CH_2). ^{13}C NMR, δ: 160.4, 138.8, 128.9, 127.9, 127.6, 98.7, 81.0, 54.2, 47.3, 44.2, 28.1, 27.2, 25.8, 24.3.

***E*-1-Methoxy-8-(2-nitro-1-phenylethyl)cyclooctene (27*a*)**, R_f 0.57 (AcOEt—hexane, 1 : 3), m.p. 58-59 °C. Found (%): C, 70.29; H, 8.24; N, 4.56. $C_{17}H_{23}NO_3$. Calculated (%): C, 70.56; H, 8.01; N, 4.84. ^{1}H NMR, δ: 7.18—7.38 (m, 5 H, Ph); 4.80 (t, 1 H, C<u>H</u>=$COCH_3$, J = 8.2 Hz); 4.64 (dd, 1 H, $CHNO_2$, J = 12.3 Hz, J = 4.5 Hz); 4.53 (dd, 1 H, $CHNO_2$, J = 12.3 Hz, J = 10.5 Hz); 3.72 (dt, 1 H, C<u>H</u>Ph, J = 4.5 Hz, J = 10.6 Hz); 3.54 (s, 3 H, OCH_3); 3.01 (dt, 1 H, C<u>H</u>CHPh, J = 4.4 Hz, J = 11.5 Hz); 2.00—2.25, 1.64—1.80 (both m, 2 H each, CH_2); 1.41—1.56 (m, 1 H, CH_2); 1.16—1.40 (m, 3 H, CH_2); 0.96—1.14 (m, 2 H, CH_2). ^{13}C NMR, δ: 155.1, 139.3, 128.9, 128.1, 127.5, 99.2, 80.1, 54.3, 45.6, 40.2, 32.4, 32.3, 27.8, 26.4, 25.5.

Study of cationic intermediates in the silylation of six-membered cyclic nitronates (general procedure). A solution of a nitronate (0.05 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (10 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) was prepared in an NMR tube filled with argon and closed with a septum. The tube was cooled to 200 K and a silyl triflate (0.075 mmol; TMSOTf for **29** and TBDMSOTf for **31**) was added with a microsyringe. The tube was rapidly shaken several times for homogenization and placed in the cooled (210 K) probe of an NMR spectrometer. The spectra of the starting nitronates and the sample with silyl triflate are given below. The cationic intermediate derived from compound **17*a*** was assigned cyclic structure **29** since its characteristic parameters in the NMR spectra were similar to the corresponding parameters of cations obtained in the silylation of six-membered cyclic nitronates.[15] The cationic intermediate derived from compound **30** was assigned acyclic structure **31** according to its spectrum. The characteristic signal in the ^{29}Si NMR spectrum is typical of silyl nitronates.

Nitronate 17*a*. ^{1}H NMR (CD_2Cl_2, −63 °C), δ: 7.25—7.40 (m, 3 H, Ph); 7.20 (d, 2 H, *o*-Ph, J = 7.3 Hz); 6.21 (d, 1 H, H(3), J = 2.5 Hz); 3.44 (dd, 1 H, H(4), J = 10.6 Hz, J = 2.3 Hz); 3.35 (s, 3 H, OMe); 2.14 (br.t, 1 H, H(4a), J ≈ 9.0 Hz); 1.92, 1.70 (both m, 1 H each, C(10)H_2); 1.10—1.66 (m, 10 H, C(5)H_2—C(9)H_2). ^{13}C NMR (CD_2Cl_2, −63 °C), δ: 138.6 (s, Ph_{ipso}); 128.6, 128.4, 127.3 (CH, Ph); 115.1 (C(3)); 108.9 (C(10a)); 49.2 (OMe); 44.2 (C(4)); 36.8 (C(4a)); 25.5 (2 C); 24.0, 23.8, 22.0, 21.0 (C(5)—C(10)).

Intermediate 29. ^{1}H NMR (CD_2Cl_2, −63 °C), δ: 8.13 (d, 1 H, H(3), J = 2.3 Hz); 7.36—7.50 (m, 3 H, Ph); 7.20 (d, 2 H, *o*-Ph, J = 7.8 Hz); 3.97 (dd, 1 H, H(4), J = 11.5 Hz, J = 2.3 Hz); 3.47 (s, 3 H, OMe); 2.44 (br.t, 1 H, H(4a), J ≈ 9.0 Hz); 2.09, 2.30 (both m, 1 H each, C(10)H_2); 1.84, 0.98—1.76 (2 m, 1 H and 9 H, C(5)H_2—C(9)H_2); 0.45 (s, 9 H, $SiMe_3$). ^{13}C NMR (CD_2Cl_2, −63 °C), δ: 143.2 (C(3)), 132.8 (s, Ph_{ipso}); 129.6, 129.0 (CH, Ph); 122.0 (C(10a)); 119.5 (q, CF_3); 51.8 (OMe); 45.0 (C(4)); 36.3 (C(4a)); 26.0, 24.4, 23.3, 22.7, 21.0, 20.4 (s, CH_2); 1.4 ($Si(CH_3)_3$). ^{29}Si NMR (CD_2Cl_2, −63 °C), δ: 49.7.

Nitronate 30. ^{1}H NMR (CD_2Cl_2, −63 °C), δ: 7.10—7.40 (m, 5 H, Ph); 3.80 (br.t, 4 H, C(11)H, C(12)H); 3.50 (d, 1 H, H(4), J = 10.6 Hz); 3.40 (br.q, 4 H, C(9)H, C(10)H); 2.65—3.00 (3 m, 3 H, C(5)H, C(8)H, C(8a)H); 1.70 (s, 3 H, C(3)Me); 1.50 (m, 6 H, C(6)H_2, C(7)H_2), C(5)H, C(8)H). ^{13}C NMR (CD_2Cl_2, −63 °C), δ: 140.9 (s, Ph_{ipso}); 128—130 (CH, Ph); 122.4 (C(3)); 100.1 (C(8a)); 67.9 (C(11), C(12)); 46.9 (C(4)); 44.7, 44.0 (C(9), C(10)); 39.8 (C(4a)); 25.3, 23.2, 22.2, 18.0 (4 CH_2); 22.0 (C(13)).

Intermediate 31. ^{1}H NMR (CD_2Cl_2, −63 °C), δ: 7.47 (d, 2 H, *o*-Ph, J = 7.3 Hz); 7.42 (t, 2 H, *m*-Ph, J = 7.2 Hz); 7.36 (t, 1 H, *p*-Ph, J = 7.1 Hz); 4.63 (d, 1 H, H(4), J = 11.7 Hz); 4.43 (ddd, 1 H, H(9), J = 13.4 Hz, J = 7.8 Hz, J = 3.2 Hz); 4.28 (m, 1 H, H(9) or H(10)); 4.21 (m, 1 H, H(9) or H(10)); 4.13 (br.d, 1 H, H(9) or H(10), J = 13.3 Hz); 4.22 (m, 1 H, H(4a)); 4.05, 3.92 (both m, 4 H, H(11), H(12)); 3.28 (td, 1 H, H(8), J = 12.5 Hz, J = 5.5 Hz); 3.20 (br.d, 1 H, H(8), J = 14.4 Hz); 2.28 (m, 1 H, H(7)); 1.96 (br.d, 1 H, H(5), J = 14.8 Hz); 1.90 (s, 3 H, C(3)Me); 1.85 (m, 2 H, H(5), H(7)); 1.65, 1.48 (both m, 2 H,

H(6)); 0.90 (s, 9 H, Bu^t); 0.22, 0.25 (both s, 6 H, $SiMe_2$). ^{13}C NMR (CD_2Cl_2, −63 °C), δ: 195.5 (C(8a)); 135.3 (s, Ph_{ipso}); 130.0, 129.5, 128.8 (CH, Ph); 125.5 (C(3)); 66.9, 66.5 (C(11), C(12)); 54.7, 54.8 (C(9), C(10)); 49.4 (C(4)); 42.9 (C(4a)); 31.4 (C(8)); 30.0 (C(5)); 28.0 (C(7)); 26.0 (CH_3, Bu^t); 24.9 (C(13)); 18.7 (C(6)); 18.6 (C_{quat}, Bu^t); −2.7, −3.9 ($Si(CH_3)_2$). ^{29}Si NMR (CD_2Cl_2, −63 °C), δ: 32.2.

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