Chemistry of *N*,*N*-Bis(silyloxy)enamines

Part 5[1])

Interaction with *N*-Trialkylsilylated Azoles. Convenient Method for the Synthesis of α-Azolyl-Substituted Oximes

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Aliphatic nitro compounds can be considered as good precursors of a wide variety of α-azolyl-substituted oximes. The double silylation of convenient aliphatic nitro compounds and the subsequent N,C-coupling of the resulting *N*,*N*-bis(silyloxy)enamines **3** with *N*-silylated azoles **4** lead to the formation of the silylated α-azolyl-substituted oximes **6**, which can be smoothly desilylated to give the target α-azolyl-substituted oximes **5**. The mechanism of the key step of this process – N,C-coupling – includes the generation of corresponding conjugated nitrosoalkenes **7** (*Schemes 4* and *5*). The contribution of the chain mechanism in the overall process is considered as well. The studies of the scope and limitations of this reaction, as well as the optimization of its conditions were accomplished. The configuration of the C=N bond in oximes was established by NMR.

1. Introduction. – *N*,*N*-Bis(silyloxy)enamines (BENA) can be used as very convenient reagents for the functionalization of the C(β) atom in readily available aliphatic nitro compounds by both electrophilic and nucleophilic reagents [2]. In former works, we already studied the interaction of BENA with various N-centered nucleophiles, including primary [3] and secondary [3][4] amines, as well as *N*-nitroamines [5]. The reactivity pattern of the BENA in these reactions is determined by the nature of the nucleophile. Alkylamines that contain an N–H bond smoothly react with BENA, while the interaction of BENA with their *N*-silylated derivatives ($>NSiMe_3$) has never been observed. In contrast to this, the reaction of BENA with *N*-nitroamines can be realized only with their silylated derivatives.

In this connection, the study of the interaction of BENA with azoles that contain two or more N-atoms in a ring is of interest. Azoles of this type resemble alkylamines as bases and, at the same time, the same azoles are close to *N*-nitroamines on the acidity scale. The successful realization of N,C-coupling of azoles with BENA would allow us to construct promising synthetic intermediates, *i.e.*, α-azolyl-substituted oximes **5** [6], from the readily available nitro compounds **1** and azoles **2** by successive silylations (**1** → **3** and **2** → **4**) followed by coupling of the resulting derivatives **3** and **4** (*Scheme 1*). The opportunity of the realization of the coupling of **3** and **4** was recently demonstrated in our preliminary communication [7]; however, various uncertainties connected with this process were also found.

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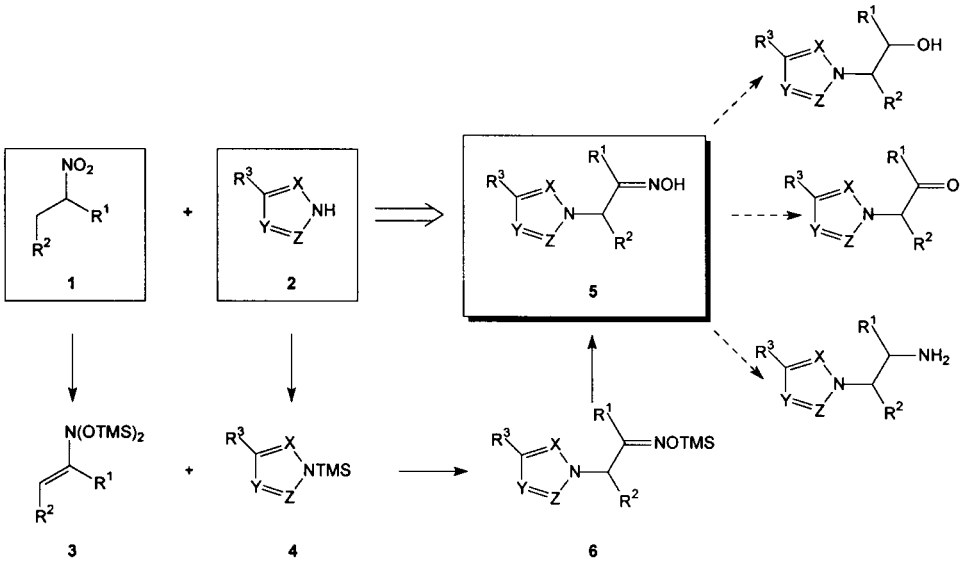
[1]) Previous communication, see [1].

Scheme 1. *Design of Azolyl Oximes* **5** *from Aliphatic Nitro Compounds*



X, Y, Z = CH, CR^3, N (no less than one fragment)
R^1, R^2, R^3 = H, alkyl, functionalized alkyl, functional group
TMS = $SiMe_3$

This paper is dedicated to the study of the mechanism, scope, and limitations of the coupling of **3** and **4**, as well as to the optimization of the reaction conditions.

2. Results and Discussion. – 2.1. *Mechanism of the Reaction of BENA with Azoles.* For the rationalization of the reactivity of BENA towards nucleophiles, a number of tentative schemes were previously suggested. *Feger* and *Simchen* proposed that BENA react with secondary amines as formal C(β) electrophiles by an S_N2' mechanism [4]. However, this interpretation is in conflict with the recently discovered [8] and quantitatively estimated [9] C(β)-nucleophilic activity of BENA[2]). The other model that was suggested for the C,C-cross-coupling reactions of BENA seems to be more realistic [10] (*Scheme 2*). According to this scheme, BENA are transformed upon the influence of Nu^1 into highly electrophilic conjugated nitrosoalkenes **7**, which can be considered as the key intermediates in the reactions of BENA with C- or N-nucleophiles (Nu^2).

For the detailed investigations of the interaction of BENA **3** with azoles **4**, we studied the reactions of the model BENA **3a** and **3a**′ with silylated 1*H*-pyrazoles **4a** and **4a**′ and 1*H*-imidazoles **4b** and **4b**′. The model reactions **3** + **4** were carried out under the standard conditions, and the process was controlled by ^{1}H-NMR monitoring of the reaction mixtures. The main results are presented in *Table 1*. These data support the formation of the active intermediate **7** (*Scheme 2*) and allow to conclude that the sp^2-

[2]) Some data presented in *Table 1* (see below) are also in conflict with the model of *Feger* and *Simchen*; this allows one to exclude this proposal from the consideration.

Scheme 2. *Possible Mechanism of Interaction of BENA* **3** *with C-Nucleophiles* (see [10])

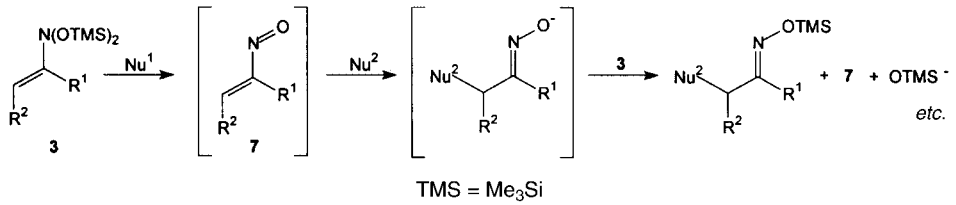
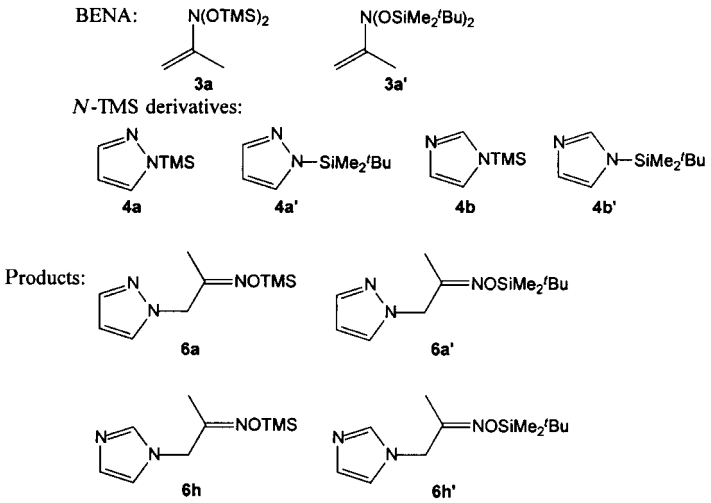


Table 1. *Study of Interaction between BENA* **3** *and* N-*Trialkylsilyl Derivatives* **4**. The starting agents:



Entry	Starting materials (mol ratio)	Reaction conditions (20°)	Catalyst or promoter (mol ratio **3**/addend)	Inductive period	Result of interaction (yield [%] by ^{1}H-NMR)
1	**3a** + **4a** (1 : 1)	0.5M in $CDCl_3$, 170 h	–	–	no reaction
2	**3a** + **4a**′ (1 : 1)	without soln., 72 h	–	–	no reaction
3	**3a** + **4b** (1 : 1)	0.5M in $CDCl_3$, 1.7 h	–	1.5 h	**6h** (93)
4	**3a** + **4b** (1 : 1)	0.5M in $CDCl_3$, 1.4 h	**6h** (1 : 0.25)	1.2 h	**6h** (89)
5	**3a** + **4b** (1 : 1)	0.5M in $CDCl_3$, 0.3 h	Et_3N (1 : 0.1)	0.15 h	**6h** (97)
6	**3a** + **4b** (1 : 1)	0.5M in petroleum ether, 0.5 h	Et_3N (1 : 0.1)	none	**6h** (85)[a])
7	**3a** + **4b**′ (1 : 1)	0.5M in $CDCl_3$, 1.7 h	–	1.5 h	**6h** + **6h**′ (96) (mol ratio **6h**/**6h**′ 1 : 9.3)
8	**3a** + **4b**′ (1 : 1)	0.5M in $CDCl_3$, 24 h	$Me_2{}^t$BuSiCl (1 : 0.1)	–	**6h**′ (97)
9	**3a**′ + **4b** (1 : 1)	neat	–	–	no reaction
10	**3a** + **4a** + **4b** (1 : 1 : 1)	0.5M in $CDCl_3$, 1.5 h	–	1.3 h	**6a** (27), **6h** (63)
11	**3a** + 1-methyl-1*H*-imidazole (1 : 1)	CH_2Cl_2, 0.2 h	–	–	decomposition of **3a** only

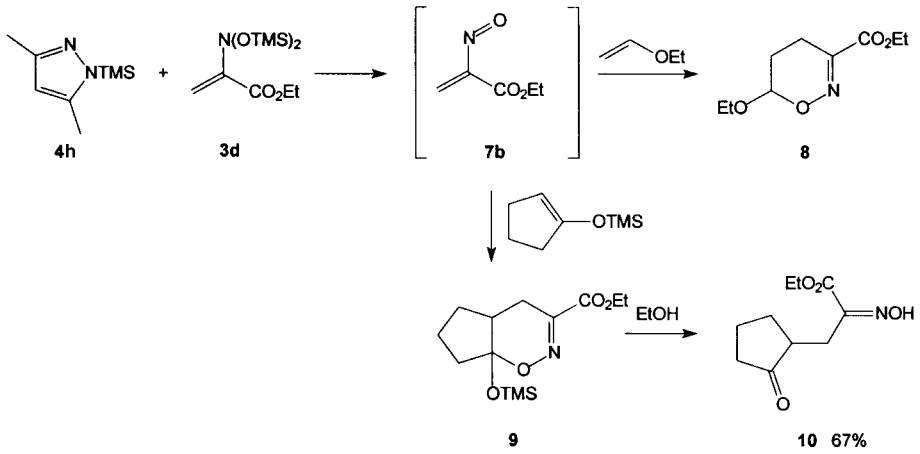
[a]) Blue color of the reaction mixture.

hybridized N-atom of the azole ring must play the role of Nu[1] triggering the transformation of BENA **3** into intermediate **7** since its shielding hampers the interaction of BENA **3** with *N*-silylated azoles (*Entries 1* and *2*, *Table 1*).

The Si-atom of BENA serves as an electrophilic center since its shielding by bulky ^{t}Bu substituents retards the reaction **3**+**4** (*cf. Entries 3* and *9*, *Table 1*). The key intermediate for the coupling of **3** and **4** should not contain any Si-fragment, and it should be less sensitive towards steric requirements than starting BENA. This was deduced from the almost quantitative transfer of the Si-label from azole **4b**′ to the target derivative **6h**′ (*Entries 7* and *8*, *Table 1*), and from the fact that the interaction of the hindered *N*-TMS-azole **4a** with BENA **3a** occurs in the presence of the less hindered azole **4b**, which is able to generate the intermediate **7** (*cf. Entries 1* and *10*, *Table 1*). An additional prove for the participation of the nitroso intermediate **7** in the reaction **3**+**4** is the appearance of a characteristic blue color [11] during the interaction of **3a** with **4b** (see *Entry 6*, *Table 1*).

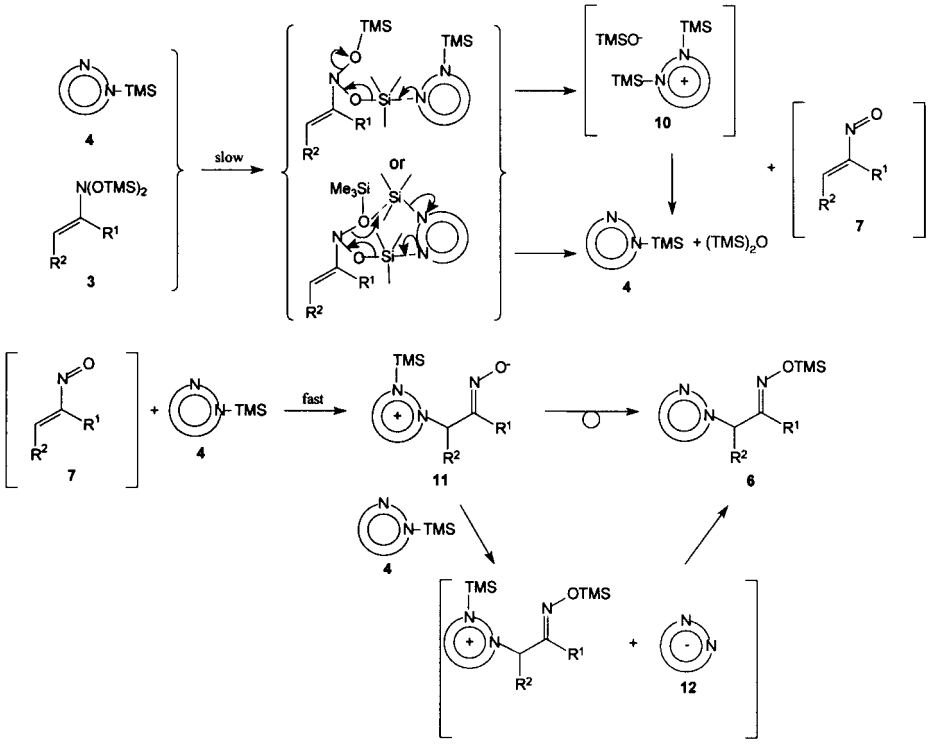
The known way of the fixation of conjugated nitrosoalkenes is their trapping by electron-enriched alkenes as the products of a [4+2] cycloaddition [11][12]; however, the reactivity of the intermediates **7** in this reaction can be very low in some cases [11]. We trapped the intermediate nitrosoalkene **7b** formed on interaction of BENA **3d** with azole **4h** by ethyl vinyl ether and by 1-[(trimethylsilyl)oxy]cyclopentene (*Scheme 3*). The cycloadducts **8** and **9**, respectively, were observed in the resulting reaction mixtures by NMR. Product **9** was also transformed into the known ketone **10** (see *Exper. Part* for the details).

Scheme 3. *Trapping of the Intermediate* **7b** *in a [4+2] Cycloaddition with Alkyl or Silyl Enolates*



The interaction of azoles with the conjugated nitrosoalkenes (step **4**+**7**) is well known [11], and therefore, the reaction **3**+**4** could be represented by *Scheme 4*. The slow step, generation of the nitroso intermediate **7**, can proceed through various transition states (in braces). The fast reaction of azole **4** with nitrosoalkene **7** results in the formation of the target product **6** *via* either intramolecular migration of the silyl group in bipolar ion **11** or interaction of the ion **11** with the next molecule of azole **4**.

Scheme 4. *Possible Mechanism of the Interaction* **3** + **4**

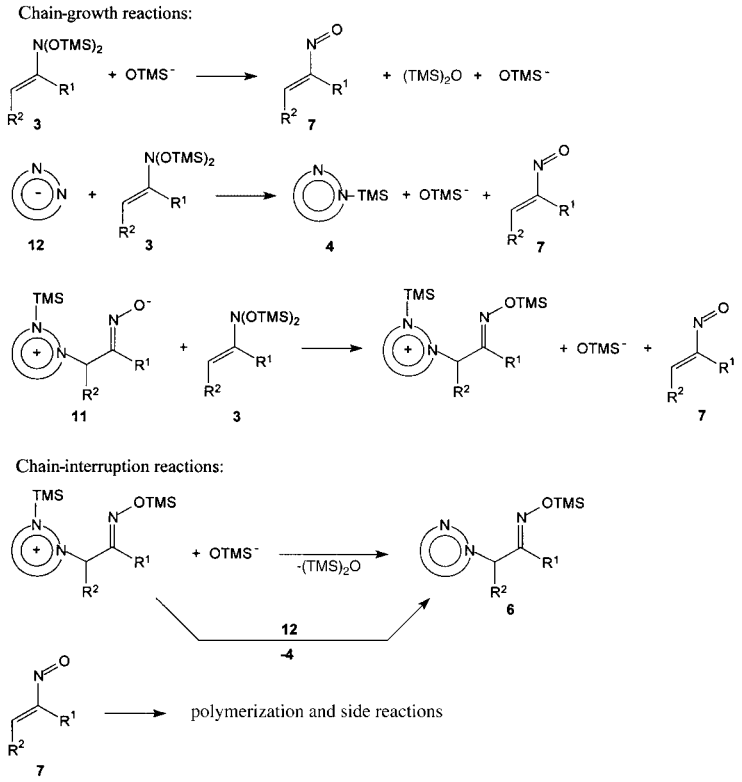


However, the observation of the inductive period (*Entries 3–5*, *7*, and *10*, *Table 1*) is not consistent with this simple model for the reaction **3** + **4** and shows that the more complicated chain mechanism is involved in the process of the N,C-coupling of **3** and **4**. Probably, the formation of the cyclic transition state, depicted in *Scheme 4* for the slow step, is likely to be retarded due to the steric demands, and Me_3SiO^-, bipolar ion **11**, and azolyl anion **12** which all exist in the reaction medium can induce the growth of the chain (*Scheme 5*).

The contribution of the chain mechanism may depend on the functionality of both interacting compounds and mainly on the sterical factors and nucleophilicity of azole **4**. Addition of the final product **6** to the reaction mixture does not affect the inductive period (*cf. Entry 3 vs. 4*, *Table 1*), while the addition of 10 mol-% of Et_3N strongly decreases the inductive period (*Entry 5*, *Table 1*). Probably, Et_3N reacts reversibly with **4**, and the generated anionic species trigger the formation of nitrosoalkenes **7** from BENA **3**.

The interaction of BENA **3** with 1-methyl-1*H*-imidazole, which can not react with the intermediate **7**, produced the polymer only (*Entry 11*, *Table 1*). The conjugated nitrosoalkenes **7** are prone to polymerization, and therefore, the very low concentration of these intermediates under the chosen reaction conditions should be maintained (*Entry 6*, *Table 1*).

Scheme 5. *Some Details of the Chain-Reaction Mechanism for the Interaction* **3** + **4**



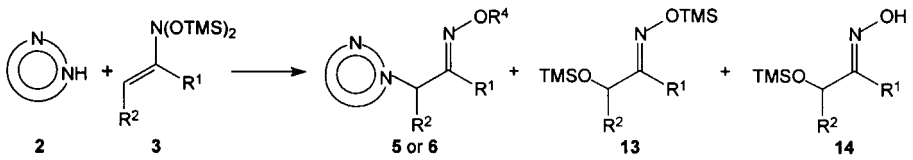
The trapping of the active anions Me_3SiO^- and **12**, which likely promote the chain reaction, can be realized with $Me_2{}^tBuSiCl$ (*Entry 8*, *Table 1*). In other words, trialkylchlorosilanes are good inhibitors of N,C-cross-coupling during the interaction of **3** and **4**.

In line with the proposed model (*Schemes 4* and *5*), the presence of at least one sp^2-hybridized N-atom in the heterocyclic counterpart is necessary to realize the process discussed. Indeed, the silylated derivatives of 1*H*-pyrrole and 1*H*-indole do not react with BENA **3**. Thus, the results obtained (*Table 1*) suggest the validity of the proposed mechanism for the interaction of BENA **3** with silylated azoles **4**, which includes a chain process and the intermediacy of the nitrosoalkenes **7** (*Schemes 4* and *5*). The sp^2-hybridized N-atom in the azoles **4** can act as a nucleophilic center twice, *i.e.*, in the first step of the process when nitrosoalkenes **7** are generated, and then on addition of the azoles **4** to **7** affording the target derivatives **6**.

Within the framework of this approach, one could try to use the N,C-coupling of non-silylated azoles **2** with BENA **3** for the preparation of the oximes **5** or **6** (*Scheme 6*). However, it is known that the reactions of BENA with various amines containing the N–H bond usually are accompanied by the rearrangement of BENA into bis-silylated derivatives **13** (the partially desilylated products **14** can also be formed

under these conditions [3][5]). The amount of the rearrangement **3** → **13** should increase along with the increase of the acidity of the N–H bond, since this process is catalyzed by *Brønsted* acids [4]. A detailed discussion of the mechanistic features of the reactions presented in *Scheme 6* will be the subject of a separate publication. Though, it is noteworthy that due to the rearrangement **3** → **13**, the reaction **2** + **3** is less convenient for the synthesis of oximes **5** than the reaction **4** + **3**.

Scheme 6. *Some Details of the Interaction* **2** + **3**



R^4 = H or TMS

2.2. *Scopes, Limitations, and Conditions Optimization of the Reaction* **4** + **3**. Based on the data concerning the mechanism of the reaction **3** + **4** (*Sect. 2.1*), a few optimized procedures for the synthesis of the final products **6** were developed. For sterically unhindered and rather nucleophilic azoles (*e.g.*, **4b** or **4c**), the reaction had to be carried out in CH_2Cl_2 solution in the presence of Et_3N (5 mol-%) as mediator (*Procedure B*). This protocol enables one to control the concentration of intermediate **7** and to control the heat production by the boiling of a solvent. The other, less reactive derivatives **4** could be converted into the products **6** by the alternative *Procedures A* or *C*, which implied the simple mixing of the components at 20° without solvent or mediator. It is noteworthy that the rearrangement **3** → **13** under the conditions of the reaction **3** + **4** was never observed. The purification of the crude target oximes **6** was performed in most cases by vacuum distillation. According to ^{1}H-NMR data, the purity of the distilled products was more than 90–95%, however, sometimes the distillation was accompanied by significant decomposition. The yields and configurations of the silyl derivatives **6a**–**w** obtained from **3a**–**e** and **4a**–**h** are summarized in *Table 2*.

The desilylation of the distilled derivatives **6** to **5** could be smoothly performed upon treatment with MeOH in the presence or absence of NH_4F. The nondistilled derivatives **6** were subjected to the disilylation after NMR analysis of the crude products (for details, see *Exper. Part*). The target oximes **5** were purified by recrystallization or by chromatography on silica gel (for yields, see *Table 2*).

In several cases, the N,C-coupling of BENA **3** with azoles **4** was not regioselective (see *Entries 6* and *11–23* in *Table 2*). The regioisomers could be separated by vacuum distillation of the derivatives **6** or by column chromatography of the desilylated oximes **5**[3]).

The preparative scope of the reaction **3** + **4** is high and allows one to synthesize a wide variety of substituted α-azolyloximes **5**, including those with the functional groups at the heterocyclic ring and at different positions of the aliphatic C-chain.

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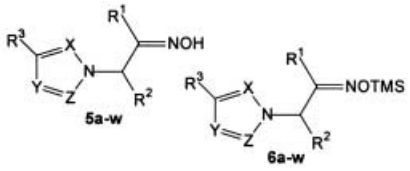
[3]) The isomerization of the derivatives **6** upon distillation *in vacuo* is likely connected with the reversibility of the addition of the azoles **4** to corresponding nitrosoalkenes **7**. It is impossible to separate the mixture **6f**/**6f′** by this way.

Table 2. *Synthesis of Derivatives* **6** *and Oxime* **5** via *the Interaction* **3** + **4**

3	R^1	R^2
a	Me	H
b	H	Me
c	CO_2Me	Me
d	CO_2Et	H
e	$(CH_2)_2CO_2Me$	H

4	X	Y	Z	R^3
a	N	CH	CH	H
b	CH	N	CH	H
c	N	N	CH	H
d	CH	N	N	H
e	[a])	N	N	[a])
f	N	N	CH	NH(TMS)
g	CH	CMe	N	CO_2Et
h	N	CH	CMe	Me

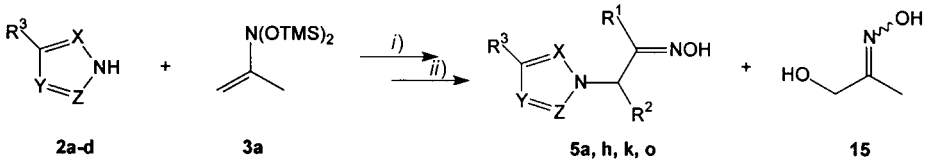


Entry	Reaction	*Procedure*[b])	*Formulae of* **5** *and* **6**						Product **6**				Product **5**			
			R^1	R^2	R^3	X	Y	Z	No.	(*E*)/(*Z*)	Yield [%] by NMR	Yield [%] after dist.	No.	(*E*)/(*Z*)	Yield [%] from distilled **6**	Yield [%] from crude **6**
1	**3a** + **4a**	*A*	Me	H	H	N	CH	CH	**6a**	(*E*)	95	58	**5a**	(*E*)	*ca.* 100	78
2	**3b** + **4a**	*A*	H	Me	H	N	CH	CH	**6b**	(*E*)	78	64	**5b**	5:2	*ca.* 100	–
3	**3c** + **4a**	*A*	CO_2Me	Me	H	N	CH	CH	**6c**	(*E*)	59	–	**5c**	(*E*)	–	60
4	**3d** + **4a**	*A*	CO_2Et	H	H	N	CH	CH	**6d**	(*E*)	88	–	**5d**	(*E*)	–	70
5	**3e** + **4a**	*A*	$(CH_2)_2CO_2Me$	H	H	N	CH	CH	**6e**	(*E*)	92	40	**5e**	7:1	76	83
6	**3a** + **4g**	*A*	Me	H	CO_2Et	CH	CMe	N	**6f**	(*E*)	64	Σ90	**5f**	5:1	*ca.* 100	–
			Me	H	CO_2Et	CMe	CH	N	**6f′**	(*E*)	30		**5f′**	4:1	*ca.* 100	–
7	**3d** + **4h**	*A*	CO_2Et	H	Me	N	CH	CMe	**6g**	(*E*)	92	–	**5g**	(*E*)	–	82
8	**3a** + **4b**	*B*	Me	H	H	CH	N	CH	**6h**	(*E*)	97	48	**5h**	(*E*)	*ca.* 100	79
9	**3b** + **4b**	*B*	H	Me	H	CH	N	CH	**6i**	8:1	97	67	**5i**	35:1	*ca.* 100	91
10	**3c** + **4b**	*B*	CO_2Me	Me	H	CH	N	CH	**6j**	(*E*)	84	–	**5j**	25:1	–	84
11	**3a** + **4c**	*B*	Me	H	H	N	N	CH	**6k**	(*E*)	92	77	**5k**	(*E*)	*ca.* 100	67
			Me	H	[c])	CH	N	CH	**6k′**	(*E*)	<5	–			–	–
12	**3b** + **4c**	*B*	H	Me	H	N	N	CH	**6l**	15:1	83	60	**5l**	30:1	*ca.* 100	59
			H	Me	[c])	CH	N	CH	**6l′**	2:1	12	–	**5l′**		–	–
13	**3c** + **4c**	*B*	CO_2Me	Me	H	N	N	CH	**6m**	40:1	71	–	**5m**	35:1	–	78
			CO_2Me	Me	[c])	CH	N	CH	**6m′**	(*E*)	17	–	**5m′**	(*E*)	–	15
14	**3e** + **4c**	*B*	$(CH_2)_2CO_2Me$	H	H	N	N	CH	**6n**	(*E*)	78	41	**5n**	(*E*)	62	53
			$(CH_2)_2CO_2Me$	H	[c])	CH	N	CH	**6n′**	4:3	18	–	**5n′**		–	–
15	**3a** + **4d**	*C*	Me	H	H	CH	N	N	**6o**	(*E*)	64	12	**5o**	(*E*)	*ca.* 100	57
			Me	H	H	N	CH	N	**6o′**	(*E*)	33	7	**5o′**	(*E*)	*ca.* 100	22
16	**3b** + **4d**	*C*	H	Me	H	CH	N	N	**6p**	5:1	38	21	**5p**	3:1	*ca.* 100	32
			H	Me	H	N	CH	N	**6p′**	5:1	57	32	**5p′**	2:1	*ca.* 100	50
17	**3c** + **4d**	*C*	CO_2Me	Me	H	CH	N	N	**6q**	3:1	72	–	**5q**	4:1	–	64
			CO_2Me	Me	H	N	CH	N	**6q′**	2:1	18	–	**5q′**	5:2	–	9
18	**3e** + **4d**	*C*	$(CH_2)_2CO_2Me$	H	H	CH	N	N	**6r**	(*E*)	98	30	**5r**	(*E*)	81	76
19	**3a** + **4e**	*C*	Me	H	[d])	[d])	N	N	**6s**	(*E*)	75	–	**5s**	(*E*)	–	68
			Me	H	[e])	N	[e])	N	**6s′**	(*E*)	12	–	**5s′**	(*E*)	–	10
20	**3b** + **4e**	*C*	H	Me	[d])	[d])	N	N	**6t**	–	25	–	**5t**	7:2	–	22
			H	Me	[e])	N	[e])	N	**6t′**	–	71	–	**5t′**	2:1	–	68
21	**3c** + **4e**	*C*	CO_2Me	Me	[d])	[d])	N	N	**6u**	–	78	–	**5u**	(*E*)	–	71
			CO_2Me	Me	[e])	N	[e])	N	**6u′**	–	19	–	**5u′**	(*E*)	–	14
22	**3e** + **4e**	*C*	$(CH_2)_2CO_2Me$	H	[d])	[d])	N	N	**6v**	–	65	–	**5v**	(*E*)	–	63
			$(CH_2)_2CO_2Me$	H	[e])	N	[e])	N	**6v′**	–	33	–	**5v′**	(*E*)	–	31
23	**3a** + **4f**	*B*[f])	Me	H	NH(TMS)[g])	N	N	CH	**6w**	(*E*)	69	–	**5w**	(*E*)	–	56
			Me	H	H	N	N	CNH(TMS)[h])	**6w′**	(*E*)	27	–	**5w′**	(*E*)	–	24

[a]) $-CH=CH-CH=CH-$ instead of X and CR^3. [b]) *A:* without solvent, 20°, 24–72 h; *B:* CH_2Cl_2, Et_3N (5 mol-%), 0°, 1 h; *C:* addition of BENA **3** in petroleum ether to **4**, followed by evaporation and exposition of the residue for 5 h to 20°. [c]) N instead of CH. [d]) $-CH=CH-CH=CH-$ instead of X and CR^3. [e]) $-CH=CH-CH=CH-$ instead of Y and CR^3. [f]) In C_6H_6 without Et_3N, 12 h at 0°. [g]) $R^3=NH_2$ for **5w**. [h]) $Z=CNH_2$ for **5w′**.

In several cases, it is possible to prepare the target oximes **5** by the N,C-coupling of BENA **3** with the nonsilylated azoles **2** (*Scheme 7*). Sometimes the yields of target oximes were high; however, this procedure is not general, and BENA **3** rearranged partially to the products **13** as a rule. This circumstance complicated the isolation and purification of resulting oximes **5**. Therefore, the protocol **3** + **4** (*Table 2*) is more convenient as a general procedure.

Scheme 7. *Preparation of Oximes* **5** via *Interaction of Azoles* **2** *with BENA* **3a**



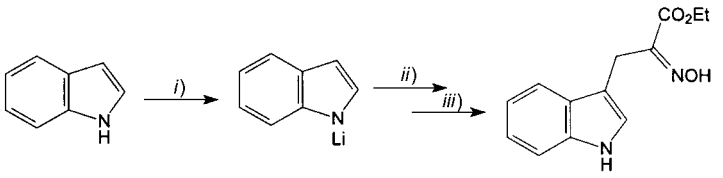
2a-d **3a** **5a, h, k, o** **15**

2	5	X	Y	Z	R^3	Yield of 5[%]	Ratio 5/15
a	**a**	N	CH	CH	H	30	1:2
b	**h**	CH	N	CH	H	5	1:9
c	**k**	N	N	CH	H	84	4.5:1
d	**o**	CH	N	N	H	76	4:1

i) CH_2Cl_2, 20 °, 6h. *ii*) MeOH, NH_4F.

In line with the discussed mechanism of the N,C-coupling **3** + **4**, 1*H*-indole and its salts or its *N*-TMS derivative did not react with BENA **3a**. However, BENA **3d**, in which the Si-atom is additionally activated by the electron-withdrawing CO_2Me-group, could be involved in the N,C-coupling with the Li salt of 1*H*-indole (*Scheme 8*). The structure of the obtained oxime **16** was established by spectroscopic methods and by comparison of its physical constants with literature data [13].

Scheme 8. *Synthesis of Oxime* **16** *by Interaction of* 1H*-Indole with BENA* **3d**



i) MeLi in pentane, Et_2O, 0 °. *ii*) **3d**, Et_2O, 20 °, 1h. *iii*) EtOH, 20 °, 6h. **16** 36%

The steric hindrances around the sp^2-hybridized N-atom in azoles **4** hamper the reaction **3** + **4** and **2** + **4**. Thus, neither silylated azole **4h** nor nonsilylated 3,5-dimethyl-1*H*-pyrazole reacted with BENA **3a** and **3b**. But N,C-coupling of **4h** was possible with the more reactive BENA **3d** (*Entry 7, Table 2*).

2.3. *Structure and Configuration of Oximes* **5** *and Derivatives* **6**. The structure of the silylated oximes **6** was established by NMR and by the chemical transformations to **5**,

and the structure of the latter was confirmed by NMR and by microanalyses. The position of the oxyiminoalkyl moiety at the azole ring was also determined by NMR; NOE difference data were employed in the case of the derivatives **6f/6f′**, **5f/5f′**, and **5w**/**5w′**. For most of the products **5** and **6**, the configuration of the oxime moiety was established by NMR by using the characteristic parameters, as described in our recent publications [3][14]. The assignment of the configuration of the C=N bond of oximes **5** prepared from BENA **3c** was achieved by a comparison of the ^{1}H-NMR chemical shifts of C*H*=N with that of analogous oximes **5**, prepared from BENA **3b**. It is noteworthy that the substitution of the proton at the C=N bond by the CO_2Me group leads to the downfield shift of the corresponding H–C(α) by 0.3 ppm.

Both stereoisomers of derivative **6m** were prepared by silylation of (*E*)-isomer **5m** followed by heating of the resulting mixture for 5 h at 150°. The silylation of the oximes **5** was also used for the attribution of the characteristic signals of silylated derivatives **6** when the yields of products **6** were determined by ^{1}H-NMR in the crude reaction mixtures. The configuration of the C=N bond of the derivatives **6u** and **6u′** was not established.

3. Conclusions. – We developed a general and convenient method for the synthesis of α-azolyl-substituted oximes **5**. These can contain the functional groups at different positions relative to the hydroxyimino group and the heterocyclic ring. In particular, the developed method allows one to prepare the direct precursors of unnatural amino acids with the carboxylic, hydroxyimino, and heterocyclic functions at different positions (see **5c–g,j,m,n,q,r,u,v**, *Table 2*). These oximes might find various applications in organic synthesis (see, *e.g.*, the products preceded by the dotted arrows in *Scheme 1*). The study of the synthetic applications of α-azolyl-substituted oximes **5** is subject of our further researches.

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Experimental Part[4])

1. *General.* All transformations of BENA **3**, the silylations of the products **2** and **5**, and experiments on the study of the mechanism of the interactions of **3** + **4** were performed under dry Ar. By known procedure were prepared BENA **3a**,**b**,**e** [16], **3a′** [9], and **3c**,**d** [17]. CH_2Cl_2 was freshly distilled before use over CaH_2 under dry Ar. Petroleum ether refers to the fraction having b.p. 60–70°. Benzene and Et_3N were distilled over Na. All other reagents were used as purchased from *Aldrich* or *Merck*. TLC: *Merck* silica gel *60 F_{254}* plates; detection with UV. Flash chromatography (FC): silica gel 230–400 mesh ASTM. NMR Spectra: *Bruker AM-300* instrument (^{1}H: 300.13 MHz; ^{13}C: 75.47 MHz; ^{29}Si: 59.63 MHz), chemical shifts δ in ppm rel. to solvent residual peak [15], internal reference ($SiMe_4$, 0 ppm); *J* values in Hz; the INEPT pulse sequence was used for ^{29}Si-signal observation.

2. *Trialkylsilyl-Derivatives* **4** *from Azoles* **2**. *1-(Trimethylsilyl)-1*H-*1,2,3-triazole* (**4d**) was prepared according to [18].

*3,5-Dimethyl-1-(trimethylsilyl)-1*H-*pyrazole* (**4h**) was synthesized under similar conditions (CH_2Cl_2, 0–20°): Yield 82%. B.p. 89°/30 Torr. ^{1}H-NMR ($CDCl_3$): 0.48 (*s*, Me_3Si); 2.21, 2.28 (2*s*, Me–C(3)), Me–C(5)); 5.81 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): 0.4 (Me_3Si); 12.9, 13.6 (*Me*–C(3), *Me*–C(5)); 107.7 (C(4)); 145.8 (C(5)); 151.4 (C(3)).

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4) With the participation of *I. V. Bliznets.*

*1-[(*tert*-Butyl)dimethylsilyl]-1*H*-imidazole* (**4b′**) was prepared with ^{t}BuMe$_2$SiCl instead of Me$_3$SiCl: Yield 69%. B.p. 61°/0.2 Torr. ^{1}H-NMR (CDCl$_3$): 0.29 (*s*, Me$_2$Si); 0.69 (*s*, Me$_3$C); 6.76, 6.97 (2*d*, ^3J = 2, H–C(4), H–C(5)); 7.37 (*s*, H–C(2)). ^{13}C-NMR (CDCl$_3$): –5.6 (Me$_2$Si); 17.5 (Me$_3$*C*); 25.4 (*Me*$_3$C); 120.6 (C(5)); 130.2 (C(4)); 140.5 (C(2)). ^{29}Si-NMR (CDCl$_3$): 17.08.

Trimethylsilyl derivatives **4a**–**4c** were prepared according to [19]. Under the same conditions were prepared 1-(*trimethylsilyl)-1*H*-benzotriazole* (**4e**), *ethyl 3-methyl-1-(trimethylsilyl)-1*H*-pyrazole-4-carboxylate* (**4g**), and N,*1-bis(trimethylsilyl)-1*H*-1,2,4-triazol-3-amine* (**4f**) (by use of 3 equiv. of (TMS)$_2$NH).

Data of **4e**: Yield 90%. B.p. 78°/0.08 Torr. ^{1}H-NMR (CDCl$_3$): 0.66 (*s*, Me$_3$Si); 7.29, 7.39 (2*t*, ^3J = 7.5, H–C(5), H–C(6)); 7.58, 8.06 (2*d*, ^3J = 7.5, H–C(4), H–C(7)). ^{13}C-NMR (CDCl$_3$): –0.4 (Me$_3$Si); 111.2, 119.8, 123.5, 127.1 (C(4), C(5), C(6), C(7)); 137.8, 146.7 (C(8), C(9)).

Data of **4g**: Yield 79%. B.p. 74°/0.05 Torr. ^{1}H-NMR (CDCl$_3$): 0.43 (*s*, Me$_3$Si); 1.28 (*t*, ^3J = 7.1, *Me*CH$_2$); 2.44 (*s*, Me); 4.23 (*q*, ^3J = 7.1, CH$_2$); 7.98 (*s*, H–C(5)). ^{13}C-NMR (CDCl$_3$): –0.9 (Me$_3$Si); 13.6 (Me); 14.4 (*Me*CH$_2$); 59.7 (CH$_2$); 113.5 (C(4)); 139.4 (C(5)); 144.2 (C(3)); 163.9 (CO).

Data of **4f**: Yield 65%. B.p. 88°/0.08 Torr. ^{1}H-NMR (CDCl$_3$): 0.22 (*s*, *Me*$_3$SiNH); 0.41 (*s*, Me$_3$SiN); 4.03 (*s*, NH); 7.75 (*s*, CH). ^{13}C-NMR (CDCl$_3$): –1.1, –0.3 (Me$_3$Si); 143.9 (C(5)); 156.4 (C(3)).

All derivatives **4** were prepared with a purity > 95% (by ^{1}H-NMR).

3. *Silylated Oximes* **6**: *Procedure A* (see *Table 2*). Compound **3** (3 mmol) was added to a stirred compound **4** (3 mmol) at 20°. The resulting mixture was kept at 20° for the indicated time (24 h for **4a**,**h** and 72 h for **4g**) by occasional shaking and then evaporated. The residue was purified by distillation *in vacuo:* **6** as a colorless oil.

*(*E*)-1-(1*H*-Pyrazol-1-yl)acetone* O-*(Trimethylsilyl)oxime* (**6a**): Yield[5]) 95%. B.p. 53°/0.06 Torr (58%). ^{1}H-NMR (CDCl$_3$): 0.19 (*s*, Me$_3$Si); 1.75 (*s*, Me); 4.80 (*s*, CH$_2$); 6.25 (*t*, ^3J = 2, H–C(4)); 7.33 (*d*, ^3J = 2, H–C(5)); 7.47 (*d*, ^3J = 2, H–C(3)). ^{13}C-NMR (CDCl$_3$): –0.8 (Me$_3$Si); 11.9 (Me); 55.9 (CH$_2$); 106.4 (C(4)); 128.9 (C(5)); 139.4 (C(3)); 157.4 (C=N).

*(*E*)-2-(1*H*-Pyrazol-1-yl)propanal* O-*(Trimethylsilyl)oxime* (**6b**): Yield[5]) 78%. B.p. 44°/0.08 Torr (64%). ^{1}H-NMR (CDCl$_3$): 0.17 (*s*, Me$_3$Si); 1.62 (*d*, ^3J = 6.7, Me); 5.1 (*m*, ^3J = 6.7, CH); 6.21 (*t*, ^3J = 2, H–C(4)); 7.36 (*d*, ^3J = 2, H–C(5)); 7.49 (*d*, ^3J = 2, H–C(3)); 7.63 (*d*, ^3J = 6.0, CH=N). ^{13}C-NMR (CDCl$_3$): –0.8 (Me$_3$Si); 18.7 (Me); 56.7 (CH); 105.8 (C(4)); 127.5 (C(5)); 139.5 (C(3)); 153.9 (CH=N).

*Methyl (*E*)-5-(1*H*-Pyrazol-1-yl)-4-{[(trimethylsilyl)oxy]imino}pentanoate* (**6e**): Yield[5]) 92%. B.p. 102–105°/0.1 Torr (40%). ^{1}H-NMR (CDCl$_3$): 0.20 (*s*, Me$_3$Si); 2.5 (*m*, CH$_2$CH$_2$); 3.63 (*s*, MeO); 4.89 (*s*, CH$_2$); 6.28 (*t*, ^3J = 2, H–C(4)); 7.41 (*d*, ^3J = 2, H–C(5)); 7.50 (*d*, ^3J = 2, H–C(3)). ^{13}C-NMR (CDCl$_3$): –0.8 (Me$_3$Si); 21.9 (*C*H$_2$CN); 29.6 (*C*H$_2$CO); 51.7 (MeO); 54.9 (CH$_2$); 106.4 (C(4)); 129.4 (C(5)); 139.7 (C(3)); 159.6 (C=N); 172.9 (CO).

*Ethyl (*E*)-3-Methyl-1-(2-{[(trimethylsilyl)oxy]imino}propyl)-1*H*-pyrazole-4-carboxylate* (**6f**) *and Ethyl (*E*)-5-Methyl-1-(2-{[(trimethylsilyl)oxy]imino}propyl)-1*H*-pyrazole-4-carboxylate* (**6f′**): Total yield[5]) after distillation 90%, **6f**/**6f′** 2:1. B.p. 90–100°/0.03 Torr (short-path apparatus).

Data of **6f**: ^{1}H-NMR (CDCl$_3$): 0.18 (*s*, Me$_3$Si); 1.30 (*t*, ^3J = 7.1, *Me*CH$_2$); 1.79 (*s*, MeC=N); 2.43 (*s*, Me); 4.20 (*q*, ^3J = 7.1, CH$_2$); 4.69 (*s*, CH$_2$); 7.80 (*s*, H–C(5)). ^{13}C-NMR (CDCl$_3$): –0.9 (Me$_3$Si); 12.0 (*Me*C=N); 13.3 (Me); 14.3 (*Me*CH$_2$); 55.9 (CH$_2$); 59.8 (CH$_2$O); 113.0 (C(4)); 133.9 (C(5)); 151.1 (C(3)); 156.5 (C=N); 163.4 (CO).

Data of **6f′**: ^{1}H-NMR (CDCl$_3$): 0.16 (*s*, Me$_3$Si); 1.31 (*t*, ^3J = 7.1, *Me*CH$_2$); 1.76 (*s*, MeC=N); 2.49 (*s*, Me); 4.23 (*q*, ^3J = 7.1, CH$_2$); 4.74 (*s*, CH$_2$); 7.81 (*s*, H–C(3)). ^{13}C-NMR (CDCl$_3$): –0.9 (Me$_3$Si); 10.3 (*Me*C=N); 11.8 (Me); 14.3 (*Me*CH$_2$); 53.7 (CH$_2$); 59.7 (CH$_2$O); 112.4 (C(4)); 140.8 (C(5)); 143.7 (C(3)); 156.2 (C=N); 163.6 (CO).

Derivatives **6c**,**d**,**g** were prepared according to *Procedure A*, without purification *via* distillation *in vacuo*.

*Methyl (*E*)-3-(1*H*-Pyrazol-1-yl)-2-{[(trimethylsilyl)oxy]imino}butanoate* (**6c**): Yield[5]) 59%. ^{1}H-NMR (CDCl$_3$): 0.23 (*s*, Me$_3$Si); 1.82 (*d*, ^3J = 6.6, Me); 3.69 (*s*, MeO); 6.01 (*q*, ^3J = 6.6, CH); 6.23 (*t*, ^3J = 2, H–C(4)); 7.48 (*d*, ^3J = 2, H–C(5)); 7.59 (*d*, ^3J = 2, H–C(3)). ^{13}C-NMR (CDCl$_3$): –0.8 (Me$_3$Si); 16.1 (Me); 52.3 (CH); 52.4 (MeO); 105.1 (C(4)); 127.9 (C(5)); 139.4 (C(3)); 155.6 (C=N); 162.8 (CO).

*Ethyl (*E*)-3-(1*H*-Pyrazol-1-yl)-2-{[(trimethylsilyl)oxy]imino}propanoate* (**6d**): Yield[5]) 88%. ^{1}H-NMR (CDCl$_3$): 0.22 (*s*, Me$_3$Si); 1.22 (*t*, ^3J = 7.4, Me); 4.22 (*q*, ^3J = 7.4, CH$_2$O); 5.17 (*s*, CH$_2$); 6.18 (*t*, ^3J = 2, H–C(4)); 7.40 (*d*, ^3J = 2, H–C(5)); 7.44 (*d*, ^3J = 2, H–C(3)). ^{13}C-NMR (CDCl$_3$): –0.9 (Me$_3$Si); 14.0 (Me); 44.3 (CH$_2$); 62.1 (CH$_2$O); 105.6 (C(4)); 130.3 (C(5)); 139.5 (C(3)); 151.6 (C=N); 162.7 (CO).

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[5]) The yield was determined by ^{1}H-NMR prior to the distillation of the crude product, after addition 1,2-dichloroethane or CH$_2$Cl$_2$ as internal standard.

*Ethyl (*E*)-3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-[[(trimethylsilyl)oxy]imino]propanoate* (**6g**): Yield[5]) 92%. ^{1}H-NMR ($CDCl_3$): 0.25 (*s*, Me_3Si); 1.22 (*t*, $^3J = 7.4$, Me); 2.18, 2.24 (2*s*, Me–C(3), Me–C(5)); 4.20 (*q*, $^3J = 7.4$, CH_2O); 5.09 (*s*, CH_2); 5.72 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 11.0, 13.5 (*Me*–C(3), *Me*–C(5)); 13.9 (MeO); 42.2 (CH_2); 61.7 (CH_2O); 104.9 (C(4)); 139.8 (C(5)); 147.9 (C(3)); 152.5 (C=N); 162.7 (CO).

4. *Silylated Oximes* **6**: *Procedure B* (see *Table 2*). Compound **3** (3 mmol) was added dropwise at 20° to a soln. of **4** (3 mmol) and Et_3N (0.02 ml, 0.15 mmol). (*Caution*! After an inductive period, the reaction can be very exotermic; use a good condenser!) The mixture was stirred for 0.5 h (after boiling started and then evaporated and the residue purified by distillation: **6** as colorless oil.

*(*E*)-1-(1*H*-Imidazol-1-yl)acetone* O-*(Trimethylsilyl)oxime* (**6h**): Yield[5]) 97%. B.p. 65°/0.08 Torr (48%). ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.74 (*s*, Me); 4.60 (*s*, CH_2); 6.87 (*s*, H–C(5)); 7.05 (*s*, H–C(4)); 7.55 (*s*, H–C(2)). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 12.3 (Me); 53.6 (CH_2); 118.3 (C(5)); 129.5 (C(4)); 137.9 (C(2)); 155.7 (C=N). ^{29}Si-NMR ($CDCl_3$): 26.1.

*2-(1*H*-Imidazol-1-yl)propanal* O-*(Trimethylsilyl)oxime* (**6i**; (*E*)/(*Z*) 8:1): Yield[5]) 97%. B.p. 73°/0.09 Torr (67%). (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.20 (*s*, Me_3Si); 1.55 (*d*, $^3J = 7.3$, Me); 4.85 (*m*, $^3J = 7.3$, CH); 6.90 (*s*, H–C(5)); 7.05 (*s*, H–C(4)); 7.51 (*d*, $^3J = 7.3$, CH=N); 7.57 (*s*, H–C(2)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 18.9 (Me); 52.3 (CH), 117.3 (C(5)); 129.5 (C(4)); 135.5 (C(2)); 153.2 (CH=N). (*Z*)-Isomer ^{1}H-NMR ($CDCl_3$): 0.20 (*s*, Me_3Si); 1.50 (*d*, $^3J = 7.3$, Me); 5.50 (*m*, $^3J = 7.3$, CH); 6.82 (*d*, $^3J = 7.3$, CH=N); 6.90 (*s*, H–C(5)); 7.05 (*s*, H–C(4)); 7.57 (*s*, H–C(2)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 17.9 (Me); 47.6 (CH); 117.2 (C(5)); 129.5 (C(4)); 135.5 (C(2)); 153.9 (CH=N).

*(*E*)-1-(1*H*-1,2,4-Triazol-1-yl)acetone* O-*(Trimethylsilyl)oxime* (**6k**): Yield[5]) 92%. B.p. 60°/0.08 Torr (77%). ^{1}H-NMR ($CDCl_3$): 0.09 (*s*, Me_3Si); 1.73 (*s*, Me); 4.87 (*s*, CH_2); 7.83 (*s*, H–C(5)); 8.02 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 12.2 (Me); 53.3 (CH_2); 143.3 (C(5)); 151.8 (C(3)); 155.7 (C=N).

*(*E*)-1-(4*H*-1,2,4-Triazol-4-yl)acetone* O-*(Trimethylsilyl)oxime* (**6k′**): Detected in the residue after distillation of **6k**. Yield ≤5%. ^{1}H-NMR ($CDCl_3$): 0.09 (*s*, Me_3Si); 1.75 (*s*, Me); 4.69 (*s*, CH_2); 8.13 (*s*, H–C(2), H–C(5)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 12.4 (Me); 49.0 (CH_2); 142.9 (C(2), C(5)); 154.8 (C=N).

*2-(1*H*-1,2,4-Triazol-1-yl)propanal* O-*(Trimethylsilyl)oxime* (**6l**; (*E*)/(*Z*) *ca.* 15:1): Yield[5]) 83%. B.p. 64°/0.08 Torr (60%). (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.15 (*s*, Me_3Si); 1.71 (*d*, $^3J = 6.7$, Me); 5.15 (*m*, $^3J = 6.7$, CH); 7.60 (*d*, $^3J = 6.0$, CH=N); 7.87 (*s*, H–C(5)); 8.07 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 18.6 (Me); 55.1 (CH); 141.8 (C(5)); 151.8 (C(3)); 152.4 (CH=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.10 (*s*, Me_3Si); 1.67 (*d*, $^3J = 6.7$, Me); 5.70 (*m*, $^3J = 6.7$, CH); 7.08 (*d*, $^3J = 6.0$, CH=N); 7.87 (*s*, H–C(5)); 8.11 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 17.8 (Me); 50.5 (CH); 142.3 (C(5)); 152.0 (C(3)); 152.7 (CH=N).

*2-(4*H*-1,2,4-Triazol-4-yl)propanal* O-*(Trimethylsilyl)oxime* (**6l′**; (*E*)/(*Z*) 2:1): Detected in residue after distillation of **6l**. Yield ≤8%. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.15 (*s*, Me_3Si); 1.60 (*d*, $^3J = 6.7$, Me); 5.04 (*m*, $^3J = 6.7$, CH); 7.54 (*d*, $^3J = 6.0$, CH=N); 8.15 (*s*, H–C(2), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 19.1 (Me); 51.2 (CH); 141.6 (C(2), C(5)); 151.9 (CH=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.15 (*s*, Me_3Si); 1.56 (*d*, $^3J = 6.7$, Me); 5.51 (*m*, $^3J = 6.7$, CH); 6.89 (*d*, $^3J = 6.0$, CH=N); 8.15 (*s*, H–C(2), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 18.0 (Me); 46.0 (CH); 141.6 (C(2), C(5)); 152.1 (CH=N).

*Methyl (*E*)-5-(1*H*-1,2,4-Triazol-1-yl)-4-[[(trimethylsilyl)oxy]imino]pentanoate* (**6n**): Yield[5]) 78%. B.p. 114–118°/0.22 Torr (41%). ^{1}H-NMR ($CDCl_3$): 0.04 (*s*, Me_3Si); 2.41 (*m*, CH_2CH_2); 3.51 (*s*, Me); 4.88 (*s*, CH_2); 7.82 (*s*, H–C(5)); 8.09 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 21.9 (*C*H_2CNO); 29.7 (*C*H_2CO); 51.6 (CH_2); 52.4 (Me); 143.7 (C(5)); 151.8 (C(3)); 157.9 (C=N); 172.8 (CO).

*Methyl 5-(4*H*-1,2,4-Triazol-4-yl)-4-[[(trimethylsilyl)oxy]imino]pentanoate* (**6n′**; (*E*)/(*Z*) *ca.* 4:3): Detected in the reaction mixture. Yield *ca.* 18%. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.04 (*s*, Me_3Si); 2.41 (*m*, CH_2CH_2); 3.51 (*s*, Me); 4.78 (*s*, CH_2); 8.10 (*s*, H–C(2), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 21.5 (*C*H_2CNO); 29.7 (*C*H_2CO); 51.7 (CH_2); 52.4 (Me); 143.1 (C(2), C(5)); 157.9 (C=N); 172.8 (CO). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.04 (*s*, Me_3Si); 2.41 (*m*, CH_2CH_2); 3.51 (*s*, Me); 5.21 (*s*, CH_2); 8.10 (*s*, H–C(2), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 29.7 (*C*H_2CNO); 29.9 (*C*H_2CO); 48.2 (CH_2); 52.4 (Me); 143.1 (C(2), C(5)); 157.7 (C=N); 172.8 (CO).

The derivative **6j** and the mixture **6m**/**6m′** were prepared according to *Procedure B* without purification *via* distillation *in vacuo*.

*Methyl (*E*)-3-(1*H*-Imidazol-1-yl)-2-[[(trimethylsilyl)oxy]imino]butanoate* (**6j**): Yield[5]) 84%. ^{1}H-NMR ($CDCl_3$): 0.18 (*s*, Me_3Si); 1.73 (*d*, $^3J = 6.6$, Me); 3.64 (*s*, MeO); 5.78 (*q*, $^3J = 6.6$, CH); 6.87 (*s*, H–C(5)); 6.91 (*s*, H–C(4)); 7.50 (*s*, H–C(2)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 16.6 (Me); 57.0 (CH); 52.3 (MeO); 118.2 (C(5)); 128.6 (C(4)); 136.4 (C(2)); 154.5 (C=N); 162.5 (CO).

*Methyl 3-(1*H*-1,2,4-Triazol-1-yl)-2-[[(trimethylsilyl)oxy]imino]butanoate* (**6m**; (*E*)/(*Z*) 40:1): Yield[5]) 71%. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.85 (*d*, $^3J = 6.6$, Me); 3.69 (*s*, MeO); 6.00 (*q*, $^3J = 6.6$,

CH); 7.81 (H–C(5)); 8.23 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 15.7 (Me); 51.0 (CH); 52.5 (MeO); 142.3 (H–C(5)); 151.5 (H–C(3)); 153.6 (C=N); 162.4 (CO). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.90 (*d*, ^3J = 6.6, Me); 3.69 (*s*, MeO); 5.42 (*q*, ^3J = 6.6, CH); 7.88 (*s*, H–C(5)); 8.20 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 17.8 (Me); 52.4 (MeO); 56.1 (CH); 142.3 (C(5)); 151.5 (C(3)); 153.5 (C=N); 162.4 (CO).

*Methyl (*E*)-3-(4*H*-1,2,4-Triazol-4-yl)-2-{[(trimethylsilyl)oxy]imino}butanoate* (**6m′**): Yield[5]) 17%. ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.81 (*d*, ^3J = 6.6, Me); 3.76 (*s*, MeO); 5.91 (*q*, ^3J = 6.6, CH); 8.23 (*s*, H–C(3), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 16.8 (Me); 45.7 (CH); 52.8 (MeO); 142.1 (C(3), C(5)); 152.8 (C=N); 162.4 (CO).

5. *Silylated Oximes* **6**: *Procedure C* (see *Table 2*). Compound **3** (3 mmol) was added dropwise at 20° to a stirred soln. of **4** (3 mmol) in petroleum ether (3 ml). After being stirred for 5 min, the mixture was evaporated. The residue was kept for 0.5 h: **6**.

*(*E*)-1-(1*H*-1,2,3-Triazol-1-yl)acetone* O-*(Trimethylsilyl)oxime* (**6o**) *and (*E*)-1-(2*H*-1,2,3-Triazol-2-yl)acetone* O-*(Trimethylsilyl)oxime* (**6o′**). Yield[5]) 64 and 33%, resp. Careful distillation *in vacuo* gave pure **6o** (12%) and **6o′** (7%).

Data of **6o**: B.p. 71°/0.15 Torr. ^{1}H-NMR ($CDCl_3$): 0.11 (*s*, Me_3Si); 1.73 (*s*, Me); 5.05 (*s*, CH_2); 7.56 (*s*, H–C(5)); 7.62 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 12.0 (Me); 53.5 (CH_2); 123.8 (C(5)); 134.5 (C(4)); 155.7 (C=N).

Data of **6o′**: B.p. 56°/0.15 Torr. ^{1}H-NMR ($CDCl_3$): 0.11 (*s*, Me_3Si); 1.70 (*s*, Me); 5.02 (*s*, CH_2); 7.55 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 11.7 (Me); 58.2 (CH_2); 133.8 (C(4), C(5)); 155.9 (C=N).

*2-(2*H*-1,2,3-Triazol-2-yl)propanal* O-*(Trimethylsilyl)oxime* (**6p′**) *and 2-(1*H*-1,2,3-Triazol-1-yl)propanal* O-*(Trimethylsilyl)oxime* (**6p**). Yield[5]) 57 and 38%, resp. Careful distillation *in vacuo* gave pure **6p′** (21%) and **6p** (32%).

Data of **6p′** ((*E*)/(*Z*) *ca.* 5:1): B.p. 78°/0.1 Torr. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.18 (*s*, Me_3Si); 1.77 (*d*, ^3J = 6.6, Me); 5.42 (*m*, ^3J = 6.6, CH); 7.61 (*s*, H–C(4), H–C(5)); 7.72 (*d*, ^3J = 5.9, CH=N). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 18.6 (Me); 59.9 (CH); 134.3 (C(4), C(5)); 152.9 (C=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.20 (*s*, Me_3Si); 1.70 (*d*, ^3J = 6.6, Me); 6.08 (*m*, ^3J = 6.6, CH); 7.22 (*d*, ^3J = 5.9, CH=N); 7.61 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 17.9 (Me); 56.0 (CH); 134.3 (C(4), C(5)); 153.3 (C=N).

Data of **6p** ((*E*)/(*Z*) *ca.* 5:1): B.p. 92°/0.1 Torr. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.19 (*s*, Me_3Si); 1.77 (*d*, ^3J = 6.6, Me); 5.42 (*m*, ^3J = 6.6, CH); 7.58 (*s*, H–C(5)); 7.61 (*s*, H–C(4)); 7.75 (*d*, ^3J = 5.9, CH=N). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 18.8 (Me); 55.8 (CH); 122.1 (C(5)); 133.9 (C(4)); 152.3 (C=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.65 (*d*, ^3J = 6.6, Me); 5.97 (*m*, ^3J = 6.6, CH); 7.13 (*d*, ^3J = 5.9, CH=N); 7.60 (*s*, H–C(5)); 7.63 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 18.2 (Me); 51.4 (CH); 122.6 (C(5)); 133.6 (C(4)); 152.6 (C=N).

*Methyl (*E*)-5-(1*H*-1,2,3-Triazol-1-yl)-4-{[(trimethylsilyl)oxy]imino}pentanoate* (**6r**). Yield[5]) 97%. Purification by distillation. B.p. 128–130°/0.1 Torr (65%). ^{1}H-NMR ($CDCl_3$): 0.12 (*s*, Me_3Si); 2.4 (*m*, CH_2CH_2); 3.52 (*s*, MeO); 5.09 (*s*, CH_2); 7.52 (*s*, H–C(5)); 7.62 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): –0.9 (Me_3Si); 21.8 (CH_2CN); 29.4 (CH_2CO); 51.7 (MeO); 52.8 (CH_2); 123.9 (C(5)); 133.8 (C(4)); 157.8 (C=N); 172.6 (CO).

*Methyl 3-(1*H*-1,2,3-Triazol-1-yl)-2-{[(trimethylsilyl)oxy]imino}butanoate* (**6q**) *and Methyl 3-(2*H*-1,2,3-Triazol-2-yl)-2-{[(trimethylsilyl)oxy]imino}butanoate* (**6q′**). Yield[5]) 72 and 18%, resp.

Data of **6q** ((*E*)/(*Z*) 3:1): (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.27 (*s*, Me_3Si); 1.87 (*d*, ^3J = 7.4, Me); 3.71 (*s*, MeO); 6.38 (*q* ^3J = 7.4, CH); 7.65 (*s*, H–C(5)); 7.79 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 16.5 (Me); 50.7 (CH); 52.6 (MeO); 122.9 (C(5)); 133.1 (C(4)); 153.4 (C=N); 162.5 (CO). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.22 (*s*, Me_3Si); 1.82 (*d*, ^3J = 7.4, Me); 3.70 (*s*, MeO); 5.71 (*q*, ^3J = 7.4, CH); 7.60 (*s*, H–C(5)); 7.70 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 18.1 (Me); 52.4 (MeO); 56.4 (CH); 122.2 (C(5)); 133.9 (C(4)); 153.2 (C=N); 162.5 (CO).

Data of **6q′** ((*E*)/(*Z*) 2:1): (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.25 (*s*, Me_3Si); 1.91 (*d*, ^3J = 7.4, Me); 3.64 (*s*, MeO); 6.12 (*q*, ^3J = 7.4, CH); 7.69 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 15.8 (Me), 52.4 (MeO); 55.2 (CH); 134.6 (C(3), C(5)); 154.4 (C=N); 162.5 (CO). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 0.22 (*s*, Me_3Si); 1.82 (*d*, ^3J = 7.4, Me); 3.60 (*s*, MeO); 5.66 (*q*, ^3J = 7.4, CH); 7.69 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): –1.0 (Me_3Si); 17.3 (Me); 52.4 (MeO); 60.7 (CH); 134.6 (C(3), C(5)); 154.4 (C=N); 162.5 (CO).

*(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)acetone* O-*(Trimethylsilyl)oxime* (**6s**) *and (*E*)-1-(2*H*-1,2,3-Benzotriazol-2-yl)acetone* O-*(Trimethylsilyl)oxime* (**6s′**). Yield[5]) 75 and 12%, resp.

Data of **6s**: ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.77 (*s*, Me); 5.33 (*s*, CH_2); 7.3–7.5 (4*m*, H–C(4), H–C(5), H–C(6), H–C(7)). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 12.0 (Me); 52.6 (CH_2); 110.0, 119.9, 124.1, 127.5 (C(4), C(5), C(6), C(7)); 133.0, 146.2 (C(8), C(9)); 155.6 (C=N).

Data of **6s′**: ^{1}H-NMR ($CDCl_3$): 0.21 (*s*, Me_3Si); 1.81 (*s*, Me); 5.42 (*s*, CH_2); 7.51 (*d*, ^3J = 8.8, H–C(5), H–C(6)); 8.02 (*d*, ^3J = 8.8, H–C(4), H–C(7)). ^{13}C-NMR ($CDCl_3$): –0.8 (Me_3Si); 11.5 (Me); 60.2 (CH_2); 118.1 (C(5), C(6)); 126.5 (C(4), C(7)); 144.6 (C(8), C(9)); 155.6 (C=N).

The mixtures **6t**/**6t′**, **6u**/**6u′**, **6v**/**6v′**, and **6w**/**6w′**[6]) were used without any purification or full NMR identification for subsequent transformations. The yields of these products were determined by characteristic NMR signals in the presence of internal standard (see *Table 2*).

6. *Desilylation of Purified Derivatives* **6** *into Oximes* **5**. NH_4F (0.05 mmol, 2 mg) was added to a soln. of freshly distilled **6** (1 mmol) in MeOH (3 ml). The mixture was kept for 6 h at 20° and evaporated: **5**. Oximes **5a**,**b**,**h**,**i**,**k**,**l**,**o**,**o′**,**p**,**p′** and the mixture **5f**/**f′** did not require additional purification. Oximes **5e**,**n**,**r** were purified by FC or crystallization.

*(*E*)-1-(1*H*-Pyrazol-1-yl)acetone Oxime* (**5a**): Yield *ca.* 100%[7]). M.p. 94–95° (from H_2O). ^{1}H-NMR ((D_6)DMSO): 1.61 (*s*, Me); 4.79 (*s*, CH_2); 6.27 (*t*, ^3J = 2, H–C(4)); 7.46 (*d*, ^3J = 2, H–C(5)); 7.72 (*d*, ^3J = 2, H–C(3)); 10.9 (br., OH). ^{13}C-NMR ((D_6)DMSO): 11.3 (Me); 55.0 (CH_2); 105.5 (C(4)); 130.4 (C(5)); 139.1 (C(3)); 151.7 (C=N). Anal. calc. for $C_6H_9N_3O$ (139.16): C 51.79, H 6.52, N 30.20; found: C 51.95, H 6.51, N 30.29.

*2-(1*H*-Pyrazol-1-yl)propanal Oxime* (**5b**; (*E*)/(*Z*) 5:2): Yield *ca.* 100%[7]). Oil. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.66 (*d*, ^3J = 6.6, Me); 5.10 (*m*, ^3J = 6.6, CH); 6.24 (*t*, ^3J = 2, H–C(4)); 7.42 (*d*, ^3J = 2, H–C(5)); 7.53 (*d*, ^3J = 2, H–C(3)); 7.58 (*d*, ^3J = 5.9, CH=N); 9.36 (br., OH). ^{13}C-NMR ($CDCl_3$): 18.5 (Me); 56.7 (CH); 105.9 (C(4)); 128.0 (C(5)); 139.6 (C(3)); 149.6 (C=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.64 (*d*, ^3J = 6.6, Me); 5.72 (*d*, ^3J = 6.6, CH); 6.24 (*t*, ^3J = 2, H–C(4)); 6.95 (*d*, ^3J = 5.9, CH=N); 7.45 (*d*, ^3J = 2, H–C(5)); 7.55 (*d*, ^3J = 2, H–C(3)); 9.36 (br., OH). ^{13}C-NMR ($CDCl_3$): 17.7 (Me); 52.2 (CH); 105.6 (C(4)); 128.6, 139.8 (C(3), C(5)); 150.3 (C=N). Anal. calc. for $C_6H_9N_3O$ (139.16): C 51.79, H 6.52, N 30.20; found: C 51.58, H 6.59, N 29.97.

*Methyl 4-(Hydroxyimino)-5-(1*H*-pyrazol-1-yl)pentanoat* (**5e**; (*E*)/(*Z*) 7:1): Yield 76% after FC. R_f *ca.* 0.52 (AcOEt/petroleum ether 1:3). Oil. (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 2.4 (*m*, CH_2CH_2); 3.61 (*s*, Me); 4.88 (*s*, CH_2); 6.27 (*t*, ^3J = 2, H–C(4)); 7.46 (*d*, ^3J = 2, H–C(5)); 7.51 (*d*, ^3J = 2, H–C(3)); 10.3 (br., OH). ^{13}C-NMR ($CDCl_3$): 21.4 (CH_2CNO); 29.4 (CH_2CO); 51.8 (CH_2); 54.88 (Me); 106.3 (C(4)); 130.2 (C(5)); 139.8 (C(3)); 154.9 (C=N); 173.3 (CO). Anal. calc. for $C_9H_{13}N_3O_3$ (211.22): C 51.18, H 6.20, N 19.89; found: C 50.87, H 6.18, N 20.06.

*Ethyl 1-[2-(Hydroxyimino)propyl]-3-methyl-1*H*-pyrazole-4-carboxylate* (**5f**) *and Ethyl 1-[2-(Hydroxyimino)propyl]-5-methyl-1*H*-pyrazole-4-carboxylate* (**5f′**): **5f**/**5f′** 2:1. Overall yield *ca.* 100%. M.p. 65–71°. Anal. calc. for $C_{10}H_{15}N_3O_3$ (225.25): C 53.32, H 6.71, N 18.66; found: C 53.74, H 6.40, N 19.09.

Data of **5f** ((*E*)/(*Z*) 5:1): (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.32 (*t*, ^3J = 7.1, *Me*CH_2); 1.80 (*s*, MeCNO); 2.42 (*s*, Me); 4.25 (*q*, ^3J = 7.1, CH_2O); 4.71 (*s*, CH_2); 7.88 (*s*, H–C(5)); 9.5 (br., OH). ^{13}C-NMR ($CDCl_3$): 11.7 (*Me*CNO); 13.4 (Me); 14.4 (*Me*CH_2); 55.9 (CH_2); 60.1 (CH_2O); 113.1 (C(4)); 134.5 (C(5)); 151.5 (C(3)); 152.6 (C=N); 163.64 (CO). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.32 (*t*, ^3J = 7.1, *Me*CH_2); 1.80 (*s*, MeCNO); 2.42 (*s*, Me); 4.25 (*q*, ^3J = 7.1, CH_2O); 5.05 (*s*, CH_2); 7.89 (*s*, H–C(5)); 9.5 (br., OH). ^{13}C-NMR ($CDCl_3$): 13.4 (Me); 14.4 (*Me*CH_2); 17.1 (*Me*CNO); 49.0 (CH_2); 60.1 (CH_2O); 113.1 (C(4)); 135.3 (C(5)); 151.5 (C(3)); 152.9 (C=N); 163.64 (CO).

Data of **5f′** ((*E*)/(*Z*) 4:1): (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.33 (*t*, ^3J = 7.1, *Me*CH_2); 1.69 (*s*, MeCNO); 2.51 (*s*, Me); 4.22 (*q*, ^3J = 7.1, CH_2O); 4.79 (*s*, CH_2); 7.85 (*s*, H–C(5)); 9.5 (br., OH). ^{13}C-NMR ($CDCl_3$): 10.5 (*Me*CNO); 11.6 (Me); 14.4 (*Me*CH_2); 53.4 (CH_2); 60.1 (CH_2O); 112.4 (C(4)); 141.3 (C(5)); 144.0 (C(3)); 151.47 (C=N); 163.60 (CO). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.33 (*t*, ^3J = 7.1, *Me*CH_2); 1.69 (*s*, MeCNO); 2.53 (*s*, Me); 4.22 (*q*, ^3J = 7.1, CH_2O); 5.12 (*s*, CH_2); 7.85 (*s*, H–C(5)); 9.5 (br., OH). ^{13}C-NMR ($CDCl_3$): 11.6 (Me); 14.4 (*Me*CH_2); 16.6 (*Me*CNO) 46.5 (CH_2); 60.1 (CH_2O); 112.43 (C(4)); 141.1 (C(5)); 144.0 (C(3)); 151.47 (C=N); 163.60 (CO).

*(*E*)-1-(1*H*-Imidazol-1-yl)acetone Oxime* (**5h**): Yield *ca.* 100%[7]). M.p. 162–167° (from H_2O). ^{1}H-NMR ((D_6)DMSO): 1.63 (*s*, Me); 4.66 (*s*, CH_2); 6.88 (*s*, H–C(5)); 7.04 (*s*, H–C(4)); 7.61 (*s*, H–C(2)); 10.92 (*s*, OH). ^{13}C-NMR ((D_6)DMSO): 11.4 (Me); 49.9 (CH_2); 119.6 (C(5)); 128.5 (C(4)); 137.6 (C(2)); 151.6 (C=N). Anal. calc. for $C_6H_9N_3O$ (139.16): C 51.79, H 6.52, N 30.20; found: C 51.73, H 6.82, N 29.99.

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[6]) C_6H_6 instead of CH_2Cl_2.

[7]) Purity > 90% (by ^{1}H-NMR).

*2-(1*H*-Imidazol-1-yl)propanal Oxime* (**5i**; (*E*)/(*Z*) 35:1): Yield *ca.* 100%[7]). M.p. 109–112° (from H_2O). (*E*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.54 (*d*, ^3J = 6.6, Me); 5.05 (*d*, ^3J = 6.6, CH); 6.92 (*s*, H–C(5)); 7.22 (*s*, H–C(4)); 7.51 (*d*, ^3J = 5.9, CH=N); 7.72 (*s*, H–C(2)); 11.19 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 19.2 (Me); 51.5 (CH); 117.6 (C(5)); 128.5 (C(4)); 135.9 (C(2)); 148.9 (CH=N). (*Z*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.54 (*d*, ^3J = 6.6, Me); 5.55 (*d*, ^3J = 6.6, CH); 6.89 (*d*, ^3J = 5.9, CH=N); 6.92 (*s*, H–C(5)); 7.22 (*s*, H–C(4)); 7.72 (*s*, H–C(2)); 11.62 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 18.3 (Me); 46.8 (CH); 117.6 (C(5)); 128.5 (C(4)); 136.2 (C(2)); 149.2 (CH=N). Anal. calc. for $C_6H_9N_3O$ (139.16): C 51.79, H 6.52, N 30.20; found: C 51.97, H 6.63, N 30.18.

*(*E*)-1-(1*H*-1,2,4-Triazol-1-yl)acetone Oxime* (**5k**): Yield *ca.* 100%[7]). M.p. 149–151° (from EtOH). ^{1}H-NMR ((D$_6$)DMSO): 1.65 (*s*, Me); 4.89 (*s*, CH_2); 7.98 (*s*, H–C(5)); 8.55 (*s*, H–C(3)); 11.00 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 11.5 (Me); 52.4 (CH_2); 144.7 (C(5)); 150.7 (C=N); 151.7 (C(3)). Anal. calc. for $C_5H_8N_4O$ (140.14): C 42.85, H 5.75, N 39.98; found: C 42.82, H 5.78, N 39.95.

*2-(1*H*-1,2,4-Triazol-1-yl)propanal Oxime* (**5l**; (*E*)/(*Z*) 30:1): Yield *ca.* 100%[7]). M.p. 109–113° (from H_2O). (*E*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.59 (*d*, ^3J = 7.7, Me); 5.28 (*m*, ^3J = 7.7, CH); 7.49 (*d*, ^3J = 7.7, CH=N); 8.00 (*s*, H–C(5)); 8.60 (*s*, H–C(3)); 11.10 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 18.3 (Me); 54.2 (CH); 143.1 (C(5)); 148.1 (C(3)); 151.4 (CH=N). (*Z*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.59 (*d*, ^3J = 7.7, Me); 5.73 (*m*, ^3J = 7.7, CH); 6.92 (*d*, ^3J = 7.7, CH=N); 8.00 (*s*, H–C(5)); 8.60 (*s*, H–C(3)); 11.50 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 17.4 (Me); 50.2 (CH); 143.1 (C(5)); 148.1 (C(3)); 151.6 (CH=N). Anal. calc. for $C_5H_8N_4O$ (140.14): C 42.85, H 5.75, N 39.98; found: C 43.05, H 5.82, N 40.11.

*Methyl (*E*)-4-(Hydroxyimino)-5-(1*H*-1,2,4-triazol-1-yl)pentanoate* (**5n**): Yield 62%. M.p. 103–105°. ^{1}H-NMR ((D$_6$)DMSO): 2.41 (*m*, CH_2CH_2); 3.58 (*s*, MeO); 4.96 (*s*, CH_2); 7.97 (*s*, H–C(5)); 8.55 (*s*, H–C(3)); 11.1 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 21.3 (*C*H_2CN); 28.8 (*C*H_2CO); 51.3 (MeO); 53.4 (CH_2); 144.8 (C(5)); 151.5 (C(3)); 152.6 (C=N); 172.3 (CO). Anal. calc. for $C_8H_{12}N_4O_3$ (212.21): C 45.28, H 5.70, N 26.40; found: C 45.20, H 5.72, N 26.62.

*(*E*)-1-(1*H*-1,2,3-Triazol-1-yl)acetone Oxime* (**5o**): Yield *ca.* 100%[7]). M.p. 128–129° (from EtOH). ^{1}H-NMR ((D$_6$)DMSO): 1.71 (*s*, Me); 5.12 (*s*, CH_2); 7.78 (*s*, H–C(5)); 8.10 (*s*, H–C(4)); 11.03 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 11.6 (Me); 52.9 (CH_2); 125.4 (C(5)); 133.4 (C(4)); 150.6 (C=N). Anal. calc. for $C_5H_8N_4O$ (140.14): C 42.85, H 5.75, N 39.98; found: C 42.76, H 5.53, N 40.18.

*(*E*)-1-(2*H*-1,2,3-Triazol-2-yl)acetone Oxime* (**5o′**): Yield *ca.* 100%[7]). M.p. 123–127° (from EtOH). ^{1}H-NMR ($CDCl_3$): 1.73 (*s*, Me); 5.11 (*s*, CH_2); 7.62 (*s*, H–C(4), H–C(5)); 9.78 (*s*, OH). ^{13}C-NMR ($CDCl_3$): 11.7 (Me); 58.3 (CH_2); 134.8 (C(4), C(5)); 152.4 (C=N). Anal. calc. for $C_5H_8N_4O$ (140.14): C 42.85, H 5.75, N 39.98; found: C 43.08, H 5.63, N 40.22.

*2-(1*H*-1,2,3-Triazol-1-yl)propanal Oxime* (**5p**: (*E*)/(*Z*) 3:1): Yield *ca.* 100%[7]). M.p. 91–94° (from H_2O). (*E*)-Isomer: ^{1}H-NMR (CD_3CD_2OD): 1.71 (*d*, ^3J = 7.2, Me); 5.42 (*m*, ^3J = 6.6, CH); 7.54 (*d*, ^3J = 5.9, CH=N); 7.63 (*s*, H–C(5)); 7.94 (*s*, H–C(4)); 11.5 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 18.8 (Me); 55.1 (CH); 123.6 (C(5)); 133.5 (C(4)); 148.0 (C=N). (*Z*)-Isomer: ^{1}H-NMR (CD_3CD_2OD): 1.71 (*d*, ^3J = 7.2, Me); 5.99 (*m*, ^3J = 6.6, CH); 6.92 (*d*, ^3J = 5.9, CH=N); 7.63 (*s*, H–C(5)); 7.99 (*s*, H–C(4)); 11.5 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 18.1 (Me); 50.5 (CH); 123.8 (C(5)); 133.3 (C(4)); 148.2 (C=N). Anal. calc. for $C_5H_8N_4O$ (140.14): C 42.85, H 5.75, N 39.98; found: C 43.05, H 5.82, N 40.03.

*2-(2*H*-1,2,3-Triazol-2-yl)propanal Oxime (***5p′***: (*E*)/(*Z*) 2:1)*: Yield *ca.* 100%. Oil (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.75 (*d*, ^3J = 7.2, Me); 5.45 (*m*, ^3J = 6.6, CH); 7.50 (*d*, ^3J = 5.9, CH=N); 7.58 (*s*, H–C(4), H–C(5)); 9.6 (br., OH). ^{13}C-NMR ($CDCl_3$): 18.4 (Me); 59.9 (CH); 134.5 (C(4), C(5)); 149.2 (C=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.71 (*d*, ^3J = 7.2, Me); 6.09 (*m*, ^3J = 6.6, CH); 7.09 (*d*, ^3J = 5.9, CH=N); 7.63 (*s*, H–C(4), H–C(5)); 10.0 (br., OH). ^{13}C-NMR ($CDCl_3$): 17.8 (Me); 55.6 (CH); 134.5 (C(4), C(5)); 149.4 (C=N). Anal. calc. for $C_5H_8N_4O$ (140.14): C 42.85, H 5.75, N 39.98; found: C 42.52, H 5.56, N 40.19.

*Methyl (*E*)-4-(Hydroxyimino)-5-(1*H*-1,2,3-triazol-1-yl)pentanoate* (**5r**): Yield 81%. M.p. 123°. ^{1}H-NMR ($CDCl_3$): 2.50 (*m*, CH_2CH_2); 3.61 (*s*, MeO); 5.19 (*s*, CH_2); 7.68 (*s*, H–C(5)); 7.73 (*s*, H–C(4)); 9.7 (br., OH). ^{13}C-NMR ($CDCl_3$): 21.7 (*C*H_2CN), 29.5 (*C*H_2CO), 52.0 (MeO); 53.1 (CH_2); 124.2 (C(5)); 134.2 (C(4)); 154.0 (C=N); 173.1 (CO). Anal. calc. for $C_8H_{12}N_4O_3$ (212.21): C 45.28, H 5.70, N 26.40; found: C 45.20, H 5.70, N 26.45.

7. Oximes **5** *from the Crude Derivatives* **6** *Obtained by the Coupling of* **4** + **3**. To crude **6** obtained after the reaction of **3** (3 mmol) with **4** (3 mmol) by one of the *Procedures A–C*, MeOH (10 ml) was added by stirring at 20°. The resulting mixture was kept for 24 h and evaporated. The residue was purified by crystallization or FC: colorless **5**.

*Methyl (*E*)-2-(Hydroxyimino)-3-(1*H*-pyrazol-1-yl)butanoate* (**5c**): Yield 60%. M.p. 161–166° (from EtOH). ^{1}H-NMR ((D$_6$)DMSO): 1.75 (*d*, ^3J = 7.3, Me); 3.56 (*s*, MeO); 5.90 (*q*, ^3J = 7.3, CH); 6.24 (*t*, ^3J = 2,

H–C(4)); 7.41 (*d*, ^3J = 2, H–C(5)); 7.81 (*d*, ^3J = 2, H–C(3)); 12.60 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 15.7 (Me); 51.1 (CH); 51.9 (MeO); 104.8 (C(4)); 128.4 (C(5)); 138.7 (C(3)); 150.1 (C=N); 162.5 (CO). Anal. calc. for $C_8H_{11}N_3O_3$ (197.19): C 48.73, H 5.62, N 21.31; found: C 48.39, H 5.54, N 20.98.

*Ethyl (*E*)-2-(Hydroxyimino)-3-(1*H*-pyrazol-1-yl)propanoate* (**5d**): Yield 70%. M.p. 66–68° ([20]: 68–69°). ^{1}H-NMR ((D$_6$)DMSO): 1.21 (*t*, ^3J = 7.4, Me); 4.20 (*q*, ^3J = 7.4, CH$_2$O); 5.28 (*s*, CH$_2$); 6.18 (*t*, ^3J = 2, H–C(4)); 7.50 (*d*, ^3J = 2, H–C(5)); 7.54 (*d*, ^3J = 2, H–C(3)); 12.4 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 13.9 (Me); 44.2 (CH$_2$); 61.8 (CH$_2$O); 105.8 (C(4)); 130.8 (C(5)); 139.6 (C(3)); 151.7 (C=N); 163.0 (CO).

*Ethyl (*E*)-3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-(hydroxyimino)propanoate* (**5g**): Yield 82%. M.p. 174° ([20]: 164–165°): ^{1}H-NMR ((D$_6$)DMSO): 1.16 (*t*, ^3J = 7.3, Me); 2.01, 2.23 (2*s*, Me–C(3), Me–C(5)); 4.13 (*q*, ^3J = 7.3, CH$_2$O); 4.91 (*s*, CH$_2$); 5.74 (*s*, H–C(4)); 12.6 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 10.9, 13.6 (*Me*–C(3), *Me*–C(5)); 14.2 (MeO); 40.7 (CH$_2$); 61.2 (CH$_2$O); 104.6 (C(4)); 139.9 (C(5)); 146.6 (C(3)); 147.1 (C=N); 163.1 (CO). Anal. calc. for $C_{10}H_{15}N_3O_3$ (225.25): C 53.32, H 6.71, N 18.66; found: C 53.31, H 6.72, N 18.59.

*Methyl 2-(Hydroxyimino)-3-(1*H*-imidazol-1-yl)butanoate* (**5j**; (*E*)/(*Z*) 25:1): Yield 84%. M.p. 195–198° (from EtOH). (*E*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.72 (*d*, ^3J = 7.2, Me); 3.67 (*s*, MeO); 5.79 (*q*, ^3J = 7.2, CH); 6.87 (*s*, H–C(5)); 7.16 (*s*, H–C(4)); 7.70 (*s*, H–C(2)); 13.0 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 16.6 (Me); 46.4 (CH); 52.2 (MeO); 118.7 (C(5)); 128.1 (C(4)); 136.6 (C(2)); 149.4 (C=N); 162.8 (CO). (*Z*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.68 (*d*, ^3J = 7.2, Me); 3.67 (*s*, MeO); 5.38 (*q*, ^3J = 7.2, CH); 6.87 (*s*, H–C(5)); 7.16 (*s*, H–C(4)); 7.70 (*s*, H–C(2)); 12.1 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 18.1 (Me); 50.1 (CH); 52.2 (MeO); 118.7 (C(5)); 128.1 (C(4)); 136.6 (C(2)); 149.9 (C=N); 162.8 (CO). Anal. calc. for $C_8H_{11}N_3O_3$ (197.19): C 48.73, H 5.62, N 21.31; found: C 48.94, H 5.60, N 21.09.

*Methyl 2-(Hydroxyimino)-3-(1*H*-1,2,4-triazol-1-yl)butanoate* (**5m**; (*E*)/(*Z*) 35:1): Yield 78%. M.p. 225–227° (from EtOH). (*E*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.81 (*d*, ^3J = 7.4, Me); 3.60 (*s*, MeO); 5.88 (*q*, ^3J = 7.4, CH); 7.92 (*s*, H–C(5)); 8.64 (*s*, H–C(3)); 12.9 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 15.1 (Me); 50.0 (CH); 52.0 (MeO); 143.1 (C(5)); 151.1 (C(3)); 148.6 (C=N); 162.2 (CO). (*Z*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.70 (*d*, ^3J = 7.4, Me); 3.61 (*s*, MeO); 5.54 (*q*, ^3J = 7.4, CH); 7.99 (*s*, H–C(5)); 8.61 (*s*, H–C(3)); 12.0 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 17.4 (Me); 52.0 (MeO); 54.9 (CH); 143.6 (C(5)); 151.5 (C(3)); 149.8 (C=N); 162.2 (CO). Anal. calc. for $C_7H_{10}N_4O_3$ (198.18): C 42.42, H 5.09, N 28.27; found: C 42.41, H 5.07, N 28.25.

*Methyl (*E*)-2-(Hydroxyimino)-3-(4*H*-1,2,4-triazol-4-yl)butanoate* (**5m′**): Identified in the reaction mixture. Yield *ca.* 15%[7]). ^{1}H-NMR ((D$_6$)DMSO): 1.76 (*d*, ^3J = 7.4, Me); 3.71 (*s*, MeO); 5.82 (*q*, ^3J = 7.4, CH); 8.52 (*s*, H–C(3), H–C(5)); 13.0 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 16.2 (Me); 45.5 (CH); 52.3 (MeO); 142.5 (C(3), C(5)); 148.3 (C=N); 162.2 (CO).

*Methyl 2-(Hydroxyimino)-3-(1*H*-1,2,3-triazol-1-yl)butanoate* (**5q**; (*E*)/(*Z*) 4:1): Yield 64%. M.p. 177–179° (from EtOH). R_f 0.28 (AcOEt/petroleum ether 1:1). (*E*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.82 (*d*, ^3J = 7.2, Me); 3.62 (*s*, MeO); 6.14 (*q*, ^3J = 7.2, CH); 7.72 (*s*, H–C(5)); 8.23 (*s*, H–C(4)); 12.96 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 15.9 (Me); 49.8 (CH); 52.1 (MeO); 123.9 (C(5)); 132.7 (C(4)); 148.3 (C=N); 162.2 (CO). (*Z*)-Isomer: ^{1}H-NMR ((D$_6$)DMSO): 1.73 (*d*, ^3J = 7.2, Me); 3.62 (*s*, MeO); 5.77 (*q*, ^3J = 7.2, CH); 7.75 (*s*, H–C(5)); 8.21 (*s*, H–C(4)); 12.07 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 17.7 (Me); 52.1 (MeO); 55.5 (CH); 123.9 (C(5)); 133.3 (C(4)); 148.4 (C=N); 162.2 (CO). Anal. calc. for $C_7H_{10}N_4O_3$ (198.18): C 42.42, H 5.09, N 28.27; found: C 42.41, H 5.14, N 28.31.

*Methyl 2-(Hydroxyimino)-3-(2*H*-1,2,3-triazol-2-yl)butanoate* (**5q′**; (*E*)/(*Z*) 5:2): Yield 9%. Oil. R_f 0.82 (AcOEt/petroleum ether 1:1). (*E*)-Isomer: ^{1}H-NMR (CDCl$_3$): 2.03 (*d*, ^3J = 7.2, Me); 3.71 (*s*, MeO); 6.23 (*q*, ^3J = 7.2, CH); 7.65 (*s*, H–C(5), H–C(4)); 10.9 (br., OH). ^{13}C-NMR (CDCl$_3$): 15.7 (Me); 52.4 (MeO); 54.6 (CH); 134.4 (C(4), C(5)); 150.7 (C=N); 162.2 (CO). (*Z*)-Isomer: ^{1}H-NMR (CDCl$_3$): 1.87 (*d*, ^3J = 7.2, Me); 3.74 (*s*, MeO); 5.76 (*q*, ^3J = 7.2, CH); 7.65 (*s*, H–C(5), H–C(4)); 10.1 (*s*, OH). ^{13}C-NMR (CDCl$_3$): 17.4 (Me); 52.4 (MeO); 60.7 (CH); 134.41 (C(4), C(5)); 150.7 (C=N); 162.24 (CO). Anal. calc. for $C_7H_{10}N_4O_3$ (198.18): C 42.42, H 5.09; found: C 43.35, H 5.85.

*(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)acetone Oxime* (**5s**): Yield 68% after FC. M.p. 187–190° (from EtOH). R_f 0.73 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ((D$_6$)DMSO): 1.72 (*s*, Me); 5.47 (*s*, CH$_2$); 7.3–8.1 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)); 11.00 (*s*, OH). ^{13}C-NMR ((D$_6$)DMSO): 11.9 (Me); 51.4 (CH$_2$); 110.8, 119.3, 124.1, 127.5 (C(4), C(5), C(6), C(7)); 133.3, 145.3 (C(8), C(9)); 150.5 (C=N). Anal. calc. for $C_9H_{10}N_4O$ (190.20): C 56.83, H 5.30, N 29.46; found: C 56.81, H 5.30, N 29.45.

*(*E*)-1-(2*H*-1,2,3-Benzotriazol-2-yl)acetone Oxime* (**5s′**): Yield 10% after FC. M.p. 130–132° (from EtOH). R_f 0.32 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ((D$_6$)DMSO): 1.73 (*s*, Me); 5.49 (*s*, CH$_2$); 7.42 (*m*, H–C(5), H–C(6)); 7.93 (*m*, H–C(4), H–C(7)); 11.15 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 11.8 (Me); 59.8 (CH$_2$); 117.8,

126.5 (C(4), C(5), C(6), C(7)); 143.8 (C(8), C(9)); 150.1 (C=N). Anal. calc. for $C_9H_{10}N_4O$ (190.20): C 56.83, H 5.30, N 29.46; found: C 56.79, H 5.25, N 29.38.

*2-(1*H*-1,2,3-Benzotriazol-1-yl)propanal Oxime* (**5t**; (*E*)/(*Z*) 7:2): Yield 22% after FC. Oil. R_f 0.65 (AcOEt/petroleum ether 1:1). (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.95 (*d*, ^3J = 6.6, Me); 5.70 (*m*, ^3J = 6.6, CH); 7.3–8.1 (*m*, H–C(5), H–C(6), H–C(7), H–C(8)); 7.53 (*d*, ^3J = 7.2, CH=N); 8.7 (br., OH). ^{13}C-NMR ($CDCl_3$): 17.9 (Me); 54.7 (CH); 109.8, 120.1, 124.3, 127.6 (C(4), C(5), C(6), C(7)); 132.4, 146.1 (C(8), C(9)); 149.1 (C=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.92 (*d*, ^3J = 6.6, Me); 6.30 (*m*, ^3J = 6.6, CH); 7.10 (*d*, ^3J = 6.5, CH=N); 7.3–8.1 (*m*, H–C(5), H–C(6), H–C(7), H–C(8)); 9.4 (br., OH). ^{13}C-NMR ($CDCl_3$): 17.7 (Me); 49.1 (CH); 109.4, 120.0, 124.2, 127.5 (C(4), C(5), C(6), C(7)); 132.6, 146.1 (C(8), C(9)); 149.4 (C=N). Anal. calc. for $C_9H_{10}N_4O$ (190.20): C 56.83, H 5.30, N 29.46; found: C 57.07, H 5.62, N 29.82.

*2-(2*H*-1,2,3-Benzotriazol-2-yl)propanal Oxime* (**5t′**; (*E*)/(*Z*) 2:1): Yield 68% after FC. Oil. R_f 0.48 (AcOEt/petroleum ether 1:1). (*E*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.95 (*d*, ^3J = 7.2, Me); 5.74 (*m*, ^3J = 6.6, C*H*Me); 7.38 (*m*, H–C(5), H–C(6)); 7.80 (*d*, ^3J = 6.0, CH=N); 7.86 (*m*, H–C(4), H–C(7)); 8.8 (br., OH). ^{13}C-NMR ($CDCl_3$): 19.0 (Me); 61.6 (CH); 118.1, 126.7 (C(4), C(5), C(6), C(7)); 144.2 (C(8), C(9)); 148.9 (C=N). (*Z*)-Isomer: ^{1}H-NMR ($CDCl_3$): 1.92 (*d*, ^3J = 7.2, Me); 6.35 (*m*, ^3J = 6.6, CH); 7.20 (*d*, ^3J = 6.0, CH=N); 7.38 (*m*, H–C(5), H–C(6)); 7.86 (*m*, H–C(4), H–C(7)); 9.20 (br., OH). ^{13}C-NMR ($CDCl_3$): 18.4 (Me); 57.3 (CH); 118.1, 126.7 (C(4), C(5), C(6), C(7)); 144.2 (C(8), C(9)); 148.8 (C=N). Anal. calc. for $C_9H_{10}N_4O$ (190.20): C 56.83, H 5.30, N 29.46; found: C 56.73, H 5.58, N 29.56.

*Methyl (*E*)-2-(Hydroxyimino)-3-(1*H*-1,2,3-benzotriazol-1-yl)butanoate* (**5u**): Yield 71% after FC. M.p. 190–192° (from EtOH). R_f 0.79 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ((D$_6$)DMSO): 2.01 (*d*, ^3J = 7.2, Me); 3.61 (*s*, MeO); 6.47 (*m*, ^3J = 7.2, CH); 7.4–8.1 (*m*, H–C(5), H–C(6), H–C(7), H–C(8)); 13.0 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 15.6 (Me); 49.2 (CH); 52.2 (MeO); 110.9, 119.2, 123.9, 127.3 (C(4), C(5), C(6), C(7)); 132.3, 145.2 (C(8), C(9)); 147.92 (C=N) 162.34 (CO). Anal. calc. for $C_{11}H_{12}N_4O_3$ (248.24): C 53.22, H 4.87, N 22.57; found: C 53.46, H 4.99, N 22.30.

*Methyl (*E*)-2-(Hydroxyimino)-3-(2*H*-1,2,3-benzotriazol-2-yl)butanoate* (**5u′**): Yield 14% after FC. M.p. 180–184° (from EtOH). R_f 0.36 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ((D$_6$)DMSO): 2.03 (*d*, ^3J = 7.2, Me); 3.57 (*s*, MeO); 6.44 (*m*, ^3J = 7.2, CH); 7.42 (*m*, H–C(5), H–C(6)); 7.90 (*m*, H–C(4), H–C(7)); 13.7 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 15.5 (Me); 52.1 (MeO); 55.7 (CH); 117.9, 126.4 (C(4), C(5), C(6), C(7)); 144.8 (C(8), C(9)); 148.1 (C=N); 162.2 (CO). Anal. calc. for $C_{11}H_{12}N_4O_3$ (248.24): C 53.22, H 4.87, N 22.57; found: C 53.61, H 5.11, N 22.97.

*Methyl (*E*)-4-(Hydroxyimino)-5-(1*H*-1,2,3-benzotriazol-1-yl)pentanoate* (**5v**): Yield 63% after FC. M.p. 101–102° (from EtOH). R_f 0.30 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ($CDCl_3$): 2.57 (*m*, CH_2CH_2); 3.66 (*s*, MeO); 5.47 (*s*, CH_2); 7.4–8.1 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)); 9.0 (br., OH). ^{13}C-NMR ($CDCl_3$): 21.7 (*C*H_2CN); 29.5 (*C*H_2CO); 51.5 (CH_2); 52.0 (MeO); 110.8, 119.9, 124.3, 127.8 (C(4), C(5), C(6), C(7)); 133.2, 154.3 (C(8), C(9)); 154.3 (C=N); 173.1 (CO). Anal. calc. for $C_{12}H_{14}N_4O_3$ (262.27): C 54.96, H 5.38, N 21.36; found: C 54.96, H 5.37, N 21.32.

*Methyl (*E*)-4-(Hydroxyimino)-5-(2*H*-1,2,3-benzotriazol-2-yl)pentanoate* (**5v′**): Yield 31% after FC. Oil. R_f 0.65 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ($CDCl_3$): 2.59 (*m*, CH_2CH_2); 3.63 (*s*, MeO); 5.53 (*s*, CH_2); 7.46 (*m*, H–C(5), H–C(6)); 7.92 (*m*, H–C(4), H–C(7)); 9.3 (br., OH). ^{13}C-NMR ($CDCl_3$): 21.9 (*C*H_2CN); 29.5 (*C*H_2CO); 51.8 (MeO); 59.2 (CH_2); 118.1 (C(5), C(6)); 126.7 (C(4), C(7)); 144.6 (C(8), C(9)); 154.0 (C=N); 173.1 (CO). Anal. calc. for $C_{12}H_{14}N_4O_3$ (262.27): C 54.96, H 5.38, N 21.36; found: C 56.21, H 5.50, N 22.87.

*(*E*)-1-(1*H*-3-Amino-1,2,4-triazol-1-yl)acetone Oxime* (**5w**): Yield 56% after FC. M.p. 116–118°. R_f 0.18 (^{i}PrOH). ^{1}H-NMR ((D$_6$)DMSO): 1.62 (*s*, Me); 4.57 (*s*, CH_2); 5.26 (*s*, NH_2); 8.01 (*s*, CH); 10.9 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 11.3 (Me); 52.0 (CH_2); 143.3 (CH); 151.0 (C=N); 164.2 (CNH_2).

*(*E*)-1-(1*H*-5-Amino-1,2,4-triazol-1-yl)acetone Oxime* (**5w′**): Yield 24% after FC. M.p. 154–159°. R_f 0.14 (^{i}PrOH). ^{1}H-NMR ((D$_6$)DMSO): 1.62 (*s*, Me); 4.52 (*s*, CH_2); 6.21 (*s*, NH_2); 7.31 (*s*, CH); 10.8 (br., OH). ^{13}C-NMR ((D$_6$)DMSO): 11.5 (Me); 49.4 (CH_2); 148.5 (CH); 155.4 (C=N); 166.2 (CNH_2). **5w**/**5w′**. Anal. calc. for $C_5H_9N_5O$ (155.16): C 38.70, H 5.85, N 45.14; found: C 38.39, H 5.82, N 44.78.

8. *Silylation of Oximes* **5c,d,g,j,m,q,s,s′**, **5m**/**5m′**, *and* **5q**/**5q′**. $(TMS)_2NH$ (0.5 mmol, 0.1 ml) was added to the oxime **5** (0.5 mmol). The mixture was boiled for 5 h and then evaporated: **6** (*ca.* 100%) as colorless oil. Purity > 90% by ^{1}H-NMR (internal standard CH_2Cl_2).

9. *(*E*)-1-(1*H*-Imidazol-1-yl)acetone* O-*[(*tert*-Butyl)dimethylsilyl]oxime* (**6h′**). To a stirred soln. of **5h** (1 mmol, 0.14 g) in CH_2Cl_2 (5 ml) at 0° was added successively Et_3N (1.5 mmol, 0.21 ml) and a soln. of Me_2*t*BuSiCl (1.3 mmol, 0.20 g) in CH_2Cl_2 (1 ml). The mixture was kept for 6 h at 0° and evaporated. The residual oil was treated with petroleum ether (10 ml), the resulting suspension was filtered under dry Ar, and the filtrate evaporated: 0.21 g (81%) of **6h′**. Reddish oil. Purity > 90% by ^{1}H-NMR in the presence of CH_2Cl_2 as a standard.

^{1}H-NMR ($CDCl_3$): 0.05 (*s*, Me_2Si); 0.87 (*s*, Me_3C); 1.72 (*s*, Me); 4.57 (*s*, CH_2); 6.81 (*s*, H–C(5)); 6.99 (*s*, H–C(4)); 7.45 (*s*, H–C(2)). ^{13}C-NMR ($CDCl_3$): –5.4 (Me_2Si); 11.7 (Me); 17.9 (Me_3C); 25.8 (Me_3C); 50.8 (CH_2); 119.0 (C(5)); 129.4 (C(4)); 137.2 (C(2)); 156.4 (C=N). ^{29}Si-NMR ($CDCl_3$): 27.3.

10. *Ethyl 2-(Hydroxyimino)-3-(1*H*-indol-3-yl)propanoate* (**16**). To a stirred soln. of 1*H*-indole (2.7 mmol, 0.32 g) in Et_2O (3 ml) was added MeLi (0.60 g as 0.05% soln. in pentane) at 0°. The mixture was stirred for 10 min, then a soln. of **3d** (1.35 mmol, 0.39 g) in Et_2O (3 ml) was added dropwise at 20°. The mixture was kept for 1 h at 20°, EtOH (3 ml) added, and the mixture evaporated after 1 h. The residue was purified by FC: **16** (0.12 g, 36%). Colorless solid. M.p. 155–158° ([13]: 156–158°). R_f 0.46 (AcOEt/petroleum ether 1:1). ^{1}H-NMR (CD_3CN): 1.22 (*t*, ^3J = 6.9, Me); 4.02 (*d*, ^4J = 0.9, CH_2); 4.19 (*q*, ^3J = 6.9, CH_2O); 7.03–7.17 (*m*, H–C(2), H–C(5), H–C(6)); 7.36, 7.67 (2*m*, H–C(4), H–C(7)); 9.1 (br., NH); 10.0 (br., OH). ^{13}C-NMR (CD_3CN): 14.4 (Me); 21.0 (CH_2); 62.3 (CH_2O); 112.3, 118.3, 119.7, 119.9, 122.5, 124.6 (C(2), C(3), C(4), C(5), C(6), C(7)); 128.1, 137.2 (C(8), C(9)); 152.8 (C=N); 163.2 (CO).

11. *Oximes* **5** via *Interaction between Azoles* **2** *and BENA* **3a**. To a stirred soln. of **2** (1 mmol) in CH_2Cl_2 (5 ml) was added a soln. of **3a** (1 mmol) in CH_2Cl_2 (2 ml). The mixture was kept for 6 h at 20° and evaporated. To the residue was added a soln. of NH_4F (0.05 mmol, 2 mg) in MeOH (3 ml). The mixture was kept for 12 h at 20°. The yields of **5** and **15** were determined by ^{1}H-NMR (internal standard $C_2H_4Cl_2$). Results: see *Scheme 7*. **5k** and **5o** were purified by recrystallization.

12. *Study of the Mechanism for the Interaction of BENA* **3** *with* N-*TMS Derivatives* (see *Table 1*). *a*) To **4b** (0.2 mmol, 28 mg) were added successively at 20° 0.5M **3a** in $CDCl_3$ (0.2 mmol, 0.4 ml) and CH_2Cl_2 (0.5 mmol, 32 µl; internal standard for ^{1}H-NMR monitoring). Every 10 min, the mixture was analyzed by ^{1}H-NMR. The inductive period (conversion **3a** < 5%) was 1.5 h, whereupon within the next 10 min, only derivative **6h** was identified in the mixture (yield 93%; see *Table 1*). The procedure was repeated, but in the presence of **6h** (25 mol-%), Et_3N (10 mol-%), or $Me_2{}^t$BuSiCl (0.02 mmol, 3 mg), as well as after replacement of derivative **4b** by **4b**′ (0.2 mmol, 36 mg) (see *Table 1*).

In the above cited procedure, **3a** was replaced by 0.5M **3a**′ in $CDCl_3$ (0.2 mmol, 0.4 ml). After 6 h, no change was detected by ^{1}H-NMR monitoring. The mixture was evaporated and then kept for 7 d at 20°. $CDCl_3$ (0.3 ml) and CH_2Cl_2 (0.5 mmol, 32 µl) were added for ^{1}H-NMR analysis (see *Table 1*).

b) To **4a** (0.2 mmol, 28 mg) were added successively at 20° 0.5M **3a** in $CDCl_3$ (0.2 mmol, 0.4 ml) and CH_2Cl_2 (0.5 mmol, 32 µl; internal standard for ^{1}H-NMR monitoring). No change was observed by ^{1}H-NMR after 170 h (see *Table 1*).

c) To **4a**′ (0.2 mmol, 36 mg) was added 0.5M **3a** in $CDCl_3$ (0.2 mmol, 0.4 ml) at 20°. The mixture was evaporated and kept for 72 h at 20°. Then $CDCl_3$ (0.3 ml) and CH_2Cl_2 (0.5 mmol, 32 µl) were added. Only **3a** and **4a**′ were observed by ^{1}H-NMR (see *Table 1*).

d) At 20°, 0.5M **3a** in $CDCl_3$ (0.2 mmol, 0.4 ml) and CH_2Cl_2 (0.5 mmol, 32 µl; internal standard for NMR monitoring) were added successively to the mixture of **4a** (0.2 mmol, 28 mg) and **4b** (0.2 mmol, 28 mg). Results of ^{1}H-NMR monitoring: see *Table 1*.

e) At 20°, 0.5M **3a** in $CDCl_3$ (0.2 mmol, 0.4 ml) was added dropwise to the stirred soln. of 1-methyl-1*H*-imidazole (0.2 mmol, 16 mg) in CH_2Cl_2 (1 ml). According to ^{1}H-NMR, only decomposition of **3a** was observed immediately, with no change of 1-methyl-1*H*-imidazole.

13. *Fixation of Ethyl 2-Nitrosoacrylate* (**7b**) *by Trapping Agents*. *a*) The soln. of **3d** (5 mmol, 1.45 g) in CH_2Cl_2 (7 ml) was added to a stirred mixture of **4d** (5 mmol, 1.45 g) and 1-[(trimethylsilyl)oxy]cyclopentene (25 mmol, 4.4 ml). The mixture was kept for 24 h at 20°, then EtOH (10 ml) was added. After 24 h, the mixture was separated by FC: *ethyl 2-(hydroxyimino)-3-(2-oxocyclopentyl)propanoate* (**10**; 0.72 g, 67%). 90–94° ([21]: 94–96°). R_f 0.31 (AcOEt/petroleum ether 1:1). ^{1}H-NMR ($CDCl_3$): 1.37 (*t*, ^3J = 7.4, Me); 1.54–3.01 (CH_2, CH); 4.31 (*q*, ^3J = 7.4, CH_2O); 9.7 (br., OH). ^{13}C-NMR ($CDCl_3$): 14.0 (Me); 20.6, 24.6, 29.6, 37.3, 46.2 (CH_2, CH); 61.9 (CH_2O); 151.2 (C=N); 163.4 (CO_2); 219.2 (CO).

b) The procedure *a* was repeated till the moment of EtOH addition. Instead, the mixture was evaporated and distilled *in vacuo* to give *ethyl 4,4a,5,6,7,7a-hexahydro-7a-[(trimethylsilyl)oxy]cyclopenta[e][1,2]oxazine-3-carboxylate* (**9**; 0.44 g, 31%). Purity of **9** > 90% (by ^{1}H-NMR); but **9** was decomposed completely in the NMR tube after 30 min. ^{1}H-NMR ($CDCl_3$): 0.24 (*s*, Me_3Si); 1.31 (*t*, ^3J = 7.4, Me); 1.68–1.92, 2.12–2.40 (*m*, CH_2); 4.21 (*q*, ^3J = 7.4, CH_2O). ^{13}C-NMR ($CDCl_3$): 1.3 (Me_3Si); 14.2 (Me); 21.9, 26.3, 30.1, 37.6, 39.2 (CH_2, CH); 62.1 (CH_2O), 111.6 (COSi); 158.4 (C=N); 163.7 (CO).

c) The procedure *b* was repeated replacing 1-[(trimethylsilyl)oxy]cyclopentene with ethyl vinyl ether (50 mmol, 4.8 ml). The mixture was kept for 24 h, and then *ethyl 6-ethoxy-5,6-dihydro-4*H*-1,2-oxazine-3-carboxylate* (**8**) was identified by NMR (see [22]). ^{1}H-NMR ($CDCl_3$): 1.12 (*t*, ^3J = 7.4, *Me*CH_2O–C(6)); 1.33 (*t*, ^3J = 7.4, *Me*CH_2OCO); 1.67–1.89 (*m*, 1 H–C(5)); 1.93–2.08 (*m*, 1 H–C(5)); 2.30–2.60 (*m*, 2 H–C(4));

3.57 (q, $^3J = 7.4$, 1 H, CH_2O); 3.87 (q, $^3J = 7.4$, 1 H, CH_2O); 4.21 (q, $^3J = 7.4$, CH_2OCO); 5.23 (dd, $^3J = 3.5$, 3.0, H–C(6)). ^{13}C-NMR ($CDCl_3$): 14.0 ($MeCH_2O$); 14.6 (Me); 20.4 (C(4)); 27.1 (C(5)); 62.1 (CH_2OCO); 64.5 (CH_2O); 101.0 (C(6)); 151.6 (C=N); 164.2 (CO_2).

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