Transformations of conjugated enamines of the imidazolidine 1-oxide series in the Vilsmeier—Haack reaction*

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In some cases, the reactions of enaminones of the imidazolidine 1-oxide series with the Vilsmeier reagent afford electrophilic substitution products containing the dimethylaminomethylene group. In an acidic medium, these products undergo either hydrolytic elimination of the dimethylaminomethylene moiety or hydrolysis of the latter to form the aldehyde group. The reaction of nitroenamine, which is a derivative of imidazolidine 1-oxide, with the Vilsmeier reagent produces furoxane, *viz.*, the nitroxyl biradical. Reduction of the latter affords the dioxime biradical.

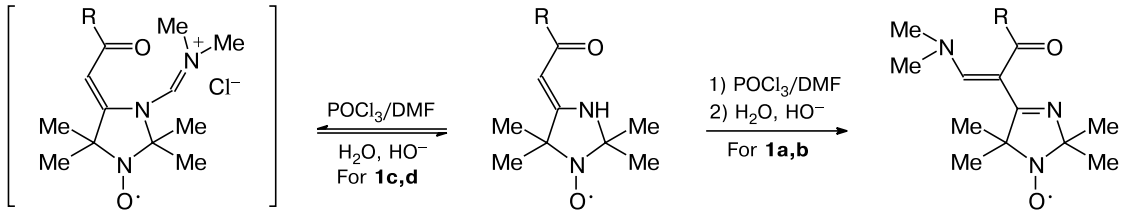
Key words: nitroxides, enaminones, nitroenamine, Vilsmeier—Haack reaction, imidazolidines.

Conjugated paramagnetic enamines, *viz.*, enaminones and nitroenamines of the imidazolidine 1-oxide series, are of interest primarily because these compounds are applied as paramagnetic ligands in the design of magnetoactive materials.[1] They can be subjected to chemical modifications due to the presence of the enaminone or nitroenamine group.[2,3] The reactions of nitroenamines and enaminones, on the whole, and nitroxides of the imidazolidine series, in particular,[4—6] with electrophilic reagents generally proceed at the enamine carbon atom (β-carbon atom). To our knowledge, data on the transformations of conjugated enamines in the Vilsmeier—Haack reaction are scarce. The reactions with the Vilsmeier reagent would be expected to proceed at the enamine carbon atom to form the corresponding enamino aldehydes, which are of interest as paramagnetic ligands.

Results and Discussion

In the present study, we demonstrated that the reaction of enamines **1a,b**, which are derivatives of imidazolidine, with the Vilsmeier reagent followed by alkaline hydrolysis of the reaction mixture afforded enamino imines **2a,b** (Scheme 1).

Scheme 1



3 **1a—d** **2a,b**

R = Bu^t (**a**), OEt (**b**), Ph (**c**), CF_3 (**d**)

* Dedicated to the memory of Academician N. N. Vorozhtsov on the 100th anniversary of his birth.

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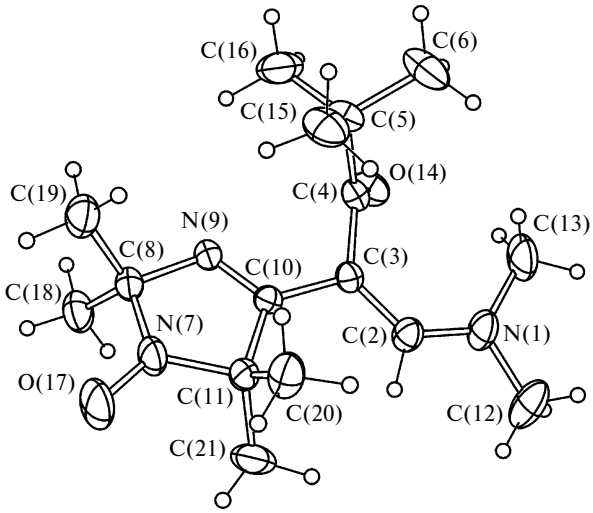


Fig. 1. Three-dimensional structure of compound **2a**.

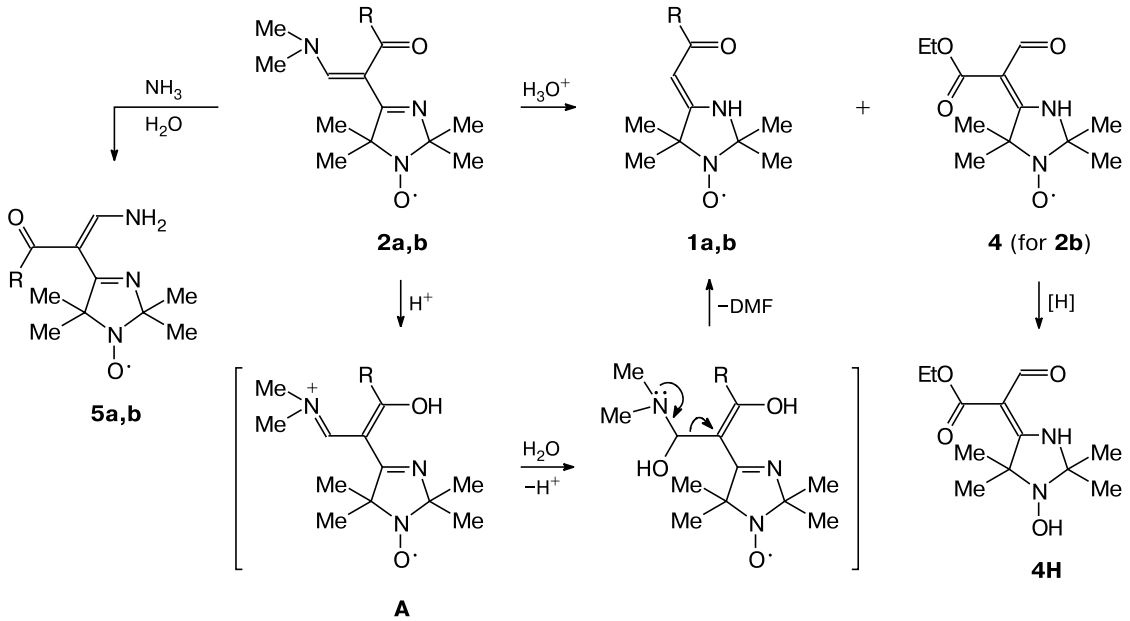
The structure of product **2a** was confirmed by X-ray diffraction analysis (Fig. 1). The bond lengths in the 1-oxyl-2,5-dihydroimidazole moiety of compound **2a** agree well with the average lengths of the corresponding bond lengths in the same fragment in six structures retrieved from the Cambridge Crystallographic Data Centre (*cf.*, for example, Ref. 7). The imidazoline ring is planar (within ±0.029(1) Å). The angle between this ring and the plane of the N(1)C(2)C(3)C(4) fragment (planar within ±0.039(1) Å) is 20.1(2)°. The C(10)—C(3)—C(4)—C(5) torsion angle is 66.6(2)°. It should be noted that in the crystal structure, molecules **2a** form layers parallel to the *bc* plane. In the layers, the molecules are arranged in networks (2D architecture) through the shortened O(14)...H—C(20) and O(17)...H—C(13) van der Waals contacts (O...H, 2.50(3) and 2.54(3) Å; C—H...O, 157(2) and 158(3)°, respectively; *cf.* lit. data[8,9]).

In contrast to the aforesaid, the starting compounds are completely consumed in the reactions of enaminones **1c,d** with the Vilsmeier reagent (TLC data for the reaction mixture); however, only the starting compounds were isolated in these reactions. Apparently, these reactions proceed at the nitrogen atom to give salt **3**, whose hydrolysis affords starting compound **1**. The reactions of enaminones **1e** (R = Me) and **1f** (R = Pr) and enamino aldehyde **1g** (R = H) with the Vilsmeier reagent give complex mixtures of nonidentified products.

Stability of enamino imines **2a,b** to alkaline hydrolysis seems rather unusual. In order to transform the enamino fragment into the aldehyde group, we attempted to perform acid hydrolysis of compounds **2a**,**b**. In the case of compound **2a**, only enaminone **1a** was isolated as the reaction product, whereas hydrolysis of compound **2b** gave rise to enaminone **1b** and target aldehyde **4** in a ratio of 1 : 2.4 (Scheme 2).

Apparently, unsubstituted products **1** are generated as follows (see Scheme 2). Initially, the carbonyl group is protonated at the oxygen atom, and the subsequent nucleophilic addition of the water molecule at the iminium group leads to elimination of the DMF molecule and the formation of enaminone **1**. In this connection, the isolation of the starting compounds in the Vilsmeier—Haack reaction involving enaminones **1c,d** could be attributed to

Scheme 2



R = Bu^t (**a**), OEt (**b**)

the analogous transformation in the course of the treatment of the reaction mixture, *i.e.*, as a result of the nucleophilic addition of water at the $C=N^+$ bond of the initially formed electrophilic substitution product, *viz.*, iminium salt **A**.

Ammonolysis of dimethylaminomethylene-substituted compounds **2a,b** in an aqueous ethanolic medium gives aminomethylene-substituted compounds **5a,b**, respectively, *i.e.*, the dimethylamino group is replaced by the amino group. The formation of unsubstituted enaminone **1a** and enamino ester **1b** was not observed. It should be emphasized that the ester group of enamino ester **2b** remains intact in the reaction with ammonia (see Scheme 2).

The X-ray diffraction data for the diamagnetic analog of aldehyde **4** (compound **4H**) are presented in Fig. 2. The imidazolidine ring in compound **4H** adopts an envelope conformation. The deviation of the N(4) atom from the plane of the C(5)N(6)C(7)C(8) fragment (planar within ±0.012(1) Å) is 0.360(3) Å. The folding angle of the ring along the line between the C(5) and C(8) atoms is 25.0(2)°. The N(4) atom is pyramidal. The C(5)—N(4)—C(8), C(5)—N(4)—O(14), and C(8)—N(4)—O(14) bond angles are 110.8(1), 110.2(1), and 110.8(1)°, respectively. The N(6)C(7)C(2)C(3)O(13) fragment is planar within ±0.023 Å due, apparently, to the conjugation between the bonds in this fragment (N(6)—C(7), 1.315(2) Å; C(7)—C(2), 1.414(2) Å; C(2)—C(3), 1.425(3) Å; C(3)—O(13), 1.234(2) Å) and the formation of the intramolecular N(6)—H...O(13) hydrogen bond (H...O, 1.92(2) Å; N—H...O, 131(2)°; *cf.* lit. data[8,9]). The ethoxycarbonyl group, which also lies in the plane of the above-mentioned amino enone fragment, is involved in conjugation to a substantially lesser extent (taking into account that the C(1)—C(2) bond length is 1.459(2) Å). Information on the structures of several compounds, for example, of methyl (*E*)-2-acetyl-3-aminopent-2-enoate,[11] containing the analogous amino enedione fragment with similar bond lengths are available in the Cambridge Crystallographic Data Centre (CCDC).[10] The crystal structure of compound **4H** is characterized by the formation of head-to-tail chains running along the *c* axis through the intermolecular O(14)—H...O(9) hydrogen bonds (H...O, 1.88(3) Å; O—H...O, 153(3)°). The chains are linked to each other to form corrugated layers parallel to the *ac* plane through the weaker N(6)—H...O(13) hydrogen bonds (H...O, 2.40(2) Å; N—H...O, 140(2)°).

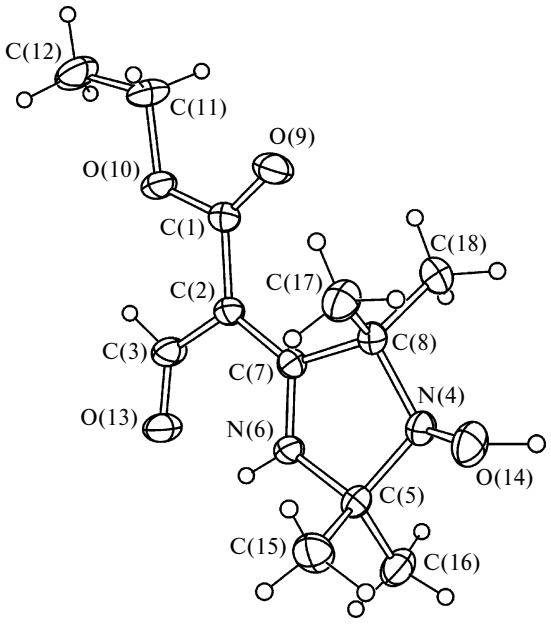


Fig. 2. Three-dimensional structure of compound **4H**.

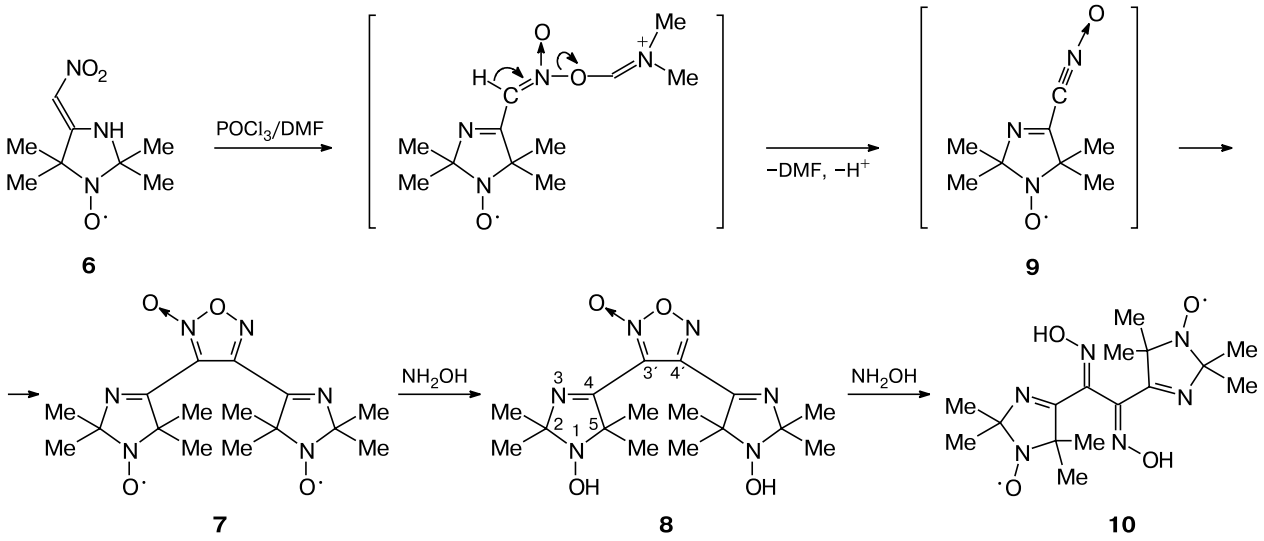
The reaction of nitroenamine **6**, which is a derivative of imidazolidine nitroxide, with the Vilsmeier reagent, unlike the reactions of enaminones, produces the biradical, *viz.*, furoxane derivative **7**. The structure of the latter is confirmed, in particular, by the NMR spectra of its diamagnetic analog **8**, which was synthesized by reduction of biradical **7** with hydroxylamine (Scheme 3). For example, the ^{13}C NMR spectrum shows signals for the carbon atoms of the furoxane ring at δ 108.0 (C=N→O) and 149.7 (C=N—O) (*cf.* Ref. 12). It should also be noted that the spectrum contains two sets of signals for the carbon atoms of the imidazoline heterocycle.

Apparently, the reaction involves the electrophilic attack of the Vilsmeier reagent on the oxygen atom of the nitro group followed by elimination[13] and the formation of nitrile oxide **9**, which undergoes dimerization to give the furoxane ring.[14] It is noteworthy that the formation of furoxane **7** was not observed when another procedure was used for the generation of this nitrile oxide (thermolysis of 4-hydroxyiminonitromethyl-2,2,5,5-tetramethyl-2,5-dihydro-1*H*-imidazole 1-oxide), although the corresponding cycloadducts were detected in the reaction performed in the presence of alkenes.[15] This difference in the results of the reaction is, most likely, associated with low thermal stability of nitrile oxide **9**.

Further reduction of compound **8** with hydroxylamine leads to the furoxane ring opening to form dioxime **10** (*cf.* Ref. 14). The fact that the nitroxide groups of dioxime **10** remain intact in a reducing medium is rather unusual and can be attributed to oxidation of the initially formed hydroxylamino derivative by atmospheric oxygen in the course of isolation giving rise to biradical **10**. Compound **10** is the promising paramagnetic ligand for coordination chemistry.[16]

Thus, some reactions of enaminones, which are derivatives of imidazolidine nitroxides, with the Vilsmeier reagent produce dimethylaminomethylene-substituted derivatives of 3-imidazoline 1-oxide. In an acidic medium, these derivatives either undergo hydrolytic elimination of the dimethylaminomethylene moiety or this moiety is hydrolyzed to give the aldehyde group, two

Scheme 3



reaction pathways being competitive. It was found that the reaction of nitroenamine, which is a derivative of imidazolidine 1-oxide, with the Vilsmeier reagent produces the nitroxyl biradical, *viz.*, furoxane, which can be transformed into the dioxime biradical.

Experimental

The IR spectra were recorded on a Bruker IFS-66 spectrometer in KBr pellets (the concentration was 0.25%, the pellet thickness was 1 mm). The UV spectra were measured on a Specord M-40 spectrometer in ethanol. The ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 and Bruker AV-300 spectrometers for 5—10% solutions in $CDCl_3$. The high-resolution mass spectra were obtained on a Finnigan MAT 8200 spectrometer with a resolution of 10000 using a direct inject system. The ESR spectra were recorded on a Bruker ESP-300 spectrometer in chloroform (the concentration of solutions was $5 \cdot 10^{-4}$ mol L^{-1}).

The melting points were measured on a Boetius micro-melting point apparatus and are uncorrected. The course of the reactions was monitored by TLC on Silufol UV-254 and aluminium oxide 60 F254 plates. Column chromatography was carried out on silica gel (0.063—0.200 mm, Merck) and neutral Al_2O_3 (Brockmann activity IV). All solutions were concentrated under reduced pressure. The synthesis of compounds **1a—g** and **6** has been described earlier.[4,17—19]

Reaction of enamines 1 and 6 with the Vilsmeier reagent (general procedure). Phosphorus oxychloride (0.19 mL, 2.00 mmol) was added to DMF (2.3 mL) at 0 °C. The reaction mixture was stirred for 10 min, enamine **1a—g** or **6** (1.00 mmol) was added, and the mixture was stirred at 0 °C for 4 h (compound **1a**), 5 h (compound **1b**), or 2 h (other compounds). Then the reaction mixture was poured into a saturated ice-cold Na_2CO_3 solution. The resulting mixture was kept at 20 °C and extracted with chloroform (3×25 mL). The combined extracts were washed several times with water and dried with $MgSO_4$. The solution was concentrated. The product was purified as described below.

1-(Dimethylamino)-2-(2,2,5,5-tetramethyl-1-oxyl-2,5-dihydro-1*H*-imidazol-4-yl)-4,4-dimethylpent-1-en-3-one (2a) was purified by alumina chromatography using chloroform as the eluent. The yield was 50%, m.p. 142—144 °C (from a hexane—AcOEt mixture). Found (%): C, 65.14; H, 9.77; N, 14.10. $C_{16}H_{28}N_3O_2$. Calculated (%): C, 65.31; H, 9.52; N, 14.29. IR (KBr), ν/cm^{-1}: 1660, 1607, 1558 (C=O, C=C, C=N). UV (EtOH), λ_{max}/nm (logε): 293 (4.29).

Ethyl 3-(dimethylamino)-2-(2,2,5,5-tetramethyl-1-oxyl-2,5-dihydro-1*H*-imidazol-4-yl)acrylate (2b). The mixture was concentrated, and the residue was crystallized upon the addition of hexane and cooling. The precipitate of compound **2b** was filtered off. The yield was 87%, m.p. 79.5—81.5 °C (from hexane). Found (%): C, 59.72; H, 8.63; N, 14.77. $C_{14}H_{24}N_3O_3$. Calculated (%): C, 59.55; H, 8.57; N, 14.88. IR (KBr), ν/cm^{-1}: 1683, 1607 (O—C=O, C=C, C=N). UV (EtOH), λ_{max}/nm (logε): 275 (4.22). High-resolution mass spectrum, found: *m/z* 282.18175 $[M]^+$. $C_{14}H_{24}N_3O_3$. Calculated: M = 282.18177.

In the reactions of enaminones 1c,d with the Vilsmeier reagent, the starting compounds **1c,d** were isolated by silica gel chromatography using diethyl ether as the eluent. The yield was 33 (**1c**) and 14% (**1d**).

3,4-Bis(2,2,5,5-tetramethyl-1-oxyl-2,5-dihydro-1*H*-imidazol-4-yl)-1,2,5-oxadiazole 2-oxide (7) was purified by alumina chromatography using chloroform as the eluent. The yield was 50%, m.p. 114.5—116.5 °C (from hexane). Found (%): C, 52.22; H, 6.54; N, 22.69. $C_{16}H_{24}N_6O_4$. Calculated (%): C, 52.75; H, 6.59; N, 23.08. IR (KBr), ν/cm^{-1}: 1627, 1614 (C=N, C=N→O); 1479, 1465 (O=N→O). UV (EtOH), λ_{max}/nm (logε): 270 (3.68). ESR ($CHCl_3$): quintet with the hyperfine constant a_N = 7.1 G.

Diamagnetic analogs of compounds 2b and **4** were prepared by reduction of these compounds with hydrogen in ethyl acetate on Pd/C at atmospheric pressure for 1—2 h. After completion of hydrogenation, the catalyst was filtered off, the solution was concentrated, and the products, **ethyl 3-(dimethylamino)-2-**

(1-hydroxy-2,2,5,5-tetramethyl-2,5-dihydro-1*H*-imidazol-4-yl)acrylate (2bH) and **ethyl 2-(1-hydroxy-2,2,5,5-tetramethylimidazolidin-4-ylidene)-3-oxopropanoate (4H)**, were crystallized after the addition of hexane.

Compound **2bH**. The yield was 50%. ^{1}H NMR ($CDCl_3$, 300.13 MHz), δ: 1.22 (t, 3 H, Me, $^3J_{H,H}$ = 6.4 Hz); 1.26 (s, 6 H, C(5)Me_2); 1.43 (s, 6 H, C(2)Me_2); 2.94 (s, 6 H, NMe_2); 4.08 (q, 2 H, OCH_2, $^3J_{H,H}$ = 6.4 Hz); 5.92 (br.s, 1 H, NOH); 7.50 (s, 1 H, CH).

Compound **4H**. The yield was 93%, m.p. 133—136 °C (from a hexane—AcOEt mixture). IR (KBr), ν/cm^{-1}: 3460 (NH, OH); 1687 (C=O); 1609, 1551 (O=CH—C=C—N). UV (EtOH), λ_{max}/nm (logε): 235 (4.05), 296 (4.17). ^{1}H NMR ($CDCl_3$, 300.13 MHz), δ: 1.29 (t, 3 H, Me, $^3J_{H,H}$ = 7.1 Hz); 1.45 (s, 6 H, C(5)Me_2); 1.60 (s, 6 H, C(2)Me_2); 4.19 (q, 2 H, OCH_2, $^3J_{H,H}$ = 7.1 Hz); 4.63 (br.s, 1 H, OH); 9.80 (s, 1 H, O=C—H); 12.46 (br.s, 1 H, NH).

3,4-Bis(1-hydroxy-2,2,5,5-tetramethyl-2,5-dihydro-1*H*-imidazol-4-yl)-1,2,5-oxadiazole 2-oxide (8) (diamagnetic analog of compound 7). A mixture of compound **7** (0.10 g, 0.27 mmol), hydroxylamine hydrochloride (0.2 g, 2.88 mmol), and MeONa (0.10 g, 1.85 mmol) in methanol (7 mL) was stirred at 20 °C for 2 h and then concentrated. The residue was diluted with water (4 ml). The precipitate of compound **8** that formed was filtered off and purified by silica gel chromatography using chloroform and a mixture of chloroform—methanol, 30 : 1, as the eluent. The yield was 50%, m.p. 101—104 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz), δ: 1.39, 1.44, 1.52, and 1.56 (all s, 6 H each, 8 Me); 6.10—7.00 (br.s, 2 H, OH). ^{13}C NMR ($CDCl_3$, 100.32 MHz), δ: 22.9, 23.1, 24.9, 25.3 (8 Me); 72.3, 74.7 (C(5)); 92.3, 93.0 (C(2)); 108.0 (C(3′)=N→O); 149.7 (C(4′)=N—O); 160.4, 161.6 (C(4)).

Hydrolysis of compound 2a. A solution of enaminone **2a** (0.09 g, 0.31 mmol) in a 1 : 1 water—methanol mixture (6 mL) was acidified with a 5% aqueous HCl solution to pH 2 and kept at ~20 °C for 19 h. The precipitate of compound **1a** was filtered off and washed with a small amount of water. The filtrate was concentrated to 1/2 of the initial volume, and the precipitate of compound **1a** that formed was filtered off. The total yield was 0.05 g (68%).

Hydrolysis of compound 2b. A solution of enaminone **2b** (0.1 g, 0.35 mmol) in a 2 : 1 water—methanol mixture (5 mL) was acidified with a 5% aqueous HCl solution to pH 2 and kept at ~20 °C for 9 h. The precipitate of **ethyl 2-(2,2,5,5-tetramethyl-1-oxylimidazolidin-4-ylidene)-3-oxopropanoate (4)** was filtered off and washed with a small amount of water. The reaction mixture was again acidified to pH 3 and kept at ~20 °C for 12 h. An additional portion of compound **4** was filtered off and washed with a small amount of water. The filtrate was concentrated to 1/2 of the initial volume and extracted with $CHCl_3$ (2×5 mL), the extract was dried with $MgSO_4$, and the solution was concentrated. A mixture of compounds **4** and **1b** was separated by alumina chromatography using chloroform as the eluent. The yield of compounds **4** and **1b** was 0.06 g (63%) and 0.02 g (25%), respectively.

Compound **4**. M.p. 106.5—108 °C (from hexane). Found (%): C, 52.67; H, 7.72; N, 10.15. $C_{12}H_{19}N_2O_4 \cdot H_2O$. Calculated (%): C, 52.74; H, 7.74; N, 10.25. IR (KBr), ν/cm^{-1}: 3104 (NH); 1717, 1698, 1616, 1550 (O=C(OEt)—C=C—N, O=CH—C=C—N). UV (EtOH), λ_{max}/nm (logε): 231 (4.01), 296 (4.11).

Ammonolysis of compound 2a. A solution of enaminone **2a** (0.2 g, 0.68 mmol) in a 2 : 3 ethanol—20% aqueous ammonia mixture (10 mL) was kept at ~20 °C for 240 h. The precipitate of **1-amino-2-(2,2,5,5-tetramethyl-1-oxyl-2,5-dihydro-1*H*-imidazol-4-yl)-4,4-dimethylpent-1-en-3-one (5a)** that formed was filtered off and washed with a small amount of water. The filtrate was concentrated to 1/2 of the initial volume. An additional amount of the precipitate of compound **5a** was filtered off and washed with a small amount of water. The yield was 0.14 g (75%), m.p. 177—178 °C (from a hexane—AcOEt mixture). IR (KBr), ν/cm^{-1}: 3344, 3140 (NH_2); 1612, 1630 (O=C—C=C—N, N=C—C=C—N). UV (EtOH), λ_{max}/nm (logε): 277 (4.18). High-resolution mass spectrum, found: *m*/*z* 266.18690 [M]$^+$. $C_{14}H_{24}N_3O_2$. Calculated: M = 266.18684.

Ammonolysis of compound 2b. A solution of enaminone **2b** (0.2 g, 0.71 mmol) in a 1 : 5 methanol—20% aqueous ammonia mixture (6 mL) was kept at ~20 °C for 48 h. The precipitate of **ethyl 3-amino-2-(2,2,5,5-tetramethyl-1-oxyl-2,5-dihydro-1*H*-imidazol-4-yl)acrylate (5b)** that formed was filtered off and washed with a small amount of water. The yield was 0.15 g (85%), m.p. 140.5—141.5 °C (from a hexane—AcOEt mixture). Found (%): C, 56.93; H, 8.17; N, 16.74. $C_{12}H_{20}N_3O_3$. Calculated (%): C, 56.68; H, 7.93; N, 16.52. IR (KBr), ν/cm^{-1}: 3401, 3300, 3122 (NH_2); 1698, 1638 (O=C(OEt)—C=C—N, N=C—C=C—N). UV (EtOH), λ_{max}/nm (logε): 243 (4.24), 290 (4.10).

1,2-Bis(2,2,5,5-tetramethyl-1-oxyl-2,5-dihydro-1*H*-imidazol-4-yl)ethane-1,2-dione dioxime (10). A saturated aqueous NaOH solution was added dropwise with stirring to a mixture of compound **7** (0.10 g, 0.27 mmol) and hydroxylamine hydrochloride (0.10 g, 1.37 mmol) in a 5 : 1 ethanol—water mixture (6 mL) to pH 10. After 72 h, the reaction mixture was concentrated almost to dryness, the residue was acidified with a 5% HCl solution to pH 3, and the precipitate of compound **10** was filtered off, washed with a brine and distilled water, and recrystallized from aqueous ethanol. The yield was 0.06 g (62%), m.p. 198—199 °C. Found (%): C, 52.90; H, 7.50; N, 22.95. $C_{16}H_{26}N_6O_4$. Calculated (%): C, 52.45; H, 7.15; N, 22.94. IR (KBr), ν/cm^{-1}: 3262, 3202 (OH); 1607, 1467, 1439, 1361 (N=C—C=N). UV (EtOH), λ_{max}/nm (logε): 227 (4.39). ESR ($CHCl_3$): quintet with the hyperfine constant a_N = 7.5 G.

X-ray diffraction study of compound 2a was performed on a Bruker P4 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scanning technique, 2θ < 50°). Crystals of **2a** suitable for X-ray diffraction were grown by recrystallization from a hexane—AcOEt mixture. The crystals are monoclinic: a = 27.466(5) Å, b = 11.072(2) Å, c = 12.867(3) Å, β = 115.75(1)°, V = 3524(1) Å^3, space group $C2/c$, $C_{16}H_{28}N_3O_2$, Z = 8, molecular weight 294.41, d_{calc} = 1.110 g cm^{-3}, μ = 0.074 mm^{-1}, the crystal dimensions were 1.00×0.80×0.08 mm, 3103 independent reflections were collected. The structure of compound **2a** was solved by direct methods using the SIR2002 program package and refined by the least-squares method with anisotropic displacement parameters for nonhydrogen atoms and isotropic displacement parameters for hydrogen atoms using the SHELXL-97 program package. The absorption correction was applied based on the crystal shape (transmission was 0.96—0.99), wR_2 = 0.1386, S = 1.022 for all reflections (R = 0.0468 for 2189 reflections with $F > 4\sigma$). The hydrogen atoms were located in difference electron density maps. The coordinates and equiva-

lent displacement parameters of the nonhydrogen atoms and the geometric parameters of molecule **2a** were deposited at the Cambridge Crystallographic Data Centre (refcode CCCD 632002).

X-ray diffraction study of compound 4H was performed on a Bruker P4 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scanning technique, $2\theta < 52°$). Transparent colorless crystals of **4H** suitable for X-ray diffraction were grown by recrystallization from a hexane—AcOEt mixture. The crystals are orthorhombic: $a = 12.686(1)$ Å, $b = 9.820(1)$ Å, $c = 21.611(2)$ Å, $V = 2692.1(5)$ Å^3, space group *Pbca*, $C_{12}H_{20}N_2O_4$, $Z = 8$, molecular weight 256.30, $d_{calc} = 1.265$ g cm^{-3}, $\mu = 0.095$ mm^{-1}, the crystal dimensions were 0.70×0.60×0.35 mm, 2646 independent reflections were collected. The structure of compound **4H** was solved by direct methods using the SHELXS-97 program package and refined by the least-squares method with anisotropic displacement parameters for nonhydrogen atoms and isotropic displacement parameters for hydrogen atoms using the SHELXL-97 program package. The empirical absorption correction was applied (transmission was 0.52—0.60), $wR_2 = 0.1333$, $S = 1.015$ for all reflections ($R = 0.0465$ for 1913 reflections with $F > 4\sigma$). The hydrogen atoms were located in difference electron density maps. The coordinates and equivalent displacement parameters of the nonhydrogen atoms and the geometric parameters of molecule **4H** were deposited at the Cambridge Crystallographic Data Centre (refcode CCCD 632001).

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