Reactions of *Z*-isomers of alkylaromatic 1,2-hydroxylamino oximes with methyl- and arylglyoxals*

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Reactions of the *Z*-isomers of alkylaromatic 1,2-hydroxylamino oximes (that contain the hydroxylamino group at the primary or secondary carbon atom) with methylglyoxal gave 6-acetyl-5,6-dihydro-4*H*-1,2,5-oxadiazines. Analogous reactions with arylglyoxals in the presence of trifluoroacetic acid afforded 6-aroyl-5,6-dihydro-4*H*-1,2,5-oxadiazines. It was found that phenylglyoxal in the absence of the acid yielded *N*-substituted α-aroylnitrone which undergoes cyclization into the corresponding oxadiazine under the action of CF_3COOH.

Key words: hydroxylamino oximes, nitrones, 1,2,5-oxadiazines, glyoxals.

Alkylaromatic 1,2-hydroxylamino oximes with the *Z*-configuration of the hydroxyimino group (*syn*-isomers) react with biacetyl to give 6-acetyl-5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines and with alkyl aryl 1,2-diketones to give *N*-substituted α-aroylnitrones or 6-aroyl-5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines, or their tautomeric mixture.[1] The use of glyoxals (α-oxo aldehydes) could be expected to afford 5,6-dihydro-4*H*-1,2,5-oxadiazines because the formyl group of glyoxals and the aldonitrone group are more reactive than the oxo group of 1,2-diketones and oxo nitrones, respectively.[2] Data on 5,6-dihydro-4*H*-1,2,5-oxadiazines are very scarce[3] (which is confirmed by the modern Beilstein CrossFire information and search system) and their formation from 1,2-hydroxylamino oximes and glyoxals are of interest for both the synthesis of new functionalized derivatives of this series and the investigation of their reactivities.

1,2-Hydroxylamino oximes **1a—d** react with methylglyoxal (**2**) at room temperature to give 6-acetyl-5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines **3a—d** (Scheme 1).

The IR spectra of oxadiazines **3a—d** contain a band at 1730—1736 cm^{-1} due to the C=O stretching vibrations in the isolated acetyl fragment and the UV spectra show a peak at 240—260 nm. This indicates that the chromophore system of the compounds obtained is similar to that of the starting hydroxylamino oximes **1a—d**. In the ^1H NMR spectra of compounds **3a—c**, the characteristic features are a singlet or a doublet (spin-spin coupling with the H(4) proton of the oxadiazine ring) for the H(6) proton of the heterocycle (δ 4.85—5.07) and a singlet for the protons of the acetyl group in position 6 (δ 2.27—2.45). The ^1H NMR spectra of compounds **3b—d** show signals for only one isomer (most likely, it is the most stable *trans*-isomer). We cannot exclude the formation of the second isomer that undergoes *in situ* transformation *via* open structure **4** into the more stable isomer.

Reactions of arylglyoxals **5** with the *Z*-isomers of alkylaromatic 1,2-hydroxylamino oximes **1a—c** in methanol in the presence of trifluoroacetic acid gave 6-aroyl-5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines **6a—j** (see Scheme 1). It should be noted that alkyl aryl 1,2-diketones, in contrast to arylglyoxals, react with the *Z*-isomers of alkylaromatic 1,2-hydroxylamino oximes to produce both α-aroyl-α-methylnitrones and 6-aroyl-5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines and their tautomeric mixtures.[1] The ^1H NMR spectra of compounds **6e—j** show signals for only one diastereomer of two, as for condensation products **3b—d** obtained from methylglyoxal. In the IR spectra of oxadiazines **6a—j**, the band of the carbonyl group conjugated with the benzene ring appears at 1661—1703 cm^{-1} and the UV spectra show a peak at 248—261 (**6a—c,e—j**) and 280 nm (**6d**), which results from superposition of the absorption peaks due to the aryloxime chromophore and the 4-methoxybenzoyl group in position 6 of the heterocycle. In the ^1H NMR

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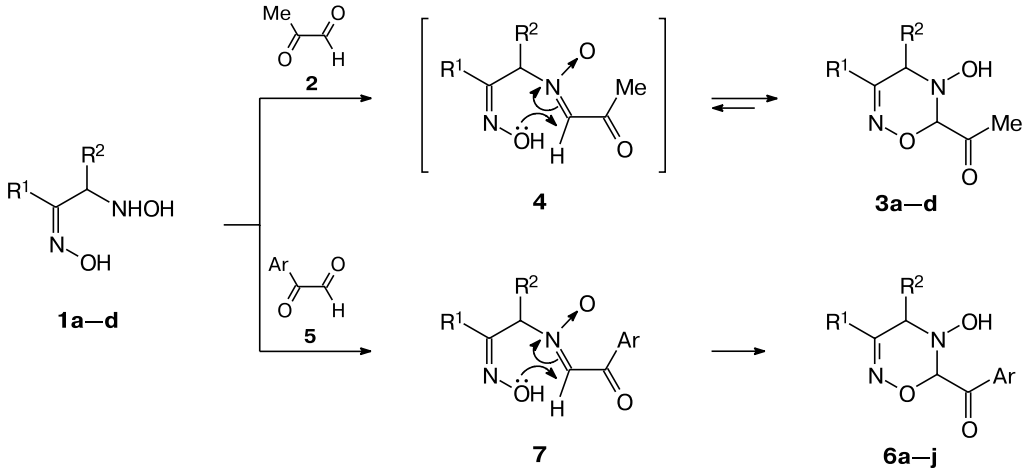
Scheme 1



1, 3	R^1	R^2	6	R^1	R^2	Ar	6	R^1	R^2	Ar
a	Ph	H	**a**	Ph	H	Ph	**f**	Ph	Me	4-BrC_6H_4
b	Ph	Me	**b**	Ph	H	4-BrC_6H_4	**g**	Ph	Me	4-ClC_6H_4
c	4-ClC_6H_4	Me	**c**	Ph	H	4-ClC_6H_4	**h**	4-ClC_6H_4	Me	Ph
d	*o*-$C_6H_4(CH_2)_2$		**d**	Ph	H	4-$MeOC_6H_4$	**i**	4-ClC_6H_4	Me	4-BrC_6H_4
			e	Ph	Me	Ph	**j**	4-ClC_6H_4	Me	4-ClC_6H_4

spectra of compounds **6a**—**j**, the signal for the H(6) proton appears at δ 5.86—6.20.

In the ^{1}H NMR spectra of compounds **3a** and **6a**—**d**, the methylene protons in position 4 of the heterocycle are diastereotopic: one of them reveals itself at room temperature as a broadened singlet, while the other, as a doublet or a doublet of doublets. Broadening of the signal for the former proton can be explained by slow (on the time scale of the NMR experiment) inversion of the N atom of the ring hydroxylamino group (position 5 of the heterocycle) and a larger difference between the chemical shifts for the exchanged protons of two stereoisomers. The high energy barrier of the N atom to inversion is probably due to intramolecular hydrogen bonding between the OH proton of the ring hydroxylamino group and the carbonyl O atom.[4] Indeed, the spectrum of compound **6c** recorded in deuterated acetone at −50 °C shows signals for two stereoisomers in the ratio ~3 : 1; the methylene protons of the major stereoisomer appear as an AB system (J = 19.2 Hz) at δ 4.17 and 4.74, while the methylene protons of the minor stereoisomer appear as an AB system (J = 18.8 Hz) at δ 3.97 and 4.03.

The reactions of 1,2-hydroxylamino oximes **1** with arylglyoxals **5** could be assumed to proceed through intermediate *N*-substituted α-aroylnitrones **7**, which undergo *in situ* cyclization into oxadiazines **6**. Indeed, a reaction of 1,2-hydroxylamino oxime **1a** with phenylglyoxal **5** (Ar = Ph) in the absence of an acid gave the corresponding α-aroylnitrone **7a**, which was transformed into oxadiazine **6a** upon addition of trifluoroacetic acid. The ^{1}H NMR spectrum of compound **6a** in DMSO-d_6 contains no signals for α-aroylnitrone **7a**, while the spectrum of α-aroylnitrone **7a** in DMSO-d_6 exhibits no signals for oxadiazine **6a**. This allows these compounds to be regarded as isomers rather than tautomers.

To summarize, we obtained new functionalized 5,6-dihydro-4*H*-1,2,5-oxadiazines by condensation of alkylaromatic 1,2-hydroxylamino oximes with the *Z*-configuration of the hydroxyimino group (*syn*-isomers) with methyl- and arylglyoxals.

Experimental

The course of the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates with $CHCl_3$—MeOH (9 : 1) as an eluent; spots were visualized under UV light. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200.13 and 50.3 MHz, respectively) and Bruker AM-400 spectrometers (400.13 MHz) in $CDCl_3$, DMSO-d_6, and $(CD_3)_2CO$ with the signals for the residual protons of the solvents as the internal standards (δ 7.24, 2.50, and 2.05, respectively). IR spectra were recorded on a Bruker Vector 22 spectrometer (pellets with KBr). UV spectra were recorded on a Hewlett-Packard 8453 spectrophotometer in 96% EtOH.

The starting 1,2-hydroxylamino oximes **1a**—**d** were prepared according to known procedures[5—7] and arylglyoxals were synthesized by the Riley reaction.[8] The melting points of arylglyoxal hydrates are identical with the literature data.[9]

Condensation of 1,2-hydroxylamino oximes 1a—d with methylglyoxal 2 (general procedure). A solution of hydroxylamino oxime **1a**—**d** (2.0 mmol) and aqueous 40% methylglyoxal **2** (0.54 g, 3.0 mmol) in MeOH (5 mL) was kept at ~20 °C for 3 days. The precipitate of product **3a**—**d** that formed was filtered off and washed with MeOH. The filtrate was concentrated and

the residue was treated with ether to give an additional crop of the condensation product.

6-Acetyl-5-hydroxy-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (3a). Yield 50%, m.p. 136 °C (decomp., from MeOH). Found (%): C, 59.79; H, 5.43; N, 12.66. $C_{11}H_{12}N_2O_3$. Calculated (%): C, 59.99; H, 5.49; N, 12.72. UV (EtOH), λ_{max}/nm (log ε): 244 (4.00). IR (KBr), ν/cm^{-1}: 1732 (C=O). ^{1}H NMR (DMSO-d_6), δ: 2.27 (s, 3 H, Ac); 3.94 (d, 1 H, H(4), J = 17.6 Hz); 4.27 (br.s, 1 H, H(4)); 5.07 (s, 1 H, H(6)); 7.40—7.50, 7.60—7.70 (both m, 5 H, Ar); 9.00 (br.s, 1 H, OH).

6-Acetyl-5-hydroxy-4-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (3b). Yield 55%, m.p. 145 °C (decomp., from MeOH). Found (%): C, 61.89; H, 6.19; N, 12.08. $C_{12}H_{14}N_2O_3$. Calculated (%): C, 61.52; H, 6.02; N, 11.96. UV (EtOH), λ_{max}/nm (log ε): 242 (3.99). IR (KBr), ν/cm^{-1}: 1736 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.35 (d, 3 H, C(4)Me, J = 7.2 Hz); 2.45 (s, 3 H, Ac); 4.20 (dq, 1 H, H(4), J = 1.6 Hz, J = 7.2 Hz); 4.85 (d, 1 H, H(6), J = 1.6 Hz); 5.97 (s, 1 H, OH); 7.37—7.44, 7.54—7.60 (both m, 5 H, Ar).

6-Acetyl-3-(4-chlorophenyl)-5-hydroxy-4-methyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (3c). Yield 41%, m.p. 142 °C (decomp., from AcOEt). Found (%): C, 53.67; H, 4.87; Cl, 12.96; N, 10.25. $C_{12}H_{13}ClN_2O_3$. Calculated (%): C, 53.64; H, 4.88; Cl, 13.20; N, 10.43. UV (EtOH), λ_{max}/nm (log ε): 250 (4.04). IR (KBr), ν/cm^{-1}: 1734 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.36 (d, 3 H, C(4)Me, J = 7.2 Hz); 2.30 (s, 3 H, Ac); 4.23 (dq, 1 H, H(4), J = 2.0 Hz, J = 7.2 Hz); 5.03 (d, 1 H, H(6), J = 2.0 Hz); 7.44—7.48, 7.67—7.71 (both m, 4 H, Ar); 8.10 (s, 1 H, OH).

2-Acetyl-1-hydroxy-1,9,10,10a-tetrahydro-2*H*-3-oxa-1,4-diazaphenanthrene (3d). Yield 61%, m.p. 164 °C (decomp., from MeOH). Found (%): C, 63.15; H, 5.68; N, 11.37. $C_{13}H_{14}N_2O_3$. Calculated (%): C, 63.40; H, 5.73; N, 11.38. UV (EtOH), λ_{max}/nm (log ε): 257 (4.04), 287 sh (3.69), 298 (3.55). IR (KBr), ν/cm^{-1}: 1732 (C=O). ^{1}H NMR (DMSO-d_6), δ: 1.75—1.90 (m, 1 H, H(10)); 2.26 (s, 3 H, Ac); 2.92 (m, 2 H, H(9)); 3.90 (br.s, 1 H, H(10a)); 4.80—5.30 (br.s, 1 H, H(2)); 7.20—7.37 (m, 3 H, Ar); 7.86 (m, 1 H, Ar); 8.73 (br.s, 1 H, OH) (the signal for one of the H(10) protons coincides with the signal for the protons of the acetyl group).

Condensation of 1,2-hydroxylamino oximes 1a—c with arylglyoxals 5 (general procedure). Arylglyoxal **5** (2.0 mmol) was added to a warm solution of hydroxylamino oxime **1a—c** (2.0 mmol) in MeOH (5—8 mL). Then trifluoroacetic acid (0.3 mL) was added and the mixture was kept for two days. The precipitate of condensation products **6a—j** that formed was filtered off, washed with MeOH, and dried. The filtrate was concentrated and the residue was treated with ether to give an additional crop of the condensation product.

6-Benzoyl-5-hydroxy-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6a). Yield 62%, m.p. 120—121 °C (decomp., from MeOH). Found (%): C, 68.06; H, 5.03; N, 9.91. $C_{16}H_{14}N_2O_3$. Calculated (%): C, 68.07; H, 5.00; N, 9.92. UV (EtOH), λ_{max}/nm (log ε): 250 (3.97). IR (KBr), ν/cm^{-1}: 1700 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 4.11 (dd, 1 H, H(4), J = 18.4 Hz, J = 1.2 Hz); 4.22—4.39 (br.s, 1 H, H(4)); 5.95 (dd, 1 H, H(6), J = 1.2 Hz, J = 1.2 Hz); 7.40—7.74, 8.12—8.18 (both m, 10 H, Ar); 8.35 (br.s, 1 H, OH).

6-(4-Bromobenzoyl)-5-hydroxy-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6b). Yield 76%, m.p. 146 °C (decomp., from MeOH). Found (%): C, 53.19; H, 3.60; Br, 22.19; N, 7.53. $C_{16}H_{13}BrN_2O_3$. Calculated (%): C, 53.20; H, 3.63; Br, 22.12; N, 7.76. UV (EtOH, saturated solution (the concentration not measured)), λ_{max}/nm: 260. IR (KBr), ν/cm^{-1}: 1677 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 4.14 (dd, 1 H, H(4), J = 18.4 Hz, J = 1.5 Hz); 4.25—4.38 (br.s, 1 H, H(4)); 5.86 (br.s, 1 H, H(6)); 7.41—7.46, 7.69—7.75, 8.07—8.12 (all m, 9 H, Ar); 8.25 (br.s, 1 H, OH).

6-(4-Chlorobenzoyl)-5-hydroxy-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6c). Yield 68%, m.p. 144 °C (decomp., from MeOH). Found (%): C, 60.30; H, 4.10; Cl, 10.95; N, 8.77. $C_{16}H_{13}ClN_2O_3$. Calculated (%): C, 60.67; H, 4.14; Cl, 11.19; N, 8.84. UV (EtOH, saturated solution (the concentration not measured)), λ_{max}/nm: 256. IR (KBr), ν/cm^{-1}: 1698 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 4.14 (dd, 1 H, H(4), J = 18.4 Hz, J = 1.5 Hz); 4.24—4.39 (br.s, 1 H, H(4)); 5.87 (br.s, 1 H, H(6)); 7.41—7.46, 7.55—7.59, 7.69—7.73, 8.15—8.19 (all m, 9 H, Ar); 8.29 (br.s, 1 H, OH).

5-Hydroxy-6-(4-methoxybenzoyl)-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6d). Yield 58%, m.p. 134 °C (decomp., from MeOH). Found (%): C, 65.38; H, 5.13; N, 9.01. $C_{17}H_{16}N_2O_4$. Calculated (%): C, 65.37; H, 5.16; N, 8.97. UV (EtOH), λ_{max}/nm (log ε): 221 (4.29), 280 (4.28). IR (KBr), ν/cm^{-1}: 1661 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 3.90 (s, 3 H, OMe); 4.12 (d, 1 H, H(4), J = 18.5 Hz); 4.18—4.35 (br.s, 1 H, H(4)); 5.86 (s, 1 H, H(6)); 7.02—7.06, 7.41—7.45, 7.69—7.73, 8.13—8.17 (all m, 9 H, Ar); 8.15—8.30 (br.s, 1 H, OH).

6-Benzoyl-5-hydroxy-4-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6e). Yield 56.5%, m.p. 139 °C (decomp., from MeOH). Found (%): C, 69.20; H, 5.46; N, 9.48. $C_{17}H_{16}N_2O_3$. Calculated (%): C, 68.90; H, 5.44; N, 9.45. UV (EtOH), λ_{max}/nm (log ε): 248 (4.31). IR (KBr), ν/cm^{-1}: 1703 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.51 (d, 3 H, C(4)Me, J = 7.6 Hz); 4.32 (dq, 1 H, H(4), J = 1.6 Hz, J = 7.6 Hz); 6.01 (d, 1 H, H(6), J = 1.6 Hz); 7.42—7.46, 7.49—7.55, 7.61—7.66, 7.67—7.71, 8.11—8.15 (all m, 10 H, Ar); 7.99 (s, 1 H, OH).

6-(4-Bromobenzoyl)-5-hydroxy-4-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6f). Yield 76%, m.p. 162 °C (decomp., from MeOH). Found (%): C, 54.41; H, 4.02; Br, 21.30; N, 7.20. $C_{17}H_{15}BrN_2O_3$. Calculated (%): C, 54.42; H, 4.03; Br, 21.30; N, 7.47. UV (EtOH, saturated solution), λ_{max}/nm: 260. IR (KBr), ν/cm^{-1}: 1701 (C=O). ^{1}H NMR (DMSO-d_6), δ: 1.39 (d, 3 H, C(4)Me, J = 7.2 Hz); 4.13 (q, 1 H, H(4), J = 7.2 Hz); 6.09 (s, 1 H, H(6)); 7.40—7.49, 7.55—7.65, 7.70—7.80, 7.89—7.98 (all m, 9 H, Ar); 8.89 (s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 19.18 (4-Me); 55.80 (C(4)); 84.77 (C(6)); 126.27 (d); 128.15 (s); 129.35, 130.44, 131.60, 132.05 (all d); 134.08, 134.32 (both s); 158,65 (C=N); 191.26 (C=O).

6-(4-Chlorobenzoyl)-5-hydroxy-4-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6g). Yield 54%, m.p. 148 °C (decomp., from MeOH). Found (%): C, 61.63; H, 4.51; Cl, 10.85; N, 8.49. $C_{17}H_{15}ClN_2O_3$. Calculated (%): C, 61.73; H, 4.57; Cl, 10.72; N, 8.47. UV (EtOH), λ_{max}/nm (log ε): 256 (4.04). IR (KBr), ν/cm^{-1}: 1702 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.51 (d, 3 H, C(4)Me, J = 7.2 Hz); 4.32 (dq, 1 H, H(4), J = 1.6 Hz, J = 7.2 Hz); 5.88 (d, 1 H, H(6), J = 1.6 Hz); 7.42—7.49, 7.54—7.61, 7.66—7.72, 8.12—8.17 (all m, 9 H, Ar); 8.05 (br.s, 1 H, OH).

6-Benzoyl-3-(4-chlorophenyl)-5-hydroxy-4-methyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6h). Yield 61%, m.p. 149 °C (decomp., from MeOH). Found (%): C, 61.42; H, 4.83; Cl, 10.47; N, 8.50. $C_{17}H_{15}ClN_2O_3$. Calculated (%): C, 61.73;

H, 4.57; Cl, 10.72; N, 8.47. UV (EtOH, saturated solution (the concentration not measured)), λ_{max}/nm: 250. IR (KBr), ν/cm^{-1}: 1699 (C=O). ^{1}H NMR (DMSO-d_6), δ: 1.43 (d, 3 H, C(4)Me, J = 7.2 Hz); 4.15 (dq, 1 H, H(4), J = 1.4 Hz, J = 7.2 Hz); 6.20 (d, 1 H, H(6), J = 1.4 Hz); 7.47—7.74, 7.98—8.07 (both m, 9 H, Ar); 8.88 (s, 1 H, OH).

6-(4-Bromobenzoyl)-3-(4-chlorophenyl)-5-hydroxy-4-methyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6i). Yield 97%, m.p. 156 °C (decomp., from MeOH). Found (%): C, 50.07; H, 3.50; Br, 19.52; N, 6.73. $C_{17}H_{14}BrClN_2O_3$. Calculated (%): C, 49.84; H, 3.44; Br, 19.51; N, 6.84. UV (EtOH, saturated solution), λ_{max}/nm: 261. IR (KBr), ν/cm^{-1}: 1692 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.52 (d, 3 H, C(4)Me, J = 7.2 Hz); 4.32 (dq, 1 H, H(4), J = 1.8 Hz, J = 7.2 Hz); 6.01 (s, 1 H, H(6), J = 1.8 Hz); 7.46—7.50, 7.70—7.75, 8.03—8.07 (all m, 8 H, Ar); 8.13 (s, 1 H, OH).

6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-5-hydroxy-4-methyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6j). Yield 91%, m.p. 153 °C (decomp., from MeOH). Found (%): C, 55.90; H, 3.49; Cl, 19.10; N, 7.73. $C_{17}H_{14}Cl_2N_2O_3$. Calculated (%): C, 55.91; H, 3.86; Cl, 19.42; N, 7.67. UV (EtOH), λ_{max}/nm (logε): 258 (4.46). IR (KBr), ν/cm^{-1}: 1700 (C=O). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.52 (d, 3 H, C(4)Me, J = 7.2 Hz); 4.32 (dq, 1 H, H(4), J = 1.6 Hz, J = 7.2 Hz); 6.00 (d, 1 H, H(6), J = 1.6 Hz); 7.46—7.50, 7.54—7.59, 7.70—7.74, 8.11—8.15 (all m, 8 H, Ar); 8.10 (s, 1 H, OH).

***N*-(α-Benzoylmethylidene)-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (7a).** A suspension of hydroxylamino oxime **1a** (498 mg, 2 mmol) in MeOH (5 mL) was heated to complete homogenization and cooled. Phenylglyoxal hydrate (456 mg, 2 mmol) was added and the reaction mixture was kept for a day. The yellow precipitate that formed was filtered off, washed with MeOH, and dried. The yield of compound **7a** was 0.40 g (47%), yellow plates, m.p. 115 °C (decomp., from MeOH). Found (%): C, 67.92; H, 4.99; N, 9.96. $C_{16}H_{14}N_2O_3$. Calculated (%): C, 68.07; H, 5.00; N, 9.92. UV (EtOH), λ_{max}/nm (logε): 246 (4.29), 274 sh (3.75), 322 (3.91). IR (KBr), ν/cm^{-1}: 1661 (C=O). ^{1}H NMR (DMSO-d_6), δ: 5.45 (s, 2 H, CH_2); 7.30—8.10 (m, 10 H, Ar); 8.48 (s, 1 H, CH=N); 12.20 (s, 1 H, OH). The colorless crystals that formed in the mother liquor on storage were filtered off to give oxadiazine **6a** (0.10 g, 12%).

Transformation of nitrone 7a into oxadiazine 6a. A solution of CF_3COOH (20 drops) in MeOH (1 mL) was added to a suspension of nitrone **7a** (282 mg, 1 mmol) in MeOH (3 mL). The mixture was stirred at ~20 °C for 1 h until the yellow solution became colorless. The precipitate was filtered off, washed with MeOH, and dried. The yield was 0.20 g (71%), m.p. 120—121 °C (decomp.). The IR spectrum of the compound obtained was identical with the IR spectrum of oxadiazine **6a** obtained by condensation of hydroxylamino oxime **1a** with phenylglyoxal in the presence of CF_3COOH.

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