Reaction of *Z* isomers of alkylaromatic 1,2-hydroxylamino oximes with 1,2-diketones*

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The reactions of *Z* isomers of alkylaromatic 1,2-hydroxylamino oximes containing the hydroxylamino group at the primary or secondary carbon atom with diacetyl afford 6-acetyl-5,6-dihydro-4*H*-1,2,5-oxadiazines. The reactions of these compounds with alkylaromatic 1,2-diketones produce *N*-substituted α-aroylnitrones or 6-aroyl-5,6-dihydro-4*H*-1,2,5-oxadiazines or, alternatively, their tautomeric mixtures.

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

The results of the reactions of 1,2-hydroxylamino oximes with carbonyl compounds depend on both the configuration of the oxime group and the nature of the carbonyl compound. For example, condensation of monocarbonyl compounds with *E* isomers of 1,2-hydroxylamino oximes affords five-membered heterocycles, *viz.*, 1-hydroxy-3-imidazoline 3-oxides, whereas condensation with *Z* isomers gives rise to six-membered heterocycles, *viz.*, 5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines.[1] The resulting heterocycles can exist in the tautomeric equilibrium with the open forms (the corresponding nitrones).[1] The reactions of *E* isomers of 1,2-hydroxylamino oximes with 1,2-diketones produce either 2-acyl-1-hydroxy-3-imidazoline 3-oxide or pyrazine 1,4-dioxide derivatives or, alternatively, their mixtures. Under certain conditions, 3-imidazoline 3-oxides are transformed into pyrazine 1,4-dioxides.[2] For 2-acyl-1-hydroxy-3-imidazoline 3-oxides, the tautomeric equilibrium with the open forms was not detected.[2] In the present study, we examined the reactions of *Z* isomers of 1,2-hydroxylamino oximes **1a—e** with 1,2-diketones with the aim of preparing functional 5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazine derivatives containing the acyl group at position 6. Data on such compounds are lacking in the literature. However, these compounds are of interest for the synthesis of new functional derivatives of this series of compounds. Systems with the 1,2,5-oxadiazine moiety were documented[3] but data on 5,6-dihydro-4*H*-1,2,5-oxadiazines are scarce.

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

The IR spectra of oxadiazines **3a—d** show a band of the isolated carbonyl group at 1720—1740 cm^{-1}. The UV spectra have a maximum at 234—256 nm, which is evidence that the chromophoric systems of the reaction products are identical to those of the starting hydroxylamino oximes **1a—d**. The ^1H NMR spectra of compounds **3a—d** in $CDCl_3$ show characteristic singlets for the protons of the Me group at position 6 of the oxadiazine ring (δ 1.44—1.80) and the protons of the acetyl group (δ 2.20—2.43). The ^1H NMR spectra provide evidence that oxadiazines **3b—d** exist in a $CDCl_3$ solution as mixtures of two diastereomers (*cis* and *trans* isomers), the substituent at position 4 of the oxadiazine ring having only a slight effect on their ratio (62 and 38% for **3b** (R^2 = Me), 63 and 37% for **3c** (R^2 = Pr^i), and 72 and 28% for **3d**). However, the isomer ratio depends on the nature of the solvent. For example, the ^1H NMR spectrum of compound **3b** in DMSO-d_6 shows that the cyclic isomers are present in a ratio of 71 : 29. This can be attributed to the fact that cyclic form **3** exists in solution in the equilibrium with open form **4**, the concentration of the latter being too small to be observed in the ^1H NMR spectrum. The ratio of diastereomers of **3** depends on their relative stability in the solvent used. The spatial arrangement of the substituents was not determined.

Unlike diacetyl, alkylaromatic 1,2-diketones **5** react with *Z* isomers of alkylaromatic 1,2-hydroxylamino oximes **1a—e** to give α-aroyl-α-methylnitrones **6A** and 6-aroyl-5-hydroxy-5,6-dihydro-4*H*-1,2,5-oxadiazines **6B**, as well as their tautomeric mixtures (see Scheme 1), whereas condensation of *E* isomers with 1,2-diketones affords only heterocyclic compounds.[2] In the crystalline state, most of

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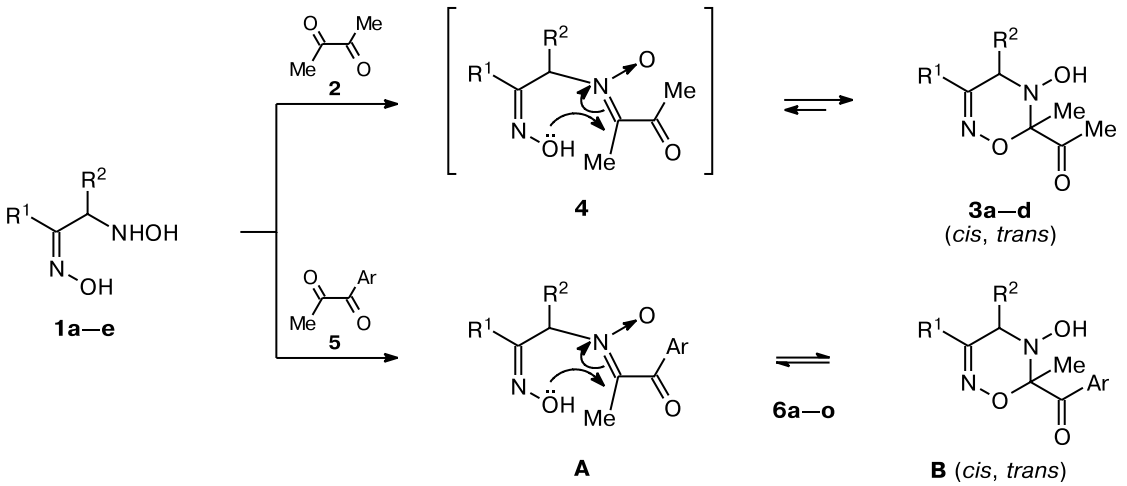
Scheme 1



1, 3	R^1	R^2	6	R^1	R^2	Ar	6	R^1	R^2	Ar	6	R^1	R^2	Ar
1a, **3a**	Ph	H	**a**	Ph	H	Ph	**f**	Ph	H	4-$C_5H_{11}OC_6H_4$	**k**	Ph	Pr^i	4-MeC_6H_4
1b, **3b**	Ph	Me	**b**	Ph	H	4-FC_6H_4	**g**	Ph	Me	Ph	**l**	Ph	Pr^i	4-FC_6H_4
1c, **3c**	Ph	Pr^i	**c**	Ph	H	4-BrC_6H_4	**h**	Ph	Me	4-BrC_6H_4	**m**	Ph	Pr^i	4-BrC_6H_4
1d, **3d**	*o*-$C_6H_4(CH_2)_2$		**d**	Ph	H	4-Cl-3-MeC_6H_3	**i**	4-ClC_6H_4	Me	Ph	**n**	Ph	Pr^i	4-ClC_6H_4
1e	4-ClC_6H_4	Me	**e**	Ph	H	4-$EtOC_6H_4$	**j**	Ph	Pr^i	Ph	**o**	*o*-$C_6H_4(CH_2)_2$		Ph

the condensation products (**6a—f,i—o**) presumably have the structure of α-aroyl-α-methylnitrones **6A**, because the IR spectra of these compounds (in KBr) show a C=O stretching band at 1650—1674 cm^{-1}, which is evidence for the conjugation between the aroyl and nitrone groups.[4] The position of the C=O stretching band in the IR spectrum of compound **6h** (in KBr) at 1692 cm^{-1} is indicative of the absence of the conjugation between the aroyl and nitrone groups (tautomer **B**). Consequently, this compound exists in the crystalline state as oxadiazine **6hB**. The IR spectrum of compound **6g** (in KBr) shows two C=O stretching bands at 1662 and 1685 cm^{-1}, due to which it is difficult to determine the structure of this compound in the crystalline state.

Study by ^{1}H NMR spectroscopy demonstrated that condensation products **6a—f,j—n** in DMSO-d_6 have the structures of α-aroyl-α-methylnitrones **6A**, whereas compounds **6a,g,i,k** in $CDCl_3$ (the other condensation products are poorly soluble in chloroform) exist in the ring-chain tautomeric equilibrium (nitrone **A** and oxadiazine **B**), with the cyclic form **B** predominating. Consequently, the equilibrium in the polar solvent (DMSO-d_6) is shifted toward the more polar open form, *viz.*, nitrone **A**, and the equilibrium in the nonpolar solvent ($CDCl_3$) is shifted toward the less polar cyclic form, *viz.*, oxadiazine **B**. For condensation products **6g,o**, the ring-chain tautomeric equilibrium between nitrone **A** and oxadiazine **B** is observed also in DMSO-d_6, the percentage of cyclic form **6gB** being 60%. The ^{1}H NMR spectrum of condensation product **6h** in the same solvent shows signals only of cyclic form **6hB**. Apparently, the Me group at position 4 of the oxadiazine ring stabilizes heterocyclic form **6B** to a greater extent compared to compounds unsubstituted at this position or compounds containing the isopropyl group.[5] The ^{1}H NMR spectra of the open form **A** of nitrones **6** in DMSO-d_6 show a characteristic singlet for the protons of the α-methylnitrone group at δ 1.93—2.35; in $CDCl_3$, a singlet for these protons is observed at δ 2.28—2.43. In the ^{1}H NMR spectra of the cyclic form **B** of oxadiazines **6** in DMSO-d_6, a singlet for the protons of the Me group at position 6 of the heterocycle is observed at δ 1.65—1.68; in $CDCl_3$, a singlet for these protons is observed at δ 1.72—1.95. It should be noted that the ratio of isomers of 4*H*-1,2,5-oxadiazine **6B** is more sensitive to the bulkiness of the aroyl group compared to the acetyl group. For example, the ratio of the cyclic forms of compound **6gB** containing the Me group at position 4 of the heterocycle is 2 : 1, whereas the corresponding ratio for compound **6kB** containing the isopropyl group at the same position is 17 : 1. This suggests that the major isomer of oxadiazine **6kB** is characterized by the *trans* arrangement of the isopropyl and aroyl groups.

To conclude, condensation of *Z* isomers of alkylaromatic 1,2-hydroxylamino oximes with diacetyl provides an approach to the synthesis of 5-hydroxy-6-methyl-5,6-dihydro-4*H*-1,2,5-oxadiazines containing the acetyl group at position 6 of the heterocycle, whereas most of the condensation products of the same 1,2-hydroxylamino oximes with alkylaromatic 1,2-diketones have the structure of α-aroyl-α-methylnitrones, which can

exist in the tautomeric equilibrium with 5-hydroxy-6-methyl-5,6-dihydro-4*H*-1,2,5-oxadiazines containing the aroyl group at position 6 of the heterocycle.

Experimental

The course of the reactions was monitored and the purity of the reaction products was checked by TLC on Silufol UV-254 plates ($CHCl_3$—MeOH, 9 : 1, as the eluent); spots were visualized with UV light or iodine vapor. The ^{1}H NMR spectra were recorded on a Bruker WP-200SY spectrometer (200.13 MHz) in $CDCl_3$ and DMSO-d_6 with the use of the residual protons of the solvent as the internal standard (δ 7.24 and 2.50, respectively). The IR spectra were measured on a Bruker Vector 22 spectrometer in KBr pellets. The UV spectra were recorded on a Hewlett-Packard 8453 spectrophotometer in 96% EtOH. The high-resolution mass spectrum of 1-(4-pentyloxyphenyl)propane-1,2-dione was obtained on a Finnigan MAT 8200 instrument (the ionizing electron energy was 70 eV, a direct inlet system, the ion source temperature was 180 °C).

The starting 1,2-hydroxylamino oximes **1a,b,d** were prepared according to known procedures (see Refs 6—8, respectively). The configuration of the oxime group in 1,2-hydroxylamino oximes **1c,e** was established by ^{1}H NMR and UV spectroscopy as described earlier.[6—8] 1-Arylpropane-1,2-diones were synthesized according to a procedure published in the literature.[9]

1-Arylpropane-1,2-diones 5 (general procedure).[9] 1) Concentrated aqueous HCl (44 mL) was added to a solution of 1-arylpropan-1-one (0.1 mol) in MeOH (200 mL), the temperature of the reaction mixture being maintained at 20 °C. Then freshly distilled *n*-butyl nitrite (0.11 mol) was added portionwise for 1 h, the mixture was kept for ~14 h, the solution was cooled to 10 °C, and a 10% NaOH solution was added at this temperature to pH 4—5. Methanol and *n*-butanol were evaporated. The precipitate was filtered off, washed with water, dried, and recrystallized.[10] The melting points of 1-aryl-2-hydroxyiminopropan-1-ones were identical to those reported earlier.[10]

2-Hydroxyimino-1-(4-pentyloxyphenyl)propan-1-one. The yield was 71%, m.p. 105—106 °C (from CCl_4). Found (%): C, 67.56; H, 7.58; N, 5.60. $C_{14}H_{19}NO_3$. Calculated (%): C, 67.44; H, 7.68; N, 5.62. IR (KBr), ν/cm^{-1}: 1652 (C=O), 3384 (OH). ^{1}H NMR ($CDCl_3$), δ: 0.92 (t, 3 H, Me, J = 6.8 Hz); 1.41 (m, 4 H, CH_2CH_2); 1.79 (m, 2 H, CH_2); 2.14 (s, 3 H, Me); 4.00 (t, 2 H, OCH_2, J = 6.6 Hz); 6.89 and 7.92 (both m, 2 H each, Ar); 8.57 (s, 1 H, =NOH).

2) Concentrated aqueous HCl (70 mL) and a 30% aqueous formaldehyde solution (125 mL, 2.5 mol) were added to a suspension of 1-aryl-2-hydroxyiminopropan-1-one (0.05 mol) in water (200 mL). The reaction mixture was magnetically stirred at ~20 °C for 10—20 h (TLC control). 1-(4-Bromophenyl)propane-1,2-dione was filtered off, washed with water, and dried. In other cases, the reaction mixture was extracted with chloroform. The chloroform extract was washed with water and a sodium bicarbonate solution, dried with $MgSO_4$, and concentrated. The residue was distilled off *in vacuo*. All diketones, except for 1-(4-pentyloxyphenyl)propane-1,2-dione, were characterized. Their melting and boiling points are consistent with those published in the literature.[10]

1-(4-Pentyloxyphenyl)propane-1,2-dione. The yield was 80%, the yellow liquid, purified by silica gel chromatography ($CHCl_3$ as the eluent). ^{1}H NMR ($CDCl_3$), δ: 0.92 (t, 3 H, Me, J = 7.0 Hz); 1.39 (m, 4 H, CH_2CH_2); 1.77 (m, 2 H, CH_2); 2.46 (s, 3 H, Me); 3.99 (t, 2 H, OCH_2, J = 6.6 Hz); 6.90 and 7.95 (both m, 2 H each, Ar). High-resolution mass spectrum, found: m/z 234.12614 $[M]^+$. Calculated: M = 234.12559.

2-Hydroxyamino-1-hydroxyimino-3-methyl-1-phenylbutane (1c). A solution of NaOH (33.4 g, 0.84 mol) in water (30 mL) was added with stirring to a suspension of hydroxylamine hydrochloride (69.5 g, 1.0 mol) in a mixture of MeOH (500 mL) and water (20 mL) at a temperature no higher than 20 °C. The precipitate of NaCl was filtered off and washed with MeOH (3×50 mL). 2-Bromo-3-methyl-1-phenylbutan-1-one (48.2 g, 0.2 mol) was added to the resulting hydroxylamine solution. The reaction mixture was refluxed for 13 h, MeOH was evaporated, and the mixture was cooled. The aqueous layer was decanted from the oil, and the oil was dissolved in 3% aqueous HCl (200 mL). The acidic aqueous solution was decanted from the oil that remained undissolved and extracted with diethyl ether (3×40 mL). Then the acidic aqueous solution was treated with aqueous ammonia to pH 8. After 2 day, the oil that precipitated crystallized out. The precipitate was filtered off, washed with water, and dried. Compound **1c** was obtained in a yield of 21.8 g (53%) (a mixture of *Z* and *E* isomers). After crystallization from MeOH (80 mL), the pure *Z* isomer was obtained in a yield of 13.4 g. Methanol was evaporated. Crystallization of the residue from benzene afforded a substance (3.65 g) consisting of 18% of the *Z* isomer and 82% of the *E* isomer (^{1}H NMR spectroscopic data). Crystallization of this mixture from AcOEt afforded the pure *E* isomer in a yield of 0.85 g.

***(Z)*-1c.** M.p. 148—149 °C (from MeOH). Found (%): C, 63.52; H, 7.78; N, 13.48. $C_{11}H_{16}N_2O_2$. Calculated (%): C, 63.44; H, 7.74; N, 13.45. UV (EtOH), λ_{max}/nm (logε): 240 (3.99). ^{1}H NMR (DMSO-d_6), δ: 0.76 and 1.02 (both d, 3 H each, Me, J = 6.7 Hz); 2.06 (m, 1 H, CH); 3.94 (d, 1 H, CH, J = 10.0 Hz); 7.25—7.40 (m, 3 H, Ar); 7.52 (s, 1 H, NH); 7.50—7.70 (m, 2 H, Ar); 11.23 (br.s, 1 H, =NOH).

***(E)*-1c.** M.p. 124—125 °C (from AcOEt). Found (%): C, 63.50; H, 7.82; N, 13.53. $C_{11}H_{16}N_2O_2$. Calculated (%): C, 63.44; H, 7.74; N, 13.45. UV (EtOH), λ_{max}/nm (logε): 229 (3.77). ^{1}H NMR ($CDCl_3$), δ: 0.87 and 0.97 (both d, 3 H each, Me, J = 6.8 Hz); 1.76 (m, 1 H, CH); 3.74 (d, 1 H, CH, J = 7.0 Hz); 7.38 (m, 5 H, Ar).

1-(4-Chlorophenyl)-2-hydroxyamino-1-hydroxyiminopropane (1e). A solution of NaOH (25.2 g, 0.63 mol) in water (25 mL) was added with stirring to a suspension of hydroxylamine hydrochloride (52.0 g, 0.75 mol) in a mixture of MeOH (370 mL) and water (15 mL) at a temperature no higher than 20 °C. The precipitate of NaCl was filtered off and washed with MeOH (3×35 mL). 2-Bromo-1-(4-chlorophenyl)propan-1-one (37.0 g, 0.15 mol) was added to the resulting hydroxylamine solution. The reaction mixture was refluxed for 8 h and then MeOH was evaporated. The residue was cooled and mixed with 5% aqueous HCl (200 mL) and benzene (100 mL). The colorless precipitate of dioxime (methyl(4-chlorophenyl)glyoxime) that remained undissolved was filtered off, washed with water, and dried. The yield of methyl(4-chlorophenyl)glyoxime was 7.1 g (13%). The aqueous solution was separated from the benzene solution and treated with aqueous ammonia. The precipitate that formed was

filtered off, washed with water, and dried. Compound **1e** (a mixture of the *Z* and *E* isomers) was obtained in a yield of 31.6 g (59%). The *Z* and *E* isomers were separated by crystallization from EtOH as described earlier[7] for compound **1b**.

(*Z*)-1e. M.p. 136—137 °C (from EtOH). Found (%): C, 50.23; H, 5.12; Cl, 16.56; N, 13.14. $C_9H_{11}ClN_2O_2$. Calculated (%): C, 50.36; H, 5.17; Cl, 16.52; N, 13.05. UV (EtOH), λ_{max}/nm (logε): 245 (3.00). ^{1}H NMR (DMSO-d_6), δ: 1.18 (d, 3 H, Me, J = 7.0 Hz); 4.51 (q, 1 H, CH, J = 7.0 Hz); 7.32 (br.s, 1 H, NH); 7.38 (d, 2 H, *o*-H_{Ar}, J = 8.5 Hz); 7.61 (d, 2 H, *m*-H_{Ar}, J = 8.5 Hz); 11.45 (br.s, 1 H, OH).

(*E*)-1e. M.p. 175—176 °C (from EtOH). Found (%): C, 50.18; H, 4.99; Cl, 16.56; N, 12.99. $C_9H_{11}ClN_2O_2$. Calculated (%): C, 50.36; H, 5.17; Cl, 16.52; N, 13.05. UV (EtOH), λ_{max}/nm (logε): 224 (3.94). ^{1}H NMR (DMSO-d_6), δ: 1.00 (d, 3 H, Me, J = 6.3 Hz); 3.77 (q, 1 H, CH, J = 6.3 Hz); 7.34 and 7.43 (both d, 2 H each, Ar, J = 8.8 Hz); 10.79 (s, 1 H, OH).

6-Acetyl-5-hydroxy-6-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (3a). A solution of hydroxylamino oxime **1a** (0.83 g, 5 mmol) and diacetyl (**2**) (0.435 mL, 5 mmol) in MeOH (8 mL) was kept at ~20 °C for 1 day. The solvent was concentrated, the residue was treated with diethyl ether, and the precipitate was filtered off. The yield was 1.05 g (90%), m.p. 153—155 °C (from EtOH). Found (%): C, 61.90; H, 5.72; N, 12.00. $C_{12}H_{14}N_2O_3$. Calculated (%): C, 61.53; H, 6.02; N, 11.96. UV (EtOH), λ_{max}/nm (logε): 246 (4.14). IR (KBr), ν/cm^{-1}: 1720 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.53 (s, 3 H, Me); 2.38 (s, 3 H, Ac); 4.09 (s, 2 H, H(4)); 6.20 (br.s, 1 H, OH); 7.30—7.45 (m, 3 H, Ar); 7.55—7.70 (m, 2 H, Ar).

Condensation of 1,2-hydroxylamino oximes 1b—d with diacetyl (2) (general procedure). A solution of hydroxylamino oxime **1b—d** (5 mmol) and diacetyl (**2**) (1.3 g, 15 mmol) in MeOH (15 mL) was refluxed for 7 h. The solvent was concentrated, and the residual yellow oil was chromatographed on a silica gel column ($CHCl_3$—MeOBu^t, 1 : 1, as the eluent for **3b,c** and $CHCl_3$ as the eluent for **3d**). The condensation product was isolated as a mixture of two diastereomers (^{1}H NMR spectroscopic data).

6-Acetyl-5-hydroxy-4,6-dimethyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (3b). The yield was 72%, m.p. 123—124 °C (from AcOEt). Found (%): C, 62.68; H, 6.56; N, 11.32. $C_{13}H_{16}N_2O_3$. Calculated (%): C, 62.89; H, 6.50; N, 11.28. UV (EtOH), λ_{max}/nm (logε): 237 (3.97). IR (KBr), ν/cm^{-1}: 1737 (C=O). The major diastereomer (62%), ^{1}H NMR ($CDCl_3$), δ: 1.33 (d, 3 H, C(4)Me, J = 7.0 Hz); 1.72 (s, 3 H, C(6)Me); 2.31 (s, 3 H, Ac); 4.25 (q, 1 H, H(4), J = 7.0 Hz); 5.84 (s, 1 H, OH); 7.40 (m, 5 H, Ar). The minor diastereomer (38%), ^{1}H NMR ($CDCl_3$), δ: 1.31 (d, 3 H, C(4)Me, J = 7.2 Hz); 1.50 (s, 3 H, C(6)Me); 2.40 (s, 3 H, Ac); 4.15 (q, 1 H, H(4), J = 7.2 Hz); 5.40 (s, 1 H, OH); 7.40 (m, 5 H, Ar).

6-Acetyl-5-hydroxy-4-isopropyl-6-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (3c). The yield was 25%, m.p. 113—114 °C (from hexane). Found (%): C, 64.92; H, 7.43; N, 10.00. $C_{15}H_{20}N_2O_3$. Calculated (%): C, 65.19; H, 7.30; N, 10.14. UV (EtOH), λ_{max}/nm (logε): 234 (3.98). IR (KBr), ν/cm^{-1}: 1723 (C=O). The major diastereomer (63%), ^{1}H NMR ($CDCl_3$), δ: 0.73 and 1.09 (both d, 3 H each, CH<u>Me</u>, J = 6.8 Hz); 1.77 (s, 3 H, C(6)Me); 1.89 (m, 1 H, C<u>H</u>Me); 2.23 (s, 3 H, Ac); 4.25 (d, 1 H, H(4), J = 2.6 Hz); 6.41 (s, 1 H, OH); 7.30—7.60 (m, 5 H, Ar). The minor diastereomer (37%), ^{1}H NMR ($CDCl_3$), δ: 0.78 and 1.09 (both d, 3 H each, CH<u>Me</u>, J = 6.8 Hz); 1.45 (s, 3 H, C(6)Me); 1.89 (m, 1 H, C<u>H</u>Me); 2.38 (s, 3 H, Ac); 3.90 (d, 1 H, H(4), J = 3.0 Hz); 5.52 (s, 1 H, OH); 7.30—7.60 (m, 5 H, Ar).

2-Acetyl-1-hydroxy-2-methyl-1,9,10,10a-tetrahydro-2*H*-3-oxa-1,4-diazaphenanthrene (3d). The yield was 56%, m.p. 142 °C (decomp., from AcOEt). Found (%): C, 64.66; H, 6.03; N, 10.76. $C_{14}H_{16}N_2O_3$. Calculated (%): C, 64.60; H, 6.20; N, 10.76. UV (EtOH), λ_{max}/nm (logε): 256 (4.10), 288 (3.67), 299 (3.57). IR (KBr), ν/cm^{-1}: 1723 (C=O). The major diastereomer (72%), ^{1}H NMR ($CDCl_3$), δ: 1.46 (s, 3 H, Me); 2.00—2.40 (m, 2 H, H(10)); 2.43 (s, 3 H, Ac); 2.90—3.05 (m, 2 H, H(9)); 3.73 (dd, 1 H, H(10a), J = 4.5 Hz, J = 12.5 Hz); 5.37 (s, 1 H, OH); 7.10—7.35 (m, 3 H, Ar); 8.50 (dd, 1 H, H(5), J = 1.4 Hz, J = 7.6 Hz). The minor diastereomer (28%), ^{1}H NMR ($CDCl_3$), δ: 1.62 (s, 3 H, Me); 2.32 (s, 3 H, Ac); other signals overlap with more intense signals of the major diastereomer.

Condensation of 1,2-hydroxylamino oxime 1a with 1-arylpropane-1,2-diones 5 (general procedure). A suspension of hydroxylamino oxime **1a** (1.1 g, 6.6 mmol) and diketone **5** (6.6 mmol) in MeOH (30 mL) was heated at 60 °C until dissolution was achieved and then the reaction mixture was kept for 7 days. The precipitate that formed was filtered off, washed with MeOH, and dried. Condensation products **6a—f** were obtained. An additional amount of the condensation product was obtained from the mother liquor after evaporation of the solvent followed by treatment of the residue with diethyl ether.

Condensation product 6a. The yield was 56%, m.p. 150 °C (decomp., from MeOH). Found (%): C, 68.88; H, 5.51; N, 9.45. $C_{17}H_{16}N_2O_3$. Calculated (%): C, 68.90; H, 5.44; N, 9.45. UV (EtOH), λ_{max}/nm (logε): 251 (4.29), 300 sh (3.79). IR (KBr), ν/cm^{-1}: 1657 (C=O). ***N*-(α-Benzoylethylidene)-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (6aA)** (100%), ^{1}H NMR (DMSO-d_6), δ: 2.07 (s, 3 H, Me); 5.34 (s, 2 H, CH_2); 7.30—7.55 (m, 10 H, Ar); 11.79 (s, 1 H, OH). **Nitrone 6aA** (45%), ^{1}H NMR ($CDCl_3$), δ: 2.43 (s, 3 H, Me); 5.20 (s, 2 H, CH_2); 7.30—7.80 (m, 10 H, Ar); 10.10 (br.s, 1 H, OH). **6-Benzoyl-5-hydroxy-6-methyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6aB)** (55%), ^{1}H NMR ($CDCl_3$), δ: 1.83 (s, 3 H, Me); 4.15 (s, 2 H, H(4)); 5.88 (br.s, 1 H, OH); 6.97 (t, 2 H, *m*-H_{Ar}, J = 7.5 Hz); 7.30—7.80 (m, Ar); 8.32 (d, 2 H, *o*-H_{Ar}, J = 7.2 Hz).

***N*-[α-(4-Fluorobenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (6bA).** The yield was 74%, m.p. 155 °C (decomp., from MeOH). Found (%): C, 65.15; H, 4.79; F, 6.04; N, 8.96. $C_{17}H_{15}FN_2O_3$. Calculated (%): C, 64.96; H, 4.81; F, 6.04; N, 8.91. UV (EtOH), λ_{max}/nm (logε): 251 (4.22), 313 sh (3.64). IR (KBr), ν/cm^{-1}: 1666 (C=O). ^{1}H NMR (DMSO-d_6), δ: 2.10 (s, 3 H, Me); 5.36 (s, 2 H, CH_2); 7.30—7.45 (m, 5 H, Ar); 7.60—7.85 (m, 4 H, Ar); 11.70 (s, 1 H, OH).

***N*-[α-(4-Bromobenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (6cA).** The yield was 81%, m.p. 162 °C (decomp., from MeOH). Found (%): C, 54.47; H, 3.97; Br, 21.26; N, 7.55. $C_{17}H_{15}BrN_2O_3$. Calculated (%): C, 54.42; H, 4.03; Br, 21.30; N, 7.47. UV (EtOH), λ_{max}/nm (logε): 261 (4.34), 314 (3.59). IR (KBr), ν/cm^{-1}: 1661 (C=O). ^{1}H NMR (DMSO-d_6), δ: 2.09 (s, 3 H, Me); 5.35 (s, 2 H, CH_2); 7.30—7.45 (m, 5 H, Ar); 7.60—7.85 (m, 4 H, Ar); 11.70 (s, 1 H, OH).

***N*-[α-(4-Chloro-3-methylbenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (6dA).** The yield was 79%, m.p. 153 °C (decomp., from MeOH). Found (%): C, 62.74; H, 4.94; Cl, 9.66; N, 8.27. $C_{18}H_{17}ClN_2O_3$. Calculated (%): C, 62.70; H, 4.97; Cl, 10.28; N, 8.12. UV (EtOH),

λ_{max}/nm (logε): 259 (4.28), 315 sh (3.71). IR (KBr), ν/cm^{-1}: 1668 (C=O). ^{1}H NMR (DMSO-d_6), δ: 2.08 (s, 3 H, α-Me); 2.40 (s, 3 H, Me); 5.35 (s, 2 H, CH_2); 7.30—7.80 (m, 8 H, Ar); 11.77 (s, 1 H, OH).

***N*-[α-(4-Ethoxybenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (6eA).** The yield was 83%, m.p. 160 °C (decomp., from MeOH). Found (%): C, 67.28; H, 5.85; N, 8.31. $C_{19}H_{20}N_2O_4$. Calculated (%): C, 67.04; H, 5.92; N, 8.23. UV (EtOH), λ_{max}/nm (logε): 231 (4.37), 293 (4.35). IR (KBr), ν/cm^{-1}: 1650 (C=O). ^{1}H NMR (DMSO-d_6), δ: 1.36 (t, 3 H, Me, J = 7.0 Hz); 2.09 (s, 3 H, α-Me); 4.14 (q, 2 H, CH_2, J = 7.0 Hz); 5.27 (s, 2 H, CH_2); 7.07 (d, 2 H, Ar, J = 8.8 Hz); 7.30—7.40 and 7.60—7.80 (both m, 5 H, Ar); 7.70 (d, 2 H, Ar, J = 8.8 Hz); 11.71 (s, 1 H, OH).

***N*-[α-(4-Pentyloxybenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-2-phenylethyl]amine *N*-oxide (6fA).** The yield was 60%, m.p. 142 °C (decomp., from MeOH). Found (%): C, 69.06; H, 6.73; N, 7.28. $C_{22}H_{26}N_2O_4$. Calculated (%): C, 69.09; H, 6.85; N, 7.32. UV (EtOH), λ_{max}/nm (logε): 230 (4.22), 293 (4.22). IR (KBr), ν/cm^{-1}: 1656 (C=O). ^{1}H NMR (DMSO-d_6), δ: 0.91 (t, 3 H, Me, J = 7.0 Hz); 1.37 (m, 4 H, CH_2CH_2); 1.73 (m, 2 H, CH_2); 2.08 (s, 3 H, α-Me); 4.08 (t, 2 H, OCH_2, J = 7.0 Hz); 5.25 (s, 2 H, CH_2); 7.07 (d, 2 H, Ar, J = 8.8 Hz); 7.30—7.40 and 7.60—7.70 (both m, 5 H, Ar); 7.69 (d, 2 H, Ar, J = 8.8 Hz); 11.70 (s, 1 H, OH).

Condensation of 1,2-hydroxylamino oximes 1b,c with 1-arylpropane-1,2-diones 5 (general procedure). A suspension of the *Z* isomer of 1,2-hydroxylamino oximes (7 mmol) and the corresponding 1-arylpropane-1,2-dione **5** (7 mmol) in MeOH (20 mL) was heated until complete dissolution was achieved and then refluxed for 6 h. The solvent was evaporated, the residue was chromatographed on a silica gel column ($CHCl_3$—MeOBu^t, 1 : 1, as the eluent), and the condensation product was isolated.

Condensation product 6g. The yield was 39%, m.p. 142 °C (decomp., from AcOEt). Found (%): C, 69.34; H, 5.83; N, 9.00. $C_{18}H_{18}N_2O_3$. Calculated (%): C, 69.66; H, 5.85; N, 9.03. UV (EtOH), λ_{max}/nm (logε): 247 (4.25), 283 sh (3.65). IR (KBr), ν/cm^{-1}: 1662, 1685 (C=O). ***N*-(α-Benzoylethylidene)-*N*-[2-(*Z*)-hydroxyimino-1-methyl-2-phenylethyl]amine *N*-oxide (6gA)** (40%), ^{1}H NMR (DMSO-d_6), δ: 1.45 (d, 3 H, Me, J = 7.5 Hz); 2.09 (s, 3 H, α-Me); 6.21 (q, 1 H, CH, J = 6.8 Hz); 7.30—7.70 (m, 10 H, Ar); 11.67 (s, 1 H, OH). **6-Benzoyl-5-hydroxy-4,6-dimethyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6gB)** (60%), ^{1}H NMR (DMSO-d_6), δ: 1.15 (d, 3 H, C(4)Me, J = 6.8 Hz); 1.67 (s, 3 H, C(6)Me); 4.09 (q, 1 H, H(4), J = 6.8 Hz); 7.30—7.70 (m, 8 H, Ar); 8.28 (d, 2 H, Ar, J = 7.2 Hz); 8.87 (s, 1 H, OH). **Nitrone 6gA** (27%), ^{1}H NMR ($CDCl_3$), δ: 1.60 (d, 3 H, Me, J = 7.0 Hz); 2.30 (s, 3 H, α-Me); 5.95 (q, 1 H, CH, J = 6.8 Hz); 7.10—7.80 (m, 10 H, Ar); 9.95 (br.s, 1 H, OH). The major isomer of **oxadiazine 6gB** (48%), ^{1}H NMR ($CDCl_3$), δ: 1.36 (d, 3 H, C(4)Me); 1.94 (s, 3 H, C(6)Me); 4.42 (q, 1 H, H(4), J = 7.0 Hz); 6.31 (s, 1 H, OH); 7.10—7.50 (m, 8 H, Ar); 8.25—8.35 (m, 2 H, Ar). The minor isomer of **oxadiazine 6gB** (25%), ^{1}H NMR ($CDCl_3$), δ: 1.27 (d, 3 H, C(4)Me); 1.73 (s, 3 H, C(6)Me); 4.20 (q, 1 H, H(4), J = 7.0 Hz); 5.88 (s, 1 H, OH); 7.10—7.50 (m, 8 H, Ar); 8.25—8.35 (m, 2 H, Ar).

6-(4-Bromobenzoyl)-5-hydroxy-4,6-dimethyl-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6hB). The yield was 72%, m.p. 168 °C (decomp., from MeOH). Found (%): C, 55.50; H, 4.45; Br, 20.75; N, 7.11. $C_{18}H_{17}BrN_2O_3$. Calculated (%): C, 55.54; H, 4.40; Br, 20.53; N, 7.20. UV (EtOH), λ_{max}/nm (logε): 259 (4.25). IR (KBr), ν/cm^{-1}: 1692 (C=O). ^{1}H NMR (DMSO-d_6), δ: 1.14 (d, 3 H, C(4)Me, J = 7.0 Hz); 1.66 (s, 3 H, C(6)Me); 4.10 (q, 1 H, H(4), J = 7.0 Hz); 7.37 (s, 5 H, Ar); 7.76 and 8.19 (both d, 2 H each, Ar, J = 6.8 Hz); 8.94 (s, 1 H, OH).

Condensation product 6i. The yield was 50%, m.p. 148 °C (decomp., from AcOEt). Found (%): C, 62.76; H, 4.98; Cl, 10.47; N, 8.16. $C_{18}H_{17}ClN_2O_3$. Calculated (%): C, 62.70; H, 4.97; Cl, 10.28; N, 8.12. UV (EtOH), λ_{max}/nm (logε): 248 (4.35), 295 sh (3.72). IR (KBr), ν/cm^{-1}: 1673 (C=O). ***N*-(α-Benzoylethylidene)-*N*-[2-(4-chlorophenylethyl)-2-(*Z*)-hydroxyimino-1-methyl]amine *N*-oxide (6iA)** (37%), ^{1}H NMR ($CDCl_3$), δ: 1.58 (d, 3 H, Me, J = 7.2 Hz); 2.29 (s, 3 H, α-Me); 5.95 (q, 1 H, CH, J = 7.2 Hz); 7.15—7.70 (m, 9 H, Ar); 9.73 (br.s, 1 H, OH). **6-Benzoyl-3-(4-chlorophenyl)-5-hydroxy-4,6-dimethyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6iB)** (63%), the major diastereomer (70%), ^{1}H NMR ($CDCl_3$), δ: 1.36 (d, 3 H, C(4)Me); 1.94 (s, 3 H, C(6)Me); 4.36 (q, 1 H, H(4), J = 6.8 Hz); 6.19 (s, 1 H, OH); 7.15—7.70 (m, 7 H, Ar); 8.31 (m, 2 H, Ar). The minor diastereomer (30%), ^{1}H NMR ($CDCl_3$), δ: 1.26 (d, 3 H, C(4)Me, J = 7.2 Hz); 1.72 (s, 3 H, C(6)Me); 4.18 (q, 1 H, H(4), J = 7.2 Hz); 5.75 (s, 1 H, OH); 7.15—7.70 (m, 7 H, Ar); 8.31 (m, 2 H, Ar).

***N*-(α-Benzoylethylidene)-*N*-[2-(*Z*)-hydroxyimino-1-isopropyl-2-phenylethyl]amine *N*-oxide (6jA).** The yield was 71%, m.p. 176 °C (decomp., from MeOH). Found (%): C, 71.10; H, 6.53; N, 8.41. $C_{20}H_{22}N_2O_3$. Calculated (%): C, 70.98; H, 6.55; N, 8.28. UV (EtOH), λ_{max}/nm (logε): 246 (4.38), 285 sh (3.72). IR (KBr), ν/cm^{-1}: 1672 (C=O). ^{1}H NMR (DMSO-d_6), δ: 0.73 and 1.03 (both d, 3 H each, Me, J = 6.4 Hz); 2.35 (s, 3 H, α-Me); 5.60 (d, 1 H, CH, J = 11.0 Hz); 7.30—7.80 (m, 10 H, Ar); 12.36 (s, 1 H, OH); the signal of C<u>H</u>Me$_2$ overlaps with the signal of the solvent.

Condensation product 6k. The yield was 78%, m.p. 176 °C (decomp., from MeOH). Found (%): C, 71.47; H, 6.74; N, 8.05. $C_{21}H_{24}N_2O_3$. Calculated (%): C, 71.57; H, 6.86; N, 7.95. UV (EtOH), λ_{max}/nm (logε): 260 (4.19), 304 sh (3.79). IR (KBr), ν/cm^{-1}: 1663 (C=O). ***N*-[2-(*Z*)-Hydroxyimino-1-isopropyl-2-phenylethyl]-*N*-[α-(4-methylbenzoyl)ethylidene]amine *N*-oxide (6kA)** (100%), ^{1}H NMR (DMSO-d_6), δ: 0.63 and 0.99 (both d, 3 H each, Me, J = 6.6 Hz); 2.13 (s, 3 H, α-Me); 2.40 (s, 3 H, C(4)Me); 5.96 (d, 1 H, CH, J = 11.0 Hz); 7.30—7.40 (m, 5 H, Ar); 7.60—7.85 (m, 4 H, Ar); 11.61 (s, 1 H, OH); the signal of C<u>H</u>Me$_2$ overlaps with the signal of the solvent. **Nitrone 6kA** (20%), ^{1}H NMR ($CDCl_3$), δ: 0.78 and 1.09 (both d, 3 H each, Me, J = 6.8 Hz); 2.28 (s, 3 H, α-Me); 2.37 (s, 3 H, C(4)Me); 2.92 (m, 1 H, CH); 5.68 (d, 1 H, CH, J = 11.0 Hz); 7.10—7.70 (m, 9 H, Ar). **5-Hydroxy-4-isopropyl-6-methyl-6-(4-methylbenzoyl)-3-phenyl-5,6-dihydro-4*H*-1,2,5-oxadiazine (6kB)** (80%), the major diastereomer (94%), ^{1}H NMR ($CDCl_3$), δ: 0.79 and 1.15 (both d, 3 H each, Me, J = 6.8 Hz); 1.95 (s, 3 H, C(6)Me); 2.34 (s, 3 H, Me); 4.43 (d, 1 H, H(4), J = 2.5 Hz); 6.87 (s, 1 H, OH); 7.10—7.70 (m, 7 H, Ar); 8.19 (d, 2 H, Ar, J = 8.4 Hz). The minor diastereomer (6%), ^{1}H NMR ($CDCl_3$), δ: 3.99 (d, 1 H, H(4), J = 2.6 Hz); 5.58 (s, 1 H, OH); other signals overlap with more intense signals.

***N*-[α-(4-Fluorobenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-1-isopropyl-2-phenylethyl]amine *N*-oxide (6lA).** The yield was 80%, m.p. 174 °C (decomp., from MeOH). Found (%): C, 67.25; H, 5.89; F, 5.34; N, 7.86. $C_{20}H_{21}FN_2O_3$. Calculated (%): C, 67.40; H, 5.94; F, 5.33; N, 7.86. UV (EtOH), λ_{max}/nm (logε): 249 (4.26), 292 sh (3.61). IR (KBr), ν/cm^{-1}: 1666 (C=O).

^{1}H NMR (DMSO-d_6), δ: 0.61 and 0.99 (both d, 3 H each, Me, J = 6.5 Hz); 2.15 (s, 3 H, α-Me); 5.95 (d, 1 H, CH, J = 10.8 Hz); 7.30—7.50 (m, 5 H, Ar); 7.70—7.90 (m, 4 H, Ar); 11.66 (s, 1 H, OH); the signal of C<u>H</u>Me_2 overlaps with the signal of the solvent.

***N*-[α-(4-Bromobenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-1-isopropyl-2-phenylethyl]amine *N*-oxide (6mA).** The yield was 86%, m.p. 171 °C (decomp., from MeOH). Found (%): C, 57.50; H, 5.07; Br, 18.90; N, 6.73. $C_{20}H_{21}BrN_2O_3$. Calculated (%): C, 57.56; H, 5.07; Br, 19.15; N, 6.71. UV (EtOH), λ_{max}/nm (logε): 227 (4.22), 266 (4.23), 303 (3.84). IR (KBr), ν/cm^{-1}: 1666 (C=O). ^{1}H NMR (DMSO-d_6), δ: 0.60 and 0.99 (both d, 3 H each, Me, J = 6.6 Hz); 1.93 (s, 3 H, α-Me); 5.96 (d, 1 H, CH, J = 10.8 Hz); 7.30—7.40 (m, 3 H, Ar); 7.60—7.90 (m, 6 H, Ar); 11.68 (s, 1 H, OH); the signal of C<u>H</u>Me_2 overlaps with the signal of the solvent.

***N*-[α-(4-Chlorobenzoyl)ethylidene]-*N*-[2-(*Z*)-hydroxyimino-1-isopropyl-2-phenylethyl]amine *N*-oxide (6nA).** The yield was 80%, m.p. 178 °C (decomp., from MeOH). Found (%): C, 64.57; H, 5.68; Cl, 9.20; N, 7.57. $C_{20}H_{21}ClN_2O_3$. Calculated (%): C, 64.43; H, 5.68; Cl, 9.51; N, 7.51. UV (EtOH), λ_{max}/nm (logε): 255 (4.33), 299 sh (3.76). IR (KBr), ν/cm^{-1}: 1665 (C=O). ^{1}H NMR (DMSO-d_6), δ: 0.60 and 0.99 (both d, 3 H each, Me, J = 6.6 Hz); 2.15 (s, 3 H, α-Me); 5.96 (d, 1 H, CH, J = 10.8 Hz); 7.30—7.40 (m, 3 H, Ar); 7.60—7.85 (m, 6 H, Ar); 11.68 (s, 1 H, OH); the signal of C<u>H</u>Me_2 overlaps with the signal of the solvent.

Condensation product 6o. The yield was 75%, m.p. 178 °C (decomp., from MeOH). Found (%): C, 70.79; H, 5.64; N, 8.69. $C_{19}H_{18}N_2O_3$. Calculated (%): C, 70.79; H, 5.63; N, 8.69. UV (EtOH), λ_{max}/nm (logε): 254 (4.31), 290 (4.05). IR (KBr), ν/cm^{-1}: 1661 (C=O). ***N*-(α-Benzoylethylidene)-*N*-[1-(*Z*)-hydroxyimino-1,2,3,4-tetrahydronaphthyl-2]amine *N*-oxide (6oA)** (92%), ^{1}H NMR (DMSO-d_6), δ: 2.10 (s, 3 H, α-Me); 2.20—2.35, 2.60—2.75, and 3.00—3.20 (all m, 4 H, CH_2CH_2); 5.90 (t, 1 H, CH, J = 5.5 Hz); 7.15—7.35 (m, 3 H, Ar); 7.55—7.85 (m, 6 H, Ar); 11.67 (s, 1 H, OH). **2-Benzoyl-1-hydroxy-2-methyl-1,9,10,10a-tetrahydro-2*H*-3-oxa-1,4-diazaphenanthrene (6oB)** (8%), ^{1}H NMR (DMSO-d_6), δ: 1.68 (s, 3 H, Me); 1.15 (d, 3 H, Me, J = 6.8 Hz); 8.30 (d, 2 H, Ar, J = 8.0 Hz); 8.92 (s, 1 H, OH); other signals overlap with more intense signals.

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