Reactions of heterocyclic paramagnetic aldonitrone, 2,2,5,5-tetramethyl-3-imidazoline-1-oxyl 3-oxide, with alkynes

T. A. Berezina, V. A. Reznikov, L. B. Volodarsky, I. Yu. Bagryanskaya, and Yu. V. Gatilov*

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 35 6387. E-mail: mslf@nioch.nsc.ru

The reactions of heterocyclic paramagnetic aldonitrone, *viz.*, 2,2,5,5-tetramethyl-3-imidazoline-1-oxyl 3-oxide, with mono- and disubstituted alkynes afford unstable isoxazoline derivatives. The reactions with monosubstituted alkynes yield predominantly 5-substituted regioisomers. The resulting isoxazoline derivatives are readily (and often spontaneously) converted into enaminoketones, *viz.*, imidazolidine-1-oxyl derivatives. In the presence of tolan, the title paramagnetic aldonitrone gives a dimer in which one imidazoline ring undergoes profound transformation. The structure of the resulting dimer was established by X-ray diffraction analysis.

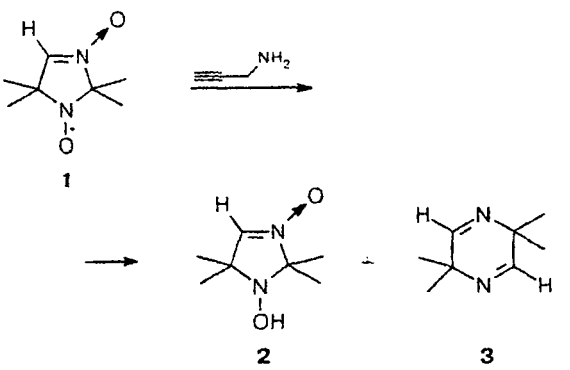
Key words: nitrones, nitroxyl radicals, 3-imidazoline 3-oxides, alkynes, enaminoketones, 1,3-dipolar cycloaddition.

Nitrones can enter into 1,3-dipolar cycloaddition reactions with a wide range of dipolarophiles containing multiple bonds. This fact provides the basis for a method for the construction of various heterocyclic systems.[1,2] The cycloaddition reactions of nitrones with alkynes are characterized by lower regioselectivity compared to the analogous reactions with alkenes. Generally, the reactions of nitrones with terminal alkynes afford both possible regioisomers (5- and 4-substituted 4-isoxazolines).[3,4] Analysis of the compositions of the reaction mixtures was complicated by instability of the cycloadducts that formed and the ease of their subsequent conversions.[5,6] The aim of the present work is to study the reactions of heterocyclic paramagnetic aldonitrone, *viz.*, 2,2,5,5-tetramethyl-3-imidazoline-1-oxyl 3-oxide (**1**), with alkynes.

Aldonitrone **1** does not react with nonactivated alkynes, *viz.*, acetylene, hex-1-yne, 3-methyl-3-hydroxybut-1-yne, and propargylamine. In these cases, only the nitroxyl group of molecule **1** is slowly reduced to the hydroxylamino group to form *N*-oxide **2**. The reaction of aldonitrone **1** with propargylamine (14 h, 7 °C) gave pyrazine **3** (the yield was 11%) along with hydroxyimidazoline **2** (the yield was 35%). Compound **3** was identified by comparing with the known sample (Scheme 1).[7]

The reaction of aldonitrone **1** with phenylacetylene at ~20 °C (72 h) afforded 4,4,6,6-tetramethyl-2-phenyl-5,6(4*H*)-dihydroimidazo[1,5-*b*]isoxazole-5-oxyl (**4a**) (the yield was 5%) and enaminoketone **6a** (the yield was 6%), which is a product of opening of the isoxazoline ring of compound **4a** (Scheme 2; *cf.* Ref. 5). The structure of compound **6a** was established by comparing

Scheme 1



with the known sample.[8] In addition, reduction product **2** was formed in a substantial amount (40%). The reaction performed at 50 °C (3 h) gave enaminoaldehyde **7a** (3%) along with the above-mentioned compounds **4a** (4%), **6a** (6%), and **2** (25%). Compound **7a** is a product of opening of 3-phenyl-substituted regioisomer **5a**, which is unstable under these conditions. Therefore, as one would expect, the regioselectivity of the reaction decreases upon heating. Note that in the other cases under study, derivatives of 3-substituted imidazo[1,5-*b*]isoxazolines or products of their conversions were not detected.

The reactions of aldonitrone **1** with methyl propiolate and propargylaldehyde afforded enaminoketones **6b,c**, which are products of opening of the isoxazoline ring of compounds **4b,c**, respectively (see Scheme 2).

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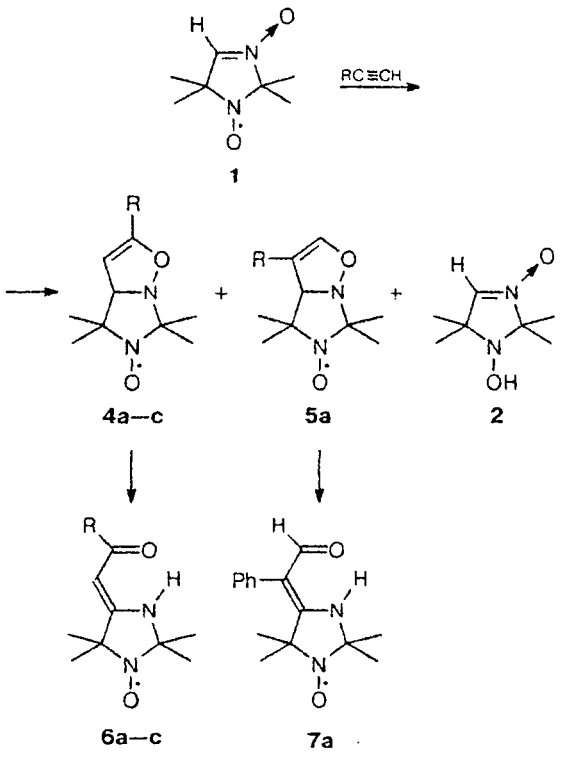
Scheme 2

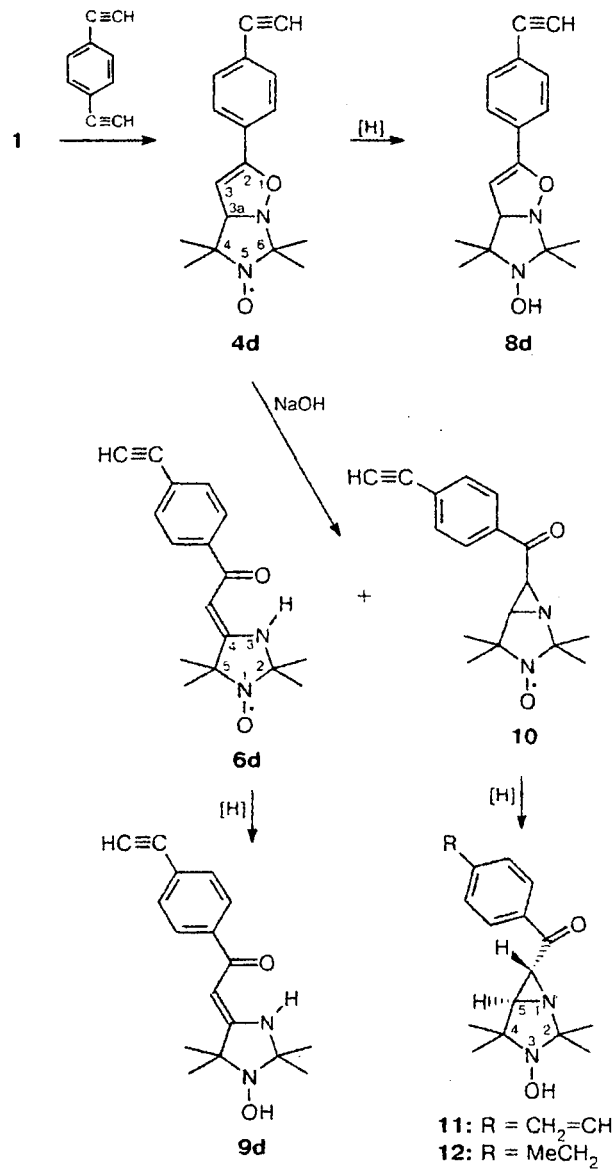


R = Ph (**a**), CHO (**b**), or AcO (**c**)

The reaction of aldonitrone **1** with *p*-diethylbenzene gave 2-aryl-substituted regioisomer **4d** as the only product. The structure of **4d** was established by ^{1}H and ^{13}C NMR spectroscopy of diamagnetic analog **8d**, which was prepared by reduction of compound **4d** (Scheme 3). Treatment of isoxazoline **4d** with an aqueous-alcoholic solution of NaOH afforded two isomeric compounds, one of which, *viz.*, enaminoketone **6d**, is the major reaction product. The structure of compound **6d** was confirmed by the ^{1}H and ^{13}C NMR spectra of diamagnetic analog **9d**. The second reaction product, *viz.*, compound **10**, was reduced by catalytic hydrogenation to diamagnetic compounds **11** and **12**. Based on the ^{1}H and ^{13}C NMR spectra of these compounds and on a comparison of these spectra with the published data for the analogs,[9,10] it is believed that products **11** and **12** are aziridine derivatives. Note that the spin-spin coupling constant of the protons at the C(5) and C(6) atoms (2.5 Hz) is indicative of their *trans* arrangement. Evidently, the vinyl group of molecule **11** and the ethyl group of molecule **12** are formed as a result of reduction of the ethynyl group of the initial compound **10**. Based on the data of ^{1}H NMR spectroscopy, the **11** : **12** ratio was 3 : 1.

The reaction of aldonitrone **1** with dimethyl acetylenedicarboxylate gave dihydroimidazoisoxazoline **13**, which was converted into enaminoketone **15** upon

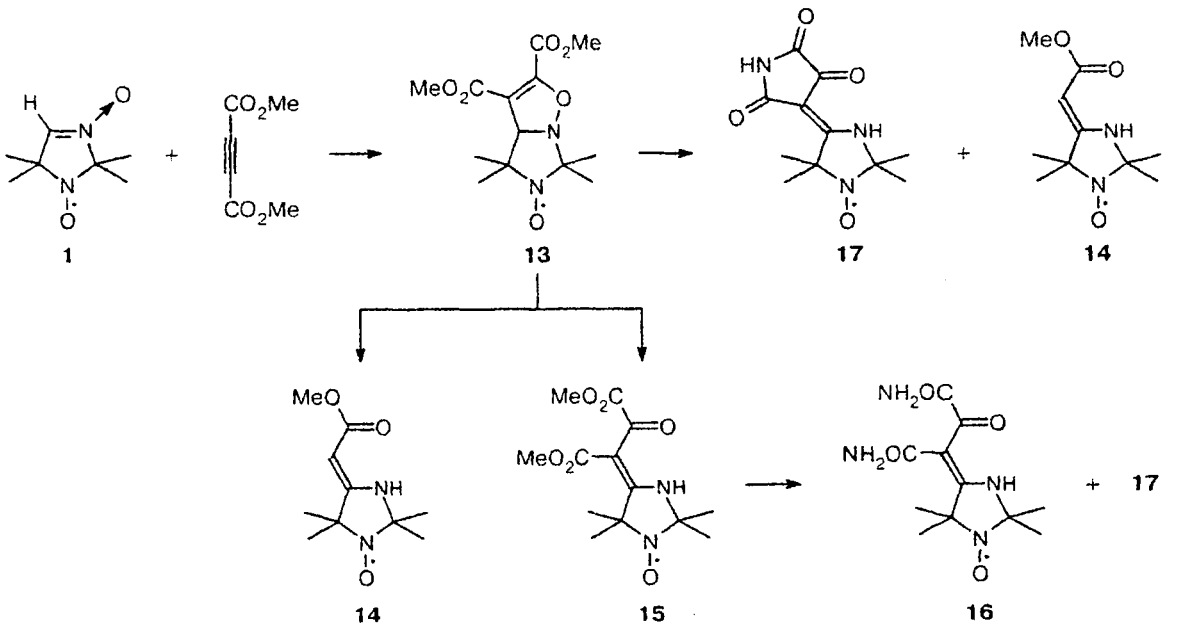
Scheme 3



treatment with a 0.2 *M* aqueous-alcoholic solution of NaOH or upon storage at room temperature (Scheme 4). Treatment of isoxazoline **13** with a more concentrated (3.3 *M*) alkaline solution yielded enamino ester **14**. The reaction of cycloadduct **13** with aqueous ammonia afforded imide **17** along with a small amount of enamino ester **14** (the yield was 7%). The reaction of diester **15** with ammonia in an alcoholic solution afforded imide **17** as the major product and diamide **16** in trace amounts (2%).

The reaction of aldonitrone **1** with tolan took an unusual pathway to give compound **18**. We succeeded in establishing the structure of compound **18** only by X-ray

Scheme 4



diffraction analysis (Fig. 1). In molecule **18**, the 3-imidazoline ring adopts an envelope conformation with the N(1) atom deviating from the plane of the double bond by 0.379(5) Å. The analogous conformation is observed in 4,4-dibromomethyl-1-hydroxy-2,2,5,5-tetramethyl-3-imidazoline 3-oxide (**19**),[11] in which this deviation is 0.48(1) Å. The bond lengths of the corresponding fragments in molecules **18** (Table 1) and **19** have close values except for the C=N bond lengths (1.272(4) and 1.32(1) Å, respectively). Note that the C(4)=N(3) bond length in molecule **18** is smaller than the average value (1.307(19) Å) for nine 3-imidazoline 3-oxides available in the Cambridge Structural Database[12] and coincides with the analogous bond length (1.26(1) Å) in 4,4-dibromomethyl-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide.[11] The bond lengths in the remaining portion of molecule **18** are close to the expected values.[13] According to the molecular formula, compound **18** is a dimer of the initial aldonitrone **1** in which one heterocycle remains unchanged, while the second heterocycle undergoes profound transformation. The role of tolan in this reaction is still unclear, but compound **18** is formed only in its presence. A hypothetical pattern of this reaction consisting in the addition of the oxygen atom of the nitroxyl group of one

Table 1. Principal bond lengths (*d*) in molecule **18**

Bond	*d*/Å*	Bond	*d*/Å*
N(1)—C(2)	1.470	C(4)—C(5)	1.479
C(2)—N(3)	1.502	C(5)—N(1)	1.497
N(3)—O(3)	1.284	N(1)—O(6)	1.439
N(3)—C(4)	1.272		

* Errors are 0.03—0.05 Å.

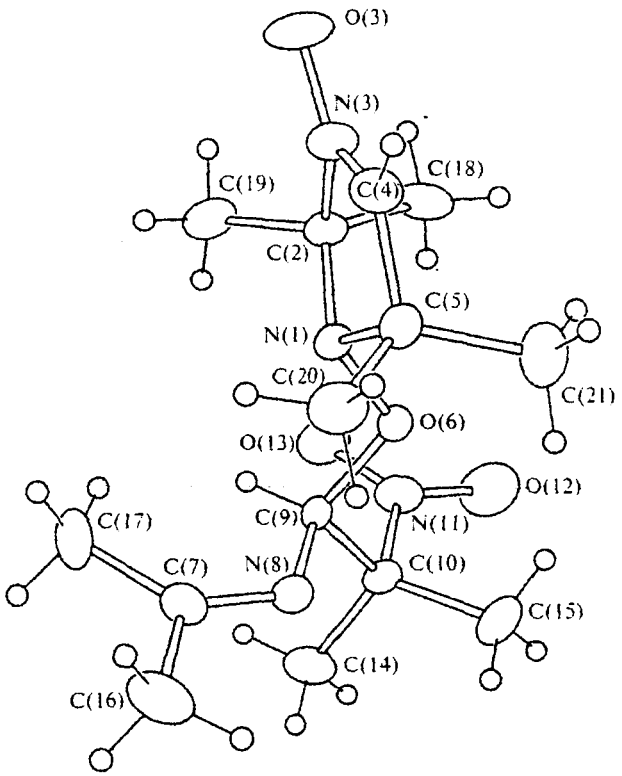
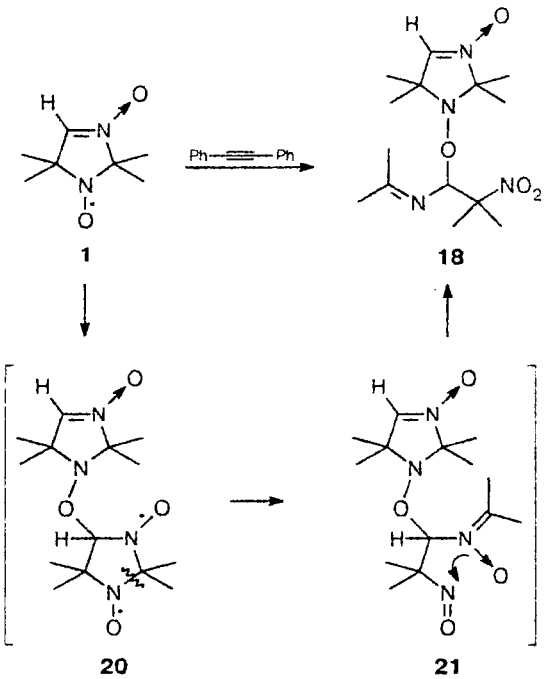


Fig. 1. Crystal structure of compound **18**.

heterocycle at the aldonitrone group of the second molecule can be suggested (Scheme 5). It is known that aldonitrones can capture short-lived radicals, including O-centered radicals. In particular, the method of spin traps is based on this transformation. However, examples of addition of the stable nitroxyl radical at the aldonitrone group are lacking. Probably, it is the presence of tolan that governs the course of this reaction. In biradical adduct **20** that formed, the imidazolidine heterocycle undergoes homolytic cleavage to form nitrosonitrone **21** and then the nitroso group is oxidized to the nitro group by the nitrone grouping, which, in turn, is reduced to the imino group.

Scheme 5



The ^{1}H NMR spectrum of compound **18** has 13 singlet signals of 16 methyl groups, two signals at δ 5.39 and 5.44 (N—C<u>H</u>—O), and one signal at δ 6.50 (s, 2 H) belonging to the protons at the C=N bond, which is apparently associated with hindered inversion of the heterocycle. This statement cannot be verified because compound **18** decomposes upon heating in DMSO or DMF.

Experimental

The IR spectra were recorded on UR-20 and Specord M-80 instruments in KBr pellets. The UV spectra were measured on a Specord UV-VIS spectrometer in ethanol. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-200 instrument (200.13 and 50.32 MHz, respectively). The yields, the melting points, the molecular formulas, and the IR and UV spectra of the synthesized compounds are given in Table 2. The compounds were purified by chromatography on a column with silica gel using chloroform as the eluent. The course of the reactions was monitored by TLC (Silufol; a 10 : 1 chloroform—methanol mixture as the eluent).

Reaction of 2,2,5,5-tetramethyl-3-imidazoline-1-oxyl 3-oxide (1) with alkynes (general procedure). A solution of aldonitrone **1** (0.1 mol; **1** was synthesized according to a procedure reported previously[15]; the structure was confirmed by comparing with the IR spectrum of the known sample) and a dipolarophile (0.15 mol) in chloroform (10 mL) was kept under conditions described below and concentrated under reduced pressure. The residue was chromatographed on a column. The reactions of compound **1** with propargylamine and propargylaldehyde were carried out at 7 °C for 14 h. The reaction with *p*-diethylbenzene was carried out at 50 °C for 2 h. The reactions with dimethyl acetylenedicarboxylate, methyl propiolate, and tolan were performed at 20 °C for 2 h, at 20 °C for 14 h, and at 50 °C for 12 h, respectively.

Reduction of radicals 4d and 6d. A solution of compound **4d** or **6d** (0.01 mol) and 80% hydrazine hydrate (0.1 mol) in methanol (2 mL) was kept at 20 °C for 10—18 h and concentrated under reduced pressure. The residue was washed with water. The precipitate of hydroxylamino derivative **8d** or **9d** was filtered off and dried *in vacuo*. Oxidation of compounds **8d** and **9d** with MnO_2 afforded the initial radicals **4d** and **6d**, respectively.

2-(4′-Ethynylphenyl)-5-hydroxy-4,4,6,6-tetramethyl-3a,4,5,6-tetrahydroimidazo[1,5-*b*]isoxazole (8d). ^{1}H NMR (CD_3OD), δ: 7.50 (m, 4 H, C_6H_4); 5.51 (d, 1 H, H(3), J = 3 Hz); 4.61 (d, 1 H, H(3a), J = 3 Hz); 3.61 (s, 1 H, <u>H</u>C≡); 1.48, 1.38, 1.28, and 1.17 (all s, 3 H each, C(4)Me_2, C(6)Me_2). ^{13}C NMR (CD_3OD), δ: 153.99 (C(2)); 133.10, 129.73, 126.37, and 124.23 (C_6H_4); 96.89 (C(3)); 87.74 (C(6)); 83.98 (≡<u>C</u>H); 80.07 (C(3a)); 77.69 (<u>C</u>≡CH); 65.49 (C(4)); 26.39, 24.85, 24.23, and 23.16 (C(4)<u>Me</u>$_2$, C(6)<u>Me</u>$_2$).

4-(4′-Ethynylphenacetylidene)-1-hydroxy-2,2,5,5-tetramethylimidazolidine (9d). ^{1}H NMR ($CDCl_3$), δ: 10.36 (s, 1 H, NH); 7.66 (m, 4 H, C_6H_4); 5.62 (s, 1 H, HC=C); 5.48 (s, 1 H, OH); 3.12 (s, 1 H, C≡CH); 1.45 and 1.40 (both s, 6 H each, C(2)Me_2, C(5)Me_2). ^{13}C NMR ($CDCl_3$), δ: 187.55 (C=O); 169.48 (C(4)); 139.78, 134.77, 126.70, and 123.66 (C_6H_4); 83.54 (C≡<u>C</u>H); 83.54 (C=<u>C</u>H); 80.36 (C(2)); 78.84 (<u>C</u>≡CH); 67.93 (C(5)); 28.71 and 24.98 (C(2)<u>Me</u>$_2$, C(5)<u>Me</u>$_2$).

4-(4′-Ethynylphenacetylidene)-2,2,5,5-tetramethylimidazolidine-1-oxyl (6d) and 6-(4′-ethynylbenzoyl)-2,2,4,4-tetramethylperhydroazirino[1,2-*c*]imidazole-3-oxyl (10). A 15% NaOH soution (0.5 mL) was added to a solution of compound **4d** (282 mg, 1 mmol) in methanol (7 mL). The reaction mixture was kept at 70 °C for 6 h and concentrated under reduced pressure. The residue was chromatographed on a column.

Reduction of radical 10 to hydroxylamines 11 and 12 was performed by hydrogenation of a solution of compound **10** (0.2 g) in ethyl acetate (10 mL) with hydrogen in the presence of Pd/C (0.1 g) under atmospheric pressure at ~20 °C until ~10 mL of hydrogen was absorbed. The catalyst was filtered off, the solution was concentrated under reduced pressure, the residue was washed with hexane, and the precipitate of compounds **11** and **12** was filtered off.

3-Hydroxy-2,2,4,4-tetramethyl-6-(4′-vinylbenzoyl)perhydroazirino[1,2-*c*]imidazole (11). ^{1}H NMR ($CDCl_3$), δ: 7.97 (d, 2 H, C_6H_4, J = 8 Hz); 7.49 (d, 2 H, C_6H_4, J = 8 Hz); 6.75 (dd, 1 H, =C<u>H</u>Ph); 5.86 (d, 1 H, <u>H</u>CH=, J = 17.0 Hz); 5.48

Table 2. Characteristics of the synthesized compounds

Compound	Yield (%)	M.p./°C	IR, ν/cm^{-1}	UV, λ_{max}/nm (log ε)	Found / Calculated (%) C	H	N	Molecular formula
4a	5	101–102[a]	1650 (C=C)	330 (4.02)	69.3 69.5	7.5 7.4	10.5 10.8	$C_{15}H_{19}N_2O_2$
4d	44	114–115[b]	2100 (C≡C); 3200 (≡CH)	260 (4.26); 300 (4.02)	72.5 72.1	6.8 6.8	9.9 9.9	$C_{17}H_{19}N_2O_2$
6b	10	167–168[c]	1630 (C=O); 1660 (C=O); 2950 (NH)	230 (3.54); 295 (4.00)	57.0 56.9	7.2 7.2	13.4 13.3	$C_{10}H_{15}N_2O_3$
6c	25	104–105[d]	1605 (C=O); 1690 (C=O); 3400 (NH)	230 (3.65); 290 (3.67)	54.9 54.9	7.1 7.1	11.6 11.6	$C_{11}H_{17}N_2O_4$
6d	60	169–171[b]	1620 (C=O); 2100 (C≡C); 3370 (NH)	268 (4.15); 339 (4.34)	71.9 72.1	6.8 6.8	9.3 9.9	$C_{17}H_{19}N_2O_2$
7a	3	90–95[a]	1675 (C=O); 3450 (NH)	250 (4.20); 330 (3.54)	69.2 69.5	7.4 7.4	10.7 10.8	$C_{15}H_{19}N_2O_2$
8d	89	127–128[b]	2100 (C≡C); 3200 (≡CH)	260 (4.18); 305 (3.98)	71.7 71.8	7.3 7.1	9.8 9.9	$C_{17}H_{20}N_2O_2$
10	15	170–171[e]	1675 (C=O); 2100 (C≡C); 3200 (≡CH)	275 (4.30)	71.9 72.1	6.6 6.8	9.7 9.9	$C_{17}H_{19}N_2O_2$
13	90	78–79[d]	1710 (C=O); 1750 (C=O)	300 (3.85)[g]	52.5 52.2	6.6 6.4	9.4 9.4	$C_{13}H_{19}N_2O_6$
14	47	81–87[d]	1650 (C=O); 3300 (NH)	272 (4.44)	56.0 56.3	8.1 8.0	13.0 13.1	$C_{10}H_{17}N_2O_3$
15	91	167–168[f]	1715 (C=O); 1725 (C=O); 3100 (NH)	235 (4.04); 300 (4.23)	52.1 52.2	6.4 6.4	9.4 9.4	$C_{13}H_{19}N_2O_6$
16	5	221–222[b]	1715 (C=O); 1770 (C=O); 3500 (NH)	270 (4.25); 400 (4.06)	49.3 49.1	6.3 6.4	20.4 20.8	$C_{11}H_{17}N_4O_4$
17	45	222–223[b]	1710 (C=O); 1765 (C=O); 3220 (NH)	270 (4.25)	48.7 48.9	5.9 5.9	15.5 15.6	$C_{11}H_{14}N_3O_4 \cdot H_2O$
18	43	123–124[a]	1655 (C=N)	235 (3.7)	53.4 53.5	8.7 8.3	17.7 17.8	$C_{14}H_{26}N_4O_4$

[a–f] The synthesized compounds were purified by: [a] recrystallization from hexane; [b] from a 1 : 1 hexane–ethyl acetate mixture; [c] from a 1 : 2 hexane–ethyl acetate mixture; [d] by chromatography; [e] by recrystallization from a 3 : 1 hexane–ethyl acetate mixture; [f] from methanol.
[g] *Cf.* Ref. 14.

(d, 1 H, HCH=, J = 10.0 Hz); 3.60 (d, 1 H, H(6), J = 2.5 Hz); 2.89 (d, 1 H, H(5), J = 2.5 Hz); 1.47, 1.37, and 1.33 (all s, 6 H + 3 H + 3 H each, C(2)Me_2, C(4)Me_2). ^{13}C NMR ($CDCl_3$), δ: 194.52 (C=O); 141.43 and 135.34 (C_6H_4, C_i); 135.04 (H_2C=CHPh); 127.71 and 125.53 (C_6H_4); 116.03 (PhCH=CH_2); 82.50 (C(4)); 61.22 (C(2)); 53.65 (C(5)); 37.72 (C(6)); 26.09, 25.36, 24.94, and 22.53 (C(2)Me_2, C(4)Me_2).

6-(4′-Ethylbenzoyl)-2-hydroxy-2,2,4,4-tetramethylperhydroazirino[1,2-*c*]imidazole (12). ^1H NMR ($CDCl_3$), δ: 7.92 (d, C_6H_4, J = 8 Hz); 7.29 (d, C_6H_4, J = 8 Hz); 2.72 (q, CH_3CH_2); 1.25 (t, CH_3CH_2). ^{13}C NMR ($CDCl_3$), δ: 141.00 and 133.84 (C_6H_4, C_i); 127.55 and 127.28 (C_6H_4).

4-Methoxycarbonylmethylene-2,2,5,5-tetramethylimidazolidine-1-oxyl (14). A solution of NaOH (0.4 g, 10 mmol) in water (1 mL) was added to a solution of isoxazoline **13** (0.6 g, 2 mmol) in methanol (2 mL). The reaction mixture was kept at 20 °C for 14 h and concentrated under reduced pressure. The residue was chromatographed on a column.

4-(1′,2′-Dimethoxycarbonyl)-2′-oxoethylidene-2,2,5,5-tetramethylimidazolidine-1-oxyl (15). A solution of NaOH (0.08 g, 2 mmol) in water (1 mL) was added to a solution of isoxazoline **13** (0.6 g, 2 mmol) in methanol (10 mL). The reaction mixture was kept at 20 °C for 14 h and the crystals that precipitated were filtered off. The resulting enaminoketone **15** was purified by recrystallization from methanol.

2,2,5,5-Tetramethyl-4-(2,3,5-trioxopyrrolidin-4-ylidene)-imidazolidine-1-oxyl (17) and 4-methoxycarbonylmethylene-2,2,5,5-tetramethylimidazoline-1-oxyl (14). Aqueous ammonia (2 mL) was added to a solution of compound **13** (0.05 mol) in methanol (10 mL). The reaction mixture was kept at 20 °C for 1 h and concentrated under reduced pressure. The residue was chromatographed on a column. Products **16** and **17** were prepared from compound **15** under analogous conditions.

1-(2,5-Dimethyl-5-nitro-3-azahex-2-ene-4-oxy)-2,2,5,5-tetramethyl-3-imidazoline 3-oxide (18). Tolan (1.78 g, 10 mmol) was added to a solution of compound **1** (1.57 g, 10 mmol) in chloroform (10 mL). The reaction mixture was kept at 50 °C for 12 h and concentrated under reduced pressure. The residue was chromatographed on a column. ^1H NMR (DMSO-d_6), δ: 1.09, 1.17, 1.27, 1.296, 1.30, 1.32, 1.35, 1.44, 1.49, 1.62, 1.94, 1.95, and 2.02 (all s, 3 H and 6 H each,

16 Me); 5.39 and 5.44 (both s, 1 H each, N—CH—O); 6.50 (s, 2 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 166.25 and 155.23 (C=N); 135.10 and 134.41 (CH=N); 92.77, 92.62, 92.01, and 90.57 (N—CH—O); 66.85, 66.00, 65.14, and 64.50 (C(2), C(4)); 57.92 (C—NO_2); 29.73, 28.39, 27.49, 26.56, 23.24, 21.79, 21.52, 21.02, 19.35, 19.05, and 18.97 (C(2)$\underline{Me}_2$, C(5)$\underline{Me}_2$, =CMe_2, Me_2C—NO_2).

X-ray diffraction analysis of a single crystal of compound 18 was performed on a Syntex $P2_1$ diffractometer (Cu-Kα radiation, graphite monochromator). The crystals of compound **18** ($C_{14}H_{26}O_4N_4$) belong to the monoclinic system, a = 13.369(3) Å, b = 9.363(2) Å, c = 14.733(3) Å, β = 108.79(2)°, V = 1745.9(6) Å, space group $P2_1/n$, Z = 4, μ = 0.729 mm^{-1}, d_{calc} = 1.196 g cm^{-3}. The intensities of 2377 independent reflections with 2θ < 115° were measured using the θ/2θ scanning technique. Corrections were made for a decrease in the intensities of the check reflections (to 81.4%) and for absorption (correction was 0.84—1.37) The structure was solved by the direct method using the SHELX-86 program package. The final anisotropic refinement of the structural parameters was performed by the full-matrix least-squares method using the SHELXL-93 program package to wR_2 = 0.1460 for all F^2 and to R = 0.0555 for 1415 $F_0 > 4\sigma$ (226 parameters were refined). At each stage, the positions of the hydrogen atoms were calculated geometrically and only the isotropic thermal parameters were refined. The principal bond lengths in molecule **18** are given in Table 1. The coordinates and the equivalent thermal parameters of the nonhydrogen atoms as well as complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database.

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