Silylation of γ-nitro ketones as a convenient approach to the synthesis of 2-[*N*,*N*-bis(silyloxy)amino]-2,3-dihydrofurans and conjugated enoximes*[1,*2]

K. P. Birin, A. A. Tishkov, S. L. Ioffe,* Yu. A. Strelenko, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: iof@cacr.ioc.ac.ru

Silylation of γ-nitro ketones of the general formula $R^1COCH(R^2)CH(R^3)CH(R^4)NO_2$ proceeded stereoselectively to give 2-[*N*,*N*-bis(trimethylsilyloxy)amino]-2,3-dihydrofurans, conjugated enoximes, silylation products of the carbonyl group or both functional groups, or *N*,*N*-bis(trimethylsilyloxy)enamine depending on the nature and positions of the substituents in the carbon skeleton. Dihydrofuran derivatives are formed for R^1 = Ar or *cyclo*-C_3H_5. Enoximes are generated as the silylation products of the starting ketones with enhanced β-proton mobility (R^3 = CO_2Me or 4-$NO_2C_6H_4$). The presence of an alkyl group at the carbonyl function (R^1 = Alk) is favorable for the formation of enoximes. Finally, the introduction of a substituent at the α position with respect to the nitro group (R^4 = Me, CO_2Me, or Ph) leads to the formation of silyl enolates. Under the action of NH_4F in MeOH, dihydrofurans can be transformed into substituted furans in moderate yields.

Key words: aliphatic nitro compounds, silylation, dihydrofurans, enoximes, furans.

Silylation of aliphatic nitro compounds (ANC) is an original and versatile process, which substantially extends the possibilities for the preparative use of these reactive nitrogen-containing substrates.[2] This process involves various reactions, which generally proceed with high chemoselectivity to give diverse functionalized compounds. The formation of a particular product upon silylation of ANC depends on the nature of substituents in the carbon skeleton of the starting nitro compounds, acid-base properties of silylating reagents, and reaction conditions.

Earlier, with a number of examples, we have demonstrated that silylation of γ-nitro ketones **1** (ANC containing the carbonyl group) can afford different products, *viz.*, 2-[*N*,*N*-bis(silyloxy)amino]-2,3-dihydrofurans,[1] conjugated enoximes,[3,4] *N*,*N*-bis(silyloxy)enamines (BSENA),[5] and some other derivatives[6] (Scheme 1). However, it is difficult to predict the pathway of the process in each particular case. Consequently, additional information on the influence of various factors on this process is required.

The aim of the present study was to systematically examine silylation of γ-nitro ketones **1** of the general formula $R^1COCH(R^2)CH(R^3)CH(R^4)NO_2$ (**1a—r**) (R^1, R^2, R^3, and R^4 are listed in Table 1). Particular attention was given to a search for the reaction conditions favorable for the generation of 2-[*N*,*N*-bis(silyloxy)amino]-2,3-dihydrofurans and conjugated enoximes. The $Me_3SiBr—Et_3N$ system was generally used as the silylating reagent.*

Results and Discussion

Based on the earlier data[1,3—6] on the silylation of a number of γ-nitro ketones **1**, a rather justified model of this complicated process can be proposed (see Scheme 1). The first step of the process involves competitive silylation of nitro ketone **1** at the carbonyl group or the nitro fragment giving rise to silyl enolate **2** or silyl nitronate **3**, respectively (steps (*1*) and (*2*)). Silyl enolate **2** can undergo further silylation to form nitronate **4**.**

If the carbonyl group is retained in the first step of silylation of γ-nitro ketones **1**, the resulting silyl nitronate **3** can undergo a series of interesting transformations involving this group.***

*1 Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

*2 For a preliminary communication, see Ref. 1.

* Below, the choice of the silylating reagent will be substantiated in more detail.

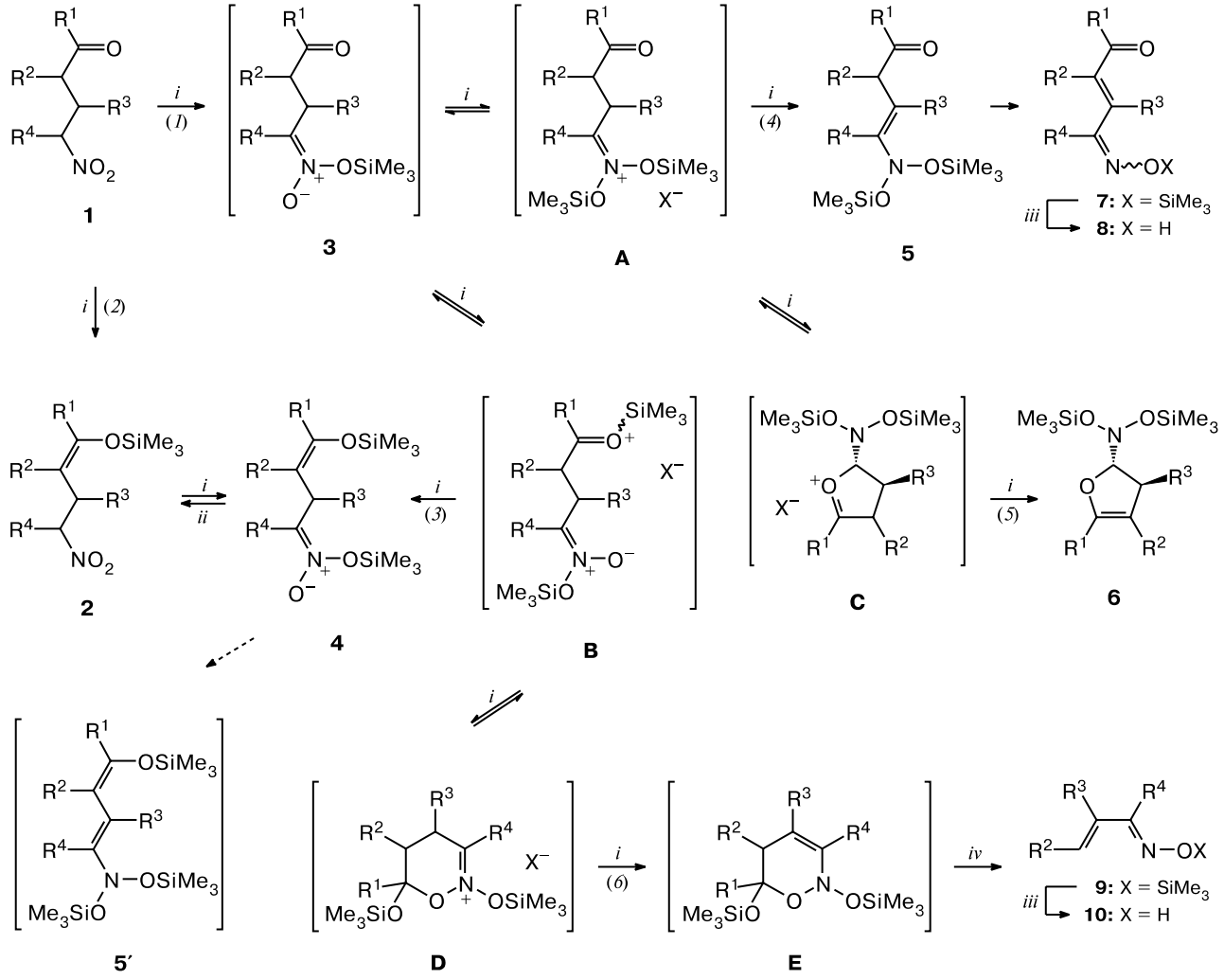
** In some cases,[6] nitronate **4** can be transformed into BSENA **5´**.

*** In the present study, we chose the silylating reagent in an attempt to retain the carbonyl group in the first step of the process. It is known that Me_3SiCl exhibits a rather weak reactivity and does not silylate the carbonyl group in some nitro ketones,[6] whereas Me_3SiOTf is a very strong silylating reagent and can silylate the carbonyl group in the presence of the nitro fragment.[6] We believed that Me_3SiBr, which is intermediate in its reactivity between the above-mentioned compounds, was the reagent of choice for our purposes.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 620—631, March, 2003.

1066-5285/03/5203-647 $25.00

Scheme 1



i. Me_3SiY, Et_3N (Y = Br or OTf); *ii*. aqueous treatment; *iii*. NH_4F, MeOH; *iv*. *retro*-[4+2].

Thus the reaction of nitronate **3** with a silylating reagent can produce one of two cations (**A** or **B**), which exist in equilibrium with nitronate **3**.* The immonium cation **A** can exist in equilibrium with its cyclic isomer **C**, both these tautomers being able to undergo deprotonation under the action of bases to produce BSENA **5** or dihydrofuran **6**, respectively.

Cation **B** also occurs in equilibrium with the cyclic immonium cation **D** and deprotonation of this pair of tautomers should lead to silyl nitronate **4** or cyclic enamine **E**, respectively. It is known[3] that the latter can undergo [4+2]-cyclofragmentation to form conjugated silylated enoxime **9**.

In addition, BSENA **5** can eliminate trimethylsilanol either spontaneously or under the action of a base to give silylated enoxime **7**.*

Therefore, silylation of γ-nitro ketones **1a—r** can afford directly silyl enolates **2**, silyl nitronates **3** or **4**, enoximes **7** or **9**, or dihydrofurans **6**. The composition of the resulting mixture depends on the ratio between the rates of the reactions (*1*)—(*6*) and (or) thermodynamic parameters of the complex equilibrium between cations **A—D** and nitronate **3**.

Since it is difficult to determine *a priori* the overall effect of different factors on the rates of the reac-

* The oxonium cations **B** are generated as intermediates in many reactions of the carbonyl group with neutral nucleophiles,[7] whereas the carboimmonium cations of the type **A** are involved in intramolecular alkylation.[2]

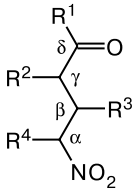
* Earlier, it has been demonstrated[4,8] that the introduction of electron-withdrawing substituents at the γ position with respect to the nitro group of BSENA substantially facilitates elimination of trimethylsilanol giving rise to the corresponding silylated conjugated enoximes, which are close analogs of **8**.

Table 1. Silylation of γ-nitro ketones **1** [a]

AHC	R^1	R^2	R^3	R^4	τ/day[b]	Product	Yield (%)
	Variation of the substituent at the δ-carbon atom with respect to the nitro group						
1a	Ph	H	4-$MeOC_6H_4$	H	7	**6a**	89
1b	4-MeC_6H_4	H	4-$MeOC_6H_4$	H	7	**6b**	92
1c	4-$MeOC_6H_4$	H	4-$MeOC_6H_4$	H	7	**6c**	96
1d[c,d]	4-$NO_2C_6H_4$	H	4-$MeOC_6H_4$	H	7	**6d**, **4d**	23, 60
1e	*cyclo*-C_3H_5	H	4-$MeOC_6H_4$	H	7	**6e**	85
1f	*cyclo*-C_6H_{11}	H	4-$MeOC_6H_4$	H	3	**9f**	40
1g	Bu[i]	H	4-$MeOC_6H_4$	H	7	**9f**	66
1h	Me	H	Ph	H	3	**9h**	53
	Variation of the substituent at the γ-carbon atom with respect to the nitro group						
1i	Ph	Ph	Ph	H	14	**6i**	51
1j	Me	Ac	Ph	H	8	**6j**	78
	Variation of the substituent at the β-carbon atom with respect to the nitro group						
1k	Ph	H	Me	H	7	**6k**	94
1l	Ph	H	Ph	H	7	**6l**	88
1m	Ph	H	4-ClC_6H_4	H	6	**6m**	86
1n	Ph	H	4-$NO_2C_6H_4$	H	14	**6n**, **7n**	72, 20
1o	Ph	H	COOMe	H	1	**7o**	86
	Variation of the substituent at the α-carbon atom with respect to the nitro group						
1p[e,f]	Ph	H	Ph	Me	7	**13p**, **2p**	64, 33
1q	Ph	H	Ph	Ph	7	**2q**	51
1r[c]	Ph	H	Ph	CO_2Me	7	**4r**, **3r**	23, 63

[a] Silylation was carried out at −30 °C.
[b] The reaction time is given for silylation with a Me_3SiBr (2.5 equiv.)—Et_3N (3 equiv.) mixture, unless the reagent is otherwise specified.
[c] The products were isolated without aqueous workup.
[d] Aqueous workup of the reaction mixture afforded a mixture of **6d** (23%) and **2d** (54%).
[e] Data on silylation with a Me_3SiOTf (3.5 equiv.)—Et_3N (4 equiv.) mixture.
[f] An increase in the time of silylation did not lead to a change in the **2p** : **13p** ratio.

tions (*1*)—(*6*) and stabilities of cations **A—D**, we studied the influence of the substituents R^1—R^4 at all atoms of the carbon skeleton on the direction of silylation of γ-nitro ketones **1**.



1

The principal data on the silylation of nitro ketones **1a—r** are presented in Table 1. In most cases, the compositions of the reaction mixtures were determined after their aqueous workup, which made it possible to separate the resulting triethylammonium salt and to remove an excess of the silylating reagent. Derivatives of types **2**, **5**, **6**, **7**, and **9** were resistant to aqueous workup. In contrast, aqueous workup of nitronates **3** and **4** recovered the starting nitro ketones **1** and silyl enolates **2**, respectively. Treatment of the reaction mixtures with methanol in the presence of fluoride anions resulted in complete desilylation of enoximes **7** and **9** (see Scheme 1).*

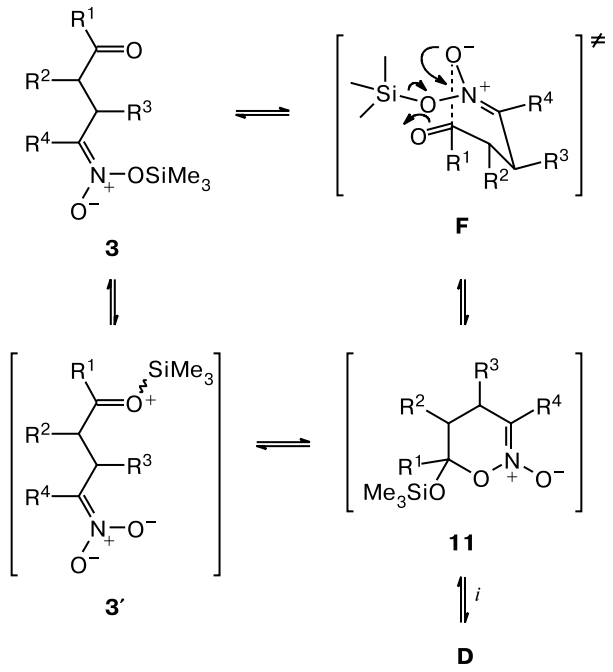
As can be seen from Table 1, most of the silylation reactions of ketones **1a—r** generally proceeded with high chemoselectivity and the character of the reaction products was determined primarily by the nature of the substituents R^1 and R^4.

The general conclusion is as follows. Silylation of compounds with the substituent R^1 involved in the conjugation with the carbonyl group produces the corresponding dihydrofuran **6** (*i.e.*, the process follows the **3** → **A** → **C** → **6** pathway), whereas compounds with alkyl substituents R^1 give rise to enoximes **9** regardless of the steric parameters of the substituent (*i.e.*, the process follows the **3** → **B** → **D** → **E** → **9** pathway). At the same time, it can be suggested that the formation of cations **D** and, as a consequence, of enoximes **9** is favored by an increase in the electrophilicity of the carbonyl group due to localization of the positive charge on its carbon atom, whereas dihydrofurans **6** are formed on condition that the cationic center in the intermediate **B** is sufficiently stabilized. However, the results of our study did not provide a more detailed explanation of high chemoselectivity of these two processes.

Apparently, silylation of ketone **1d** afforded silyl nitronate **4d** as the main product (**2d** after aqueous workup) due to the fact that the keto fragment in this ANC is highly prone to silylation (pK_a(PhCOMe) = 18.4, whereas pK_a(4-$NO_2C_6H_4$COMe) = 16.7 [9]).

* Desilylation of dihydrofurans **6** will be considered in detail below.

Scheme 2



i. Me_3SiY, Et_3N (Y = Br or OTf).

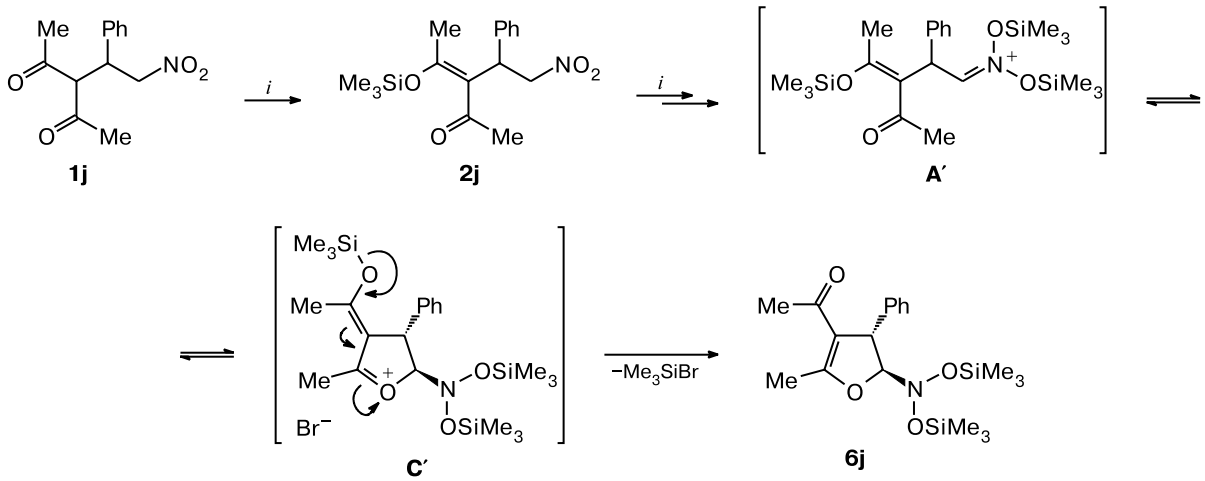
Cations **D** could be derived from silyl nitronates **3** not only by the pathway presented in Scheme 1 but also according to a mechanism involving intermediate cyclic nitronates **11** (Scheme 2), which are generated either directly from **3** (through a transition state **F**) or through the bipolar ion **3´** produced upon reversible 1,6-*O*,*O*-migration of the Me_3Si group. The possibility of the transformation **11** → **D** → **E** → **9** was confirmed by independent experiments.[3] This pathway of generation of cations **D** should involve an equilibrium between **3** and **11**. However, this seems to be unlikely, because authentic nitronates of type **3** or **11** were described as individual compounds and these compounds were not transformed into each other under ordinary conditions.[1,3,6]

The introduction of the phenyl substituent at the γ-carbon atom (with respect to the nitro group) of nitro ketone **1** (R^2 = Ph) did not change the direction of the reaction and the corresponding dihydrofuran **6i** was generated from nitro ketone **1i**. In contrast, the introduction of the acetyl group into ketone **1h** (R^2 = Ac) resulted in the formation of dihydrofuran **6j** rather than of the expected enoxime **9j**. Presumably, the scheme of formation of dihydrofuran **6j** differs from that of other dihydrofurans **6** (Scheme 3).

Apparently, the dicarbonyl fragment in nitro ketone **1j** is silylated more rapidly than the nitro fragment ($pK_a(MeNO_2)$ = 10.6, $pK_a(Ac_2CH_2)$ = 9 [10]). As a consequence, cation **A´** in which the carbonyl group is conjugated with the electron-donating π system can be a precursor of dihydrofuran **6j**. Such a conjugation causes an increase in the nucleophilicity of the oxygen atom of the carbonyl group and is favorable for the formation of cation **C´**.

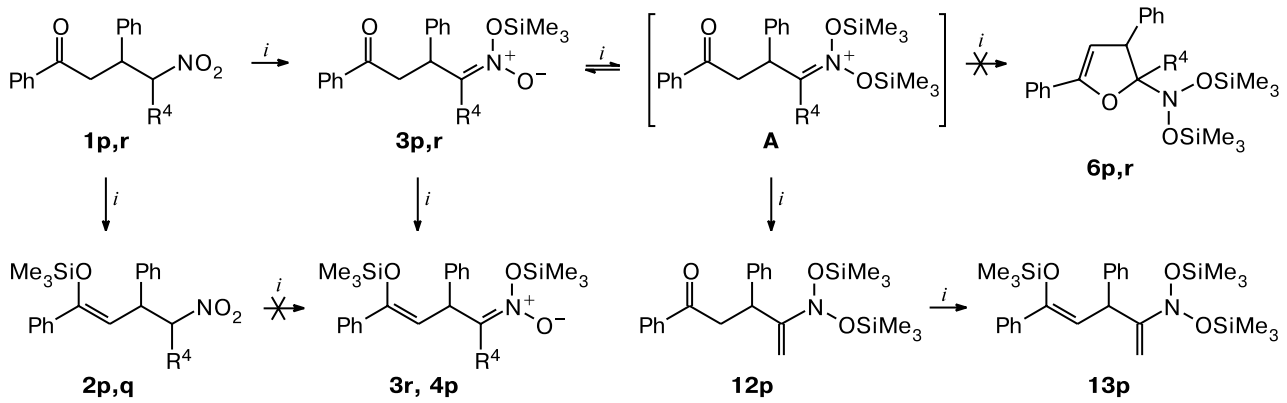
The electronic and steric properties of the substituent R^3 at the β-carbon atom exert a strong effect on the selectivity of silylation of γ-nitro ketones. The introduction of the methyl or aryl group at the β position of nitro ketone **1** ensures the formation of dihydrofurans **6** (see Table 1). Apparently, this is associated with deceleration of β-deprotonation of the carboimmonium ion **A** (see Scheme 1, step (*4*)) due to steric hindrance for the approach of a base to the β-proton. An increase in the rate of β-deprotonation of cations **A** due to an increase in the ability of the β-substituent (R^3) to stabilize the negative charge leads to an increase in the proportion of enoximes

Scheme 3



i. Me_3SiBr, Et_3N.

Scheme 4



i. Me_3SiOTf, Et_3N.

7 among the silylation products of compounds **1** in the series **1m** < **1n** < **1o** (see Table 1).

The introduction of the substituents R^4 at the α-carbon atom (with respect to the nitro group) sharply changed the silylation pathway of nitro ketones **1**. In this case, dihydrofurans **6** were not formed. Silylation of ketone **1p** with the $Me_3SiBr—Et_3N$ system afforded unidentified products. The use of a stronger silylating agent, *viz*., $Me_3SiOTf—Et_3N$, made it possible to obtain a mixture of silyl enolate **2p** and BSENA **13p** after aqueous workup (Scheme 4).

A twofold increase in the time of exposure did not lead to a change in the **2p** : **13p** ratio, *i.e*., silyl enolate **2p** was not transformed into BSENA **13p** under the reaction conditions. Presumably, this is associated with the fact that γ-silyl oxo nitronate **3p** rather than silyl enolate **2p** was the precursor of *N*,*N*-bis(silyloxy)enamine **13p**, the transformation of compound **3p** into BSENA **13p** being preceded by its transformation into BSENA **12p**. Silylation of the nitro group is very sensitive to the steric demands of the adjacent substituents, which is presumably responsible for the observed selectivity of the process.

Apparently, steric hindrances cause termination of silylation of ketone **1q** in the step of formation of silyl enolate **2q**.*

Evidently, silylation of compound **1r** containing an electron-withdrawing substituent at the α position with respect to the nitro group ($R^4 = CO_2Me$) proceeded differently and gave a mixture of nitronate **3r** and its silylation product at the carbonyl group (**4r**) in a molar ratio of approximately 1 : 3 (see Scheme 4; the reaction mixture was analyzed without its aqueous workup). It is highly probable that the presence of an electron-withdrawing substituent leads to acceleration of silylation of the nitro group in **1r** to give nitronate **3r** followed by its slow silylation at the carbonyl group. The formation of cation **A** from **3r** is prevented by both a decrease in the nucleophilicity of the oxygen atom of the nitronate group under the influence of the adjacent electron-withdrawing substituent R^4 (kinetic factor) and destabilization of the cationic center by the same substituent R^4 (thermodynamic factor).

Proof of the structures of silylation products of γ-nitro ketones 1a—r

To summarize, silylation of nitro ketones **1a—r** afforded dihydrofurans **6a—n**, conjugated enoximes **7n,o** and **9f,h**, and BSENA **13p** as the main synthetically valuable products.

N,*N*-Bis(silyloxy)aminodihydrofurans **6** contain the ill-studied structural fragment, *viz*., the *N*,*N*-bis(silyloxy)amino group, bound to the sp^3-hybridized carbon atom.*

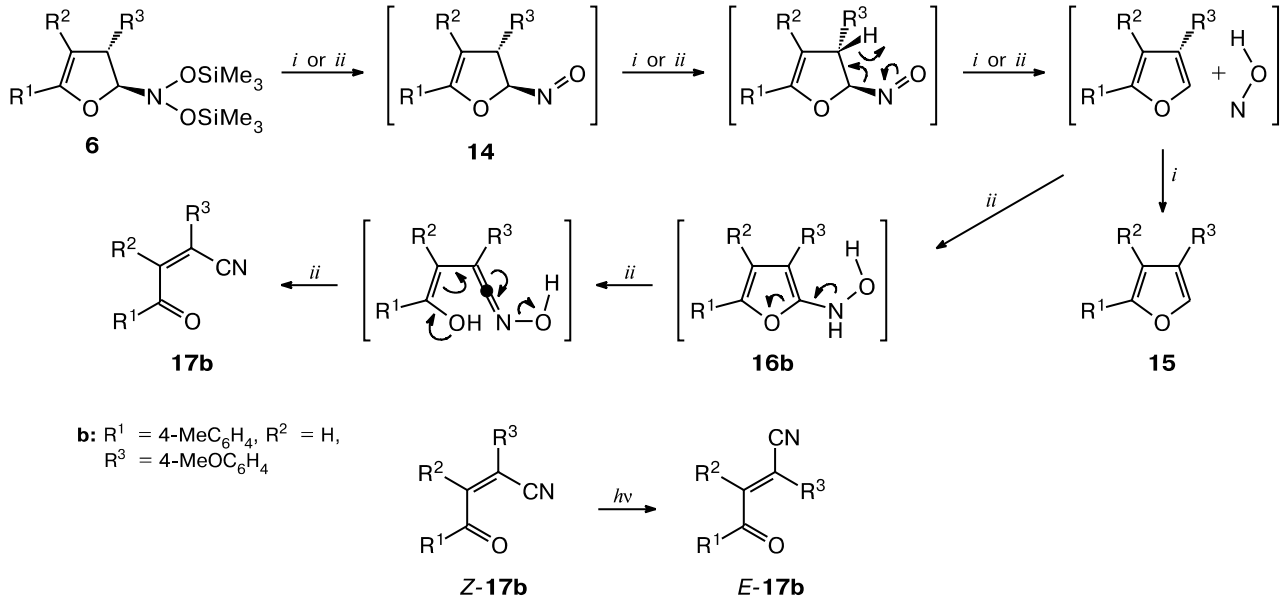
Dihydrofurans **6** are thermally labile oils, which remain intact upon aqueous workup but do not withstand chromatographic purification.** Hence, their structures were confirmed only by heteronuclear NMR spectroscopy and chemical transformations (see below). The presence of all structural fragments in products **6** was supported by the data from ^1H and ^{13}C NMR spectroscopy. The *N*,*N*-bis(silyloxy)amino group was additionally identified

* Taking into account that the treatment of the reaction mixture, which was obtained after silylation of compound **1q**, with methanol-d_4 did not afford deuterated silyl enolate **2q** (^1H and ^{13}C NMR spectroscopic data), the possibility of the formation of silyl nitronate **4q** in this process can be rejected.

* Compounds containing this fragment have been described only in two recent studies.[1,11]

** Due to the difficulties associated with the purification of dihydrofurans **6**, the reaction mixtures obtained by silylation were kept over a long period of time (7 days) to achieve complete conversions of the starting nitro ketones **1**. According to the ^1H NMR spectroscopic data, the purities of dihydrofurans **6** were no less than 90%.

Scheme 5



i. NH_4F, MeOH; *ii*. Bu_4NF, CH_2Cl_2.

based on the ^{15}N and ^{29}Si NMR spectroscopic data (for example, $\delta(^{15}N)$ is −145.0 and $\delta(^{29}Si)$ are 24.5 and 26.9 for product **6l**; for comparison, $\delta(^{15}N)$ is −143.8 and $\delta(^{29}Si)$ is 23.4 for $CH_2{=}C(Me)N(OSiMe_3)_2$ [12]). Based on the $^3J_{H,H}$ values and NOE data, the *trans* configuration was assigned to the substituents at the C(2) and C(3) carbon atoms of the stereoisomers of dihydrofurans **6** obtained.

The presence of two signals for the $OSiMe_3$ groups of the *N*,*N*-bis(silyloxy)amino fragment in the ^1H, ^{13}C, and ^{29}Si NMR spectra of derivatives **6** is attributed to the hindered inversion of the nitrogen atom in these products. It should be noted that we failed to find evidence of coalescence or exchange broadening of these signals in the temperature range up to 60 °C. Consequently, the inversion barrier in dihydrofurans **6** should be no lower than 80 kJ mol^{-1} (barrier was determined according to a procedure described earlier[13]). This is much higher than the inversion barrier of the nitrogen atom estimated recently for BSENA,[14] but it is consistent with the inversion barriers of the nitrogen atom in bis-alkoxyamines[15] and *N*-alkoxy- or *N*-silyloxyisoxazolidines.[16]

The structures of silyl derivatives of enoximes **7** and **9** were confirmed by spectroscopic characteristics (NMR) and desilylation giving rise to the corresponding oximes **8** and **10**, which have been characterized not only by spectroscopic methods but also by the satisfactory results of elemental analysis. The configurations of the oximino groups and the C=C double bonds in the resulting enoximes were determined based on the rules reported in our earlier studies (see, for example, Ref. 4).

The structures of BSENA **13p**, silyl nitronate **3r**, and silyl enolates **2d**, **2p**, and **2q** were confirmed by ^1H, ^{13}C, ^{29}Si, and ^{14}N NMR spectroscopy. The structure of silyl enolate **2d** was additionally confirmed by the introduction of the deuterium label at the γ-C atom (with respect to the nitro group) upon desilylation of **2d** in a CD_3OD—CD_3COOD medium.

Desilylation of *N*,*N*-bis(silyloxy)aminodihydrofurans 6

Earlier,[2,11,17] we have demonstrated that BSENA containing the bis(silyloxy)amino fragment were readily transformed into unstable conjugated nitrosoalkenes under the conditions of nucleophilic catalysis. Hence, *N*,*N*-bis(silyloxy)aminodihydrofurans **6** would be expected to be synthetic equivalents of 2-nitrosodihydrofurans **14**.

However, treatment of derivatives **6** with methanol in the presence of NH_4F afforded furans **15** in moderate yields, whereas the reaction of dihydrofuran **6b** with Bu_4NF in CH_2Cl_2 gave *Z*-enenitrile **17b** (Scheme 5, Table 2).*

The structures of substituted furans **15** and enenitrile **17b** were confirmed by NMR spectroscopy and elemental analysis. These data for known furans **15** are in good agreement with those published in the literature.** The structure and configuration of enenitrile **17b** were additionally confirmed by comparing its physicochemical characteristics and properties with the published data** for analogous derivatives. For instance, when exposed to sunlight,

* Unfortunately, we failed to extend the transformation **6** → **17** to other dihydrofurans **6**.

** See the Experimental section.

Table 2. Desilylation of *N*,*N*-bis(silyloxy)aminodihydrofurans **6**

Dihydrofuran	Reagent*	Conditions		Product	Yield (%)
		T/°C	τ/h		
6a	NH_4F	0	48	**15a**	35
6b	NH_4F	0	0.5	**15b**	51
6b	Bu_4NF	25	24	**17b**	38
6c	NH_4F	0	2	**15c**	22
6e	NH_4F	0	168	**15e**	48
6j	NH_4F	0	1.5	**15j**	38
6l	NH_4F	0	0.5	**15m**	85
6m	NH_4F	0	24	**15n**	61
6n	NH_4F	0	1	**15o**	40

* 20 mol.% with respect to dihydrofuran **6** in an excess of MeOH or in CH_2Cl_2.

enenitrile *Z*-**17b** underwent the rearrangement into the *E* isomer typical of this class of substituted alkenes.[18]

The assumed mechanism of desilylation of dihydrofurans **6** is presented in Scheme 5.

Apparently, nitrosodihydrofuran **14** is initially generated. The next step involves elimination of the nitrene-like H—O—N species, which can occur both by ionic and synchronous pathways involving both the dimer and monomer of nitrosodihydrofuran **14**. Subsequently, the H—O—N → H—N=O rearrangement and(or) dimerization of nitrene into hyponitrous acid HO—N=N—OH take place in methanol due to solvation. In contrast, the reaction in aprotic dichloromethane led to the insertion of nitrene into the C—H bond of furan **15b** that formed (as was exemplified by **15b**) to give the corresponding 2-hydroxyaminofuran **16b**, which was transformed into enenitrile **17b**.*

It could be assumed that oximes **18** are direct precursors of 2-hydroxyaminofurans **16** (Scheme 6). However, analogous authentic oxime **18a** did not undergo such an isomerization even under more drastic conditions than those used for desilylation of dihydrofurans **6** (see Scheme 6).

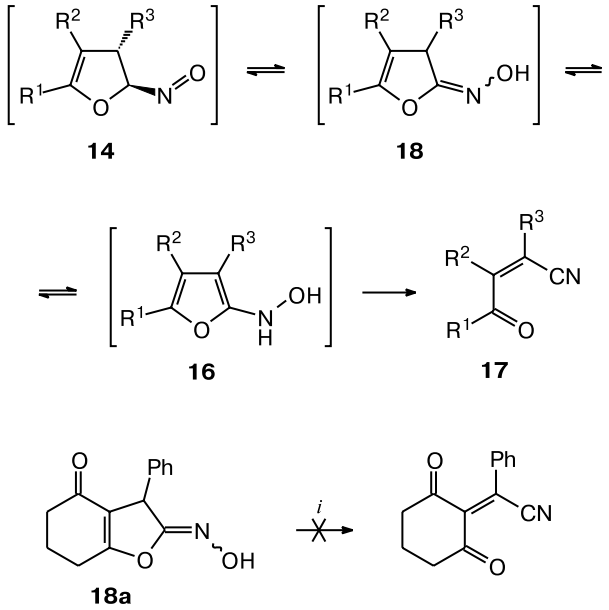
* * *

To summarize, the present as well as earlier[3,4,6] studies provided evidence that readily accessible γ-nitro ketones **1a—o** can be considered as convenient precursors of substituted furans **15** and conjugated enoximes **10** (Scheme 7).

It should be noted that aryl γ-nitroalkyl ketones **1a—c,e,j,m—o** serve as convenient sources of di- and trisubstituted furans **16**, whereas alkyl γ-nitroalkyl ketones **1f—h** give enoximes **10** upon an analogous silylation—desilylation procedure. It remains unclear whether aliphatic nitro compounds of types **1n** and **1o** can be successfully used in the synthesis of other type of conjugated enoximes, *viz.*, of products **8**. However, one would expect that this problem will be solved by changing the nature of the silylating agent and directing the silylation along the **1** → **2** → **4** pathway and further to functionalized BSENA **5**´ followed by 1,6-*N*,*C*-elimination of Me_3SiOH analogously to a procedure described earlier.[6]

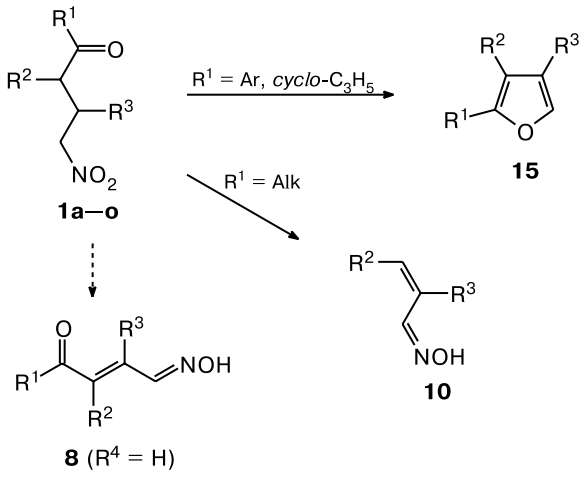
In our opinion, the chemistry of dihydrofurans **6** containing the *N*,*N*-bis(silyloxy)amino fragment holds additional promise. It should be noted that these compounds have been subjected only to such transformations in which

Scheme 6



i. Bu_4NF, CH_2Cl_2, refluxing.

Scheme 7



* According to the published data,[19] 2-hydroxyaminofurans generated by reduction of 2-nitrofurans can undergo fragmentation to give conjugated enenitriles, which is indirect evidence in favor of Scheme 5.

the proton and $N(OSiMe_3)_2$ group were eliminated with a loss of two asymmetric centers. In the future, we plan to investigate other aspects of the chemistry of dihydrofurans **6**.

Experimental

The NMR spectra were recorded on a Bruker AM-300 instrument in $CDCl_3$. The chemical shifts were measured relative to the residual signal of the solvent (^1H and ^{13}C), Me_4Si as the internal standard (^{29}Si), and $MeNO_2$ as the external standard (^{14}N and ^{15}N). The ^{29}Si and ^{15}N signals were observed using the INEPT technique.

The IR spectra were measured on a Bruker Vektor 22 instrument in KBr pellets. The mass spectra were obtained on a Finnigan MAT Incos 50 instrument (EI, 70 eV).

All experiments were carried out under dry argon. The solvents were purified according to standard procedures.

The starting ANC were synthesized according to known procedures: **1a**;[20] **1b,e,h,l,o**;[21] **1c**;[22] **1i**;[23] **1j**;[24] **1m**;[25] **1n**;[26] **1p**;[27] and **1q**.[28]

Synthesis of aliphatic nitro compounds 1d, 1f, 1g, and 1k (general procedure). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (1.5 mL, 10 mmol) was added to a stirred solution of α,β-unsaturated ketone $R^1C(O)C(R^2)=CHR^3$ (8.7 mmol) in CH_2Cl_2 (34 mL) and $MeNO_2$ (7 mL) at 0 °C. The reaction mixture was stirred under specified conditions (see below) and then a solution of $NaHSO_4 \cdot H_2O$ (1.93 g, 14 mmol) in H_2O (50 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed with H_2O (2×20 mL) and a saturated NaCl solution (10 mL), dried with Na_2SO_4, and concentrated *in vacuo*. The residue was recrystallized from MeOH (for **1d** and **1g**), distilled *in vacuo* (for **1k**), or purified by column chromatography on silica gel (for **1f**).

3-(4-Methoxyphenyl)-4-nitro-1-(4-nitrophenyl)butan-1-one (1d). Reaction conditions: 1 h at 0 °C. The yield was 1.53 g (51%). Yellow crystals, m.p. 106—107 °C (MeOH). Found (%): C, 59.00; H, 4.49; N, 7.89. $C_{17}H_{16}N_2O_6$. Calculated (%): C, 59.30; H, 4.68; N, 8.14. ^1H NMR ($CDCl_3$), δ: 3.48 (m, 2 H, CH_2CO); 3.78 (s, 3 H, OMe); 4.17 (m, 1 H, CH—Ar); 4.66 (dd, 1 H, CH_2NO_2, ^3J = 7.2 Hz, ^3J = 12.2 Hz); 4.78 (dd, 1 H, CH_2NO_2, ^3J = 7.2 Hz, ^3J = 12.2 Hz); 6.86 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.18 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 8.05 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 8.30 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz).

1-Cyclohexyl-3-(4-methoxyphenyl)-4-nitrobutan-1-one (1f). Reaction conditions: 2.5 h at 20 °C. The yield was 1.01 g (38%). Colorless oil. Found (%): C, 66.81; H, 7.40; N, 4.69. $C_{17}H_{23}NO_4$. Calculated (%): C, 66.86; H, 7.59; N, 4.59. ^1H NMR ($CDCl_3$), δ: 1.12—1.35 (m, 4 H, 2 CH_2); 1.58—1.84 (m, 6 H, 3 CH_2); 2.26 (m, 1 H, CHCO); 2.87 (m, 2 H, CH_2CO); 3.78 (s, 3 H, OMe); 3.96 (m, 1 H, CH—Ar); 4.56 (dd, 1 H, CH_2NO_2, ^3J = 7.4 Hz, ^3J = 12.5 Hz); 4.66 (dd, 1 H, CH_2NO_2, ^3J = 7.4 Hz, ^3J = 12.5 Hz); 6.84 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.12 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz).

2-(4-Methoxyphenyl)-6-methyl-1-nitroheptan-4-one (1g). Reaction conditions: 1.5 h at 0 °C. The yield was 1.58 g (65%). White crystals, m.p. 50—51 °C (MeOH). Found (%): C, 64.43; H, 7.51; N, 5.00. $C_{15}H_{21}NO_4$. Calculated (%): C, 64.50; H, 7.58; N, 5.01. ^1H NMR ($CDCl_3$), δ: 0.84 (d, 6 H, 2 Me, ^3J = 6.6 Hz); 2.07 (m, 1 H, C<u>H</u>Me_2); 2.22 (m, 2 H, C<u>H</u>$_2Pr^i$); 2.83 (m, 2 H, CH_2CO); 3.78 (s, 3 H, OMe); 3.97 (m, 1 H, CH—Ar); 4.55 (dd, 1 H, CH_2NO_2, ^3J = 7.2 Hz, ^3J = 12.2 Hz); 4.66 (dd, 1 H, CH_2NO_2, ^3J = 7.2 Hz, ^3J = 12.2 Hz); 6.84 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.13 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz).

3-Methyl-4-nitro-1-phenylbutan-1-one (1k). Reaction conditions: 0.25 h at 0 °C. The yield was 1.53 g (85%). Colorless oil, b.p. 98—108 °C (0.1 Torr). Found (%): C, 63.61; H, 6.18; N, 6.49. $C_{11}H_{13}NO_3$. Calculated (%): C, 63.76; H, 6.32; N, 6.76. ^1H NMR ($CDCl_3$), δ: 1.14 (d, 3 H, Me, ^3J = 5.9 Hz); 2.90—3.22 (m, 3 H, CH_2CO and C<u>H</u>—Me); 4.52 (dd, 1 H, CH_2NO_2, ^3J = 6.6 Hz, ^3J = 11.8 Hz); 4.52 (dd, 1 H, CH_2NO_2, ^3J = 5.9 Hz, ^3J = 11.8 Hz); 7.46 (m, 2 H, CH_{Ph}); 7.57 (m, 1 H, CH_{Ph}); 7.94 (m, 2 H, CH_{Ph}).

Methyl 2-nitro-5-oxo-3,5-diphenylpentanoate (1r). Triethylamine (2.1 mL, 15 mmol) and $NO_2CH_2CO_2Me$ (1.79 g, 15 mmol) were added to a stirred solution of chalcone (2.08 g, 10 mmol) in CH_2Cl_2 (40 mL) at 0 °C. The reaction mixture was stirred at 20 °C for 48 h and then a solution of $NaHSO_4 \cdot H_2O$ (2.07 g, 15 mmol) in H_2O (20 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (4×20 mL). The combined organic phases were washed with H_2O (2×20 mL) and a saturated NaCl solution (10 mL), dried with Na_2SO_4, and concentrated *in vacuo*. After recrystallization of the residue from MeOH, compound **1r** was obtained in a yield of 1.31 g (40%) as white crystals, m.p. 114—116 °C (MeOH). Found (%): C, 65.90; H, 5.07; N, 4.39. $C_{18}H_{17}NO_5$. Calculated (%): C, 66.05; H, 5.23; N, 4.28. ^1H NMR ($CDCl_3$), δ: 3.48 (dd, 1 H, CH_2CO, ^3J = 4.4 Hz, ^3J = 17.7 Hz); 3.60 (s, 3 H, OMe); 3.69 (dd, 1 H, CH_2CO, ^3J = 8.8 Hz, ^3J = 17.7 Hz); 4.45 (m, 1 H, CH—Ph); 5.51 (d, 1 H, $CHNO_2$, ^3J = 8.1 Hz); 7.25 (m, 5 H, CH_{Ph}); 7.41 (m, 2 H, CH_{Ph}); 7.53 (m, 1 H, CH_{Ph}); 7.86 (m, 2 H, CH_{Ph}).

Silylation of aliphatic nitro compounds 1 with a Me_3SiBr—Et_3N mixture (general procedure). Bromotrimethylsilane (0.4 mL, 3.0 mmol) was added to a stirred solution of ANC **1** (1 mmol) in CH_2Cl_2 (3 mL) and Et_3N (0.5 mL, 3.5 mmol) at −40 °C for 2 min. The reaction mixture was kept at −30 °C over a period of time given in Table 1, diluted with light petroleum (10 mL), and poured into a mixture of H_2O (10 mL) and light petroleum (5 mL). The organic layer was separated, washed with a solution of $NaHSO_4 \cdot H_2O$ (70 mg, 0.5 mmol) in H_2O (10 mL), H_2O (2×10 mL) and a saturated NaCl solution (10 mL), dried with Na_2SO_4, and concentrated *in vacuo*. The product was analyzed by NMR spectroscopy using a quantitative standard ($ClCH_2CH_2Cl$, δ_H = 3.73).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3-(4-methoxyphenyl)-5-phenyl-2,3-dihydrofuran (6a), colorless thick oil. ^1H NMR ($CDCl_3$), δ: 0.17 and 0.18 (both s, 9 H both, 2 $SiMe_3$); 3.76 (s, 3 H, OMe); 4.69 (dd, 1 H, CH_{Ar}, ^3J = 4.0 Hz, ^3J = 3.4 Hz); 5.00 (d, 1 H, CH—N, ^3J = 4.0 Hz); 5.54 (d, 1 H, CH=C, ^3J = 3.4 Hz); 6.83 (d, 2 H, CH_{Ar}, ^3J = 8.7 Hz); 7.23 (d, 2 H, CH_{Ar}, ^3J = 8.7 Hz); 7.28—7.38 (m, 3 H, CH_{Ph}); 7.64 (d, 2 H, CH_{Ar}, ^3J = 7.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.3 and 0.5 (2 $SiMe_3$); 48.1 (<u>C</u>H_{Ar}); 100.2 (<u>C</u>H=C); 107.3 (CH—N); 114.0, 125.3, 128.3, 128.5, 129.0 (<u>C</u>H_{Ph} and <u>C</u>H_{Ar}); 130.4, 135.5 and 158.5 (2 C_{Ar} and C_{Ph}); 155.1 (<u>C</u>=CH). ^{29}Si NMR ($CDCl_3$), δ: 24.42 and 26.03 (2 $SiMe_3$).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3-(4-methoxyphenyl)-5-(4-tolyl)-2,3-dihydrofuran (6b), colorless viscous oil. ^1H NMR ($CDCl_3$), δ: 0.17 and 0.18 (both s, 9 H each, 2 $SiMe_3$); 2.34 (s, 3 H, Me); 3.75 (s, 3 H, OMe); 4.67 (dd, 1 H, C<u>H</u>$_{Ar}$, ^3J = 4.0 Hz,

^3J = 3.4 Hz); 4.99 (d, 1 H, CH—N, ^3J = 4.0 Hz); 5.47 (d, 1 H, CH=C, ^3J = 3.4 Hz); 6.82 (d, 2 H, CH_{Ar}, ^3J = 8.7 Hz); 7.15 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 7.22 (d, 2 H, CH_{Ar}, ^3J = 8.7 Hz); 7.53 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.4 and 0.5 (2 $SiMe_3$); 21.4 (Me); 48.1 ($\underline{C}H_{Ar}$); 55.3 (OMe); 99.3 ($\underline{C}H$=C); 107.3 (CH—N); 114.0, 125.3, 128.9, and 129.0 (all $\underline{C}H_{Ar}$); 127.7, 135.7, 138.4, and 158.5 (all $\underline{C}_{Ar}$); 155.3 ($\underline{C}$=CH). ^{29}Si NMR ($CDCl_3$), δ: 24.31 and 25.89 (2 $SiMe_3$).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3,5-bis(4-methoxyphenyl)-2,3-dihydrofuran (6c), colorless thick oil. ^{1}H NMR ($CDCl_3$), δ: 0.17 and 0.18 (both s, 9 H each, 2 $SiMe_3$); 3.79 (s, 3 H) and 3.84 (s, 9 H) (2 OMe); 4.65 (dd, 1 H, $C\underline{H}_{Ar}$, ^3J = 3.8 Hz, ^3J = 2.9 Hz); 4.96 (d, 1 H, CH—N, ^3J = 3.8 Hz); 5.39 (d, 1 H, CH=C, ^3J = 2.8 Hz); 6.69 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 6.83 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.23 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.57 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.3 and 0.4 (2 $SiMe_3$); 48.1 ($\underline{C}H_{Ar}$); 55.2 (2 OMe); 98.1 ($\underline{C}H$=C); 107.2 (CH—N); 113.7, 113.8, 126.6, and 128.9 (all $\underline{C}H_{Ar}$); 123.1, 135.7, 158.4, and 159.8 (all $\underline{C}_{Ar}$); 154.9 ($\underline{C}$=CH). ^{29}Si NMR ($CDCl_3$), δ: 24.26 and 25.86 (2 $SiMe_3$).

A mixture of 2-[*N*,*N*-bis(trimethylsilyloxy)amino]-3-(4-methoxyphenyl)-5-(4-nitrophenyl)-2,3-dihydrofuran (6d) and [3-(4-methoxyphenyl)-4-nitro-1-(4-nitrophenyl)-but-1-enyloxy]trimethylsilane (2d), viscous yellowish oil.

Compound 6d. ^{1}H NMR (C_6D_6), δ: 0.21 and 0.25 (both s, 9 H each, 2 $SiMe_3$); 3.42 (s, 3 H, OMe); 5.07 (dd, 1 H, CH_{Ar}, ^3J = 3.7 Hz, ^3J = 3.0 Hz); 5.29 (d, 1 H, CH—N, ^3J = 3.7 Hz); 5.53 (d, 1 H, CH=C, ^3J = 3.0 Hz); 6.85 (d, 2 H, CH_{Ar}, ^3J = 8.6 Hz); 7.27 (d, 2 H, CH_{Ar}, ^3J = 8.6 Hz); 7.47 (d, 2 H, CH_{Ar}, ^3J = 8.9 Hz); 7.93 (d, 2 H, CH_{Ar}, ^3J = 8.9 Hz). ^{13}C NMR (C_6D_6), δ: 0.3 and 0.6 (2 $SiMe_3$); 48.6 ($\underline{C}H_{Ar}$); 54.9 (OMe); 105.7 ($\underline{C}H$=C); 107.7 (CH—N); 114.5, 123.9, 125.9, and 129.4 (all $\underline{C}H_{Ar}$); 135.1, 136.9, 147.7, and 159.3 (all $\underline{C}_{Ar}$); 153.5 ($\underline{C}$=CH). ^{29}Si NMR (C_6D_6), δ: 23.62 and 25.19 (2 $SiMe_3$).

Compound 2d. ^{1}H NMR (C_6D_6), δ: 0.09 (s, 9 H, $SiMe_3$); 3.40 (s, 3 H, OMe); 4.29 (m, 2 H, CH_2NO_2); 4.70 (m, 1 H, CH—Ar); 5.31 (d, 1 H, CH=C, ^3J = 9.2 Hz); 6.79 (d, 2 H, CH_{Ar}, ^3J = 8.6 Hz); 7.07 (d, 2 H, CH_{Ar}, ^3J = 8.6 Hz); 7.20 (d, 2 H, CH_{Ar}, ^3J = 8.9 Hz); 7.88 (d, 2 H, CH_{Ar}, ^3J = 8.9 Hz). ^{13}C NMR (C_6D_6), δ: 0.6 ($SiMe_3$); 41.1 ($\underline{C}$H—Ar); 54.9 (OMe); 80.1 (CH_2NO_2); 112.6 (OC=$\underline{C}$H); 114.8, 123.7, 126.7, and 128.8 (all $\underline{C}H_{Ar}$); 131.3, 144.5, 147.9 and 159.6 ($\underline{C}_{Ar}$); 150.4 (O$\underline{C}$=CH). ^{29}Si NMR (C_6D_6), δ: 22.09 ($SiMe_3$). ^{14}N NMR (C_6D_6), δ: –9.3 (NO_2, $\Delta\nu_{1/2} \approx 1100$ Hz).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-5-cyclopropyl-3-(4-methoxyphenyl)-2,3-dihydrofuran (6e), viscous colorless oil. ^{1}H NMR (C_6D_6), δ: 0.19 and 0.31 (both s, 9 H each, 2 $SiMe_3$); 0.50—0.58 (m, 2 H, CH_2); 0.75—0.82 (m, 2 H, CH_2); 1.40 (m, 1 H, CH); 3.32 (s, 3 H, OMe); 4.70 (d, 1 H, CH—N, ^3J = 2.9 Hz); 4.75 (dd, 1 H, CH—Ar, ^3J = 3.7 Hz, ^3J = 2.9 Hz); 5.12 (d, 1 H, CH=C, ^3J = 3.7 Hz); 6.79 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.28 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz). ^{13}C NMR (C_6D_6), δ: 0.5 and 0.6 (2 $SiMe_3$); 5.8 (CH_2); 6.2 (CH_2); 9.2 (CH); 48.7 ($\underline{C}$H—Ar); 54.8 (OMe); 98.0 ($\underline{C}$H=C); 108.2 (CH—N); 114.3 and 129.3 (2 $\underline{C}H_{Ar}$); 136.7 and 159.0 (2 $\underline{C}_{Ar}$); 159.4 ($\underline{C}$=CH). ^{29}Si NMR (C_6D_6), δ: 23.01 and 24.43 (2 $SiMe_3$).

2-(4-Methoxyphenyl)propenal *O*-trimethylsilyloxime (9f), thick yellowish oil. ^{1}H NMR ($CDCl_3$), δ: 0.23 (s, 9 H, $SiMe_3$); 3.83 (s, 3 H, OMe); 5.46 (s, 1 H, CH_2); 5.61 (s, 1 H, CH_2); 6.89 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 7.44 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 8.09 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$), δ: 0.6 ($SiMe_3$); 55.4 (OMe); 113.4 and 129.6 (2 $\underline{C}H_{Ar}$); 121.3 (CH_2); 125.5 and 159.6 (2 $\underline{C}_{Ar}$); 142.2 ($\underline{C}$=CH_2); 155.4 (CH=N). ^{29}Si NMR ($CDCl_3$), δ: 26.28 ($SiMe_3$).

2-Phenylpropenal *O*-trimethylsilyloxime (9h), thick yellowish oil. ^{1}H NMR ($CDCl_3$), δ: 0.21 (s, 9 H, $SiMe_3$); 5.53 (s, 1 H, CH_2); 5.65 (s, 1 H, CH_2); 7.33 (m, 3 H, CH_{Ph}); 7.46 (m, 2 H, CH_{Ph}); 8.09 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$), δ: –0.8 ($SiMe_3$); 122.3 (CH_2); 127.8, 128.2, and 128.0 (all $\underline{C}H_{Ph}$); 137.4 ($\underline{C}_{Ph}$); 142.8 ($\underline{C}$=CH_2); 154.9 (CH=N). ^{29}Si NMR ($CDCl_3$), δ: 26.29 ($SiMe_3$).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3,4,5-triphenyl-2,3-dihydrofuran (6i), colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.10 and 0.14 (both s, 9 H each, 2 $SiMe_3$); 4.91 (d, 1 H, CH—Ar, ^3J = 3.3 Hz); 4.94 (d, 1 H, CH—N, ^3J = 3.3 Hz); 7.00—7.47 (m, 13 H, CH_{Ph}); 7.75 (m, 2 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: –2.8 and –2.7 (2 $SiMe_3$); 50.8 ($\underline{C}$H—Ph); 102.0 (CH—N); 111.9 ($\underline{C}$=CO); 123.4, 123.7, 124.7, 125.0, 125.2, 125.4, 125.6, 125.8, and 126.6 (all $\underline{C}H_{Ph}$); 130.2, 131.4, and 139.1 (all $\underline{C}_{Ph}$); 146.9 (C=$\underline{C}$O). ^{29}Si NMR ($CDCl_3$), δ: 24.64 and 25.97 (2 $SiMe_3$).

4-Acetyl-2-[*N*,*N*-bis(trimethylsilyloxy)amino]-5-methyl-3-phenyl-2,3-dihydrofuran (6j), thick colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.17 and 0.22 (both s, 9 H each, 2 $SiMe_3$); 1.92 (d, 3 H, MeC=C, ^4J = 1.5 Hz); 2.39 (s, 3 H, MeC=O); 4.73 (br.s, 1 H, CH—Ar); 4.84 (d, 1 H, CH—N, ^3J = 3.7 Hz); 7.15—7.39 (m, 5 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: 0.3 and 0.4 (2 $SiMe_3$); 14.9 ($\underline{Me}$C=C); 29.8 ($\underline{Me}$C=O); 48.9 (CH—Ph); 96.3 ($\underline{C}$=CO); 107.0 (CH—N); 127.3, 127.8, and 129.0 (all $\underline{C}H_{Ph}$); 142.3 ($\underline{C}_{Ph}$); 167.5 (C=$\underline{C}$O); 195.2 (C=O). ^{29}Si NMR ($CDCl_3$), δ: 25.56 and 26.51 (2 $SiMe_3$).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3-methyl-5-phenyl-2,3-dihydrofuran (6k), thick colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.17 and 0.23 (both s, 9 H each, 2 $SiMe_3$); 1.20 (d, 3 H, Me, ^3J = 7.2 Hz); 3.39 (m, 1 H, C$\underline{H}$—Me); 4.76 (d, 1 H, CH—N, ^3J = 4.6 Hz); 5.37 (d, 1 H, CH=C, ^3J = 2.6 Hz); 7.20—7.37 (m, 3 H, CH_{Ph}); 7.55 (d, 2 H, CH_{Ph}, ^3J = 7.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.4 and 0.5 (2 $SiMe_3$); 20.4 (Me); 38.9 ($\underline{C}$H—Me); 102.2 ($\underline{C}$H=C); 107.5 (CH—N); 125.1, 128.2, and 128.3 (all $\underline{C}H_{Ph}$); 130.5 ($\underline{C}_{Ph}$); 153.6 ($\underline{C}$=CH). ^{29}Si NMR ($CDCl_3$), δ: 24.53 and 25.78 (2 $SiMe_3$).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3,5-diphenyl-2,3-dihydrofuran (6l), thick colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.17 and 0.19 (both s, 9 H each, 2 $SiMe_3$); 4.75 (dd, 1 H, CH—Ph, ^3J = 3.8 Hz, ^3J = 3.0 Hz); 5.05 (d, 1 H, CH—N, ^3J = 3.8 Hz); 5.58 (d, 1 H, CH=C, ^3J = 3.0 Hz); 7.18—7.39 (m, 8 H, CH_{Ph}); 7.65—7.68 (m, 2 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: 0.2 and 0.3 (2 $SiMe_3$); 48.6 ($\underline{C}$H—Ph); 99.8 ($\underline{C}$H=C); 106.9 (CH—N); 125.1, 126.6, 127.9, 128.2, and 128.4 (all $\underline{C}H_{Ph}$); 130.2 and 143.3 (2 $\underline{C}_{Ph}$); 155.1 ($\underline{C}$=CH). ^{29}Si NMR ($CDCl_3$), δ: 24.54 and 26.19 (2 $SiMe_3$). ^{15}N NMR ($CDCl_3$), δ: –145.0 (d, $N(OSiMe_3)_2$, ^2J = 9.7 Hz).

2-[*N*,*N*-Bis(trimethylsilyloxy)amino]-3-(4-chlorophenyl)-5-phenyl-2,3-dihydrofuran (6m), thick colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.21 and 0.22 (both s, 9 H each, 2 $SiMe_3$); 4.81 (dd, 1 H, CH—Ar, ^3J = 4.0 Hz, ^3J = 3.4 Hz); 5.04 (d, 1 H, CH—N, ^3J = 4.0 Hz); 5.56 (d, 1 H, CH=C, ^3J = 3.4 Hz); 7.29 (m, 3 H, CH_{Ph}); 7.34 (d, 2 H, CH_{Ar}, ^3J = 7.4 Hz); 7.38 (d, 2 H, CH_{Ar}, ^3J = 7.4 Hz); 7.68 (d, 2 H, CH_{Ph}, ^3J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.3 and 0.4 (2 $SiMe_3$); 48.1 ($\underline{C}$H—Ar); 99.3 ($\underline{C}$H=C); 106.9 (CH—N); 125.3, 128.3, 128.4, 128.5, and 129.5 (all $\underline{C}H_{Ph}$ and all $\underline{C}H_{Ar}$); 130.1 and 142.1 ($\underline{C}_{Ar}$ and $\underline{C}_{Ph}$); 155.6 ($\underline{C}$=CH). ^{29}Si NMR ($CDCl_3$), δ: 24.71 and 26.42 (2 $SiMe_3$).

A mixture of 2-[*N*,*N*-bis(trimethylsilyloxy)amino]-3-(4-nitrophenyl)-5-phenyl-2,3-dihydrofuryan (6n) and 2-(4-nitrophenyl)-4-oxo-4-phenylbut-2-enal *O*-trimethylsilyloxime (7n), viscous yellow oil.

Compound 6n. ^{1}H NMR ($CDCl_3$), δ: 0.16 and 0.18 (both s, 9 H each, 2 $SiMe_3$); 4.96 (dd, 1 H, CH—Ar, ^3J = 3.9 Hz, ^3J = 3.3 Hz); 5.00 (d, 1 H, CH—N, ^3J = 3.9 Hz); 5.55 (d, 1 H, CH=C, ^3J = 3.3 Hz); 7.30—7.42 (m, 3 H, CH_{Ph}); 7.51 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.60—7.68 (m, 2 H, CH_{Ph}); 8.17 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.2 and 0.4 (2 $SiMe_3$); 48.4 (CH—Ar); 98.4 (CH=C); 106.4 (CH—N); 123.8, 125.4, 128.5, 128.6, and 129.0 (all CH_{Ph} and CH_{Ar}); 130.3, 146.9, and 151.3 (all C_{Ar} and C_{Ph}); 156.4 (C=CH). ^{29}Si NMR ($CDCl_3$), δ: 25.17 and 27.00 (2 $SiMe_3$).

Compound 7n. ^{1}H NMR ($CDCl_3$), δ: 7.15 (s, 1 H, CH=C); 7.56—7.68 (m, 3 H, CH_{Ph}); 7.98 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 8.10 (m, 2 H, CH_{Ph}); 8.26 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 9.01 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$), δ: 0.1 ($SiMe_3$); 123.1, 128.3, 128.6, 128.8, and 129.0 (all CH_{Ar} and CH_{Ph}); 130.2 (CH=C); 137.9, 144.8, and 148.0 (all C_{Ar} and C_{Ph}); 146.2 (CH=C); 152.4 (CH=N); 190.1 (C=O). ^{29}Si NMR ($CDCl_3$), δ: 28.55 ($SiMe_3$).

Methyl 4-oxo-4-phenyl-2-(trimethylsilyloxyiminomethyl)-but-2-enoate (7o), viscous yellow oil. *Z-anti*-**7o** : *E-anti*-**7o** = 1 : 1.

***Z-anti*-7o.** ^{1}H NMR ($CDCl_3$), δ: 0.20 (s, 9 H, $SiMe_3$); 3.80 (s, 3 H, OMe); 7.16 (s, 1 H, CH=C); 7.40 (m, 3 H, CH_{Ph}); 7.88 (m, 2 H, CH_{Ph}); 7.99 (s, 1 H, CH=N). Irradiation of the CH=C signal at δ7.16 led to an increase in the intensity of the CH=N signals at δ 7.99. ^{13}C NMR ($CDCl_3$), δ: −1.0 ($SiMe_3$); 52.5 (OMe); 127.5 (CH=C); 128.4, 128.7, and 133.5 (all CH_{Ph}); 135.6 and 141.0 (CH=C and C_{Ph}); 151.3 (CH=N); 165.2 (COOMe); 192.6 (COPh). ^{29}Si NMR ($CDCl_3$), δ: 28.33 ($SiMe_3$). ^{15}N NMR ($CDCl_3$), δ: 16.1 (d, CH=N, ^2J = 2.5 Hz).

***E-anti*-7o.** ^{1}H NMR ($CDCl_3$), δ: −0.09 (s, 9 H, $SiMe_3$); 3.80 (s, 3 H, OMe); 7.40 (m, 3 H, CH=C + CH_{Ph}); 7.52 (m, 1 H, CH_{Ph}); 7.88 (m, 2 H, CH_{Ph}); 8.19 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$), δ: −1.3 ($SiMe_3$); 52.2 (OMe); 128.6, 128.7, and 133.6 (all CH_{Ph}); 131.1 and 136.6 (CH=C and C_{Ph}); 136.8 (CH=C); 147.6 (CH=N); 166.1 (COOMe); 188.4 (COPh). ^{29}Si NMR ($CDCl_3$), δ: 29.64 ($SiMe_3$). ^{15}N NMR ($CDCl_3$), δ: 9.1 (d, CH=N, ^2J = 3.0 Hz).

Trimethyl(4-nitro-1,3,4-triphenylbut-1-enyloxy)silane (2q), white crystals, m.p. 103—105 °C (C_5H_{14}). Found (%): C, 76.32; H, 5.38; N, 4.24. $C_{22}H_{19}NO_3$. Calculated (%): C, 76.50; H, 5.54; N, 4.06. ^{1}H NMR ($CDCl_3$), δ: 0.05 (s, 9 H, $SiMe_3$); 4.93—5.06 (m, 2 H, 2 CH—Ph); 5.76 (m, 1 H, CH=C); 7.13—7.47 (m, 13 H, CH_{Ph}); 7.65 (m, 2 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: 0.9 ($SiMe_3$); 46.3 (CH—Ph); 96.9 (CH=C); 107.7 (CH—NO_2); 126.4, 127.5, 128.0, 128.1, 128.3, 128.6, 128.7, 129.0, and 129.9 (all CH_{Ph}); 133.5, 138.8, and 140.4 (all C_{Ph}); 152.2 (C=CH). ^{29}Si NMR ($CDCl_3$), δ: 20.48 ($SiMe_3$). ^{14}N NMR ($CDCl_3$), δ: 7.5 (NO_2, $\Delta\nu_{1/2} \approx 700$ Hz).

A mixture of *N*,*N*-bis(trimethylsilyloxy)-1-methylidene-2,4-diphenyl-4-(trimethylsilyloxy)but-3-enylamine (13p) and trimethyl(4-nitro-1,3-diphenylpent-1-enyloxy)silane (2p). Trimethylsilyl triflate (0.6 mL, 3.5 mmol) was added to a solution of γ-nitro ketone **1p** (285 mg, 1 mmol) in CH_2Cl_2 (3 mL) and Et_3N (0.6 mL, 4 mmol) at −40 °C for 2 min. The reaction mixture was kept at −30 °C for one or two weeks and then diluted with light petroleum (10 mL). Methanol (0.04 mL) was added to the resulting emulsion at −30 °C and the resulting mixture was poured into a mixture of H_2O (10 mL) and light petroleum (5 mL). The organic layer was separated, washed with a solution of $NaHSO_4 \cdot H_2O$ (70 mg, 0.5 mmol) in H_2O (10 mL), H_2O (2×10 mL) and a saturated NaCl solution (10 mL), dried with Na_2SO_4, and concentrated *in vacuo*. The yield and purity of the product were determined from the ^{1}H NMR spectrum using a quantitative standard ($ClCH_2CH_2Cl$, δ_H 3.73). A 2 : 1 mixture of compounds **13p** and **2p** (450 mg) was obtained as a colorless thick oil.

Compound 13p. ^{1}H NMR ($CDCl_3$), δ: 0.20 and 0.26 (both s, 9 H each, 2 $SiMe_3$); 4.87 (s, 1 H, CH_2); 5.13 (d, 1 H, CH—Ph, ^3J = 9.7 Hz); 5.39 (s, 1 H, CH_2); 5.54 (d, 1 H, CH=C, ^3J = 9.7 Hz); 7.19—7.62 (m, 10 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: 0.2 and 0.8 (2 $SiMe_3$); 42.8 (CH—Ph); 102.7 (CH_2); 107.2 (CH=CO); 125.9, 126.0, 127.7, 127.9, 128.0, and 128.3 (all CH_{Ph}); 139.4 and 144.1 (2 C_{Ph}); 148.9 (CH=CO); 162.2 (CH_2=CN). ^{29}Si NMR ($CDCl_3$), δ: 19.98 and 24.02 (2 $SiMe_3$).

Compound 2p. ^{1}H NMR ($CDCl_3$), δ: 0.21 (s, 9 H, $SiMe_3$); 1.69 (d, 3 H, Me, ^3J = 6.6 Hz); 4.57 (m, 1 H, CH—Ph); 4.90 (m, 1 H, $CHNO_2$); 5.37 (d, 1 H, CH=C, ^3J = 9.0 Hz); 7.19—7.62 (m, 10 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: 0.7 ($SiMe_3$); 17.3 (Me); 47.0 (CH—Ph); 88.4 ($CHNO_2$); 113.3 (CH=CO); 126.2, 127.3, 127.7, 128.1, 128.4, and 128.8 (all CH_{Ph}); 138.5 and 139.9 (2 C_{Ph}); 152.8 (CH=CO). ^{29}Si NMR ($CDCl_3$), δ: 20.79 ($SiMe_3$).

Silylation of aliphatic nitro compounds 1d and 1r without aqueous workup of the reaction mixture (general procedure). Bromotrimethylsilane (0.4 mL, 3.0 mmol) was added to a solution of ANC **1** (1 mmol) in CH_2Cl_2 (3 mL) and Et_3N (0.5 mL, 3.5 mmol) at −40 °C for 2 min. The reaction mixture was kept at −30 °C for one week, diluted with anhydrous toluene (15 mL), and filtered under argon. The filtrate was concentrated *in vacuo*. The resulting product was analyzed by NMR spectroscopy using a quantitative standard ($ClCH_2CH_2Cl$, δ_H 3.73).

A mixture of 2-[*N*,*N*-bis(trimethylsilyloxy)amino]-3-(4-methoxyphenyl)-5-(4-nitrophenyl)-2,3-dihydrofuran (6d) and trimethylsilyl 2-(4-methoxyphenyl)-4-(4-nitrophenyl)-4-trimethylsilyloxybut-3-ene-1-*aci*-nitronate (4d), viscous yellowish oil, **6d** : **4d** = 1 : 2.6.

Compound 4d. ^{1}H NMR ($CDCl_3$), δ: 0.26 and 0.41 (both s, 9 H each, 2 $SiMe_3$); 3.77 (s, 3 H, OMe); 5.18 (dd, 1 H, CH—Ar, ^3J = 7.7 Hz, ^3J = 9.6 Hz); 5.65 (d, 1 H, CH=C, ^3J = 9.6 Hz); 6.45 (d, 1 H, CH=N, ^3J = 7.7 Hz); 6.92 (d, 2 H, CH_{Ar}, ^3J = 8.7 Hz); 7.18 (d, 2 H, CH_{Ar}, ^3J = 8.7 Hz); 7.67 (d, 2 H, CH_{Ar}, ^3J = 8.9 Hz); 8.18 (d, 2 H, CH_{Ar}, ^3J = 8.9 Hz). ^{13}C NMR ($CDCl_3$), δ: −0.3 and 0.2 (2 $SiMe_3$); 45.8 (CH—Ar); 54.8 (OMe); 112.4 (OC=CH); 117.2 (CH=N); 113.9, 123.2, 126.2, and 128.7 (all CH_{Ar}); 131.9, 144.6, 147.1, and 158.5 (C_{Ar}); 149.1 (OC=CH). ^{29}Si NMR ($CDCl_3$), δ: 22.49 and 26.28 (2 $SiMe_3$).

A mixture of trimethylsilyl 1-methoxycarbonyl-2,4-diphenyl-4-oxobutane-1-*aci*-nitronate (3r) and trimethylsilyl 1-methoxycarbonyl-2,4-diphenyl-4-trimethylsilyloxybut-3-ene-1-*aci*-nitronate (4r). Colorless oil, **3r** : **4r** = 1 : 2.7.

Compound 4r. ^{1}H NMR ($CDCl_3$), δ: 0.14 and 0.32 (both s, 9 H each, 2 $SiMe_3$); 3.85 (s, 3 H, OMe); 5.53 (d, 1 H, CH—Ph, ^3J = 9.6 Hz); 5.69 (d, 1 H, CH=C, ^3J = 9.6 Hz); 7.15—7.58 (m, 10 H, CH_{Ph}). ^{13}C NMR ($CDCl_3$), δ: −0.2 and 0.6 (2 $SiMe_3$); 41.0 (CH—Ph); 52.5 (OMe); 107.0 (CH=CO); 122.2 (C=N); 126.2, 126.7, 127.6, 128.2, 128.3, and 128.4 (all CH_{Ph}); 138.7 and 140.3 (2 C_{Ph}); 152.2 (CH=CO); 162.5 (COOMe). ^{29}Si NMR ($CDCl_3$), δ: 20.75 and 29.69 (2 $SiMe_3$).

Compound 3r. ^{1}H NMR ($CDCl_3$), δ: 0.29 (s, 9 H, $SiMe_3$); 3.61 (dd, 1 H, CH_2C=O, ^2J = 16.5 Hz, ^3J = 6.3 Hz); 3.81 (s, 3 H, OMe); 4.07 (dd, 1 H, CH_2C=O, ^2J = 16.5 Hz, ^3J = 9.0 Hz); 4.87 (dd, 1 H, CH—Ph, ^3J = 6.3 Hz, ^3J = 9.0 Hz); 7.15—7.58 (m, 8 H, CH_{Ph}); 8.08 (d, 2 H, CH_{Ph}, ^3J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: –0.3 ($SiMe_3$); 40.1 ($\underline{C}H_2C$=O); 40.3 ($\underline{C}H$—Ph); 52.6 (OMe); 122.6 (C=N); 127.2, 128.0, 128.1, 128.5, 128.7, and 133.3 (all $\underline{C}H_{Ph}$); 136.6 and 139.0 (2 $\underline{C}_{Ph}$); 162.7 ($\underline{C}$OOMe); 197.4 ($CH_2\underline{C}$=O). ^{29}Si NMR ($CDCl_3$), δ: 30.43 ($SiMe_3$).

Desilylation of compounds 6, 7, and 9 with NH_4F in MeOH (general procedure). Crystalline NH_4F (5 mg, 0.1 mmol) was added to a solution of compound **6**, **7**, or **9** (1 mmol) in MeOH (4.4 mL) at 0 °C. The reaction mixture was kept under the conditions given in Table 2 and concentrated *in vacuo*. The products were purified by recrystallization from MeOH or chromatography on silica gel (yields are given in Table 2).

2-(4-Methoxyphenyl)propenal oxime (10f), white crystals, m.p. 65—67 °C (CH_2Cl_2—pentane). Found (%): C, 67.99; H, 6.00; N, 7.67. $C_{10}H_{11}NO_2$. Calculated (%): C, 67.78; H, 6.26; N, 7.90. ^{1}H NMR ($CDCl_3$), δ: 3.81 (s, 3 H, OMe); 5.48 (s, 1 H, CH_2); 5.58 (s, 1 H, CH_2); 6.89 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.36 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.55 (s, 1 H, CH=N); 8.01 (s, 1 H, NOH). ^{13}C NMR ($CDCl_3$), δ: 55.4 (OMe); 113.7 and 129.6 (2 $\underline{C}H_{Ar}$); 122.2 (CH_2); 129.6 and 159.7 (2 $\underline{C}_{Ar}$); 142.4 ($\underline{C}$=CH_2); 152.5 (CH=N).

2-Phenylpropenal oxime (10h), white crystals, m.p. 105—107 °C (CH_2Cl_2—pentane) (*cf.* lit. data[29]: m.p. 103 °C (MeOH)). ^{1}H NMR ($CDCl_3$), δ: 5.42 (s, 1 H, CH_2); 5.50 (s, 1 H, CH_2); 7.26 (br.s, 5 H, CH_{Ph}); 7.86 (s, 1 H, CH=N); 8.69 (s, 1 H, NOH). ^{13}C NMR ($CDCl_3$), δ: 123.0 (CH_2); 128.2 (2 $\underline{C}H_{Ph}$); 128.3 ($\underline{C}H_{Ph}$); 137.4 ($\underline{C}_{Ph}$); 143.1 (CH_2=$\underline{C}$); 151.5 (C=N).

4-(4-Methoxyphenyl)-2-phenylfuran (15a), white crystals, m.p. 136—138 °C (MeOH) (*cf.* lit. data[30]: m.p. 132—134 °C (MeOH)). ^{1}H NMR ($CDCl_3$), δ: 3.85 (s, 3 H, OMe); 6.94 (s, 1 H, CH=CO); 6.96 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.30 (m, 1 H, CH_{Ph}); 7.37—7.53 (m, 4 H, CH_{Ph}); 7.71 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.75 (s, 1 H, C=CHO). ^{13}C NMR ($CDCl_3$), δ: 55.4 (OMe); 104.2 ($\underline{C}$H=CO); 114.4, 123.9, 127.1, 127.6, and 128.8 (all $\underline{C}H_{Ar}$ and $\underline{C}H_{Ph}$); 125.1 ($\underline{C}_{Ar}$); 128.1 ($\underline{C}$=CHO); 130.8 ($\underline{C}_{Ph}$); 137.2 (C=$\underline{C}$HO); 154.8 (CH=$\underline{C}$O); 158.9 ($\underline{C}_{Ar}$).

4-(4-Methoxyphenyl)-2-(4-tolyl)furan (15b), white crystals, m.p. 135—137 °C (MeOH) (*cf.* lit. data[30]: m.p. 107 °C (MeOH)). ^{1}H NMR ($CDCl_3$), δ: 2.17 (s, 3 H, Me); 3.46 (s, 3 H, OMe); 6.78 (s, 1 H, CH=CO); 6.87 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 7.07 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 7.34 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 7.48 (s, 1 H, C=CHO); 7.67 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.2 (Me); 55.1 (OMe); 104.1 ($\underline{C}$H=CO); 114.8, 124.5, 127.5, and 129.7 (all $\underline{C}H_{Ar}$); 125.8, 129.0, 137.5, and 159.7 (all $\underline{C}_{Ar}$); 128.8 ($\underline{C}$=CHO); 137.3 (C=$\underline{C}$HO); 155.7 (CH=$\underline{C}$O).

2,4-Bis(4-methoxyphenyl)furan (15c), white crystals, m.p. 188—189 °C (MeOH) (*cf.* lit. data[31]: m.p. 188—190 °C). ^{1}H NMR ($CDCl_3$), δ: 3.57 and 3.59 (both s, 3 H each, 2 OMe); 6.90 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 6.93 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.21 (s, 1 H, CH=CO); 7.47 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.66 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.75 (s, 1 H, C=CHO). ^{13}C NMR ($CDCl_3$), δ: 55.4 (2 OMe); 103.3 ($\underline{C}$H=CO); 114.8, 114.9, 127.4, and 125.7 (all $\underline{C}H_{Ar}$); 124.3, 125.5, 159.4, and 159.8 (all $\underline{C}_{Ar}$); 128.5 ($\underline{C}$=CHO); 155.1 (CH=$\underline{C}$O).

2-Cyclopropyl-4-(4-methoxyphenyl)furan (15e), white crystals, m.p. 119—122 °C (MeOH). Found (%): C, 78.06; H, 6.70. $C_{14}H_{14}O_2$. Calculated (%): C, 78.48; H, 6.59. ^{1}H NMR ($CDCl_3$), δ: 0.73—1.03 (m, 4 H, CH_2); 1.92 (m, 1 H, CH); 3.82 (s, 3 H, OMe); 6.23 (s, 1 H, CH=CO); 6.90 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.37 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.46 (s, 1 H, C=CHO). ^{13}C NMR ($CDCl_3$), δ: 6.7 (CH_2); 9.0 (CH); 55.4 (OMe); 102.9 ($\underline{C}$H=CO); 114.3 and 126.9 (2 $\underline{C}H_{Ar}$); 125.6 ($\underline{C}$=CHO); 126.8 and 158.4 (2 $\underline{C}_{Ar}$); 135.5 (C=$\underline{C}$HO); 158.7 (CH=$\underline{C}$O).

3-Acetyl-2-methyl-4-phenylfuran (15j), viscous colorless oil (*cf.* Ref. 32). ^{1}H NMR ($CDCl_3$), δ: 2.05 (s, 3 H, Me); 2.57 (s, 3 H, MeCO); 7.29—7.39 (m, 5 H, CH_{Ph}); 7.37 (s, 1 H, C=CHO). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 31.0 ($\underline{Me}$CO); 122.3 ($\underline{C}$=CO); 126.8 ($\underline{C}$=CHO); 127.8, 128.5, and 129.3 (all CH_{Ph}); 132.5 ($\underline{C}_{Ph}$); 138.1 (C=$\underline{C}$HO); 158.7 (C=$\underline{C}$O); 196.1 (C=O).

2,4-Diphenylfuran (15l), white crystals, m.p. 110—111 °C (MeOH) (*cf.* lit. data[31]: m.p. 109 °C). ^{1}H NMR ($CDCl_3$), δ: 6.92 (s, 1 H, CH=CO); 7.21—7.29 (m, 2 H, CH_{Ph}); 7.32—7.41 (m, 4 H, CH_{Ph}); 7.47—7.53 (m, 2 H, CH_{Ph}); 7.66—7.72 (m, 2 H, CH_{Ph}); 7.70 (s, 1 H, C=CHO). ^{13}C NMR ($CDCl_3$), δ: 104.1 ($\underline{C}$H=CO); 124.0, 126.0, 127.3, 127.7, 128.8, and 129.0 (all $\underline{C}H_{Ph}$); 128.5 ($\underline{C}$=CHO); 130.8 and 132.5 (2 $\underline{C}_{Ph}$); 138.0 (C=$\underline{C}$HO); 155.0 (CH=$\underline{C}$O).

4-(4-Chlorophenyl)-2-phenylfuran (15m), white crystals, m.p. 133—134 °C (MeOH) (*cf.* lit. data[30]: m.p. 130 °C (MeOH)). ^{1}H NMR ($CDCl_3$), δ: 6.89 (s, 1 H, CH=CO); 7.22—7.47 (m, 7 H, CH_{Ph} and CH_{Ar}); 7.69 (m, 2 H, CH_{Ph}); 7.70 (s, 1 H, C=CHO). ^{13}C NMR ($CDCl_3$), δ: 103.6 ($\underline{C}$H=CO); 123.8, 126.9, 127.7, 128.7, and 128.9 (all $\underline{C}H_{Ar}$ and $\underline{C}H_{Ph}$); 128.2 ($\underline{C}$=CHO); 130.8, 131.0, and 133.1 (2 $\underline{C}_{Ar}$ and $\underline{C}_{Ph}$); 137.9 (C=$\underline{C}$HO); 153.2 (CH=$\underline{C}$O).

4-(4-Nitrophenyl)-2-phenylfuran (15n), yellow crystals, m.p. 166—167 °C (MeOH) (*cf.* lit. data[30]: m.p. 152 °C (MeOH)). ^{1}H NMR ($(CD_3)_2SO$), δ: 7.34 (m, 1 H, CH_{Ph}); 7.47 (m, 2 H, CH_{Ph}); 7.60 (s, 1 H, CH=CO); 7.76 (d, 2H, CH_{Ph}, ^3J = 7.7 Hz); 7.94 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 8.26 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 8.52 (s, 1 H, C=CHO). ^{13}C NMR ($(CD_3)_2SO$), δ: 104.1 ($\underline{C}$H=CO); 123.5, 124.0, 126.1, 127.9, and 128.8 (all $\underline{C}H_{Ar}$ and $\underline{C}H_{Ph}$); 126.1 ($\underline{C}$=CHO); 141.4 (C=$\underline{C}$HO); 129.6, 138.6, and 146.0 ($\underline{C}_{Ph}$ and 2 $\underline{C}_{Ar}$); 154.6 (CH=$\underline{C}$O).

***Z-anti*-2-(4-Nitrophenyl)-4-oxo-4-phenylbut-2-enal oxime (8n)**, yellowish crystals, m.p. 149—151 °C (MeOH). ^{1}H NMR ($(CD_3)_2SO$), δ: 7.40 (s, 1 H, CH=C); 7.56 (m, 2 H, CH_{Ph}); 7.68 (m, 1 H, CH_{Ph}); 7.81 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 8.07 (d, 2 H, CH_{Ph}, ^3J = 7.7 Hz); 8.27 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 8.83 (s, 1 H, CH=N); 11.99 (s, 1 H, OH). Irradiation of H_o of the 4-$NO_2C_6H_4$ group (δ 7.81) led to an increase in the intensities of the signals at δ 7.40 (CH=C) and 8.27 (H_m of the 4-$NO_2C_6H_4$ group). Irradiation of the proton of the OH group (δ 11.99) led to an increase in the intensity of the signal of CH=N at δ 8.83. ^{13}C NMR ($(CD_3)_2SO$), δ: 122.9, 128.6, 128.8, 130.7 and 133.6 ($\underline{C}H_{Ar}$ and $\underline{C}H_{Ph}$); 127.8 ($\underline{C}$H=C); 137.6, 144.9, and 147.4 (2 $\underline{C}_{Ar}$ and $\underline{C}_{Ph}$); 146.1 (CH=$\underline{C}$); 147.6 ($\underline{C}$H=N); 190.2 ($\underline{C}$=O).

Methyl *E-anti*-2-(hydroxyiminomethyl)-4-oxo-4-phenylbut-2-enoate (8o), yellow crystals, m.p. 124—126 °C (MeOH). Found (%): C, 61.60; H, 4.51; N, 5.83. $C_{12}H_{11}NO_4$. Calculated (%): C, 61.80; H, 4.75; N, 6.01. ^{1}H NMR ($(CD_3)_2CO$), δ: 3.86 (s, 3 H, OMe); 7.16 (s, 1 H, CHBz); 7.50 (m, 2 H, CH_{Ph}); 7.61 (m, 1 H, CH_{Ph}); 7.94 (m, 2 H, CH_{Ph}); 7.96 (s, 1 H, CH=N); 8.86 (br.s, 1 H, O$\underline{H}$). Irradiation of the proton of the CH=N group (δ 7.96) led to an increase in the intensity of the signal of C$\underline{H}$Bz at δ 7.16. ^{13}C NMR ($(CD_3)_2CO$), δ: 51.8 (OMe); 127.0 ($\underline{C}$H=C); 128.7, 129.2, and 133.9 (all $\underline{C}H_{Ph}$); 137.5 and

142.7 (CH=C and C_{Ph}); 148.2 (CH=N); 166.2 (COOMe); 188.4 (COPh).

***Z*-2-(4-Methoxyphenyl)-4-oxo-4-(4-tolyl)but-2-enonitrile (17b).** Tetrabutylammonium fluoride (0.3 mL, 0.2 mmol; a 0.73 *M* solution in THF) was added to a solution of dihydrofuran **6b** (460 mg, 1 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The reaction mixture was kept at 20 °C for 24 h and then concentrated *in vacuo*. The residue was recrystallized from a benzene—pentane mixture (3 : 1). The product was obtained as yellow crystals in a yield of 150 mg (54%), m.p. 154—156 °C (PhH—C_5H_{12}). Found (%): C, 77.67; H, 5.25; N, 4.89. $C_{18}H_{15}NO_2$. Calculated (%): C, 77.96; H, 5.45; N, 5.05. MS (EI), m/z (I_{rel} (%)): 277 $[M]^+$ (95); 246 $[M - OMe]^+$ (100). IR (KBr), ν/cm^{-1}: 1655 (C=O); 2222 (CN). ^1H NMR ($CDCl_3$), δ: 2.44 (s, 3 H, Me); 3.88 (s, 3 H, OMe); 7.00 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.32 (d, 2 H, CH_{Ar}, ^3J = 7.9 Hz); 7.78 (d, 2 H, CH_{Ar}, ^3J = 8.5 Hz); 7.80 (s, 1 H, CH=C); 7.94 (d, 2 H, CH_{Ar}, ^3J = 7.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.8 (Me); 55.6 (OMe); 114.8, 128.7, 129.0, and 129.7 (all CH_{Ar}); 116.5 (CN); 124.1 (CH=C); 130.2 (CH=C); 125.0, 134.5, 145.0, and 162.4 (all C_{Ar}); 186.3 (C=O).

***E*-2-(4-Methoxyphenyl)-4-oxo-4-(4-tolyl)but-2-enonitrile (*E*-17b).** A solution of enenitrile (20 mg, 0.07 mmol) *Z*-**17b** in benzene (5 mL) was kept in a glass vessel in sunlight for one week. Then the solvent was evaporated *in vacuo* and the residue was analyzed by ^1H NMR spectroscopy.

Compound *E*-17b. ^1H NMR ($CDCl_3$), δ: 2.41 (s, 3 H, Me); 3.78 (s, 3 H, OMe); 6.80 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.25 (d, 2 H, CH_{Ar}, ^3J = 8.8 Hz); 7.37 (s, 1 H, CH=C); 7.41 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz); 7.81 (d, 2 H, CH_{Ar}, ^3J = 8.1 Hz).

The degree of conversion of *Z*-**17b** into *E*-**17b** was 86%.

The study was carried out at the Scientific and Educational Center of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences and the Moscow Chemical Lyceum and was financially supported by the Russian Foundation for Basic Research (Project Nos. 03-98-33002 and 00-15-97455) and the Federal Target Program "Integration" (Project Nos. A0082 and B0062).

References

1. A. A. Tishkov, A. V. Kozintsev, I. M. Lyapkalo, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Tetrahedron Lett.*, 1999, **40**, 5075.
2. V. A. Tartakovsky, S. L. Ioffe, A. D. Dilman, and A. A. Tishkov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1850 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1936].
3. A. A. Tishkov, I. M. Lyapkalo, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 2000, 3229.
4. V. M. Danilenko, A. A. Tishkov, S. L. Ioffe, I. M. Lyapkalo, Yu. A. Strelenko, and V. A. Tartakovsky, *Synthesis*, 2002, 635.
5. A. D. Dilman, A. A. Tishkov, I. M. Lyapkalo, V. V. Kachala, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2926.
6. A. A. Tishkov, I. M. Lyapkalo, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Tetrahedron*, 2001, **57**, 2221.
7. (a) R. Noyori, S. Murata, and M. Suzuki, *Tetrahedron*, 1981, **37**, 3899; (b) B. Mathieu and L. Ghosez, *Tetrahedron Lett.*, 1997, **38**, 5497.
8. A. A. Tishkov, I. M. Lyapkalo, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 210 [*Russ. Chem. Bull.*, 1997, **46**, 205 (Engl. Transl.)].
9. J. P. Guthrie, J. Cossar, and A. Klym, *Can. J. Chem.*, 1987, **65**, 2154.
10. R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 1953, **75**, 2439.
11. V. O. Smirnov, A. A. Tishkov, I. M. Lyapkalo, S. L. Ioffe, V. V. Kachala, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2324 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2433].
12. A. D. Dilman, A. A. Tishkov, I. M. Lyapkalo, V. V. Kachala, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Synthesis*, 1998, 181.
13. R. G. Kostyanovsky, G. K. Kadorkina, V. N. Voznesensky, I. I. Chervin, M. Yu. Antipin, K. A. Lyssenko, E. V. Vorontsov, V. I. Bakhmutov, and P. Rademacher, *Mendeleev Commun.*, 1996, 69.
14. A. A. Tishkov, A. D. Dilman, V. I. Faustov, A. A. Birukov, K. S. Lysenko, P. A. Belyakov, S. L. Ioffe, Yu. A. Strelenko, and M. Yu. Antipin, *J. Am. Chem. Soc.*, 2002, **124**, 11358.
15. V. F. Rudchenko, *Chem. Rev.*, 1993, **93**, 725.
16. C. L. Ioffe, M. V. Kashutina, V. M. Shitkin, A. Z. Yankelevich, A. A. Levin, and V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 1341 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 1292 (Engl. Transl.)].
17. A. D. Dilman, I. M. Lyapkalo, P. A. Belyakov, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1659 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1649].
18. K. Nozaki, N. Sato, and H. Takaya, *Bull. Chem. Soc. Jpn.*, 1996, 1629.
19. (a) M. Largeron and M.-B. Fleury, *Tetrahedron Lett.*, 1991, 631; (b) H. Yamada, H. Yoshimura, and K. Tatsumi, *Chem. Pharm. Bull.*, 1982, 2647.
20. D. E. Warrall and C. J. Bradway, *J. Am. Chem. Soc.*, 1936, **58**, 1607.
21. A. A. Tishkov, V. O. Smirnov, M. V. Nefed´eva, I. M. Lyapkalo, S. E. Semenov, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Zh. Org. Khim.*, 2001, **37**, 416 [*Russ. J. Org. Chem.*, 2001, **37**, 390 (Engl. Transl.)].
22. W. Davey and D. J. Tivey, *J. Chem. Soc.*, 1958, 2276.
23. M. E. Kuehne and L. Foley, *J. Org. Chem.*, 1965, 4280.
24. J. H. Nelson, P. N. Howells, G. C. DeLullo, G. L. Landen, and R. A. Henry, *J. Org. Chem.*, 1980, 1246.
25. E. P. Kohler and L. I. Smith, *J. Am. Chem. Soc.*, 1922, **44**, 624.
26. K. Watanabe, K. Miyazu, and K. Irie, *Bull. Chem. Soc.*, 1982, **55**, 3212.
27. E. P. Kohler, *J. Am. Chem. Soc.*, 1916, **38**, 897.
28. E. P. Kohler, *J. Am. Chem. Soc.*, 1924, **46**, 1738.
29. P. Bravo, G. Gaudiano, C. Ticozzi, and A. Umani-Ronchi, *Gazz. Chim. Ital.*, 1969, **99**, 549.
30. P. Molina, A. Lorenzo, and P. M. Fresenda, *Synthesis*, 1983, 49.
31. I. Francesconi, A. Patel, and D. W. Boykin, *Synthesis*, 1999, 61.
32. T. Kataoka, S. Watanabe, K. Yamamoto, M. Yoshimatsu, G. Tanabe, and O. Muraoka, *J. Org. Chem.*, 1998, **63**, 6382.

Received August 1, 2002;
in revised form November 14, 2002