Recyclizations of 2-Aminobenzylimines and Thioaroylhydrazones of *N*-Substituted *N*-Hydroxy-3-oxobutanamides

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A universal scheme is proposed for the molecular design of heterocyclic recyclizations by replacing the exocyclic hydroxyl groups in *exo-trig*- ring-chain tautomeric molecules with substituted amines or hydrazines. The practical applicability of this approach is demonstrated by the condensations of 5-hydroxy-5-methyl-3-isoxazolidinones with thioaroyl-hydrazines and 2-aminomethylaniline. The condensation products were studied by modern ^{1}H, ^{13}C and ^{15}N NMR spectroscopic methods using three solvents: $CDCl_3$, DMSO[D_6] and CD_3CN. The solvent was found to have a strong effect to the relative amounts of the tautomers.

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Introduction.

Ring-chain tautomerism is an important phenomenon in heterocyclic chemistry [1-4]. Recently, our attention was drawn to multitautomeric ring-chain systems comprising more than one cyclic structure. They correspond to tautomeric interconversion of heterocycles [5,6] which phenomenon is closely related to the frequently studied ring transformations of hetero- and carbocycles occurring *via* linear intermediates [7-11].

A series of ring-linear-ring tautomeric systems generated previously [5,6] provides a basis for systematic research. In particular, the available data on ring-ring equilibria in substituted imines and hydrazones of aldoses [12-15] give a basis to the general scheme illustrating the method to achieve recyclizations by substituting amino groups (of substituted amines and hydrazines) to the exocyclic hydroxyl group in 5(6)-*exo-trig*-tautomeric (or pseudotautomeric) ring-chain systems, thereby introducing another cyclic (tautomeric or pseudotautomeric) 5(6)-*endo-trig*- structure in the end product (Scheme 1).

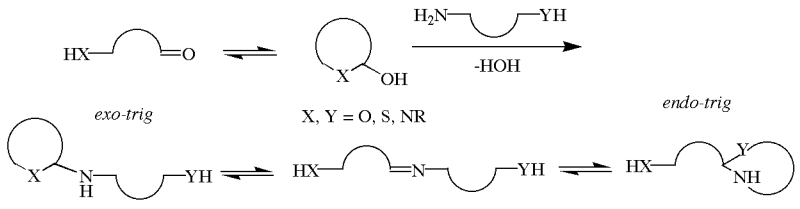
Results and Discussion.

General.

The approach was selected based on the following considerations. Compounds **Ia-c**, which do not undergo ring opening in non-polar solvents [16] exhibit ring-chain equilibria A ⇆ B when dissolved in DMSO [17]. The same is true for the products obtained by substitution of their hemiacetal hydroxyl group with certain hydrazine derivatives [18]. On the other hand, the condensation between carbonyl compounds and either 2-aminomethylaniline or thioaroylhydrazines leads to cyclic structures 1,3,4-Δ^2-thiadiazolines [19] or (1,2,3,4-tetrahydroquinazolines [20], respectively). These heterocycles can exhibit ring-chain tautomerism, which was indeed observed in 1,3,4-Δ^2-thiadiazolines [21,22].

We found that 5-hydroxyisoxazolidin-3-ones **Ia-c** react smoothly with thioaroylhydrazines **IIa**,**b** and 2-aminomethylaniline to produce compounds **IIIa-f** and **IVa**,**b**, respectively (Schemes 2 and 3) in high yields (70-90%, see Experimental).

Scheme 1 A method to achieve ring-linear-ring tautomeric systems.

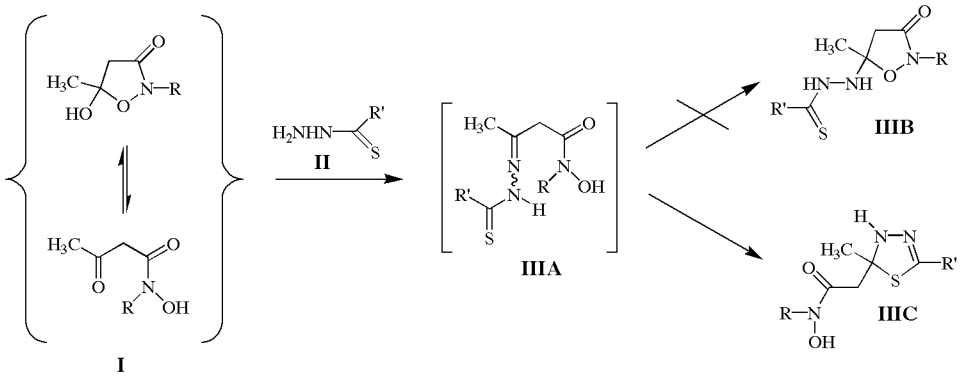


Accordingly, the products of condensation of 5-hydroxy-5-methyl-3-isoxazolidinones (**Ia-c**, Scheme 2, 5-*exo-trig*-system) with thioaroylhydrazines (**IIa-b**, Scheme 2) and 2-aminomethylaniline (the source of 5- or 6-*endo-trig*-systems in the end product) were studied in order to test the ideas proposed in Scheme 1.

Thioaroylhydrazine Derivatives.

In theory, the condensation products **III** obtained from thioaroylhydrazines may exist in either of the two cyclic structures, isoxazolidine **B** or 1,3,4-Δ^2-thiadiazoline **C** (Scheme 2).

Scheme 2 Possiblecondensation products from thioaroylhydrazines.



I a R = CH_2Ph, **b** R = Ph, **c** R = 4-MeOOC-Ph
II a R' = Ph, **b** R' = 4-Me-Ph
III a R = CH_2Ph, R' = Ph, **b** R = CH_2Ph, R' = 4-Me-Ph,
c R = Ph, R' = Ph, **d** R = Ph, R' = 4-Me-Ph,
e R = 4-MeOOC-Ph, R' = Ph, **f** R = 4-MeOOC-Ph, R' = 4-Me-Ph

It turned out that **C** was the only cyclic tautomer present in this system. The unmistakably cyclic (both in polar and non-polar solvents) structures **III** (Table 1) are identified as **IIIC** by the carbon signals at δ_C 78.2-81.4 ppm corresponding to the C-5 atoms of 1,3,4-thiadiazolines [19]. The C-5 signals of structures **IIIB** should be shifted beyond 90 ppm [18].

recyclization of isoxazolidines into 1,3,4-thiadiazolines takes place.

Aminomethylaniline Derivatives.

The situation with 2-aminomethylaniline derivatives **IVa**,**b** is more complicated. All possible tautomers (isomers) are shown in Scheme 3. Taking into account all pos-

Table 1

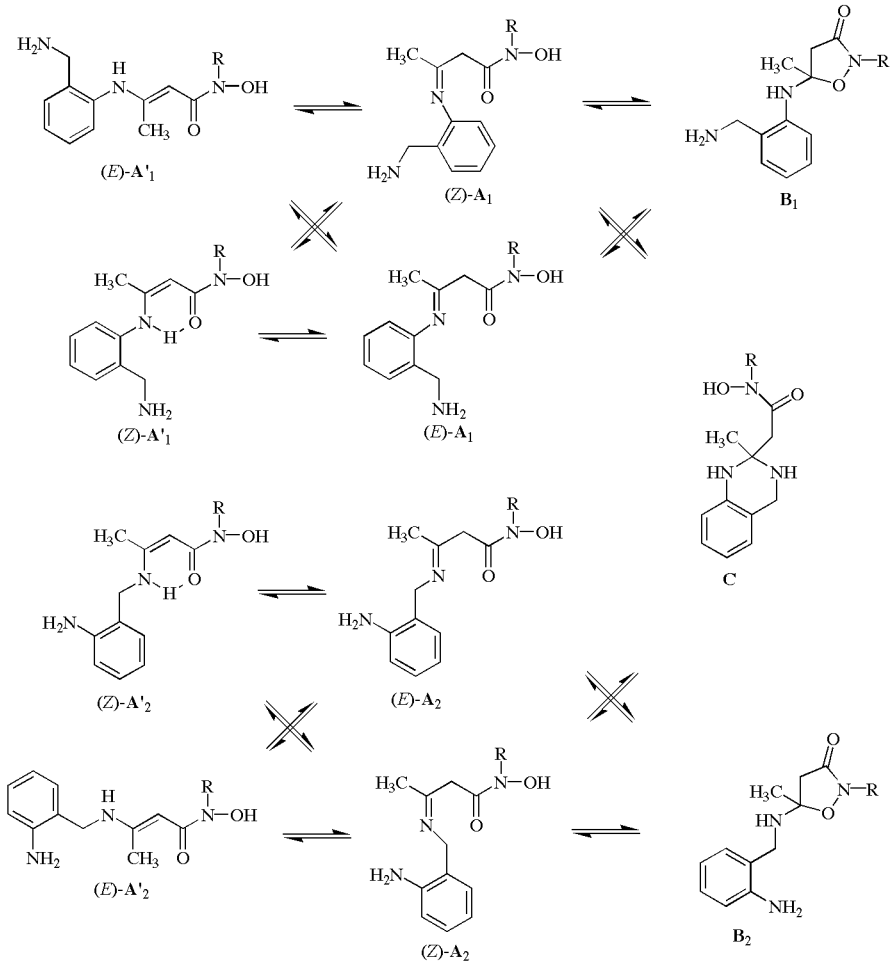
^1H and ^{13}C NMR Parameters for Compounds **IIIa-f**; Chemical shifts (in ppm) are Referenced to Tetramethylsilane (0.00 ppm); Coupling Constants are in Hz

	IIIa	**IIIb**	**IIIc**	**IIId**	**IIIe**	**IIIf**
Solvent	DMSO[D_6]	$CDCl_3$	DMSO[D_6]	$CDCl_3$	DMSO[D_6]	$CDCl_3$
C*H*$_3$	1.73	1.60	1.61	1.65	1.73	1.66
C*H*$_2$CO	3.23, 3.36	3.07, 3.25	3.29, 3.39	3.20, 3.38	3.32, 3.43	3.34, 3.49
	^2J = -16.50	^2J = -16.45	^2J = -16.35	^2J = -16.58	^2J = -16.56	^2J = -16.00
N*H*	7.96	7.82	7.69	7.85	7.63	8.13
O*H*	9.52	10.02	10.95	10.72	10.66	10.95
H_{arom}	7.07-7.80	7.20-7.46	7.12-7.65	7.21-7.65	7.29-7.96	7.38-7.91
Other ^1H signals	4.80 (C*H*$_2$Ph)	2.32 (4-Me), 4.73 (C*H*$_2$Ph)	-	2.32 (4-Me)	3.86 (COOMe)	2.33 (4-Me), 3.84 (COOMe)
*C*H$_3$	24.8	27.8	27.6	26.3	26.7	27.5
*C*H$_2$	40.9	44.0	45.5	43.1	45.1	42.1
C-5	78.2	81.4	80.8	81.4	80.6	81.2
C_{arom}	127.5-135.9 (8 signals)	127.4-151.2 (8 signals)	120.3-144.0 (8 signals)	117.4-130.3 (8 signals)	115.5-131.2 (8 signals)	127.2-136.6 (8 signals)
C-2	141.4	140.8	141.3	140.4	144.0	142.3
C=O	167.0	170.2	169.2	165.2	166.2	166.9
Other ^{13}C Signals	48.6 (*C*H$_2$Ph)	21.8 (4-Me), 52.0 (*C*H$_2$Ph)	-	21.8 (4-Me)	51.8 (OMe), 150.6 (*C*OO)	21.8 (4-Me), 52.5 (OMe), 154.5 (*C*OO)

The mass spectrum (EI, 70 eV) of **IIIa** is also consistent with the structure **IIIC**. The base peak corresponds to $C_9H_9N_2S^+$ ions formed directly from the molecular ions ($M^{+\cdot}$) *via* the loss of $RN(OH)COCH_2^{\bullet}$ radical, which rules out structure **IIIB**. Thus, in the case of compounds **III**, a

sible transformations (including imine-enamine prototropic tautomerism with ensuing (*E*)/(*Z*) isomerism, as well as ring-linear, ring-linear-ring, and linear-ring-linear transformations), a total of 11 structures can theoretically coexist in this system.

Scheme 3 All possible isomers of compounds **IVa** and **IVb**.

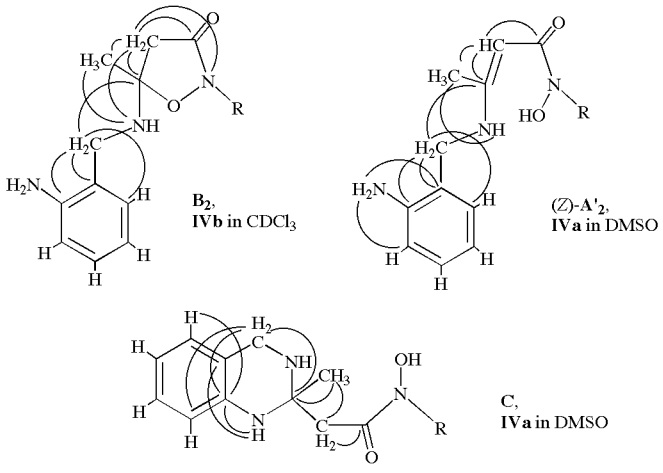


IV a R = Ph, **b** R = CH_2Ph

In the reality, both compounds **IVa** and **IVb** were found to exhibit no more than three accessible forms in equilibrium. Their ratio depended on the nature of the solvent and it took several days to reach the equilibria (Table 2). Various NMR measurements were carried out in $CDCl_3$, CD_3CN and DMSO, including a variety of 2D spectra to enable identification of the isomeric forms. Also ^{15}N NMR spectra for **IVa** were recorded in chloroform. Proton and carbon chemical shifts were mainly used to identify the isomeric structures, and the assignments were confirmed by 2D spectra. Typical HMBC correlations for isomeric structures (*Z*)-$\mathbf{A'_2}$, $\mathbf{B_2}$ and **C** are shown in Scheme 4.

Chemical shifts for **IVa** and **IVb** in selected solvents are presented in Table 3. The low solubility of the compound or the small relative amounts of some of the forms made it impossible to assign all forms in any solvent. However, this information was available for all main forms (*Z*)-$\mathbf{A'_2}$, $\mathbf{B_2}$ and **C** of compounds **IVa** and **IVb** at least in one solvent. With the help of the information given in Table 3 it is easy to reveal the presence of the various forms also in more difficult cases (low solubility or abundance).

Scheme 4 Selected HMBC correlations for different isomers.



It follows from the NMR spectra that compound **IVa** exists, immediately after dissolution in $CDCl_3$, in a single form, most likely as structure $\mathbf{B_2}$. The quinazoline structure **C** is ruled out because it should exhibit an sp^3 carbon signal (N***C***N) at 60−70 ppm, the actual shift being 95.4 ppm (Table 3), which is characteristic of 5-amino-3-isoxazolidinones [18]. Structure $\mathbf{B_1}$ is excluded because of the observed ratio of signals for the "aniline"- and "benzyl"-type amino groups, 2:1, which should be reversed for $\mathbf{B_1}$. The ^{15}N chemical shifts were determined for compound **IVa** in $CDCl_3$ (***N***−C=O −187.8, ***N***H −317.7 and ***N***H_2 −326.4 ppm). Since the nitrogen signals were obtained from $^1H-^{15}N$ HMQC and HMBC spectra by inverse detection, their accuracy is about ±1 ppm.

Unlike **IVa**, which retains structure $\mathbf{B_2}$ when dissolved in $CDCl_3$, a ring-linear-ring equilibrium, (*Z*)-$\mathbf{A'_2} \leftrightarrows \mathbf{B_2} \leftrightarrows \mathbf{C}$ (Table 2) was established in solutions of **IVb**. The presence of the (*Z*)-$\mathbf{A'_2}$ tautomer was confirmed by comparing with the spectra of **IVa** and **IVb** in DMSO, *vide infra* (Table 3). Structure $\mathbf{B_2}$ was identified as in the case of **IVa**. The assignment of structure **C** was primarily based on the chemical shift of the N***C***N carbon at 66.7 ppm.

After dissolving in DMSO **IVa** exists mainly as the enamine tautomer (*Z*)-$\mathbf{A'_2}$, as shown by the "olefinic" proton signal at 5.20 ppm and sp^2 carbon signals at 82.2 and 161.5 ppm. Its geometry is further confirmed by comparison of the N***H*** shift (9.50 ppm) with the literature data [18]. Such a high value of the amine proton shift is due to a hydrogen bond formed with the carbonyl group. This signal is a triplet, and the adjacent methylene group appears as a doublet, which rules out structure (*Z*)-$\mathbf{A'_1}$ with an "aniline" nitrogen. Immediately after dissolution of **IVa**, the amounts of the forms (*Z*)-$\mathbf{A'_2}$, $\mathbf{B_2}$, and **C** were 65, 7, and 28%, respectively. After the equilibria were established (one week), the amount of (*Z*)-$\mathbf{A'_2}$ was increased whereas that of structure **C** decreased.

Table 2

Relative Amounts of the Ring-chain Tautomers Found for **IVa** and **IVb**

Compound	Solvent		
	$CDCl_3$	CD_3CN	DMSO[D_6]
IVa	$\mathbf{B_2}$	(*Z*)-$\mathbf{A'_2} \leftrightarrows \mathbf{B_2} \leftrightarrows \mathbf{C}$ 19:80:1	(*Z*)-$\mathbf{A'_2} \leftrightarrows \mathbf{B_2} \leftrightarrows \mathbf{C}$ 83:9:8
IVb	(*Z*)-$\mathbf{A'_2} \leftrightarrows \mathbf{B_2} \leftrightarrows \mathbf{C}$ 5:63:31	(*Z*)-$\mathbf{A'_2} \leftrightarrows \mathbf{B_2} \leftrightarrows \mathbf{C}$ 28:36:36	(*Z*)-$\mathbf{A'_2} \leftrightarrows$ (*E*)-$\mathbf{A'_2} \leftrightarrows \mathbf{C}$ 55:5:40

For compound **IVb** the major forms in DMSO were also (*Z*)-$\mathbf{A'_2}$ and **C**. Structure $\mathbf{B_2}$ was not observed but the proton spectra exhibited traces of a third form, which most likely was (*E*)-$\mathbf{A'_2}$, since the "olefinic" proton signal appeared at 5.24 ppm.

In CD_3CN the relative amounts of the forms fall between the values observed in $CDCl_3$ and DMSO. The more polar the solvent, the more the equilibria shift toward the structure (*Z*)-$\mathbf{A'_2}$ (for both **IVa** and **IVb**). The amount of structure **C** also increases with the solvent polarity. Characteristic chemical shifts for different forms are shown in Table 3. The chemical shifts of the quaternary carbons located next to NH-nitrogen are most indicative of the isomer structures. The quinazoline structure **C** and the isoxazolidine structure $\mathbf{B_2}$ exhibit the signals of the sp^3 carbons at about 65 ppm and 95 ppm, respectively, and the enamine tautomers (*Z*)-$\mathbf{A'_2}$ in turn the signal of the sp^2 carbon at *ca*. 160 ppm. Chemical shifts of the carbons next to the carbonyl carbon (***C***-C=O) are very different for structures (*Z*)-$\mathbf{A'_2}$, $\mathbf{B_2}$, and **C** due to the hybridization of this carbon atom. This hybridization has also a clear effect on the chemical shifts of proton/protons attached to the ***C***-C=O carbon (Table 3). The chemical shifts of the methyl protons are also good structural indicators: 1.3-1.4 ppm for structure **C**, 1.55-1.75 ppm for structure $\mathbf{B_2}$ and 1.9-2.0 ppm for structure (*Z*)-$\mathbf{A'_2}$.

The mass spectra of **IVa**,**b** show that some amount of the open-chain forms are present in the gas phase. For both compounds, the direct loss of RNOH$^{\cdot}$ from the $M^{+\cdot}$ was confirmed by metastable ions.

Conclusion.

In conclusion, a novel ring-linear-ring equilibrium involving isoxazolidine and 1,2,3,4-tetrahydroquinazoline rings was discovered and studied in compounds **IV**. This particular case demonstrates the universal applicability of the general scheme proposed for the design of heterocyclic recyclizations, which may be either irreversible (compounds **III**) or reversible (tautomeric equilibria, compounds **IV**) depending on the relative stability of the cyclic structures involved.

EXPERIMENTAL

NMR-spectra were acquired using a JEOL JNM-A-500 spectrometer operating at 500.16 MHz for ^1H and 125.78 MHz for ^{13}C or a JEOL JNM-L-400 spectrometer operating at 399.78 MHz for ^1H and 100.54 MHz for ^{13}C. Spectra were recorded at 25 °C in $CDCl_3$ and in CD_3CN and at 30 °C in DMSO[D_6]. Proton and carbon spectra were referenced to TMS (tetramethylsilane) signal using value 0.00 ppm. Nitrogen spectra were referenced externally to the standard sample of nitromethane (10 % deuterated) using value 0.00 ppm.

1D proton spectra were acquired with normal single-pulse excitation, 45° flip-angle consisting of 32K data points. 1D carbon spectra were acquired with normal single-pulse excitation, broad-band proton decoupling, 45° flip-angle and with spectral widths of 30 kHz consisting of 65K data points and with 0.3–0.5 Hz exponential weighting applied prior to Fourier transformation. DEPT spectra were acquired as carbon spectra. 2D heteronuclear correlation experiments were acquired using carbon detected CH-shift correlation with partial homonuclear decoupling in the F1 dimension, proton detected HMQC and HMBC

Table 3

^{1}H and ^{13}C NMR Parameters for Compounds **IVa** and **IVb**; Chemical Shifts (in ppm) are Referenced toTetramethylsilane (0.00ppm); Coupling Constants are in Hz.

	IVa	**IVa**	**IVa**	**IVa**	**IVb**	**IVb**	**IVb**
Isomer	**B_2**	(*Z*)-**A'$_2$**	**C**	**B_2**	**B_2**	(*Z*)-**A'$_2$**	**C**
Solvent	$CDCl_3$	DMSO[D_6]	DMSO[D_6]	CD_3CN	$CDCl_3$	DMSO[D_6]	DMSO[D_6]
C*H*$_3$	1.73	1.99	1.37	1.67	1.56	1.93	1.32
C*H*$_2$CO/ C*H*CO	2.99	5.20	2.72, 3.08 ^2J = -15.4	2.95	2.80	5.05	2.52, 2.99 ^2J = -15.3
N*H*	2.35	9.50	5.75	2.92	2.12	9.46	5.75
N*H*$_2$	4.14	4.99	-	4.38	4.04	4.99	-
O*H*	-	10.02	9.83	-	-	9.29	10.19
C*H*$_2$NH	3.99	4.29	3.83	3.91	3.60, 3.69 ^2J = -15.6	4.24	3.81
C*H*$_2$Ph	-	-	-	-	4.54, 4.91 ^2J = -14.6	4.62	4.66, 4.77 ^2J = -15.2
H$_{arom}$	6.66-7.75 (7 signals)	6.54-7.57 (7 signals)	6.47-7.65 (7 signals)	6.59-7.72 (7 signals)	6.62-7.38 (7 signals)	6.55-7.37 (7 signals)	6.46-7.37 (7 signals)
*C*H$_3$	23.9	19.6	25.9	24.0	24.1	19.4	25.9
C=O	165.6	169.7	170.4	167.5	167.2	171.7	170.5
C-C=O	44.8	82.2	41.2	45.3	43.4	81.4	40.9
C-CH$_3$	95.4	161.5	65.4	96.9	94.7	160.1	65.3
*C*H$_2$NH	44.3	42.7	*	44.6	44.0	42.5	41.1
*C*H$_2$Ph	-	-	-	-	48.3	51.2	50.8
C$_{arom}$	116.0-145.9 (10 signals)	114.9-145.9 (10 signals)	*	116.3-147.9 (10 signals)	115.8-145.9 (10 signals)	114.8-145.8 (10 signals)	114.1-143.0 (10 signals)

* Signals were not detected.

with gradient selection and HMBC with BIRD filtering without gradient unit. One-bond coupling constant was 145 Hz in proton-carbon correlation spectra and 95 Hz in proton-nitrogen HMQC spectrum. In ^{1}H-^{13}C and ^{1}H-^{15}N HMBC spectra 8 Hz was used as a long-range coupling constant $^nJ_{CH}$ or $^nJ_{NH}$ (n = 2 or 3) between proton and hetero nuclei. 2D homonuclear H,H-correlation experiments were acquired using phase-sensitive double quantum filtered COSY and phase-sensitive NOESY. The spectral widths of 2D spectra were optimised from 1D spectra. All spectra were made using standard pulse sequences [23].

Mass spectra (EI, 70 eV, direct insertion) were recorded on a VG ZabSpec spectrometer (VG Analytical, Manchester, UK). Fragmentation patterns are confirmed by metastable ions and high-resolution measurements. The purity of the synthesized compounds was checked by tlc (Silufol UV-254 plates).

5-Hydroxy-5-methyl-2-phenylisoxazolidin-3-one (**Ia**), 2-Benzyl-5-hydroxy-5-methylisoxazolidin-3-one (**Ib**), and 5-Hydroxy-2-(4-methoxycarbonyl-phenyl)-5-methylisoxazolidin-3-one (**Ic**).

Ia was synthesized by the known method [16] in a68 % yield, mp 126 °C (acetone) (mp 126 °C [16]). **Ib** and **Ic** were synthesized similarly in a 52 % yield, mp 66-67 °C (benzene) and in a 76 % yield, mp 118 °C (benzene), respectively.

Anal. Calcd. for $C_{11}H_{13}NO_3$:C, 63.76; H, 6.32; N, 6.76. Found: C, 63.72; H, 6.35; N, 6.70 for **Ib**. Calcd. for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.41; H, 5.22; N, 5.58 for **Ic**.

General Procedure for the Reaction of Compounds **I** with Thioacylhydrazine (**II**) and 2-(Aminomethyl)aniline.

Saturated solutions of **I** (5 mmol) and thioacylhydrazine **II** or 2-(aminomethyl)aniline (5 mmol) in dry ethanol were mixed at room temperature and 2-3 drops of trifluoroacetic acid added to the mixture. The precipitate, which formed after a few hours, was isolated by filtration, washed first with cold ethanol, then with ether, and recrystallized from either ethanol (compounds **III**) or acetonitrile (compounds **IV**).

N-Benzyl-*N*-hydroxy-2-(2-methyl-5-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)acetamide (**IIIa**).

This compound was obtained in 82% yield, mp 160-162 ºC. Spectral data for this compound are presented in Table 1. MS (EI, 70 eV): 341(M, 8), 178(12), 177(100), 121(20), 107(7), 105(5), 104(6), 91(23), 77(10).

Anal. Calcd. for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31. Found: C, 63.28; H, 5.72; N, 12.29.

N-Benzyl-*N*-hydroxy-2-(2-methyl-5-(4-tolyl)-2,3-dihydro-1,3,4-thiadiazol-2-yl)acetamide (**IIIb**).

This compound was obtained in 77% yield, mp 147-148 ºC. Spectral data for this compound are presented in Table 1.

Anal. Calcd. for $C_{19}H_{21}N_3O_2S$: C, 64.20; H, 5.95; N, 11.82. Found: C, 64.24; H, 6.00; N, 11.76.

N-Hydroxy-*N*-phenyl-2-(2-methyl-5-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)acetamide (**IIIc**).

This compound was obtained in 88% yield, mp 129-130 ºC. Spectral data for this compound are presented in Table 1.

Anal. Calcd. for $C_{17}H_{17}N_3O_2S$: C, 62.37; H, 5.23; N, 12.83. Found: C, 62.42; H, 5.31; N, 12.78.

N-Hydroxy-*N*-phenyl-2-(2-methyl-5-(4-tolyl)-2,3-dihydro-1,3,4-thiadiazol-2-yl)acetamide (**IIId**).

This compound was obtained in 85% yield, mp 140 ºC. Spectral data for this compound are presented in Table 1.

Anal. Calcd. for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31. Found: C, 63.43; H, 5.50; N, 12.38.

N-Hydroxy-*N*-(4-metoxycarbonylphenyl)-2-(2-methyl-5-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)acetamide (**IIIe**).

This compound was obtained in 92% yield, mp 137-138 ºC. Spectral data for this compound are presented in Table 1.

Anal. Calcd. for $C_{19}H_{19}N_3O_4S$: C, 59.21; H, 4.97; N, 10.90. Found: C, 59.36; H, 5.02; N, 10.95.

N-Hydroxy-*N*-(4-metoxycarbonylphenyl)-2-(2-methyl-5-(4-tolyl)-2,3-dihydro-1,3,4-thiadiazol-2-yl)acetamide (**IIIf**).

This compound was obtained in 90% yield, mp 151-152 ºC. Spectral data for this compound are presented in Table 1.

Anal. Calcd. for $C_{20}H_{21}N_3O_4S$: C, 60.13; H, 5.30; N, 10.52. Found: C, 59.96; H, 5.32; N, 10.45.

5-(2-Aminobenzylamino)-5-methyl-2-phenyltetrahydroisoxazol-3-one (**IVa**).

This compound was obtained in 78% yield, mp 102-103 ºC. Spectral data for this compound are presented in Table 3.

Anal. Calcd. for $C_{17}H_{19}N_3O_2$: C, 68.67; H, 6.44; N, 14.13. Found: C, 68.70; H, 6.50; N, 14.16.

3-(2-Aminobenzylamino)-*N*-benzyl-*N*-hydroxy-2-butenamide (**IVb**).

This compound was obtained in 95% yield, mp 147-148 ºC. Spectral data for this compound are presented in Table 3.

Anal. Calcd. for $C_{18}H_{11}N_3O_2$: C, 69.43; H, 6.80; N, 13.49. Found: C, 69.55; H, 6.75; N, 13.42.

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