Reactions of chloro-substituted enaminoketones, *viz.*, derivatives of imidazolidine nitroxides, with sodium cyanide

V. A. Reznikov, 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) 33 4752. E-mail: mslf@nioch.nsc.ru

The reactions of chloro-substituted enaminoketones, *viz.*, derivatives of imidazolidine nitroxides, with sodium cyanide afford the corresponding nitriles. The reactions proceed through formation of epoxides. The structure of one of these epoxides was confirmed by X-ray diffraction analysis.

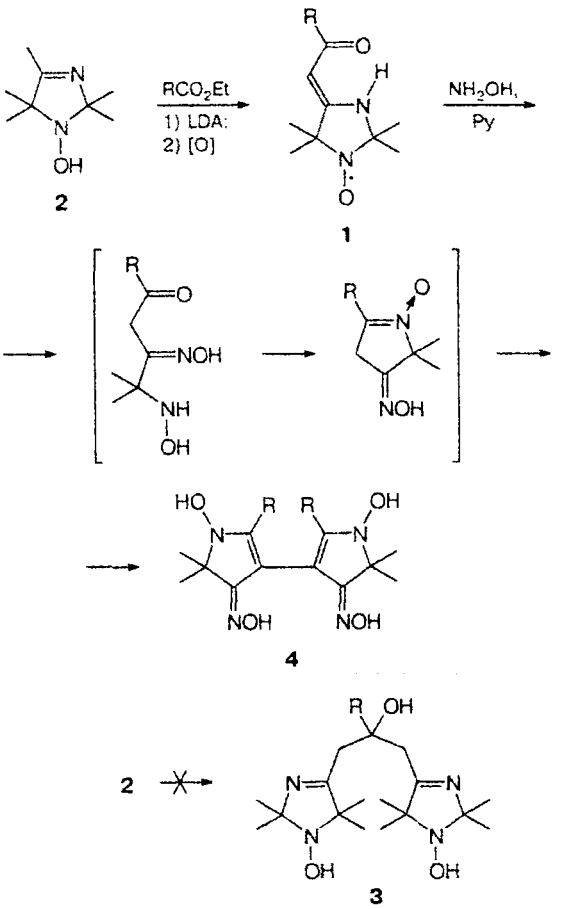
Key words: nitroxides, enaminoketones, imidazolidines, epoxides, nucleophilic substitution.

Enaminoketones are vinylogs of amides, and their carbonyl groups exhibit reduced reactivity with respect to nucleophilic addition.[1] Derivatives of imidazolidine nitroxides **1** are no exception.

Thus, compounds **1** were prepared by the reactions of imidazolidine **2** with esters in the presence of lithium diisopropylamide (LDA).[2–4] In no case was the formation of compounds **3**, which are products of the addition of two molecules **2** to the ester molecule, observed whatever the order in which the reagents were mixed and their ratio. Enaminoketones **1** do not react with amines and sodium borohydride. In the reactions of compounds **1** with hydroxylamine, only the nitroxyl group was reduced to the hydroxylamino group, while the carbonyl group remained intact.[5] Only under rather severe conditions, *viz.*, upon refluxing of enaminoketones **1** with hydroxylamine hydrochloride in pyridine, did the keto group also enter into the reaction; however, the heterocycle was initially cleaved and the subsequent reaction of the hydroxylamino group with the carbonyl group occurred as an intramolecular process to form pyrroline derivative **4** (Scheme 1).[3] Therefore, the addition of a nucleophile at the carbonyl group is less probable than the nucleophilic attack on the carbon atom bound to the nitrogen atom.

Previously, we have demonstrated that in the reactions of enaminoketones **1** with hypohalogenites in an aqueous-methanolic solution at 0 °C, the enaminoketone group was readily cleaved to form halomethyl derivatives of 3-imidazolidine.[6] Apparently, the scheme of this reaction involves the initial formation of mono- or dihalogen derivatives followed by the nucleophilic attack on the carbon atom of the carbonyl group. The possibility of this reaction proceeding according to the above-mentioned scheme was confirmed by the conversion of bromo-substituted enaminoketone **5** (X = Br) into bromomethyl derivative **6** (X = Br) in the reaction with sodium methoxide (Scheme 2). The somewhat surprising thing is that compound **6** (X = Br) did not further react with an excess of sodium methoxide. Note that unsubstituted enaminoketone **1a** (R = Ph) did not react with sodium methoxide under these conditions and even

Scheme 1



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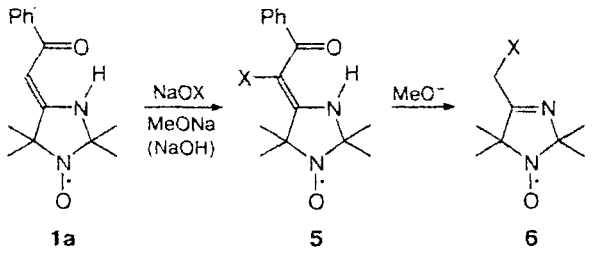
under more severe conditions. Therefore, the presence of a substituent, *viz.*, the halogen atom, at the enamine carbon atom of the enaminoketone group, leads, apparently, to an increase in the electrophilicity of the carbon atom of the carbonyl group.

Scheme 2



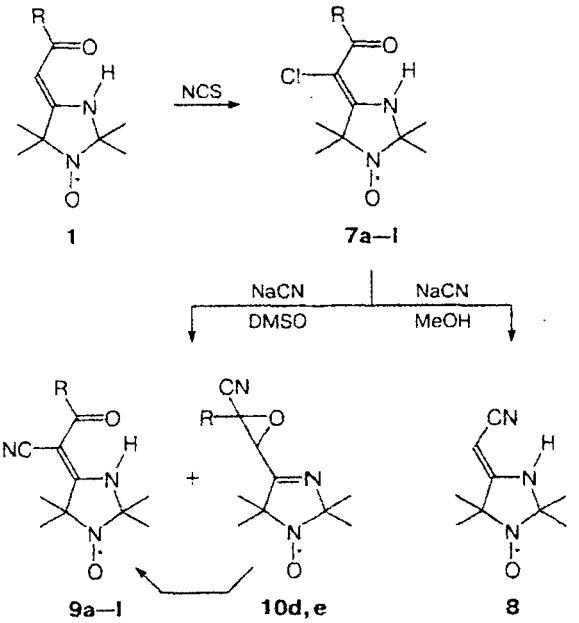
1a **5** **6**

Since the halogen atom at the enamine carbon atom is located at the double bond, its nucleophilic mobility should be extremely low. At the same time, it was of considerable interest to perform the synthesis of cyano-substituted enaminoketones. It is known that enaminoketones of type **1** can be used as paramagnetic ligands in the synthesis of coordination compounds with transition metals, certain of which are low-temperature molecular ferromagnetics.[7] First, the cyano group can substantially modify the electron and spin density distributions in the enaminoketonate molecule. Second, judging from the literature data, cyano-substituted enaminoketonates can form crystal structures favorable for magnetic phase transitions.[8,9] In this connection, the aim of this work was to study the reactions of chloro-substituted enaminoketones **7** with NaCN.

The initial enaminoketones **7** were prepared by chlorination of compounds **1** with *N*-chlorosuccinimide (NCS) in $CHCl_3$ or CCl_4 (Scheme 3). The reactions proceeded rather selectively to give compounds **7** in high yields.

The reaction of enaminoketone **7a** with NaCN in methanol did not afford cyano-substituted enaminoketone **9a**, and enaminonitrile **8** was obtained as the only paramagnetic reaction product. The reaction of compound **7a** with NaCN in acetonitrile in the presence of 15-crown-5 ether proceeded very slowly to give nitrile **9a** in low yield. When this reaction was performed in DMSO, nitrile **9a** was rapidly formed under mild conditions in high yield. Under these conditions, a series of nitriles **9b—c,f—l** were synthesized from enaminoketones **7b—c,f—l**, respectively (see Scheme 3). It was found that nitrile **9e** was formed from chloro derivative **7e** only in low yield, and isomeric epoxide **10e** was unexpectedly obtained as the major reaction product. The structure of the latter was established by X-ray diffraction analysis. The molecular structure of the nitroxyl radical under study is shown in Fig. 1. The principal bond lengths are given in Table 1. The bulkiest substituents in the oxirane ring, *viz.*, the imidazoline ring and the *tert*-butyl group, are in the mutually *trans* arrangement. The imidazoline

Scheme 3



1 **7a—l** **9a—l** **10d,e** **8**

R = Ph (**a**), Me (**b**), Et (**c**), Pr^i (**d**), Bu^t (**e**), OEt (**f**), CF_3 (**g**), 4-pyridyl (**h**), 2-pyridyl (**i**), H (**k**), $CONH_2$ (**l**)

ring is planar to within ±0.02 Å. The geometric parameters of the imidazoline ring and of its environment and the corresponding parameters of ten 3-imidazoline 3-oxides available in the Cambridge Structural Database coincide within the experimental error. The exception is the C(4)=N(3) bond length, which is somewhat smaller than the average value (1.299(19) Å) for the above-mentioned structures, but coincides with the length of the analogous bond in 4-(2-hydroxypropyl-2)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (1.270(3) Å).[10] The lengths of the remaining bonds in radical **10e** are close to the expected values.[11] Note also the shortening of the C—O bond lengths in the epoxide ring (on the average, to 1.430(3) Å) compared to the literature data (1.45(1) Å).[11] In the crystal of **10e**, the radicals are linked in infinite chains along the *a* axis through weak

Table 1. Principal bond lengths (*d*) in radical **10e**

Bond	*d*/Å	Bond	*d*/Å
N(1)—O(1)	1.266	C(5)—C(10)	1.519
N(1)—C(2)	1.483	C(5)—C(11)	1.515
N(3)—C(4)	1.267	C(6)—O(2)	1.437
C(2)—N(3)	1.461	C(6)—C(7)	1.478
C(2)—C(8)	1.509	C(7)—O(2)	1.423
C(2)—C(9)	1.528	C(7)—C(12)	1.457
C(4)—C(5)	1.511	C(7)—C(13)	1.530
C(4)—C(6)	1.488	C(12)—N(17)	1.128
C(5)—N(1)	1.471		

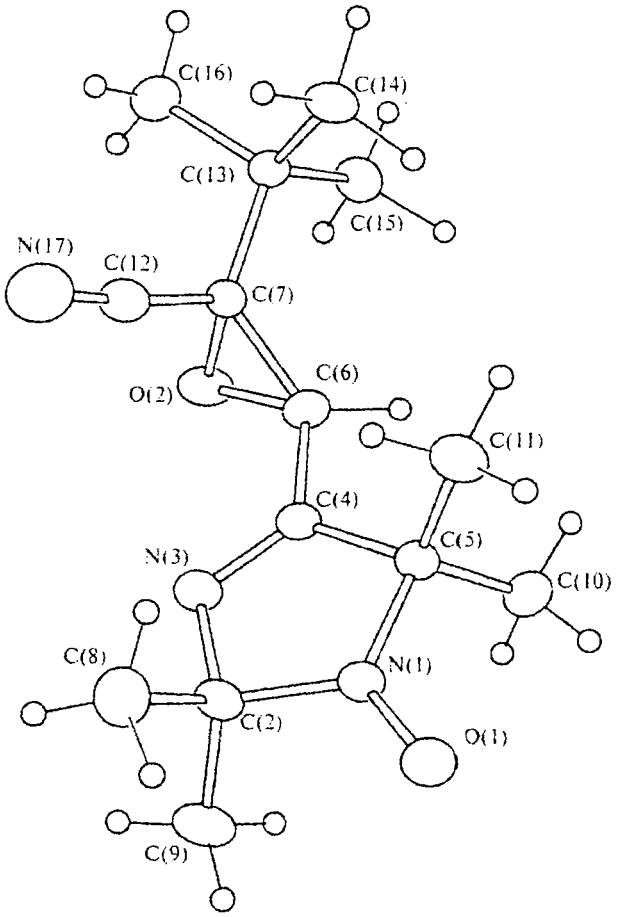


Fig. 1. Structure of nitroxyl radical **10e**.

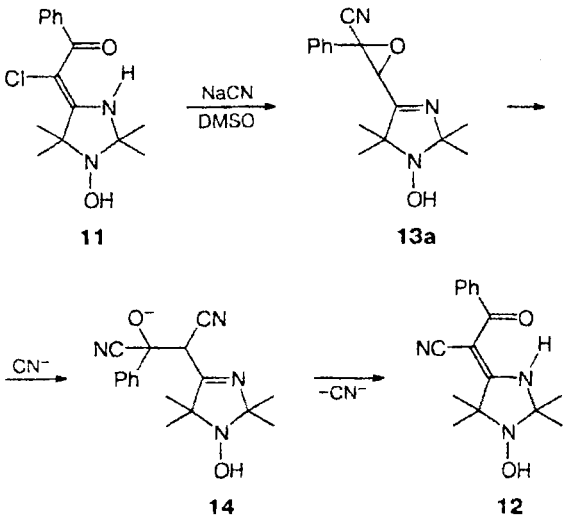
O...H hydrogen bonds (N(1)—O(1)...H(10B), 2.53 Å) (see Fig. 1).

When the reaction of chloro derivative **7d** with NaCN was carried out under the above-mentioned conditions during 1 h, nitrile **9d** and epoxide **10d** were obtained in approximately equal amounts. The amount of epoxide **10d** decreased and the content of nitrile **9d** increased as the reaction time was increased. The fact that epoxides **10d,e** are intermediates in the reactions yielding cyano-substituted enaminoketones **9e,d** was confirmed by the reactions of compounds **10d,e** with NaCN in DMSO giving nitriles **9e,d** in high yields. The slow spontaneous conversion of epoxide **10e** into nitrile **9e** was also observed upon storage of a solution of **10e** in an organic solvent or even upon storage of crystals of **10e**. In the cases of other chloro-substituted enaminoketones, the formation of epoxides was not observed (at least, in noticeable amounts).

From the aforesaid, it can be suggested that in all cases epoxides **10** are intermediates in the reactions yielding nitriles **9**. Evidently, it is due to the formation of epoxides that the substitution reactions proceed readily.

With the aim of confirming the generality of the proposed scheme of replacement of the Cl atom in chloro-substituted enaminoketones **7**, we synthesized diamagnetic analogs of chloro derivative **7a** (compound **11**), nitrile **9a** (**12**), and epoxide **10e** (**13e**) and performed the reaction of chloride **11** with NaCN in DMSO in an NMR tube (Scheme 4).

Scheme 4



The NMR spectrum of the reaction mixture has signals of the initial compound **11** and nitrile **12** along with signals, which can be assigned to epoxide **13a** or anion **14**. Thus, the ^{1}H NMR spectrum has singlets at δ 3.65 and 4.53, which, apparently, belong to the methine protons of diastereomeric epoxides **13a** (the chemical shift of the signal for the corresponding proton in the spectrum of epoxide **13e** in a solution in $CDCl_3$ is 3.65 ppm). The ^{13}C NMR spectrum has signals at δ 49.21 and 50.63, which can be assigned either to the proton-bearing carbon atom of the epoxide ring in diastereomeric epoxides **13a** (the chemical shift of the signal for this atom in the spectrum of epoxide **13e** in $CDCl_3$ is 53.70 ppm) or to the corresponding carbon atom of cyanohydrin **14**. The signals at δ 89.00 and 90.64, which are absent in the NMR spectra of the initial chloro derivative **11** and of the final nitrile **12**, can belong to the carbon atom of the epoxide ring bound to the nitrile group (at δ 92.01 for epoxide **13e**). To exclude the possibility of formation of epoxide or, which is more probable, of cyanohydrin from nitrile **12** as a result of addition of the cyanide anion, we also recorded the NMR spectra of a solution of nitrile **12** in the presence of NaCN. In this case, the spectra remain essentially the same. The observed differences in the chemical shifts may be associated with possible deprotonation of compound **12** under these conditions.

Therefore, it is believed that in all cases, the reactions of chloro-substituted enaminoketones 7 proceed through formation of the corresponding epoxide. Compounds **10d,e** were isolated from the reaction mixture only due to their relatively higher stability under the reaction conditions, all the more so since the electronic and steric effects of the isopropyl group, and, particularly, of the *tert*-butyl group are least favorable for the addition of the cyanide anion to the carbonyl group in the series of chloro-substituted enaminoketones under study.

It should be noted that the formation of epoxides in the reactions of nucleophiles, *viz.*, of cyanide or alkoxide anions, with α-haloketones is well known.[12] Although, taking into account the reduced electrophilicity of the carbonyl carbon atom of the enaminoketone, the formation of epoxides is not obvious, it accounts for the fact that the substitution proceeds readily.

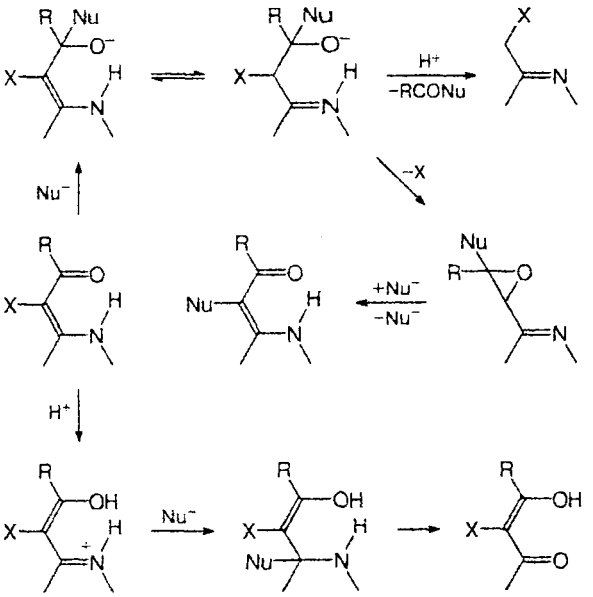
Therefore, it is believed that the reactions of halogen-substituted enaminoketones with nucleophilic reagents involve the nucleophilic attack on the carbon atom of the carbonyl group as the initial stage. The direction of subsequent conversions depends on the ratio of the reaction rates of the cleavage of the C—C bond and of intramolecular nucleophilic substitution yielding epoxide, which further gives a "nucleophilic substitution" product. The first pathway involves reactions with the participation of hydroxide and alkoxide anions. The second pathway involves reactions with the participation of cyanide anions. In particular, these facts explain the difference in the direction of the reactions of enaminoketone **7a** with NaCN in acetonitrile and methanol.

The third pathway of the reactions with nucleophiles, *viz.*, the attack on the carbon atom bound to the nitrogen atom, is also possible. However, in the case of enaminoketones, *viz.*, imidazolidine derivatives, we observed this conversion resulting in the opening of the heterocycle of imidazolidine only in an acidic medium under conditions of electrophilic catalysis (Scheme 5).

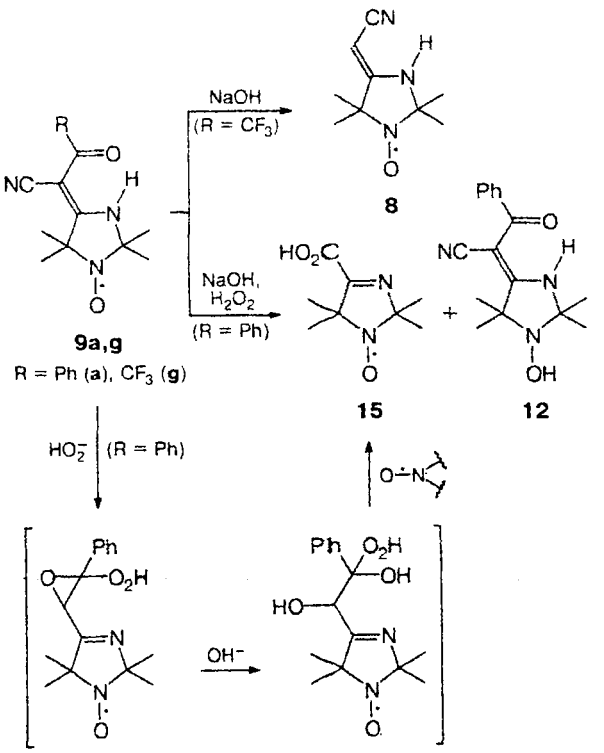
An interesting feature of nitriles **9g,h** is the fact that the IR spectra of crystalline samples of these compounds have two vibration bands of the nitrile group, whereas the IR spectra of solutions have one band. The region of the spectrum in which vibration bands of the enaminoketone group are observed is somewhat more complicated than those of other nitriles **9**. Apparently, this is associated with the possibility of existence of compounds **9** as two isomers (the *E* and *Z* isomers with respect to the exocyclic C=C bond), which occur in the equilibrium in solutions (*cf.* Ref. 1).

As expected, the reaction of nitrile **9g** with an aqueous-alcoholic solution of NaOH afforded enaminonitrile **8** (Scheme 6). Nitrile **9a** is more stable to alkaline hydrolysis and remained virtually unchanged after refluxing in an aqueous-alcoholic solution of NaOH for many hours. In attempting to perform hydrolysis of the nitrile group of compound **9a** under the action of an alkaline solution of hydrogen peroxide, reduction product **12** and carboxylic acid **15** were unexpectedly obtained in small amounts (see Scheme 6). Probably,

Scheme 5



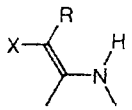
Scheme 6



acid **15** was also formed as a result of the nucleophilic attack of the hydroperoxide anion on the carbon atom of the carbonyl group of nitrile **9a** followed by intramolecular nucleophilic replacement of the cyano group by

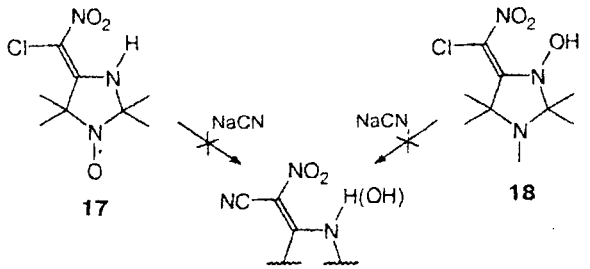
the hydroxide ion. It is believed that reduction of the nitroxyl group under these conditions is associated with oxidation of an alcoholic group, which appears as a result of the opening of the intermediate epoxide, by the above-mentioned nitroxyl group (*cf.* Ref. 13).

In conclusion, it should be noted that when the nature of the R group in halogen-substituted enamines



16

16 does not give grounds to expect the formation of epoxide, the replacement of the halogen atom does not, apparently, occur. In particular, chloro-substituted nitroenamines **17** and **18** (*cf.* Ref. 14) do not react with NaCN under the above-mentioned conditions.



To summarize, we demonstrated that the reactions of chloro-substituted enaminoketones, *viz.*, derivatives of imidazolidine nitroxides, with sodium cyanide proceed through formation of epoxides. The latter are converted into nitriles, which are formal products of nucleophilic replacement of the chlorine atom by the cyano group.

Experimental

The IR spectra were recorded on a Specord M-80 instrument in KBr pellets (the concentration was 0.25%) and in solutions in CCl_4 (the concentration was 5%). The UV spectra were measured on a Specord UV-VIS spectrometer in ethanol. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-200 instrument at 300 K (the concentration of the solutions was 5%).

The syntheses of chloro-substituted enaminoketones **7a,b,e,g—i** have been reported previously.[6,13] Compounds **7c,d,f** were prepared analogously[6,13] by the reactions of equimolar amounts of enaminoketones **1** and *N*-chlorosuccinimide in CCl_4. The reaction of enaminoaldehyde **1k** with *N*-chlorosuccinimide was carried out in $CHCl_3$. The characteristics of the newly synthesized compounds are given in Table 2.

4-(2-Carbamoyl-1-chloro-2-oxoethylidene)-2,2,5,5-tetramethylimidazolidine-1-oxyl (7l). *N*-Chlorosuccinimide (0.59 g, 4.4 mmol) was added portionwise with stirring to a suspension of amide **1l** (1 g, 4.4 mmol) in $CHCl_3$ (50 mL) for 1 h. Then the reaction mixture was stirred at 20 °C for 12 h, refluxed for 2 h, and concentrated. Compound **7l** was isolated by chromatography on a column with silica gel using a 30 : 1 $CHCl_3$—methanol mixture as the eluent.

4-(Cyanomethylene)-2,2,5,5-tetramethylimidazolidine-1-oxyl (8). A mixture of chloro derivative **7a** (0.3 g, 1 mmol) and NaCN (0.1 g, 2 mmol) in methanol (10 mL) was refluxed for 20 min and then concentrated. A saturated aqueous solution of NaCl (5 mL) and hexane (2 mL) were added to the residue. The precipitate of enaminonitrile **8** that formed was filtered off, washed with hexane, and dried.

4-(1-Cyano-2-oxo-2-phenylethylidene)-2,2,5,5-tetramethylimidazolidine-1-oxyl (9a). *A.* A suspension of chloro derivative **7a** (0.5 g, 1.7 mmol), NaCN (0.17 g, 3.4 mmol), and 15-crown-5 ether (0.05 g) in anhydrous acetonitrile (10 mL) was stirred at 20 °C for 10 days and then concentrated. Nitrile **9a** was isolated by chromatography on a column with silica gel; $CHCl_3$ was used as the eluent. The yield was 0.1 g (20%).

B. Chloro derivative **7a** (0.6 g, 2 mmol) was added to a solution of NaCN (0.2 g, 4 mmol) in anhydrous DMSO (10 mL) and the reaction mixture was stirred at 20 °C for 3 h. Then the solution was cooled to 0 °C and an aqueous saturated solution of NaCl (20 mL) was added. The precipitate of nitrile **9a** that formed was filtered off, washed with an aqueous saturated solution of NaCl and water, and dried.

4-[Carbethoxy(cyano)methylene]-2,2,5,5-tetramethylimidazolidine-1-oxyl (9f) was prepared and isolated analogously. **4-(1-Cyano-2-oxopropylidene)-2,2,5,5-tetramethylimidazolidine-1-oxyl (9b)** and **4-(1-cyano-2-oxobutylidene)-2,2,5,5-tetramethylimidazolidine-1-oxyl (9c)** were isolated by neutralizing their aqueous solutions with 5% HCl. In the cases of **4-[1-cyano-2-oxo-2-(pyridyl-4)ethylidene]-2,2,5,5-tetramethylimidazolidine-1-oxyl (9h)** and **4-[1-cyano-2-oxo-2-(pyridyl-2)ethylidene]-2,2,5,5-tetramethylimidazolidine-1-oxyl (9i)**, the solutions were acidified to pH 6. The remaining nitriles were isolated by acidifying their solutions to pH 4 followed by treatment according to the above-described procedure.

4-(1-Cyano-3-methyl-2-oxobutylidene-1)-2,2,5,5-tetramethylimidazolidine-1-oxyl (9d) and **4-(3-cyano-3-isopropyloxiranyl-2)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (10d).** Chloro derivative **7d** (1 g, 3.85 mmol) was added with stirring to a solution of NaCN (0.5 g, 7.7 mmol) in anhydrous DMSO (15 mL) and then the reaction mixture was stirred at 20 °C for 1 h. The solution was poured onto ice (25 g). The precipitate of nitrile **9d** that formed was filtered off, washed with water, dried, and purified by chromatography on a column with silica gel; $CHCl_3$ was used as the eluent. The yield was 0.3 g (30%). The filtrate was saturated with NaCl and the precipitate of epoxide **10d** that formed was filtered off, dried, and purified by recrystallization from hexane. The yield was 0.3 g (30%). When the reaction time was increased to 4 h, only nitrile **9d** was isolated.

Under analogous conditions, a mixture of **4-(1-cyano-3,3-dimethyl-2-oxobutylidene-1)-2,2,5,5-tetramethylimidazolidine-1-oxyl (9e)** and **4-(3-*tert*-butyl-3-cyanooxiranyl-2)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (10e)** was obtained from chloro derivative **7e**. The mixture was separated by chromatography on a column with silica gel ($CHCl_3$ was used as the eluent). Epoxide **10e** disappeared from the reaction mixture when the reaction time was increased to 5 h.

2,2,5,5-Tetramethyl-4-(chloronitromethylene)imidazolidine-1-oxyl (17). A solution of 2,2,5,5-tetramethyl-4-nitromethyleneimidazolidine-1-oxyl (1 g, 5 mmol) and *N*-chlorosuccinimide (0.87 g, 6.5 mmol) in $CHCl_3$ (20 mL) was stirred at 20 °C for 24 h and then concentrated. Compound **17** was isolated by chromatography on a column with silica gel ($CHCl_3$ as the eluent).

The reaction of chloro derivative **17** with NaCN was carried out under conditions described for compound **7g**. The initial compound was isolated in 90% yield.

Reduction of chloro derivative 7a and nitrile 9a with hydroxylamine in methanol yielding hydroxylamino derivatives **11** and **12**, respectively, was carried out as described previously.[5]

1-Hydroxy-4-(1-chloro-2-oxo-2-phenylethylidene)-2,2,5,5-tetramethylimidazolidine (11). ^1H NMR (DMSO-d_6), δ: 1.40 and 1.51 (both s, 6 H each, C(2)Me_2, C(5)Me_2); 7.50 (m, 5 H, Ph); 8.07 (br.s, 1 H, OH); 10.88 (br.s, 1 H, NH). ^{13}C NMR

Table 2. Characteristics of the synthesized compounds

Compound	Yield (%)	M.p.* /°C	Found / Calculated (%) C	H	N	Molecular formula	IR (KBr), ν/cm^{-1}	UV, λ_{max}/nm (log ε)
7c	90	107—109	53.5 53.8	7.1 7.3	11.3 11.4	$C_{11}H_{18}ClN_2O_2$	1540, 1620 (C=C—C=O); 3205 (NH)	316 (4.20)
7d	90	144—145	55.4 55.5	7.9 7.7	10.6 10.8	$C_{12}H_{20}ClN_2O_2$	1530, 1610 (C=C—C=O); 3180 (NH)	318 (4.18)
7f	80	127—129	50.4 50.5	6.7 6.9	10.5 10.7	$C_{11}H_{18}ClN_2O_3$	1575, 1650 (C=C—C=O); 3160 (NH)	289 (4.22)
7k	70	183—185	49.5 49.7	6.2 6.4	12.9 12.9	$C_9H_{14}ClN_2O_2$	1545, 1600, 1605 (C=C—C=O); 3150 (NH)	301 (4.42)
7l	95	193—194	46.0 46.0	5.8 5.8	15.9 16.1	$C_{10}H_{15}ClN_3O_3$	1590, 1660—1710 (C=C—C=O, $CONH_2$)	325 (3.94)
8	60	154—155	60.1 60.1	7.8 7.8	23.4 23.4	$C_9H_{14}N_3O$	1620, 1630 (C=C); 2195 (CN); 3240 (NH)	262 (4.43)
9a	90	226—228	67.4 67.6	6.3 6.3	14.6 14.8	$C_{16}H_{18}N_2O_2$	1540, 1570, 1610 (C=C—C—O); 2195 (CN); 3260 (NH)	236 (4.19), 310 (4.31)
9b	70	157—159	59.2 59.5	7.0 7.2	18.9 18.9	$C_{11}H_{16}N_2O_2$	1555, 1645 (C=C—C=O); 2195 (CN); 3180 (NH)	294 (4.28)
9c	85	154—156	60.9 61.1	7.5 7.6	17.7 17.8	$C_{12}H_{18}N_2O_2$	1550,1555, 1640 (C=C—C=O); 2190 (CN); 3190 (NH)	292 (4.27)
9d	65	189—190	62.4 62.4	8.3 8.0	16.8 16.8	$C_{13}H_{20}N_2O_2$	1560, 1640 (C=C—C=O); 2200 (CN); 3195 (NH)	292 (4.26)
9e	55	219—221	64.0 63.6	8.2 8.3	15.9 16.0	$C_{14}H_{22}N_2O_2$	1545, 1550, 1620 (C=C—C=O); 2200 (CN); 3175 (NH)	291 (4.03)
9f	85	208—209	57.0 57.1	6.9 7.1	16.5 16.7	$C_{12}H_{18}N_2O_3$	1575, 1660 (C=C—C=O); 2195 (CN); 3260 (NH)	277 (4.34)
9g	90	190—192	47.9 47.8	4.8 4.7	15.3 15.2	$C_{11}H_{13}F_3N_2O_2$	1560, 1600 (C=C—C=O); 2205, 2210 (CN); 3190 (NH)	304 (4.17)
9h	70	202—205	59.8 59.5	6.2 6.3	18.4 18.5	$C_{15}H_{17}N_4O_2 \cdot H_2O$	1550, 1620 (C=C—C=O); 2195, 2205 (CN); 3175, 3550 (NH, OH)	243 (3.99), 313 (4.20)
9i	80	232—233	63.2 63.2	6.0 6.0	19.4 19.6	$C_{15}H_{17}N_4O_2$	1525, 1550, 1575, 1605 (C=C—C=O); 2200 (CN); 3240 (NH)	238 (4.12), 315 (4.22)
9k	75	202—204	57.4 57.7	6.8 6.7	20.0 20.2	$C_{10}H_{14}N_2O_2$	1555, 1650 (C=C—C=O); 2200 (CN); 3190 (NH)	299 (4.08)
9l	65	215—217	52.6 52.6	5.9 6.0	22.1 22.3	$C_{11}H_{15}N_4O_3$	1550, 1600, 1620 (C=C—C=O); 1675, 1705 ($CONH_2$); 2200 (CN); 3200, 3400 (NH)	314 (4.08)
10d	30	83—84	62.6 62.4	8.2 8.0	16.8 16.8	$C_{13}H_{20}N_2O_2$	1645 (C=N); 2220 (CN)	—
10e	50	90—92	64.0 63.6	8.3 8.3	16.0 16.0	$C_{14}H_{22}N_2O_2$	1640 (C=N)	—
17	70	157—158	40.8 40.9	5.7 5.6	17.6 17.9	$C_8H_{13}ClN_2O_3$	1585 (C=C—NO_2); 3280 (NH)	357 (4.19)

* Compounds **7c,d,f** and **10d,e** were purified by recrystallization from hexane; compounds **8**, **9a—g,k**, and **17** were purified by recrystallization from a hexane—ethyl acetate mixture; compounds **7k,l** and **9h,i** were purified by recrystallization from ethyl acetate; and compound **9l** was purified by recrystallization from an ethyl acetate—methanol mixture.

(DMSO-d_6), δ: 23.0 and 26.3 (C(2)Me_2, C(5)Me_2); 69.1 (C(5)); 79.7 (C(2)); 93.1 (—CCl=), 127.3, 127.6, 129.3, and 140.7 (Ph); 165.1 (C(4)); 190.3 (C=O). **1-Hydroxy-4-(1-cyano-2-oxo-2-phenylethylidene)-2,2,5,5-tetramethylimidazolidine (12).** ^{1}H NMR (DMSO-d_6), δ: 1.43 and 1.51 (both s, 6 H each, C(2)Me_2, C(5)Me_2); 7.50 (m, 5 H, Ph); 8.20 (br.s, 1 H, OH); 11.40 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 23.0 and 25.7 (C(2)Me_2, C(5)Me_2); 66.8 (C(5)); 81.1 (C(2)); 73.7 (—CCN=); 120.0 (CN); 127.3, 127.9, 130.8, and 139.3 (Ph); 173.7 (C(4)); 191.3 (C=O). ^{13}C NMR of a mixture of compound **12** and NaCN (DMSO-d_6), δ: 23.3 and 26.4 (C(2)Me_2, C(5)Me_2); 69.4 (C(5)); 83.7 (C(2)); 72.7 (—CCN=); 123.7 (CN); 127.4, 127.6, 129.5, and 141.7 (Ph); 159.2 (CN^-); 173.4 (C(4)); 189.2 (C=O).

1-Hydroxy-4-(3-*tert*-butyl-3-cyanooxiranyl-2)-2,2,5,5-tetramethyl-3-imidazoline (13e). A solution of radical **10e** (0.12 g) and hydrazine hydrate (0.1 mL) in methanol (5 mL) was kept at 20 °C for 3 h and then concentrated. The residue was diluted with water (2 mL) and hexane (1 mL). Compound **13e** crystallized out upon triturating. The precipitate was filtered off, washed with water and hexane, and dried. ^{1}H NMR ($CDCl_3$), δ: 1.07 (s, 9 H, CMe_3); 1.31 and 1.35 (both s, 3 H each) and 1.41 (s, 6 H, C(2)Me_2, C(5)Me_2); 3.65 (s, 1 H); 6.50 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 23.1, 25.3, and 26.2 (C(2)Me_2, C(5)Me_2); 24.6 (CMe_3); 33.0 (CMe_3); 53.7 (CH); 62.3 (C(5)); 71.5 (C(2)); 92.0 (C—CN); 114.4 (CN); 167.6 (C(4)).

X-ray diffraction study of compound 10e was carried out on a Syntex $P2_1$ diffractometer (Cu-Kα radiation, graphite monochromator, 2θ/θ scanning technique in the range 2θ < 140°). A single crystal of **10e** of dimensions 1.20×0.70×0.5 mm was

chosen for X-ray diffraction study. Crystals of $C_{14}H_{22}N_3O_2$ are monoclinic: a = 6.064(1) Å, b = 11.799(2) Å, c = 10.878(2) Å, β = 93.67(2)°, V = 776.7(2) Å^3, space group $P2_1$, Z = 2, d_{calc} = 1.130 g cm^{-3}, μ = 0.618 mm^{-1}. Intensities of 1554 independent reflections were measured. The structure was solved by the direct method with the use of the SHELXS-86 program package. The positions of the hydrogen atoms were calculated geometrically. The final refinement of the structural parameters was performed by the full-matrix least-squares method (the H atom were not included in the refinement) in the anisotropic approximation based on all F^2 using the SHELXL-97 program package to wR_2 = 0.1097, S = 1.060; 173 parameters were refined (R = 0.0380 for 1505 $F > 4\sigma$). The complete tables of the bond lengths and bond angles, the atomic coordinates, and the thermal parameters of radical **10e** have been deposited with the Cambridge Structural Database.

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