Pergamon

Tetrahedron 57 (2001) 2221–2230

TETRAHEDRON

The exhaustive silylation of 5-nitro-pentan-2-one: novel processes and opportunities

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

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 117913 Moscow, Russian Federation

Received 6 October 2000; revised 8 December 2000; accepted 4 January 2001

Abstract—Treatment of 5-nitro-pentan-2-one (**1**) with Me_3SiOTf/Et_3N leads to initial silylation of the C(O)Me-group to give regioisomeric silyl enol ethers **2a** and **2b** followed by double silylation of the NO_2-group furnishing a mixture of *N*,*N*-bis(silyloxy)enamine **4a** and enoxime TMS ether **6**. Employment of a large excess of Me_3SiOTf/Et_3N triggers a cascade of eliminations and silylations to give a mixture of (*E*)-4-trimethylsilyloxy-2-trimethylsilyl-pent-2,4-dienenitrile (**8**) and 3-oxo-1-(1,1,1-trimethylsilyl)-1-cyclobutanecarbonitrile (**9**). The use of Me_3SiCl/DBU changes the selectivity of silylation of **1** to give silyl nitronate **2c**. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The silylation of aliphatic nitro compounds (ANC) is a promising method to broaden their reactivity.[1] The most interesting and unusual results could be obtained upon silylation of different functionalized nitro compounds. Thus, the reactivity of readily available γ-functionalized derivatives of the general formula RCHX–CHY–CHZ(NO_2) (R=H, alkyl or aryl; X=electron-withdrawing group; Y, Z=H, alkyl, aryl, functional group)[2] upon silylation depends on several factors, such as the nature of R, X, Y, Z and the silylating reagents, as well as the conditions of silylation. The silylation of these compounds could lead to enoximes,[3–6] *N*,*N*-bis(silyloxy)enamines,[4,7] *N*,*N*-bis(silyloxy)amino-dihydrofurans and cyclopropanes,[8] β-functionalized *N*,*N*-divinylhydroxylamines.[6]

Such diversity of transformations and crucial dependence of reaction pathway on a multitude of factors complicate a prediction of the result in each new case. Therefore, more experimental data on the effect of varying the substituents is required in order to be able to control the process outcome. In this study, 5-nitro-pentan-2-one (**1**) was chosen as a model polyfunctional compound, having both a nitro- and a carbonyl group capable to undergo silylation.

2. Influence of the nature of the silylating reagent

Treatment of ketone **1** with Me_3SiCl/DBU[9] gives silyl nitronate **2c** in high yield (Scheme 1).

The reaction proceeds chemoselectively affecting only the CH_2NO_2 moiety.

Utilization of a stronger silylating reagent, Me_3SiBr/Et_3N, for the silylation of ketone **1** resulted in the formation of a complicated mixture of unidentified products, which contained ca. 20% of enoxime **6**. It is noteworthy that β-aryl-γ-nitroketones were transformed under the same reaction conditions into dihydrofurans[8] or α-oxyminostyrenes[10], while a related analog of ketone **1**, methyl 4-nitrobutanoate, underwent facile double silylation.[4]

To obtain a more unambiguous result, we used 4 equiv. of one of the most powerful silylating reagent Me_3SiOTf/Et_3N. However, even in this case we observed the formation of complicated mixtures of products. Nevertheless, the employment of more than 10-fold excess of silylating reagent allowed us to isolate the nitriles **8** (44%) and **9** (17%).

Products of such kind have never been isolated before upon silylation of ANC. This unexpected result prompted us to investigate in detail the silylation of nitro-ketone **1** using Me_3SiOTf/Et_3N and varying the temperature of the process and the ratio of reagents. The main results are presented in Scheme 1 and Table 1.

Attempts to monitor directly the course of silylation by NMR failed because the presence of excess of silylating

Keywords: silylation; nitro ketones; *N*,*N*-bis(silyloxy)enamines; elimination; *E*,*Z*-isomerization.

* Corresponding authors. Tel.: +7-095-938-36-23; fax: +7-095-135-53-28; e-mail: tishkov@cacr.ioc.ac.ru

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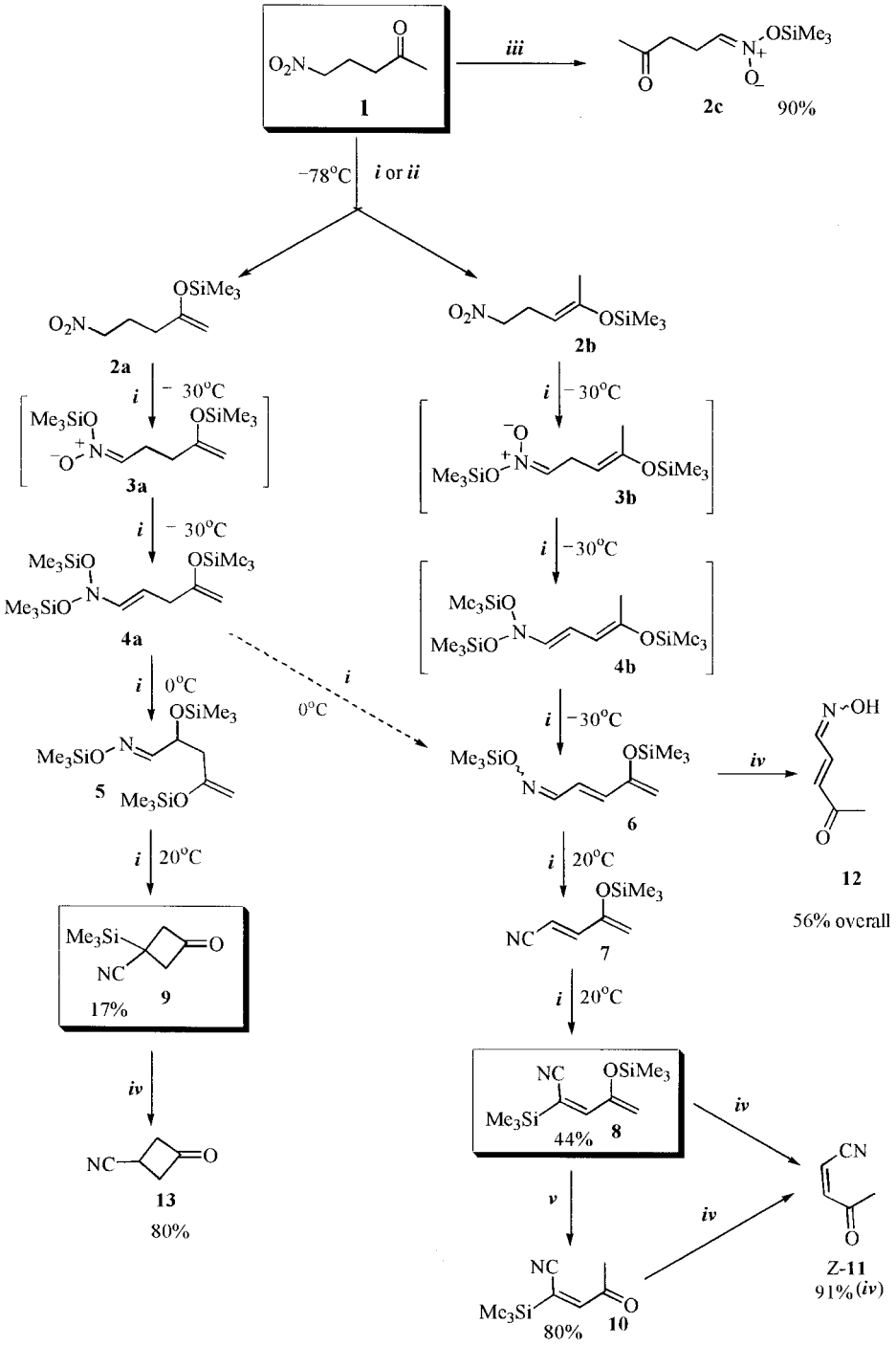
PII: S0040-4020(01)00055-2



Scheme 1. (i) Me_3SiOTf/Et_3N in CH_2Cl_2; the ratios are presented in Table 1 (**2a/2b**=1:1). (ii) (1) $(Me_3Si)_2NLi$ (2.5 equiv.) in THF; (2) Me_3SiCl (3.5 equiv.); (3) H_2O; (**2a/2b**=1:2.6). (iii) DBU/Me_3SiCl in CH_2Cl_2, 0→20°C. (iv) NH_4F in MeOH, 10°C. (v) Silica gel, 20°C.

reagent hampered the spectral registration as the precipitate of $Me_3SiNEt_3^+$ OTf^- formed. Therefore, an alternative procedure was employed.

The reagents were mixed at −78°C. The reaction mixture was stirred for the time period stated in Table 1 at the indicated temperature, and then quenched at −30°C by adding first petroleum ether, and then methanol and water (the quenching was made at −78°C in case of entry 2, Table 1). The organic layer was separated and washed in a regular manner. The residue, after solvent evaporation, was mixed with an internal standard for further NMR analysis.[†]

[†] The mild quenching conditions are meant to avoid desilylation of all products formed upon silylation of ketone **1** with Me_3SiOTf/Et_3N. The exception is the compounds containing silyl nitronate moiety CH=N(O)OSiMe$_3$, which should easily transform into CH_2NO_2-group upon such quenching.

Table 1. The silylation of substrates with Me_3SiOTf/Et_3N

Entry	Substrate for silylation (SS)	Mol. ratio SS:TMSOTf:Et_3N	*T*, °C/time, h	The yields of products and intermediates (%)							
				2a	**2b**	**4a**	**5**	**6**	**7**	**8**	**9**
1[a]	**1**	1:1.1:1.4	−78/4	47[b]	47[b]	–	–	–	–	–	–
2	**1**	1:4.2:4.5	−78/2	41[c]	41[c]	–	–	–	–	–	–
3	**1**	1:4.2:4.5	−30/1	–	–	40[b]	8[b]	51[b,d]	–	–	–
4	**2a**,**b** (**2a/2b**=1:2.6)	1:3.2:4.5	−30/1	–	–	24[b]	2[b]	72[b,e]	–	–	–
5	**1**	1:4.2:4.5	0/3	–	–	–	21[b]	61[b,f]	–	–	–
6	**1**	1:7.0:8.0	20/24	–	–	–	–	–	51[b,g]	14[b]	22[b]
7	**1**	1:11.0:12.0	20/50	–	–	–	–	–	–	52[b,h]	20[b]
8	*E*-**11**	1:3.0:3.5	20/6	–	–	–	–	–	85[c]	–	–
9	*E*-**11**	1:7.0:8.0	5/30	–	–	–	–	–	20[b]	68[b]	–
10	*E*-**11**	1:7.0:8.0	20/55	–	–	–	–	–	–	80[c]	–

[a] In NMR tube in CD_2Cl_2.
[b] By ^1H NMR spectrum with internal standard $ClCH_2CH_2Cl$ (the accuracy is ±3%).
[c] Yield for distilled product.
[d] (**4a**+**5**):**6**=1:1.06; *syn*-**6**:*anti*-**6**~1:3.3.
[e] (**4a**+**5**):**6**=1:2.7; *syn*-**6**:*anti*-**6**~1:3.3.
[f] *syn*-**6**:*anti*-**6**~1:3.4.
[g] Contained the traces of *E*-**11** and **10**.
[h] Contained the traces of **10**.

3. Mechanism of silylation of nitro-ketone 1 upon treatment with Me_3SiOTf/Et_3N

As was mentioned above, the silylation of nitro-ketone **1** with Me_3SiOTf/Et_3N is an exceptionally complicated process, which has no precedent in the practice of ANC silylation. However, the data on effects of the variation of temperature, reaction time and ratio of reagents on the reaction outcome enable us to define the nature of the intermediates formed in the sequence of the transformations leading to the main isolable products, namely silyl enol ethers **2**, the mixture of oximes **5** and **6**, and the mixture of nitriles **8** and **9** (Scheme 1, Table 1).

The silylation at −78°C proceeds chemoselectively affecting the carbonyl group, independent of the ratio of reagents and furnishes a mixture of silyl enol ethers **2a** and **2b** (only the *E*-isomer was formed) in the ratio 1:1. The mixture of **2a** and **2b** with a different ratio (1:2.6, respectively) could be prepared by method (ii) in Scheme 1.

The employment of excess of Me_3SiOTf/Et_3N does not affect the result of silylation of nitro-ketone **1** at −78°C (cf. entries 1 and 2, Table 1).‡

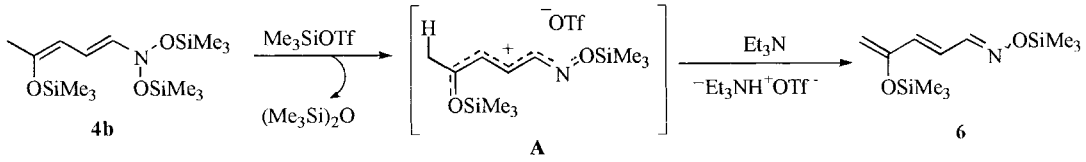
Thus, the chemoselectivity of silylation of nitro-ketone **1** entirely changes, when Me_3SiCl/DBU is substituted by Me_3SiOTf/Et_3N. This result could be rationalized from the standpoint of the difference in the electrophilicity of the silylating reagents employed.

The carbonyl group in the starting nitro-ketone **1** is more basic than the nitro group (for RNO_2H^+ pK_a~−12; for $RR'C{=}OH^+$ pK_a~−7).[11] It should be noted also, that five α-protons in the 1- and 3-positions of **1** undergo facile exchange for deuterium under acidic conditions (DCl in D_2O), whereas the CH_2NO_2 moiety remains intact.[12] At the same time, the CH-acidity of ANC (pK_a~8–10) exceeds substantially the CH-acidity of ketones (pK_a~19–20).[13] Therefore, the 'nucleophilic' silylating reagents preferentially attack the CH_2NO_2 moiety of functionalized ANC. In contrast to this, 'electrophilic' silylating reagents should silylate the carbonyl group. In this connection, the nucleophilic Me_3SiCl/Et_3N in benzene is widely used for the preparation of silyl nitronates from primary ANC at 20°C.[14] The same Me_3SiCl/Et_3N silylates ketones only under harsh conditions and heating in highly polar DMF is required.[15] The use of more basic DBU instead of Et_3N facilitates the silylation of CH_2NO_2 moiety ((iii), Scheme 1). The mixture of Me_3SiOTf and Et_3N exists, especially at low temperature, as the salt $[Et_3NSiMe_3]^+$ OTf^-,[16] i.e. it possesses a highly electrophilic character. This might be a reason why Me_3SiOTf/Et_3N silylates selectively the carbonyl group in nitro-ketone **1** in the presence of the CH_2NO_2 moiety at low temperature.

The initially formed silyl enol ethers **2a** and **2b** undergo double silylation at the $CH_2CH_2NO_2$ moiety upon temperature increase up to −30°C to give the mixture of **4a** and **6** (entries 3 and 4, Table 1). Oxime **6** was observed as a mixture of *syn*- and *anti*-isomers. All products were obtained as *E*-isomers around the internal C,C-double bond. The reaction mixture contained also a small amount of oxime **5**. The overall yield of products is close to quantitative and the ratio **4a/6** is predetermined by the ratio of silyl enol ethers **2a** and **2b**, respectively (cf. entries 3 and 4, Table 1). Hence one may conclude, that *N*,*N*-bis(silyloxy)-enamine **4a** emerged from **2a** and oxime **6** from **2b.**

The absence of silyl nitronates **3** in the reaction mixture does not seem unexpected, as the rate of silylation of silyl nitronates with Me_3SiOTf/Et_3N exceeds the rate of initial silylation of starting ANC, as was previously reported.[17] The high stereoselectivity of the formation of the C,C-double bond in *N*,*N*-bis(silyloxy)enamines upon silylation

‡ It is reasonable to suppose, that the employment of large excess of Me_3SiOTf/Et_3N gives rise to the mixture of silyl nitronates **3a** and **3b**, which transforms into the mixture of nitro compounds **2a** and **2b** upon quenching. However, the quenching of the reaction mixture (entry 2, Table 1) with MeOD (the enrichment is more then 60%) does not lead to the introduction of deuterium in the nitro compounds **2a** and **2b** (according to ^1H and ^{13}C NMR).



Scheme 2.

is well known,[7,17,18] as well as the fact that *N*,*N*-bis(silyloxy)enamines are prone to rearrange into 2-silyloxyoximes.[17] Therefore, the stereoselectivity of formation of *N*,*N*-bis(silyloxy)enamine **4a** and the observation of the product of its rearrangement in the reaction mixture seems to be a rather expected result.

Additional comments are warranted in order to explain the presence of silylated oxime **6** among the products of silylation. It is beyond any doubt, that the main precursor of **6** under these conditions is a tentative intermediate **4b**, which formed from silyl enol ether **2b** upon double silylation. Apparently, *N*,*N*-bis(silyloxy)enamine **4b** undergoes stereoselective elimination of Me_3SiOH to give the *E*-isomer of oxime **6** and the ease of this process can be explained by the facile formation of stabilized cation **A** (Scheme 2). The driving force behind this reaction is the cleavage of a weak N,O-single bond in electron enriched *N*,*N*-bis(silyloxy)enamine **4b** along with formation of the thermodynamically stable unsaturated oxime **6**.

Further increase of the temperature of silylation up to 0°C and a longer exposure allows us to obtain the mixture of oximes **5** and **6** with high overall yield (entry 5, Table 1). In the light of the above mentioned, the formation of these products does not require additional explanations. However, it should be noted, that the ratio of **5** and **6** is 1:2.9, which does not correlate with the starting ratio of silyl enol ethers **2a** and **2b** (1:1). This discrepancy might be due to well-known fact of the low yields of the rearrangement of *N*,*N*-bis(silyloxy)enamines. Obviously, the increase of the yield of **6** is connected with the competitive elimination of Me_3SiOH from **4a**.[§]

The desilylation of the mixture **5**+**6** upon treatment with NH_4F in MeOH allows us to isolate the *E*-isomer of the known enoxime **12**[19] with satisfactory yield (Scheme 1).

As was mentioned in the first part of the article, the elevation of temperature and the increase of excess of silylating reagent leads to the realization of hitherto unknown processes giving rise to nitriles **8** and **9**. The precursors of these nitriles are the oximes **6** and **5**, respectively. The rates of these reactions are essentially lower than those for already discussed transformations. Me_3SiOTf serves as Lewis acidic mediator of the transformations of **5** and **6** into **9** and **8**.

The intermediacy of the *E*-isomer of dienenitrile **7** in the transformation of **6** into **8** is unambiguously established upon variation of the ratio of reagents and the reaction time (entries 6 and 7, Table 1). The first step of this process is the stereoselective elimination of Me_3SiOH from the CH=N fragment with retention of configuration of the internal C,C-double bond. The transformation of oximes into nitriles upon treatment with Me_3SiOTf/Et_3N was previously unknown[‖]. Taking into account the formation of **9**, we assume, that this process might be general.

The second step of the observed transformation **6**→**8** is of considerable interest. It consists of the stereoselective silylation of the dienenitrile **7** affecting the α-carbon atom relative to the CN-group[¶]. This step proceeds with entire inversion of configuration of the internal C,C-double bond in dienenitrile **7**. The transformation **7**→**8** most likely includes the intermediacy of cation **B**, which eliminates triflic acid to give linear intermediate **C**. The latter suffers a smooth rearrangement into the thermodynamically stable *E*-isomer of nitrile **8** (Scheme 3). An alternative mechanism of the transformation **7**→**8** is possible (Scheme 4).

The desilylation of nitrile **8** could be realized in high yield and with entire retention of configuration of the C,C-double bond[††] (Schemes 1 and 3). Owing to this, the found process could appear to be a convenient way for the *E*,*Z*-isomerisation of β-substituted conjugated enenitriles. However, we have isomerised the known enenitrile *E*-**11** into *Z*-**11** with an overall yield of 75% (Scheme 3, 80% for the step *E*-**11**→**8**, entries 9 and 10, Table 1, and 91% for the step **8**→*Z*-**11**). The intermediacy of nitrile **7** also was rigorously established (entry 8, Table 1).

It seems reasonable to discuss briefly the other potential option for the application of enenitrile **8** and related structures. α-Silylated enenitriles are the only known equivalents of vinyl carbanions of the general type $[RR'C{=}C{-}CN]^-$ and they react with some electrophiles in the presence of F^- anions.[20] Therefore, the silylation of enenitriles or their precursors enaldoximes[‡‡] with Me_3SiOTf/Et_3N might be a

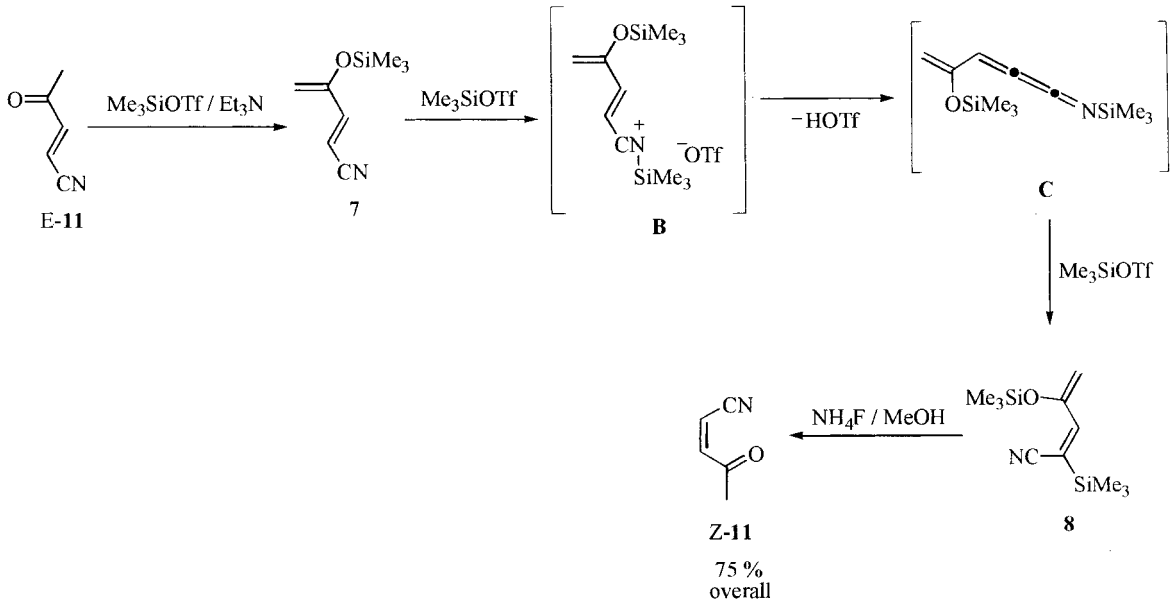
[§] A similar process has been reported previously for the example of $MeOOCCH_2CH{=}CHN(OSiMe_3)_2$, see Ref. [4]

[‖] A similar elimination was postulated once when ANC have been treated with Me_3SiI (the aldoximes have been generated in situ from primary nitro compounds). However, this process was not smooth: Olah, G. A.; Narang, S. C.; Field, L. D.; Fung, A. P. J. *Org. Chem.* **1983**, *48*, 2766 - 2767.

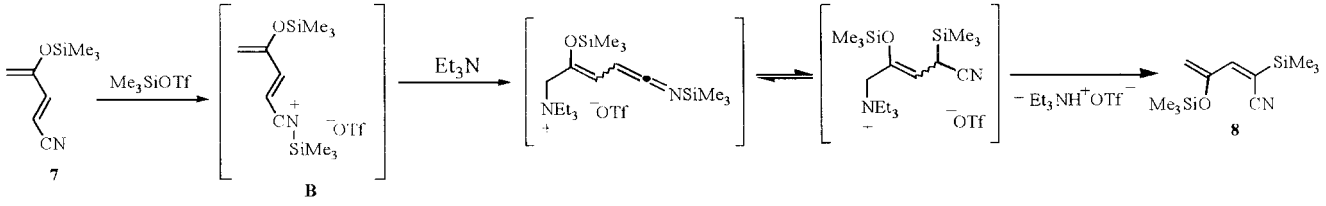
[¶] We know only two somewhat similar silylations of α,β-unsaturated nitriles mediated by Me_3SiI/Et_3N at 120°C to give moderate yields of α-silylated nitriles (see: Yamashita, H.; Reddy, N. P.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1510 - 1513). However, the authors proposed a different mechanism, which includes initial γ-C–H deprotonation. Obviously, this mechanism could not be operative in our case.

[††] This is in accordance with the normal way of protodesilylation in alkenyl silanes, indicating no free linear carbanions generation in reaction conditions (see: Weber, W. P. *Silicon Reagents for Organic Synthesis*, Springer, Berlin, **1983**, 85).

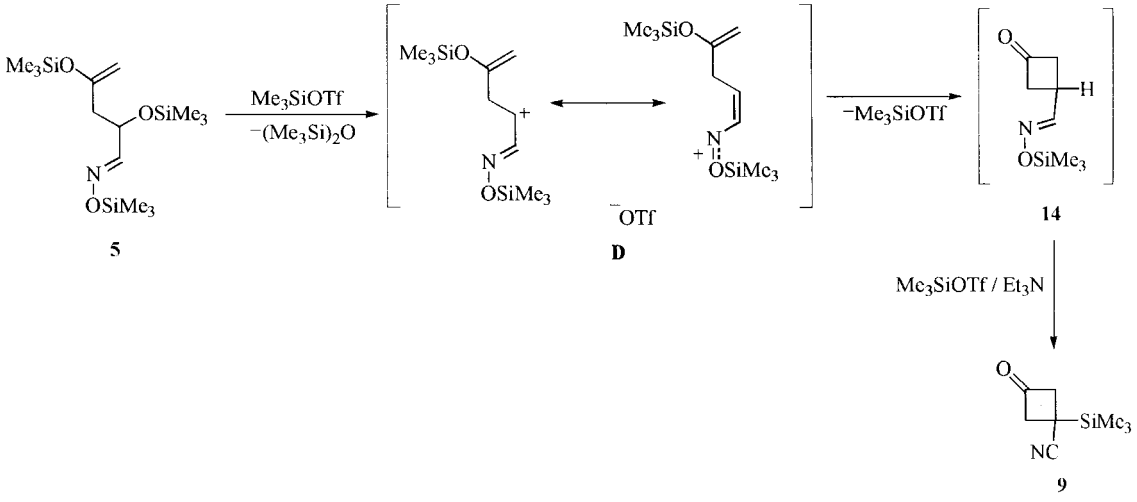
[‡‡] For the preparation of α,β-unsaturated aldoximes from ready available ANC via silylation see: ref.[3–6]



Scheme 3.



Scheme 4.



Scheme 5.

convenient method for the preparation of these interesting building blocks.

The formation of nitrile **9** is the other interesting process, which was found upon silylation of nitro-ketone **1** with an excess of Me_3SiOTf/Et_3N. The obvious pathway of its formation could be represented by the sequence **1→2a→3a→4a→5→9**.

It is likely that the step **5→9** proceeds via the generation of cationic intermediate **D**, which suffers intramolecular cyclization into ketone **14** followed by transformation of the CH=NOSiMe$_3$-group into the CN-group and silylation of the resulting nitrile affecting the α-carbon atom likewise the discussed reaction **6→8** (Scheme 5).[§§]

[§§] The sequence of steps was chosen arbitrary and the initial formation of the nitrile group followed by cyclization is possible.

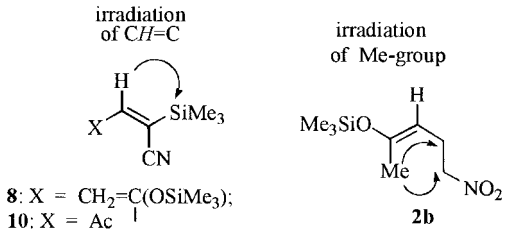


Figure 1.

The mixture of nitriles **8** and **9** could be separated by flash chromatography at low temperature (−78°C), as the regular separation at room temperature is complicated by the desilylation of nitrile **8** into keto-nitrile **10**, which has the same R_f as its cyclic isomer **9**.[IIII] The conversion of **8** into **10** on silica gel at room temperature is 80% in 1.5 h and keto-nitrile **10** could be obtained with good yield at prolonged exposure.

The complete desilylation of nitrile **9** upon the treatment with NH_4F in MeOH proceeds with good yield to give the known keto-nitrile **13**.[21]

4. Determination of the structure and double bond configuration of the products and intermediates

All obtained products and intermediates of silylation of ketone **1** were characterized with NMR and IR spectra.

The composition of isomeric silyl enol ethers **2a** and **2b**, nitriles **8** and *Z*-**11** was confirmed by means of micro-analysis. The structure of compounds **9** and **10** was confirmed by their transformations into known nitrile **13** and described herein *Z*-**11**, respectively.

The recorded NMR and IR spectra for all known products were in good agreement with literature data.

The configuration of the internal disubstituted C,C-double bond in compounds **4a**, **6**, **7**, *E*-**11**, *Z*-**11** and **12** was defined using the values of corresponding $^3J_{H,H}$ coupling constants.[¶¶] The *E*-configuration of the trisubstituted C,C-double bond in compounds **2b**, **8** and **10** was assigned by means of nuclear Overhauser effect measurements (Fig. 1).

The configuration of the C,N-double bond in oximes **6** and **12** was determined on the basis of the values of the chemical shift of the proton in the CH═N-moieties using the rule, that this proton in the *syn*-isomer is shifted 0.5–0.6 ppm upfield compared with the analogous signal in the *anti*-isomer.[22] The *anti*-configuration of product **5** was assigned by comparing the observed chemical shift of the CH═N proton with the chemical shifts of the same protons in known similar compounds.[17]

[IIII] Employment of rapid flash chromatography at 20°C gives rise to slight conversion of **8** into **10** (max. 10%) and this method is the most convenient for the isolation of **8**.

[¶¶] The large value of the $^3J_{H-H}$ coupling constant (13.4–16.4) is typical for *trans* α,β-disubstituted alkenes: Hesse, M.; Meier, H.; Zeeh, B. *Spectroskopische Methoden in der Organischen Chemie*, *Georg. Thieme Verlag*, *Stuttgart* , **1995**, 108 (in German).

5. Conclusion

The entire utilization of the oxidizing potential of the nitro group was accomplished upon silylation of the sterically unhindered nitro-ketone **1** via cleavage of the weak N–O bonds. The formation of new multiple C,C- and C,N-bonds took place.

Several interesting reactions were disclosed. Further research will be focused on the application of these processes in organic synthesis.

6. Experimental

6.1. General

NMR spectra were recorded on Bruker AM-300 instrument. Chemical shifts were measured relative to solvent residual peak (7.26 ppm for ^1H and 77.16 ppm for ^{13}C)[23], internal reference ($SiMe_4$, 0 ppm, for ^{29}Si) and external reference ($MeNO_2$, 0 ppm, for ^{14}N). The INEPT pulse sequence[24] was used for ^{29}Si signals observation. IR spectra were recorded on Bruker 'VECTOR 22'.

Reagents: commercially available Et_3N, Me_3SiCl, DBU, and $(Me_3Si)_2NH$ were freshly distilled with CaH_2, Me_3SiOTf was distilled and stored with few drops of $SiMe_4$, Me_3SiBr was freshly distilled and stored with Cu shavings. *n*-BuLi in hexane (ca. 1.5 mol/L) was used as purchased from 'Merck'. Reactions were carried out in dry argon atmosphere using CH_2Cl_2 freshly distilled with CaH_2. Dry THF and Et_2O were obtained by boiling with Na/Ph_2C═O followed by distillation. All other solvents were distilled prior to use.

Merck TLC plates were used for chromatographic analysis and Fisher silica gel (particle size 32–63 μm) was used for flash column chromatography. The flash-chromatography at −78°C was carried out using a column equipped with freezing jacket filled with dry ice/acetone.

Starting 5-nitro-pentan-2-one **1**[25] and *E*-4-oxo-pent-2-enenitrile *E*-**11**[26] were obtained according to the known procedures. **1**, colourless liquid, bp 118–120°C/10 (lit.[25] bp 117–129°C/10 Torr); ν_{max} (KBr) 1716 (s, C═O), 1554 (s, NO_2), 1372 (m, NO_2) cm^{-1} (in agreement with lit.[25] data); δ_H (300.13 MHz, $CDCl_3$) 4.40 (2H, t, ^3J=6.5 Hz, CH_2NO_2), 2.58 (2H, t, ^3J=6.5 Hz, $CH_2C(O)$), 2.21 (2H, qt, ^3J=6.5 Hz, CH_2), 2.15 (3H, s, *Me*C(O)) (in agreement with lit.[25] data); δ_C (75.47 MHz, $CDCl_3$) 206.5 (*C*═O), 74.3 (CH_2NO_2), 39.0 ($CH_2C(O)$), 29.6 (*Me*), 20.9 (CH_2); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) 0.7 ($\Delta\nu_{1/2}$ 90 Hz, NO_2). *E*-**11**, yellowish solid, 75–80°C/40 Torr (lit.[26] bp 73°C/11 Torr); mp 26–27°C (lit.[26] mp 27°C); ν_{max} (KBr) 2226 (w, CN), 1709 (s, C═O) cm^{-1} (in agreement with lit.[27] data); δ_H (300.13 MHz, $CDCl_3$) 6.94 (1H, d, ^3J=16.5 Hz, *CH*═CHCN), 6.31 (1H, d, ^3J=16.5 Hz, CH═*CH*CN), 2.37 (3H, s, *Me*) (in agreement with lit.[28] data); δ_C (75.47 MHz, $CDCl_3$) 194.5 (*C*═O), 145.1 (*CH*═CHCN), 115.9 (*C*N), 110.9 (CH═*C*HCN), 28.9 (*Me*); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −106 ($\Delta\nu_{1/2}$ 520 Hz, *CN*).

6.2. General procedure for silylation with Me_3SiOTf/Et_3N (GP)

To a vigorously stirred solution of starting compound (1.50 mmol) in CH_2Cl_2 (1.5 mL) at −78°C (dry ice/acetone) was added in one portion the defined amount of neat Et_3N. Then the defined amount of Me_3SiOTf in CH_2Cl_2 (1 mL) was added dropwise in 10 min at −78°C. Dry ice/acetone bath was removed (unless the reaction was carried out at −78°C) and the reaction mixture was stored at stirring in conditions indicated in Table 1. For quenching the reaction mixture was recooled to −30°C and petroleum ether (10 mL) was added (the quenching at −78°C was made in case of silylation at −78°C, see entry 2, Table 1). MeOH (0.5 mL) was added to vigorously stirred solution, reaction mixture was maintained for 5 min and then poured into the two-phase mixture of H_2O (20 mL) and petroleum ether (10 mL). The organic phase was washed consecutively with the solution of $NaHSO_4 \cdot H_2O$ (0.11 g) in H_2O (20 mL), H_2O (10 mL), and brine (10 mL), dried with Na_2SO_4 and concentrated in vacuo to provide the crude product. The yields were determined by means of ^1H NMR with a quantitative standard ($ClCH_2CH_2Cl$, the accuracy is ±3%) or by distillation in short-path apparatus.

6.2.1. Mixture of trimethyl-[1-(3-nitro-propyl)vinyloxy]-silane (2a) and (*E*)-trimethyl-(1-methyl-4-nitro-but-1-enyloxy)-silane (2b). a. Treatment of the ketone **1** (197 mg, 1.50 mmol) with Me_3SiOTf (1.20 mL, 6.32 mmol) and Et_3N (0.94 mL, 6.75 mmol) according to GP (−78°C, 2 h) gave the mixture of two title compounds **2a** and **2b** (167 mg, overall 82% after distillation, mol. ratio 1:1, colourless oil), bp 44–45°C/0.1 Torr; (Found: C, 47.3; H, 8.5; N, 6.9; Si, 14.0. $C_8H_{17}NO_3Si$ requires C, 47.26; H, 8.43; N, 6.89; Si, 13.81%); ν_{max} (KBr) 1555 (s, NO_2), 1381 (m, NO_2), 1254 (m, $SiMe_3$), 847 (s, $SiMe_3$) cm^{-1}. For **2a** δ_H (300.13 MHz, $CDCl_3$) 4.40 (2H, t, ^3J=7.0 Hz, CH_2NO_2), 4.09 (2H, m, CH_2=C), 2.16 (4H, m, $(CH_2)_2$), 0.21 (9H, s, SiMe_3); δ_C (75.47 MHz, $CDCl_3$) 156.7 (CH_2=*C*), 91.4 (CH_2=C), 74.7 (CH_2NO_2), 33.2 (CH_2), 24.7 (CH_2), 0.1 (SiMe_3); δ_{29Si} (59.63 MHz, $CDCl_3$) 18.1 (CO*Si*Me_3). For **2b** δ_H (300.13 MHz, $CDCl_3$) 4.40 (1H, m, C*H*=C), 4.32 (2H, t, ^3J=7.0 Hz, CH_2NO_2), 2.66 (2H, qd, ^3J=7.0, 1.0 Hz, CH_2), 1.79 (3H, m, *Me*), 0.20 (9H, s, SiMe_3); δ_C (75.47 MHz, $CDCl_3$) 150.7 (CH=*C*), 101.2 (*C*H=C), 75.3 (CH_2NO_2), 24.0 (CH_2), 22.6 (*Me*), 0.8 (SiMe_3); δ_{29Si} (59.63 MHz, $CDCl_3$) 17.5 (CO*Si*Me_3). For both **2a** and **2b** δ_{14N} (21.69 MHz, $CDCl_3$) 4.8 ($\Delta\nu_{1/2}$ 110 Hz, *N*O_2).

b. To a stirred solution of $(Me_3Si)_2NH$ (0.31 mL, 1.50 mmol) in THF (4 mL) a solution of *n*-BuLi in hexane (0.83 mL of ca. 1.5 mol/L, 1.25 mmol) was added at 0°C. The mixture was stirred for 20 min at 0°C and cooled down to −78°C. A solution of nitro ketone **1** (66 mg, 0.50 mmol) in THF (10 mL) was then added dropwise and the reaction mixture was stirred for 1 h at −78°C. After the addition of the solution of Me_3SiCl (0.21 mL, 1.67 mmol) in THF (1 mL) the resulting mixture was allowed to warm to ambient temperature and evaporated carefully in vacuo. The residue was diluted with petroleum ether (20 mL) and poured into H_2O (20 mL). The organic layer was separated, washed with H_2O (10 mL) and brine (10 mL), dried with Na_2SO_4 and evaporated in vacuo to give the mixture of two title compounds **2a** and **2b** (93 mg, 89% by NMR, mol. ratio 1:2.6, respectively, yellowish oil), which was sufficiently pure for utilization in following transformation.

6.2.2. Mixture of *O*-(1,1,1-trimethylsilyl)-*N*-[(1,1,1-trimethylsilyl)oxy]-*N*-{(1*E*)-4-[(1,1,1-trimethyl-silyl)oxy]-1,4-pentadienyl}hydroxylamine (4a), 2,4-bis[(1,1,1-trimethylsilyl)oxy]-4-pentenal O^1-(1,1,1-trimethylsilyl)oxime (5) and (2*E*)-4-[(1,1,1-trimethylsilyl)oxy]-2,4-pentadienal O^1-(1,1,1-trimethylsilyl)oxime (6). a. Treatment of the ketone **1** (197 mg, 1.50 mmol) with Me_3SiOTf (1.20 mL, 6.32 mmol) and Et_3N (0.94 mL, 6.75 mmol) according to GP (−30°C, 1 h) gave the mixture of three title compounds **4a**, **5** and **6** (447 mg, overall 99% by ^1H NMR, mol. ratio 5:1:6.4, respectively; *syn*-**6**:*anti*-**6**=1:3.3, yellowish oil). For **4a** δ_H (300.13 MHz, $CDCl_3$) 6.03 (1H, dt, ^3J=13.5, 1.5 Hz, CH=C*H*N), 5.52 (1H, dt, ^3J=13.5, 7.5 Hz, C*H*=CHN), 4.05 (2H, m, CH_2=C), 2.71 (2H, d, ^3J=7.5 Hz, CH_2), 0.20 (9H, s, COSiMe_3), 0.19 (18H, s, NOSiMe_3); δ_C (75.47 MHz, $CDCl_3$) 157.4 (CH_2=*C*), 144.3 (CH=*C*HN), 118.1 (*C*H=CHN), 90.5 (CH_2=C), 36.4 (CH_2), 0.9 (SiMe_3), 0.3 (SiMe_3); δ_{29Si} (59.63 MHz, $CDCl_3$) 25.9 (NO*Si*Me_3), 17.5 (CO*Si*Me_3). For **5** δ_H (300.13 MHz, $CDCl_3$) 7.35 (1H, d, ^3J=7.5 Hz, C*H*=N), 4.46 (1H, m, C*H*OSiMe_3), 4.07 (2H, m, CH_2=C), 2.30 (2H, m, CH_2), 0.20 (SiMe_3), 0.14 (SiMe_3), 0.11 (SiMe_3); δ_C (75.47 MHz, $CDCl_3$) 156.5 (*C*H=N), 154.7 (CH_2=*C*), 92.2 (CH_2=C), 68.1 (*C*HOSiMe_3), 43.8 (CH_2), 1.5 (SiMe_3), 0.1 (SiMe_3), −0.6 (SiMe_3); δ_{29Si} (59.63 MHz, $CDCl_3$) 25.1 (NO*Si*Me_3), 18.7 (CO*Si*Me_3), 17.2 (CO*Si*Me_3). For *anti*-**6** δ_H (300.13 MHz, $CDCl_3$) 7.86 (1H, dd, ^3J=10.0 Hz, ^4J=0.5 Hz, CH=CH–C*H*=N), 6.51 (1H, ddt, ^3J=10.0, 15.5 Hz, ^5J=0.5 Hz, CH=C*H*–CH=N), 6.26 (1H, d, ^3J=15.5 Hz, C*H*=CH–CH=N), 4.47 (2H, m, CH_2=C), 0.25 (9H, s, SiMe_3), 0.23 (9H, s, SiMe_3); δ_C (75.47 MHz, $CDCl_3$) 154.8 (CH=CH–*C*H=N), 154.5 (CH_2=*C*), 136.1 (*C*H=CH–CH=N), 123.3 (CH=*C*H–CH=N), 98.7 (CH_2=C), 0.1 (SiMe_3), −0.7 (SiMe_3); δ_{29Si} (59.63 MHz, $CDCl_3$) 25.6 (NO*Si*Me_3), 19.6 (CO*Si*Me_3). For *syn*-**6** δ_H (300.13 MHz, $CDCl_3$) 7.30 (1H, d, ^3J=9.5 Hz, CH=CH–C*H*=N), 7.09 (1H, dd, ^3J=9.5, 15.5 Hz, CH=C*H*–CH=N), 6.32 (1H, d, ^3J=15.5 Hz, C*H*=CH–CH=N), 4.54 (2H, m, CH_2=C), 0.21 (9H, s, SiMe_3), 0.20 (9H, s, SiMe_3); δ_C (75.47 MHz, $CDCl_3$) 154.4 (CH_2=*C*), 151.8 (CH=CH–*C*H=N), 136.7 (*C*H=CH–CH=N), 117.4 (CH=*C*H–CH=N), 100.5 (CH_2=C), −0.2 (SiMe_3), −0.9 (SiMe_3); δ_{29Si} (59.63 MHz, $CDCl_3$) 25.2 (NO*Si*Me_3), 19.5 (CO*Si*Me_3).

b. Treatment of the mixture of **2a** and **2b** (76 mg, 0.37 mmol, molar ratio 1:2.6, respectively) with Me_3SiOTf (0.23 mL, 1.21 mmol) and Et_3N (0.23 mL, 1.67 mmol) according to GP (−30°C, 1 h) gave the mixture of three title compounds **4a**, **5** and **6** (102 mg, overall 98% by ^1H NMR, mol. ratio 12:1:36, respectively, *syn*-**6**/*anti*-**6**=1:3.3; yellowish oil).

c. Treatment of the ketone **1** (197 mg, 1.50 mmol) with Me_3SiOTf (1.20 mL, 6.32 mmol) and Et_3N (0.94 mL, 6.75 mmol) according to **GP** (0°C, 3 h) gave the mixture of two title compounds **5** and **6** (230 mg, overall 82% by ^1H NMR, mol. ratio 1:2.9, respectively, brown oil).

6.2.3. (*E*)-4-Trimethylsilyloxy-pent-2,4-dienenitrile (7). **a**. Treatment of the nitrile *E*-**11** (71 mg, 0.75 mmol) with Me_3SiOTf (0.43 mL, 2.26 mmol) and Et_3N (0.37 mL, 2.66 mmol) according to **GP** (20°C, 6 h) gave the title compound **7** (106 mg, 85% after distillation, colourless liquid); bp 45–50°C/0.2 Torr (lit.[28] bp 54°C/2 Torr); ν_{max} (KBr) 2219 (w, CN), 1256 (m, $SiMe_3$), 850 (s, $SiMe_3$) cm^{-1}; δ_H (300.13 MHz, $CDCl_3$) 6.82 (1H, d, ^3J=16.0 Hz, C*H*=CHCN), 5.63 (1H, dt, ^3J=16.0, ^5J=0.5 Hz, CH=C*H*CN), 4.65 (1H, dd, ^2J=1.5, ^5J=0.5 Hz, CH_2=C), 4.63 (1H, dd, ^2J=1.5, ^5J=1.0 Hz, CH_2=C), 0.24 (9H, s, Si*Me*$_3$); δ_C (75.47 MHz, $CDCl_3$) 152.5 (CH_2=*C*), 147.8 (*C*H=CHCN), 118.0 (*C*N), 103.0 (CH=*C*HCN), 97.5 (*C*H_2=C), 0.0 (Si*Me*$_3$); $\delta_{^{29}Si}$ (59.63 MHz, $CDCl_3$) 21.7 (CO*Si*Me_3); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −115 ($\Delta\nu_{1/2}$ 760 Hz, C*N*).

b. Treatment of the ketone **1** (98 mg, 0.75 mmol) with Me_3SiOTf (1.00 mL, 5.26 mmol) and Et_3N (0.84 mL, 6.03 mmol) according to **GP** (20°C, 24 h) gave the mixture of the title compound **7**, (*E*)-4-trimethylsilyloxy-2-trimethylsilyl-pent-2,4-dienenitrile (**8**) and 3-oxo-2-trimethylsilyl-cyclobutane-carbonitrile (**9**) (59 mg, overall 87% by ^1H NMR, mol. ratio 3.6:1:1.6, respectively, contained traces of nitriles *E*-**11** and **10**, brown oil).

6.2.4. (*E*)-4-Trimethylsilyloxy-2-trimethylsilyl-pent-2,4-dienenitrile (8). a. Treatment of the nitrile *E*-**11** (71 mg, 0.75 mmol) with Me_3SiOTf (1.00 mL, 5.26 mmol) and Et_3N (0.84 mL, 6.03 mmol) according to **GP** (20°C, 55 h) gave the title compound **8** (144 mg, 80% after distillation, colourless liquid); bp 50–55°C/0.1 Torr; (Found: C, 55.3; H, 8.9; N, 5.9; Si, 23.6. $C_{11}H_{21}NOSi_2$ requires C, 55.17; H, 8.84; N, 5.85; Si, 23.46%); ν_{max} (KBr) 2192 (w, CN), 1254 (s, $SiMe_3$), 846 (s, $SiMe_3$) cm^{-1}; δ_H (300.13 MHz, $CDCl_3$) 6.52 (1H, s, C*H*=CCN), 4.64 (1H, d, ^2J=1.5 Hz, CH_2=C), 4.61 (1H, d, ^2J=1.5 Hz, CH_2=C), 0.31 (9H, s, Si*Me*$_3$), 0.25 (9H, s, Si*Me*$_3$); δ_C (75.47 MHz, $CDCl_3$) 154.4 (CH_2=*C*), 150.8 (*C*H=CHCN), 118.6 (*C*N), 112.5 (CH=*C*$SiMe_3$), 102.5 (*C*H_2=C), 0.0 (Si*Me*$_3$), −2.1 (Si*Me*$_3$); $\delta_{^{29}Si}$ (59.63 MHz, $CDCl_3$) 21.5 (CO*Si*Me_3), 2.3 (C*Si*Me_3); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −114 ($\Delta\nu_{1/2}$ 1085 Hz, C*N*).

b. Treatment of the ketone **1** (25 mg, 0.19 mmol) with Me_3SiOTf (0.40 mL, 2.11 mmol) and Et_3N (0.32 mL, 2.30 mmol) according to **GP** (20°C, 50 h) gave the mixture of title compound **8** and 3-oxo-2-trimethylsilyl-cyclobutane-carbonitrile (**9**) (30 mg, overall 72% by ^1H NMR, mol. ratio 2.6:1, respectively, contained traces of **10**, brown oil). The resulting mixture was distilled at 50–60°C/0.1 Torr and then subjected to rapid flash-chromatography to give pure title compound **8** (20 mg, 44%, colourless liquid, R_f (EtOAc/petrol. ether 1:3) 0.55) and the mixture of compounds **9** and **10** (5 mg, overall 15%, mol. ratio 1:1, yellowish oil, R_f (EtOAc/petrol. ether 1:3) 0.20 for both)

6.2.5. 3-Oxo-2-trimethylsilyl-cyclobutane-carbonitrile (9). The silylation of the ketone **1** (25 mg, 0.19 mmol) according to **GP** (20°C, 50 h) with Me_3SiOTf (0.40 mL, 2.11 mmol) and Et_3N (0.32 mL, 2.30 mmol) gave the mixture of title compound **9** and (*E*)-4-trimethylsilyloxy-2-trimethylsilyl-pent-2,4-dienenitrile (**8**) (30 mg, overall 72% by ^1H NMR, mol. ratio 1:2.6, respectively, contained traces of **10**, brown oil). The resulting mixture was distilled at 50–60°C/0.1 Torr and then subjected to rapid flash-chromatography at −78°C to give title compound **9** (5.4 mg, 17%, yellowish oil, R_f (EtOAc/petrol. ether 1:3) 0.20) and (*E*)-4-trimethylsilyloxy-2-trimethylsilyl-pent-2,4-dienenitrile (**8**) (22 mg, 49%, colourless liquid).

For **9**. ν_{max} (KBr) 2220 (w, CN), 1796 (s, C=O), 1258 (m, $SiMe_3$), 847 (s, $SiMe_3$) cm^{-1}; δ_H (300.13 MHz, $CDCl_3$) 3.66 (2H, ddd, ^2J=15.5, ^4J=3.5, 2.5 Hz, C$H_M H_{M'}$), 3.26 (2H, ddd, ^2J=15.5, ^4J=3.5, 2.5 Hz, C$H_A H_{A'}$), 0.27 (9H, s, CSi*Me*$_3$); δ_C (75.47 MHz, $CDCl_3$) 200.4 (*C*=O), 124.0 (*C*N), 54.8 (2 *C*H_2), 11.7 (*C*$SiMe_3$), −4.4 (Si*Me*$_3$); $\delta_{^{29}Si}$ (59.63 MHz, $CDCl_3$) 11.5 (C*Si*Me_3); the ^{14}N signal is too broad to be observed.

6.2.6. 5-*aci*-nitro-pentan-2-one trimethylsilyl ether (2c). To the stirred solution of ketone **1** (66 mg, 0.50 mmol) in CH_2Cl_2 (1 mL) at 0°C neat DBU (0.09 mL, 0.60 mmol) was added. The reaction mixture was stirred for 15 min at 0°C, then Me_3SiCl (0.15 mL, 1.18 mmol) was added. The resulting mixture was allowed to warm to ambient temperature and then concentrated in vacuo. The solid residue was treated with dry petroleum ether (10 mL), filtered in a dry atmosphere, and the precipitate of DBU·HCl was washed with petroleum ether (5 mL). The combined filtrate was concentrated in vacuo to give the title compound **2c** (102 mg, 90%, colorless oil) (Caution, the silyl nitronate **2c** is sensitive to moisture and should be stored in Ar atmosphere). δ_H (300.13 MHz, $CDCl_3$) 6.17 (1H, t, ^3J=6.5 Hz, C*H*=N), 2.70 (2H, t, ^3J=7.0 Hz, CH_2C(O)), 2.44 (2H, q, ^3J=6.5 Hz, CH_2), 2.13 (3H, s, *Me*), 0.27 (Si*Me*$_3$); δ_C (75.47 MHz, $CDCl_3$) 206.0 (*C*=O), 115.2 (*C*H=N), 38.5 (CH_2C(O)), 29.2 (*Me*), 20.4 (*C*H_2), −0.4 (Si*Me*$_3$); $\delta_{^{29}Si}$ (59.63 MHz, $CDCl_3$) 25.7 (NO*Si*Me_3); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −87.0 ($\Delta\nu_{1/2}$ 590 Hz, *N*(O)OSiMe_3).

6.2.7. (*E*)-4-Oxopent-2-enal oxime (12). The mixture of **5**, *syn*-**6** and *anti*-**6** (230 mg, 1.23 mmol, mol. ratio **5**/**6**=1:2.9, respectively) obtained by GP (see entry 5, Table 1) was dissolved in MeOH (3 mL). NH_4F (10 mg, 0.27 mmol) was added and the reaction mixture was stirred at 10°C for 3 h. Then it was evaporated in vacuo, and the residue was subjected to flash-chromatography and then distilled in short-path apparatus to give the title compound **12** (95 mg, overall 56%, the mixture of *anti*-**12** and *syn*-**12**, mol. ratio 8.5:1, respectively, white solid); bp 60–110°C/0.1 Torr (lit.[19] bp 80–100°C/0.1 Torr for pure E,*anti*-**12**); mp 40–43°C (lit.[19] mp 45°C for pure E,*anti*-**12**); ν_{max} (KBr) 3263 (br, s, OH), 1671 (s, C=O), 1640 (m, C=N), 982 (s, N–O) cm^{-1}. For *anti*-**12** δ_H (300.13 MHz, $CDCl_3$) 9.53 (1H, br, s., OH), 7.88 (1H, d, ^3J=10.0 Hz, CH=CH–C*H*=N), 7.16 (1H, dd, ^3J=10.0, 16.0 Hz, CH=C*H*–CH=N), 6.38 (1H, d, ^3J=16.0 Hz, C*H*=CH–CH=N), 2.34 (3H, s, *Me*); δ_C (75.47 MHz, $CDCl_3$) 198.7 (*C*=O), 150.0 (CH=CH–*C*H=N), 136.5 (CH=*C*H–CH=N), 135.3 (*C*H=CH–CH=N), 27.4 (*Me*). For *syn*-**12** δ_H (300.13 MHz, $CDCl_3$) 9.53 (1H, br, s, OH), 7.67 (1H, dd, ^3J=9.5, 16.5 Hz, CH=C*H*–CH=N), 7.29 (1H, d, ^3J=9.5 Hz, CH=CH–C*H*=N), 6.34 (1H, d, ^3J=16.5 Hz, C*H*=CH–CH=N), 2.38 (3H, s, *Me*); δ_C (75.47 MHz, $CDCl_3$) 199.5 (*C*=O),

146.9 (CH=CH–*C*H=N), 136.0 (CH=*C*H–CH=N), 127.8 (*C*H=CH–CH=N), 27.4 (*Me*).

6.2.8. (*Z*)-4-Oxo-2-trimethylsilyl-pent-2-enenitrile (10). The enenitrile **8** (30 mg, 0.13 mmol) was brought on the column packed with silica gel (4 g in petroleum ether) and maintained for 2.5 h. Then it was eluted with EtOAc/petroleum ether 1:1. The eluent was concentrated in vacuo to give the title compound **10** (18 mg, 80%, yellowish oil, R_f (EtOAc/petrol. ether 1:3) 0.20), ν_{max} (KBr) 2197 (w, CN), 1702 (s, C=O), 1254 (m, $SiMe_3$), 847 (s, $SiMe_3$) cm^{-1}; δ_H (300.13 MHz, $CDCl_3$) 6.79 (1H, s, C*H*=CCN), 2.46 (3H, s, *Me*), 0.32 (9H, s, $SiMe_3$); δ_C (75.47 MHz, $CDCl_3$) 194.8 (*C*=O), 150.0 (*C*H=CCN), 127.1 (CH=*C*CN), 117.5 (*C*N), 29.8 (*Me*), −2.4 (CSi*Me*$_3$); $\delta_{^{29}Si}$ (59.63 MHz, $CDCl_3$) 4.5 (CS*i*Me_3); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −126 ($\Delta\nu_{1/2}$ 650 Hz, C*N*).

6.2.9. (*Z*)-4-Oxo-pent-2-enenitrile (*Z*-11). a. The distilled nitrile **8** (35 mg, 0.15 mmol) was dissolved in MeOH (0.3 mL). NH_4F (2 mg, 0.05 mmol) was added, and the reaction mixture was stirred for 3 h at 10°C. The solvent was removed in vacuo and the residue was extracted with warm petroleum ether (5×1 mL). The resulting solution was cooled and the analytically pure title compound *Z*-**11** was crystallized (13 mg, 91%, white solid), mp 34–35°C; (Found: C, 63.2; H, 5.3; N, 14.8. C_5H_5NO requires C, 63.15; H, 5.30; N, 14.73%); ν_{max} (KBr) 2225 (w, CN), 1693 (s, C=O) cm^{-1}; δ_H (300.13 MHz, $CDCl_3$) 6.78 (1H, d, ^3J=11.5 Hz, C*H*=CHCN), 5.84 (1H, d, ^3J=11.5 Hz, CH=C*H*CN), 2.46 (3H, s, *Me*); δ_C (75.47 MHz, $CDCl_3$) 194.5 (*C*=O), 144.7 (*C*H=CHCN), 115.1 (*C*N), 107.3 (CH=*C*HCN), 30.1 (*Me*); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −108 ($\Delta\nu_{1/2}$ 340 Hz, C*N*).

b. The nitrile **10** (10 mg, 0.06 mmol) was dissolved in MeOH (0.1 mL). NH_4F (0.5 mg, 0.01 mmol) was added, and the reaction mixture was stirred for 3 h at 10°C. The solvent was removed in vacuo and the residue was extracted with warm petroleum ether (2×0.5 mL). The solvent was removed in vacuo to give the title compound *Z*-**11** (5.2 mg, 91%, white solid).

6.2.10. 3-Oxo-cyclobutanecarbonitrile (13). The obtained after rapid flash-chromatography at −78°C nitrile **9** (5 mg, 0.03 mmol) was dissolved in MeOH (0.05 mL). NH_4F (0.3 mg, 0.008 mmol) was added, and the reaction mixture was stirred for 3 h at 10°C. The solvent was carefully removed in vacuo and the residue was extracted with warm petroleum ether (2×0.5 mL). The solvent was removed in vacuo to give the title compound **13** (2.3 mg, 80%, yellowish oil). ν_{max} (KBr) 2245 (w, CN), 1798 (s, C=O) cm^{-1} (in agreement with lit.[21] data).

b. The obtained after regular flash-chromatography at room temperature mixture of **10** and **9** (60 mg, 0.36 mmol, mol. ratio 1:1) was dissolved in MeOH (0.7 mL). NH_4F (2 mg, 0.054 mmol) was added, and the reaction mixture was stirred for 3 h at 10°C. The solvent was removed in vacuo and the residue was extracted with warm petroleum ether (5→1 mL). The resulting solution was evaporated and the crude product was purified by flash-chromatography (EtOAc/petroleum ether 1:5) to give the mixture of the title compound **13** and enenitrile *Z*-**11** (30 mg, overall 88%, mol. ratio 1:1, respectively, yellowish oil, R_f (EtOAc/petroleum ether 1:1) 0.39 for both **13** and *Z*-**11**). For **13**: δ_H (300.13 MHz, $CDCl_3$) 3.56 (4H, m, 2 CH_2), 3.27 (1H, m, C*H*CN); δ_H (80 MHz on 'Bruker WP-80', $CDCl_3$) 3.50 (5H, m, 2 CH_2+C*H*CN) (in agreement with lit.[21] δ_H (60 MHz on 'Varian V-60', $CDCl_3$) 3.47 (5H, m, 2 CH_2+C*H*CN)); δ_C (75.47 MHz, $CDCl_3$) 200.1 (*C*=O), 121.1 (*C*N), 53.5 (2 *C*H_2), 12.4 (*C*HCN); $\delta_{^{14}N}$ (21.69 MHz, $CDCl_3$) −124 ($\Delta\nu_{1/2}$ 440 Hz, C*N*).

Acknowledgements

This work was performed at the Scientific Educational Center for young chemists and supported by Russian Foundation of Basic Research (grant nos. 98-03-33002, 00-15-97455), and Federal Program Integration (project no. A0082).

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