Novel Me_3Si-Mediated Intramolecular Cyclisation/[4 + 2] Cyclofragmentation of β-Substituted γ-Nitro Ketones

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5-Nitro-4-phenylpentan-2-one **(1)** was found to undergo hitherto unknown Me_3SiBr/Et_3N-promoted cyclisation into the intermediate six-membered cyclic nitronate **5**. Subsequent silylation of **5** led to the corresponding 2-trimethylsilyloxy-2*H*-[1,2]oxazine **C**, which undergoes a facile [4 + 2] cyclofragmentation to give 2-phenylpropenal oxime trimethylsilyl ether **(6)** in moderate yield. The intermediacy of the open-chain trimethylsilyl nitronate **2** and the cyclic nitronate **5** was confirmed by independent experiments. The transformation of the bicyclic nitronate **8** into the 8-trimethylsilyloxyimino-7-phenyloct-6-enoic acid trimethylsilyl ester **(9)** upon silylation proved the silylation/cycloreversion to be a key step in 1,3-azadiene moiety formation. The presented sequence of reactions could be carried out in one pot in low yield by a Me_3SiOTf/Et_3N-promoted hetero-[4 + 2] cycloaddition of 2-(trimethylsilyloxy)propene to (*E*)-2-nitro-1-phenyl-ethene, followed by silylation and fragmentation of the intermediate **C**.

Introduction

The development of methods for reactivity transfer onto carbon atoms other than that possessing the nitro group in saturated aliphatic nitro-containing compounds has become an important area of research in view of the application of readily available aliphatic nitro compounds in organic synthesis.[1−3] In this paper we describe the silylation of saturated nitro aliphatic compounds as the most convenient and fruitful approach for solving this kind of problem.[1] For example, the silylation of easily prepared nitro compounds of the general type $XC^{\gamma}H(R^3)C^{\beta}H(R^2)C^{\alpha}H(R^1)NO_2$ [X is an electron-withdrawing substituent such as RC(O), CO_2R, CN etc.] has been found to lead to a variety of chemo- and stereoselective transformations promoted by silylating reagents. We recently described new reactions leading to α,β-unsaturated oximes,[4,5] *N*,*N*-bis(trimethylsilyloxy)enamines,[3,5d] *N*,*N*-divinyl-*N*-trimethylsilyloxyamines,[4] and *N*,*N*-bis(trimethylsilyloxy)amino-substituted cyclopropane and 2,3-dihydrofuran derivatives,[6] and that the outcome of silylation depends on the character of R^1, R^2, R^3 and X.

However, more experimental data upon the effect of varying the substituents is required in order to be able to predict successfully the results of these reactions. The main subject of the present article is therefore the silylation of 5-nitro-4-phenylpentan-2-one **(1)**.

Results

To our surprise, the silylation of **1** with an excess of Me_3SiBr/Et_3N (see ***i*** in Scheme 1) gives neither the anticipated *N*,*N*-bis(trimethylsilyloxy)amine **(4)**[6] (pathway 2; see also Scheme 3), nor enoxime **3**[5d] (pathway 1), but instead gives 2-phenyl propenal oxime TMS ether **(6)** (pathway 3). The structure of compound **6** was assigned by ^1H and ^{13}C NMR spectroscopy, microanalysis (see Experimental Section) and by its conversion into the known 2-phenyl propenal oxime **(7)**.[7]

Study of the Silylation Mechanism

The proposed mechanism for product **6** formation is shown in Scheme 1 (pathway 3, i.e. **1** → **2** → **5** → **B** → **C** → **6**). According to this pathway, the cyclic nitronate **5** apparently forms from the trimethylsilyl nitronate **2**. Subsequent silylation of **5** (presumably via the transient cationic adduct **B**) leads to the 5,6-dihydro-2*H*-[1,2]oxazine **C**, which then undergoes a facile concerted [4 + 2] cyclofragmentation to give the final product **6** and trimethylsilyl acetate ($AcOSiMe_3$). This is a rather complex process and therefore the suggested mechanism required additional elucidation and experimental proof. In particular, we strove to confirm the following details of the mechanism:

- the consecutive realization of reaction steps **1** → **2** → **5** → **B** → **C** → **6**
- the formation of carbonyl and 1-aza-1,3-diene moieties upon fragmentation of **C**.

Obviously, trimethylsilyl nitronate **(2)** is an intermediate in this process since silylation of the independently prepared and isolated **2**[8] (see Experimental Section) leads to **6** in the same yield under the same conditions as for **1** (see ***i*** in Scheme 1). Unfortunately, we failed to detect either intermediates **5** or **B** in the mixture of **2** and Me_3SiBr in CD_2Cl_2 by NMR spectroscopy. In order to prove the intermediacy of the nitronate **5**, we have prepared and isolated it as a 1:1 mixture of stereoisomers according to a known procedure[9]

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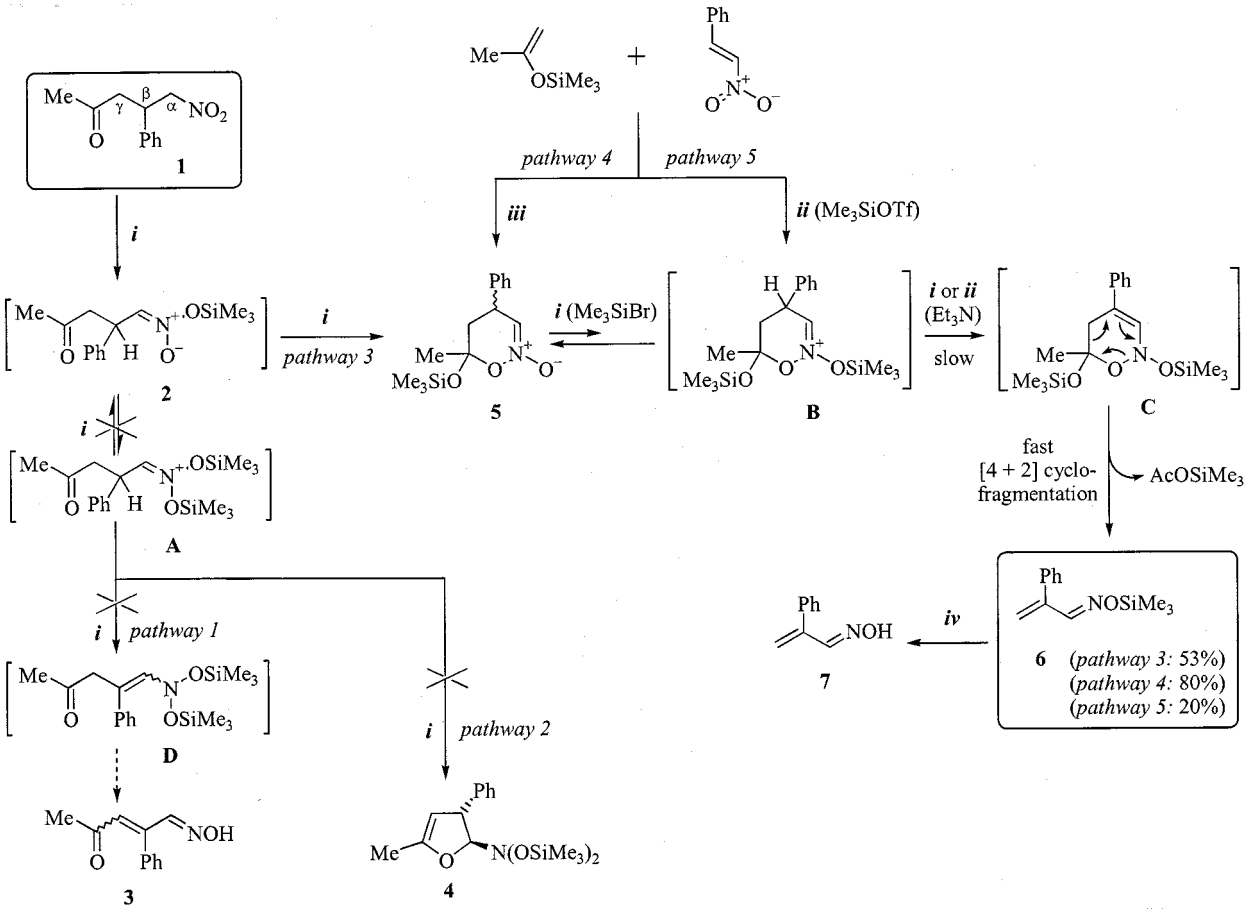


Scheme 1. i. Me_3SiBr/Et_3N in CH_2Cl_2, −30 °C; ii. Me_3SiOTf/Et_3N in CH_2Cl_2, 0 °C→20 °C; iii. (a) $(iPrO)_2TiCl_2$ in CH_2Cl_2, −30 °C, (b) $NaHCO_3$ in H_2O; iv. MeOH, 20 °C

(see ***iii*** in Scheme 1, pathway 4). Compound **5** was then subjected to the same silylation conditions (see ***i*** in Scheme 1) resulting in a high yield of the final product **6**.

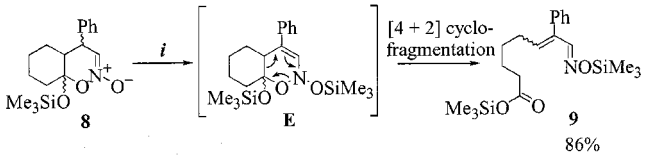
It should be noted, that the above-mentioned sequence of transformations could by carried out in one pot by Me_3SiOTf/Et_3N-promoted addition of 2-(trimethylsilyloxy)-propene to (*E*)-2-nitro-1-phenylethene (see pathway 5 in Scheme 1) followed by silylation of **5** and fragmentation of **C** to give 2-phenyl propenal oxime TMS ether **(6)**, albeit in lower yield.[10]

Thus, the cyclic nitronate **5** has been confirmed to be a key intermediate in the formation of **6**. Remarkably, such a transformation is described herein for 5,6-dihydro-4*H*-[1,2]oxazine 2-oxides for the first time.[11]

In view of the fact that the majority of trimethylsilyl nitronates react smoothly with Me_3SiBr/Et_3N to give *N*,*N*-bis(trimethylsilyloxy)enamines,[3b] the silylation of **5** under similar conditions, leading to 5,6-dihydro-2*H*-[1,2]oxazine **C** (cyclic dioxyenamine!), does not seem surprising.[12]

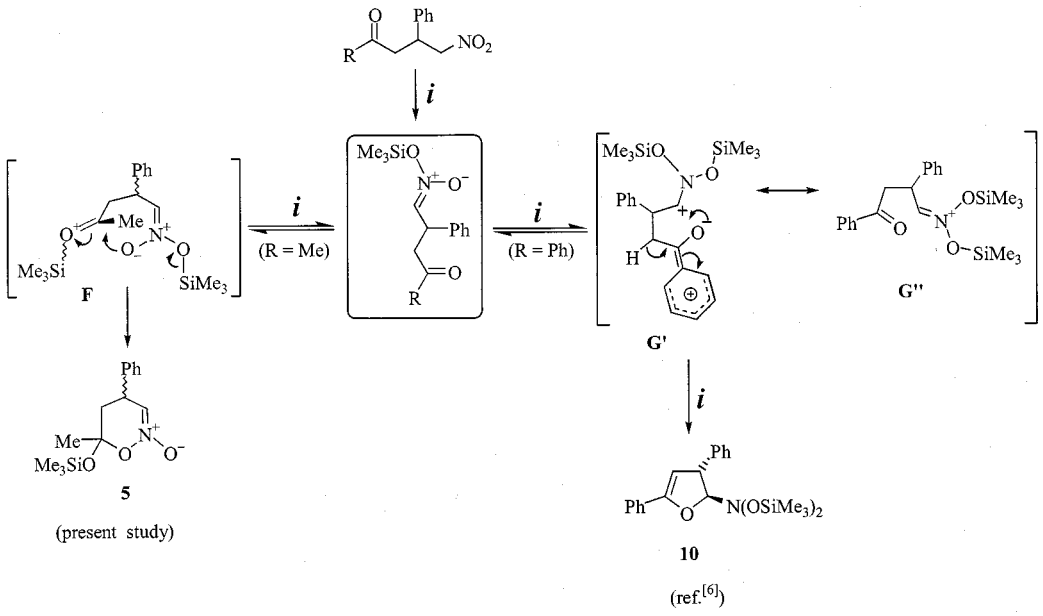
What is noteworthy is that 5,6-dihydro-2-alkyl-[13] and 5,6-dihydro-2-trimethylsilyl-2*H*-[1,2]oxazines[4] are described as isolable compounds which, however, are thermally unstable and undergo concerted [4 + 2] cycloreversion to give α,β-unsaturated imines.[4,13] The driving force behind these reactions is a cleavage of the weak endocyclic N−O bond along with formation of the strong C=O bond.[14]

The correctness of our hypothesis concerning generation of **C** with subsequent fragmentation is confirmed rigorously by the involvement of bicyclic nitronate **8** in the similar transformation upon silylation (Scheme 2) (for preparation of **8** see ref.[9]). In this case, both carbonyl and 1-aza-1,3-diene moieties emerge from the [4 + 2] cyclofragmentation of **E** and, obviously, are tethered by a carbon chain in the final product **9** (Scheme 2).



Scheme 2. i. Me_3SiBr/Et_3N in CH_2Cl_2, −30 °C

The structure of the product **9** was ascertained by ^1H and ^{13}C NMR spectroscopy, and confirmed by microanalysis. The trimethylsilyl ester **9** was obtained as a 4:1 mixture of (*E*)- and (*Z*)-isomers around the C=C double bond.[15] The assignment of the configuration of the C=C double bond was made using NOE measurements (see Experimental Section for details). A comparison of the spin-spin coupling



Scheme 3. i. Me_3SiBr/Et_3N in CH_2Cl_2, −30 °C

constant values ($^3J_{trans\text{-}^1H,^{13}C} > {}^3J_{cis\text{-}^1H,^{13}C}$)[16] supports our proposal.

Discussion

The data presented here, along with the previously reported results concerning Me_3Si-mediated transformations of γ-nitrocarbonyl derivatives,[5,6] allow us to conclude that stereoelectronic effects in silyl nitronates of type **2** have a crucial influence on the direction of the subsequent silylation. Most probably, steric requirements of the phenyl group at the β-carbon atom of **A** hinder an approach of Et_3N to the $C^β$−H bond for the proton abstraction, preventing the formation of the intermediate *N*,*N*-bis(trimethylsilyloxy)enamine (BENA) **D** (pathway 1 in Scheme 1).[17] Therefore, trimethylsilyl nitronate **(2)** undergoes another process of intramolecular cyclisation of cation **A** in dihydrofuran **4** (pathway 2 in Scheme 1) or the cyclisation of trimethylsilyl nitronate **2** into **5** followed by conversion into **C** (pathway 3 in Scheme 1).

We would like to emphasize the dramatic dependence of the course of the silylation reaction on the character of the γ-substituent in the starting nitro compounds. As seen from our preceding study,[6] the replacement of the methyl substituent by the phenyl group in the carbonyl function of **1** entirely changes the reaction course and the silylation affords 2-[*N*,*N*-bis(trimethylsilyloxy)amino]-3,5-diaryl-2,3-dihydrofurans **10** (see Scheme 3, cf. pathway 2 in Scheme 1).

This fact can be rationalized by taking into consideration the relatively higher nucleophilicity of the carbonyl oxygen in the benzoyl group as reflected in the superposition of the resonance structures **G′** and **G″**, although a specific steric influence of the carbonyl substituents on the geometry of the transition state (**F** vs. **G′**) cannot be excluded.[18] A study of the origin of this chemoselectivity is in progress.

Conclusion

In summary, we have found and studied a new transformation of some γ-functionalized aliphatic nitro compounds which is effected as a complex reaction sequence resulting in α,β-unsaturated oxime trimethylsilyl ethers with formal loss of the γ-substituent. The same result is obtained by a novel Me_3SiOTf-promoted tandem hetero[4 + 2] cycloaddition of the trimethylsilyl enol ether to the (*E*)-2-nitro-1-phenyl-ethene followed by silylation and [4′ + 2′] cyclofragmentation.

The above reactions allow us to obtain the different enoximes (including the products containing a COOH group generated by silylation), in one step, from simple and readily available starting materials. We are currently exploring the synthetic applicability of these reactions, and the results of our studies will be reported in due course.

Experimental Section

General Remarks: NMR spectra were recorded on a Bruker AM-300 instrument in $CDCl_3$ as a solvent. Chemical shifts were measured relative to internal $SiMe_4$ (δ = 0; ^1H, ^{13}C and ^{29}Si) or external $MeNO_2$ (δ = 0; ^{14}N). The INEPT pulse sequence was used for observation of the ^{29}Si signals.[19] − Starting materials were synthesized according to known procedures: 5-nitro-4-phenylpentan-2-one **(1)**,[20] (*E*)-2-nitro-1-phenylethene,[9] 2-(trimethylsilyloxy)propene (contained ca. 20 mol.% of $(Me_3Si)_2O$ as an unreactive admixture),[21] and 1-(trimethylsilyloxy)cyclohexene.[22] Reagents: commercially available Et_3N, Me_3SiCl, $Ti(OiPr)_4$, $TiCl_4$ and DBU were freshly distilled over CaH_2; Me_3SiBr was distilled with Cu shavings and Me_3SiOTf was distilled and stored with $SiMe_4$. Reactions were carried out under a dry argon atmosphere using CH_2Cl_2 freshly distilled from CaH_2. Dry toluene was obtained by boiling with Na followed by distillation. Et_2O, MeOH, and petroleum ether were distilled prior to use. The yields of products were determined by ^1H

NMR measurements (the accuracy is ±5%) relative to the internal quantitative standard $ClCH_2CH_2Cl$ [$\delta(^1H) = 3.69$] unless stated otherwise.

Preparation of 2-Phenylpropenal Oxime Trimethylsilyl Ether (6) From 5,6-Dihydro-6-methyl-4-phenyl-6-trimethylsilyloxy-4*H*-[1,2]oxazine 2-Oxide (5): The crude cyclic nitronate **5** as a 1:1 mixture of stereoisomers obtained from (*E*)-2-nitro-1-phenylethene (0.15 g, 1 mmol) (see *GP2*) was treated with Et_3N (0.32 mL, 2.3 mmol) and Me_3SiBr (0.28 mL, 2.1 mmol) according to *GP1* (vide infra) to give the desired enoxime **6** (80%). Distillation in vacuo at 64−66 °C (0.13 mbar) using a short-path apparatus provided an analytically pure sample of **6** [0.165 g, 75% isolated yield with respect to the starting (*E*)-2-nitro-1-phenylethene] as a colorless oil. − ^1H NMR: 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, Ph), 7.46 (m, 2 H, Ph), 8.09 (s, 1 H, CH=N). − ^{13}C NMR: δ = −0.8 ($SiMe_3$), 122.3 (CH_2), 127.8 and 128.2 (*C*H$_o$ and *C*H$_m$, Ph), 128.0 (*C*H$_p$, Ph), 137.4 (C_{ipso}, Ph), 142.8 (*C*=CH_2), 154.9 (C=N). − ^{29}Si NMR: δ = 26.29. − $C_{12}H_{17}NOSi$ (219.4): calcd. C 65.71, H 7.81, N 6.39; found C 65.84, H 7.72, N 6.17.

From 5-Nitro-4-phenylpentan-2-one (1). General Procedure (GP1): Neat Et_3N (0.54 mL, 3.86 mmol) was added in one portion to a solution of **1** (0.21 g, 1 mmol) in CH_2Cl_2 (2.7 mL) at −30 °C. Then the solution of Me_3SiBr (0.46 mL, 3.45 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise, and the resulting mixture was maintained with occasional stirring for 24 h at −30 °C. Petroleum ether (10 mL) was added, and the diluted reaction mixture was poured into two-phase mixture of H_2O (20 mL) and petroleum ether (10 mL). The organic phase was washed consecutively with a solution of $NaHSO_4$ (0.08 g, 0.6 mmol) in H_2O (20 mL), H_2O (10 mL), and brine (10 mL), dried with Na_2SO_4 and concentrated in vacuo to give the crude enoxime **6** (53%).

From 5-*aci*-Nitro-4-phenylpentan-2-one Trimethylsilyl Ester (2): The crude trimethylsilyl nitronate **2** obtained from **1** (0.21 g, 1 mmol) (vide infra) was treated with Et_3N (0.32 mL, 2.3 mmol) and Me_3SiBr (0.28 mL, 2.1 mmol) according to *GP1* to give the desired product **6** (53%).

From Me_3SiOTf-Promoted Addition of 2-(Trimethylsilyloxy)propene to (*E*)-2-Nitro-1-phenylethene: A solution of Me_3SiOTf (0.72 mL, 3.72 mmol) in CH_2Cl_2 (4 mL) was added to a solution of (*E*)-2-nitro-1-phenylethene (0.22 g, 1.48 mmol), Et_3N (0.54 mL, 3.87 mmol) and 2-(trimethylsilyloxy)propene (0.30 g, 1.50 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C. The resulting mixture was allowed to warm to 20 °C and maintained with occasional stirring for 18 h. Petroleum ether (10 mL) was added, and the dilute reaction mixture was poured into a two-phase mixture of saturated aqueous $NaHCO_3$ (10 mL) and petroleum ether (10 mL). The organic phase was washed consecutively with H_2O (10 mL) and brine (10 mL), dried with Na_2SO_4 and concentrated in vacuo to give the crude product **6** (20%).

Preparation of 8-Trimethylsilyloxyimino-7-phenyloct-6-enoic Acid Trimethylsilyl Ester (9): The crude bicyclic nitronate **8** as a 1:2.2:4.5:15.5 mixture of stereoisomers[9] obtained from (*E*)-2-nitro-1-phenylethene (0.15 g, 1 mmol) (see *GP2*) was treated with Et_3N (0.32 mL, 2.3 mmol) and Me_3SiBr (0.28 mL, 2.1 mmol) according to *GP1* and maintained with occasional stirring for 24 h at −30°C. The resultant mixture was then diluted with dry PhMe (10 mL) and filtered under a dry atmosphere. The precipitate of $[Et_3NH]^+ \cdot Br^-$ was washed with PhMe, and the combined filtrates were concentrated in vacuo to give the crude product **9** (86%). Distillation at 144−146 °C (0.13 mbar) using a short-path apparatus provided an analytically pure sample of **9** [0.165 g, 70% isolated yield with respect to the starting (*E*)-2-nitro-1-phenyl-ethene] as a colorless oil consisting of a 4:1 mixture of (*E*)- and (*Z*)-isomers. − **Major isomer:** ^1H NMR: δ = 0.11 (s, 9 H, $SiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 1.43 (m, 2 H, CH_2), 1.54 (m, 2 H, CH_2), 2.13 (m, 2 H, CH_2CH=C), 2.22 (t, ^3J = 7.7 Hz, 2 H, $CH_2CO_2SiMe_3$), 5.92 (t, ^3J = 7.9 Hz, 1 H, C*H*=C), 7.14−7.38 (m, 5 H, Ph), 7.95 (s, 1 H, CH=N). − NOE: upon irradiation of the signal at δ = 7.26 (*o*-protons of C_6H_5 group), there was an enhancement of the allylic CH_2 group signal at δ = 2.13. − ^{13}C NMR: δ = −0.9 ($SiMe_3$), −0.3 ($SiMe_3$), 24.4, 28.6, 28.7, and 35.5 (all CH_2), 127.0 (*C*H$_p$, Ph), 127.5 and 129.5 (*C*H$_o$ and *C*H$_m$, Ph), 135.7 (*C*=CH), 137.0 (C_{ipso}, Ph), 139.2 (*C*H=C), 157.1 (dd, $^1J^1_{H,}{}^{13}_{C}$ = 163.9 Hz, $^3J^1_{H,}{}^{13}_{C}$ = 8.9 Hz, *C*H=N), 173.9 (C=O). − ^{29}Si NMR: δ = 23.27 and 25.94. − **Minor Isomer:** ^1H NMR: δ = 0.20 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 1.53 (m, 2 H, CH_2), 1.68 (m, 2 H, CH_2), 2.33 (t, ^3J = 7.6 Hz, 2 H, $CH_2CO_2SiMe_3$), 2.40 (m, 2 H, CH_2CH=C), 5.99 (t, ^3J = 7.9 Hz, 1 H, C*H*=C), 7.14−7.38 (m, 5 H, Ph), 8.31 (s, 1 H, CH=N). − NOE: upon irradiation of the CH_2CH=C signal at δ = 2.40, there was an enhancement of the C*H*=N signal at δ = 8.31. − ^{13}C NMR: δ = −0.3 (both $SiMe_3$), 24.6, 28.3, 29.0, and 35.6 (all CH_2), 127.1 (*C*H$_p$, Ph), 127.7 and 128.2 (*C*H$_o$ and *C*H$_m$, Ph), 134.4 (*C*=CH), 138.0 (*C*H=C), 139.6 (C_{ipso}, Ph), 151.4 (dd, $^1J^1_{H,}{}^{13}_{C}$ = 164.1 Hz, $^3J^1_{H,}{}^{13}_{C}$ = 10.5 Hz, *C*H=N). − ^{29}Si NMR: δ = 23.18 and 25.47. − $C_{20}H_{33}NO_3Si_2$ (391.7): calcd. C 61.33, H 8.49, N 3.58; found C 61.05, H 8.68, N 3.61.

Preparation of 5,6-Dihydro-4-phenyl-4*H*-[1,2]oxazine-2-oxides 5 and 8. General Procedure (GP2):[9] A solution of (*E*)-2-nitro-1-phenylethene (0.15 g, 1.0 mmol) in CH_2Cl_2 (2.0 mL) was added dropwise to a solution of (iPrO)$_2TiCl_2$ at −30 °C [freshly prepared by addition of $TiCl_4$ (0.16 mL, 1.46 mmol) to a precooled (0−10 °C) solution of (iPrO)$_4$Ti (0.46 mL, 1.56 mmol) in CH_2Cl_2 (40 mL), followed by stirring at ambient temperature for 20 min)], and the resulting bright-yellow solution was stirred at this temperature for 20 min, then cooled down to −90 °C, and trimethylsilyl enol ether (1.12 mmol) was added. The reaction mixture was allowed to warm to −75 °C and stirred at this temperature for 2 h. It was then poured into a vigorously stirred Et_2O (30 mL)/sat. aq. $NaHCO_3$ (80 mL) bilayer. The H_2O layer was extracted with Et_2O (2 × 30 mL), and the combined organic phases were washed with H_2O (30 mL) and dried with $MgSO_4/NaHCO_3$ (1:1). Filtration and concentration in vacuo provided the desired nitronate **5** (91%) or **8** (90%), which was used in the following reaction without further purification.

Product 5: A 1:1 mixture of stereoisomers contaminated with ca. 7% of nitro ketone **1**. − ^1H NMR: δ = 0.18 (s, 9 H, $SiMe_3$), 0.29 (s, 9 H, $SiMe_3$), 1.63 (s, 6 H, both Me), 1.78 (t, ^2J = ^3J = 12.7 Hz, 1 H, CH_2 for one isomer), 2.15−2.38 (m, 1 H + 2 H, CH_2 for both isomers), 3.85 (m, 1 H, C*H*Ph), 3.96 (m, 1 H, C*H*Ph), 6.40 (m, 1 H, CH=N), 6.54 (d, ^3J = 3.9 Hz, 1 H, CH=N), 7.20−7.40 (m, 10 H, Ph).

The ^1H and ^{13}C NMR spectroscopic data for the product **8** consisting of a 1:2.2:4.5:15.5 mixture of stereoisomers are in good agreement with those described in the literature.[9]

Preparation of 5-*aci*-Nitro-4-phenylpentan-2-one Trimethylsilyl Ester (2): Neat DBU (0.16 g, 1.05 mmol) was added to a stirred solution of nitro compound **1** (0.207 g, 1 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, then Me_3SiCl (0.4 mL, 3.15 mmol) was added. The resulting mixture was allowed to warm to ambient temperature, and then concentrated in vacuo. The residue was treated with Et_2O (15 mL), the

resulting ethereal solution was filtered in a dry atmosphere, and the precipitate of DBU·HCl was washed with Et_2O (5 mL). The combined filtrate was concentrated in vacuo to give crystalline nitronate **2** (96%) which was used in the following transformation without further purification. – ^{1}H NMR: δ = 0.27 (s, 9 H, $SiMe_3$), 2.05 (s, 3 H, Me), 2.87 (dd, ^2J = 16.6 Hz, ^3J = 7.1 Hz, 1 H, CH_AH_B), 3.09 (dd, ^2J = 16.6 Hz, ^3J = 7.0 Hz, 1 H, CH_AH_B), 4.23 (m, 1 H, C*H*Ph), 6.31 (d, ^3J = 7.2 Hz, 1 H, CH=N), 7.12–7.30 (m, 5 H, Ph). – ^{13}C NMR: δ = −0.4 ($SiMe_3$), 29.6 (Me), 38.5 (*C*HPh), 46.0 (CH_2), 118.0 (CH=N), 126.9 (*C*H_p, Ph), 127.3 and 128.5 (*C*H_o and *C*H_m, Ph), 139.6 (C_{ipso}, Ph), 204.8 (C=O). – ^{29}Si NMR: δ = 26.67. – ^{14}N NMR: δ = −97 ($\Delta\nu_2 \approx 1400$ Hz).

Preparation of 2-Phenylpropenal Oxime (7): All the crude **6** obtained from nitro compound **1** (see *GP1*) was dissolved in MeOH (1 mL) and the mixture was stirred for 24 h at ambient temperature. Then the volatile components were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/petroleum ether (1:7) to give the product **7** (0.06 g, 41% isolated yield with respect to the starting nitro ketone **1**) as white crystals, m.p. 105–107 °C (ref.[7] m.p. 103 °C). – ^{1}H NMR: δ = 5.42 (s, 1 H, CH_2), 5.50 (s, 1 H, CH_2), 7.26 (br. s, 5 H, Ph), 7.86 (s, 1 H, CH=N), 8.69 (s, 1 H, NOH). – ^{13}C NMR: δ = 123.0 (CH_2), 128.2 (*C*H_p, Ph), 128.2 and 128.3 (*C*H_o and *C*H_m, Ph), 137.4 (C_{ipso}, Ph), 143.1 (CH_2=*C*), 151.5 (C=N).

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[7] The physical constants obtained for the oxime **7** are in complete agreement with those described in the literature: P. Bravo, G. Gaudiano, C. Ticozzi, A. Umani-Ronchi, *Gazz. Chim. Ital.* **1969**, *99*, 549–564.

[8] A general procedure is described in the following article: J. M. Aizpurua, M. Oiarbide, C. Palomo, *Tetrahedron Lett.* **1987**, *28*, 5361–5364.

[9] M. A. Brook, D. Seebach, *Can. J. Chem.* **1987**, *65*, 836–850.

[10] In early studies, Me_3SiOTf has been reported to be ineffective in promoting the addition of silyl enol ethers to regular nitro alkenes: A. Yoshikoshi, M. Miyashita, *Acc. Chem. Res.* **1985**, *18*, 284–290.

[11] Recently, 5,6-dihydro-4*H*-[1,2]oxazine-2-oxides were systematically studied and widely applied as 1,3-dipoles in highly stereoselective [3 + 2] cycloadditions to C=C double bonds: [11a] S. E. Denmark, A. Thorarensen, *Chem. Rev.* **1996**, *96*, 137–165. – [11b] S. E. Denmark, E. A. Martinborough, *J. Am. Chem. Soc.* **1999**, *121*, 3046–3056; and to C≡C triple bonds: [11c] D. Seebach, I. M. Lyapkalo, R. Dahinden, *Helv. Chim. Acta* **1999**, *82*, 1829–1842.

[12] Seemingly, the C^4–H bond in the cyclic intermediate **B** is sterically more accessible for the proton abstraction with Et_3N than the corresponding C^β–H bond in the open-chain analogue **A**.

[13] [13a] P. Gygax, T. K. DasGupta, A. Eschenmoser, *Helv. Chim. Acta* **1972**, *55*, 2205–2214. – [13b] E. Shalom, J.-L. Zenou, S. Shatzmiller, *J. Org. Chem.* **1977**, *42*, 4213–4216. – [13c] R. Faragher, T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1* **1979**, 258–262. – [13d] B. Hardegger, S. Shatzmiller, *Helv. Chim. Acta* **1976**, *59*, 2765–2767.

[14] We consider 5,6-dihydro-2-trimethylsilyloxy-2*H*-[1,2]oxazines of type **C** to be essentially less stable than their 5,6-dihydro-2-alkyl- or 5,6-dihydro-2-trialkylsilyl- analogues due to the destabilizing effect of the three heteroatoms in the O–N–O fragment. This effect may complicate their isolation or even observation by NMR spectroscopy.

[15] The stereochemical outcome of the [4 + 2] cyclofragmentation of **E** depends strongly on the stereoisomer ratio of the starting cyclic nitronate **8**. The variation of isomer ratios of **8** can be achieved by means of solvent modification in its synthesis (see ref.[11c]). Thus, the silylation of **8** (as a 1:3:5.8:20.5 mixture of isomers) leads to a 1:4 mixture of (*Z*)-**9** and (*E*)-**9** (overall yield 86%), respectively, whereas the treatment of **8** (as a 1:27:4:16 mixture) with the same Me_3SiBr/Et_3N gives rise to **9** as a 1.4:1 mixture of (*Z*)-**9** and (*E*)-**9** in 70% yield. Since the geometry of the formation of C=C bonds could testify to the mechanism of the [4 + 2] cyclofragmentation of intermediate **E**, the investigation of this problem requires separate efforts in the near future. The configuration of the CH=NOSiMe_3 group in both isomers of **9** was not determined, but it is equal according to NMR spectroscopic data.

[16] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie,* Georg. Thieme Verlag, Stuttgart, **1995**, 108 (in German).

[17] This is the usual way of transforming γ-functionalized aliphatic nitro compounds in the absence of branching at the β-carbon atom (see ref.[5d]).

[18] The observed difference of reactivity of γ-benzoyl and γ-acetyl nitro compounds is difficult to explain unambiguously nowadays. The collected experimental results of the silylation of substituted nitro aliphatics reveal that the reaction mechanisms are usually very complex and frequently vary, although high chemoselectivity is normally observed in each case. We are now studying the silylation of nitro compounds of general type $R^1C(O)CH_2CH(R^2)CH_2NO_2$ with a wide variation of R^1 and R^2. The summarized results will be published in due course.

[19] G. E. Morris, R. Freeman, *J. Am. Chem. Soc.* **1979**, *101*, 760–762.

[20] M. C. Kloetzel, *J. Am. Chem. Soc.* **1947**, *69*, 2271–2275.

[21] Obtained by silylation of acetone with Me_3SiCl/Et_3N in DMF in the conditions specified for butan-2-one in ref.[22]

[22] H. O. House, L. J. Czuba, M. Gall, H. D. Olmstead, *J. Org. Chem.* **1969**, *34*, 2324–2336.

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