Synthesis and oxidation of 1-hydroxy-3(2)-imidazoline-derived enaminones

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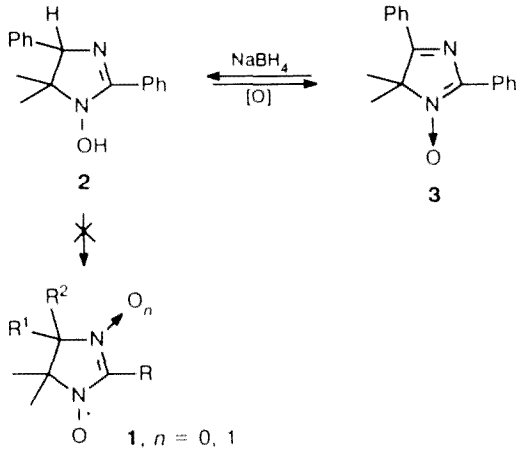
Interaction of 1-hydroxy-3-imidazoline and 3-imidazoline 3-oxide derivatives with esters in the presence of LDA gives enaminones, derivatives of imidazolidine. Oxidation of these compounds with MnO_2 leads to *4H*-imidazole *N*-oxides, oxidative dimerization products, or stable nitroxyl radicals, depending on the structure of the initial compound.

Key words: 3-imidazoline, enaminone, *4H*-imidazole oxide, oxidative dimerization, nitroxyl radicals.

Nitroxyl radicals are known to be stable when there are no hydrogen atoms at the α-carbon atom of the nitroxyl group. Stable nitroxyl radicals containing a diphenylmethyl group as one of the substituents at the nitroxyl group are an exception to this rule.[1] Iminonitroxyl radicals **1** (n = 0) with a hydrogen atom at position 2 of the heterocycle (R = H) are stable and can be isolated in the individual state.[2,3] Structures like **1**, in which substituent R^1 or R^2 is H, are unstable because the spin densities at the imine and nitroxyl nitrogen atoms are comparable. For example, when imidazoline **2** obtained by the reduction of *4H*-imidazole 3-oxide **3** is oxidized with MnO_2, PbO_2, or $K_3Fe(CN)_6$,[4] the starting imidazole is obtained rather than nitroxyl radical **1** (R = R^2 = Ph, R^1 = H) (Scheme 1).

Scheme 1



2 **3**

1, n = 0, 1

The purpose of the present work is to continue the study of possibly stable nitroxyl radicals, in particular, iminonitroxyl (n = 0) and nitronylnitroxyl radicals (n = 1), in which the environment of the nitroxyl group is unusual.

The fact found by us that enaminones derived from 2,2,5,5-tetramethylimidazolidin-1-oxyl exist exclusively as the enolized (possibly enaminone) form[5] made it possible to expect that compounds **5** would also exist in the same tautomeric form and, therefore, could be converted by oxidation into stable iminonitroxyl radicals of type **A** (Scheme 2). Compounds **5** are formed in the reaction of imidazoline **4** with esters in the presence of lithium diisopropylamide (LDA) (*cf.* Ref. 6). According to ^1H and ^{13}C NMR spectra, compounds **5** actually exist in the enaminone tautomeric form; however, their oxidation gave no stable nitroxyl radicals.

In fact, oxidation of enaminone **5b** affords compound **6b**, whose IR spectrum exhibits no absorption band due to a carbonyl group, and the ^{13}C NMR spectrum contains signals at 134.74 and 167.66 ppm, corresponding to the C-2 and C-5 atoms in the *4H*-imidazole 3-oxide molecule. The ^1H NMR spectrum of compound **6b** exhibits a signal at 11.23 ppm, corresponding apparently to a proton involved in an intramolecular hydrogen bond. Based on these data, the structure of a *4H*-imidazole derivative in which the oxo group is enolized both in solution and in the crystalline state was attributed to compound **6b**.

Oxidation of enaminone **5a** with MnO_2 for 1 min gives *4H*-imidazole **6a**, whose structure is similar to that of **6b**. Following more prolonged oxidation, compound **6a** is quantitatively converted into compound **7**. According to the data of elemental analysis and ebullioscopic molecular weight determination, the latter compound results from oxidative dimerization, which is also in agreement with its spectroscopic characteristics. It is noteworthy that oxidative dimerization is a fairly well known process for β-oxonitrones,[7] whereas enaminones do not undergo this reaction under the given conditions (*cf.* Ref. 8). This difference is probably due to the fact

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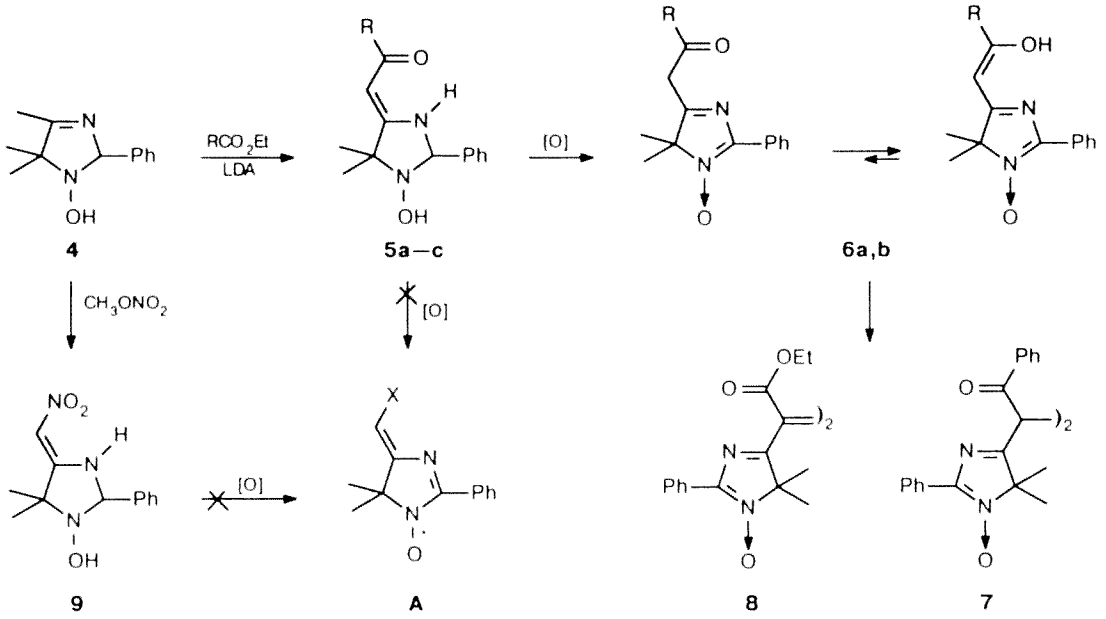
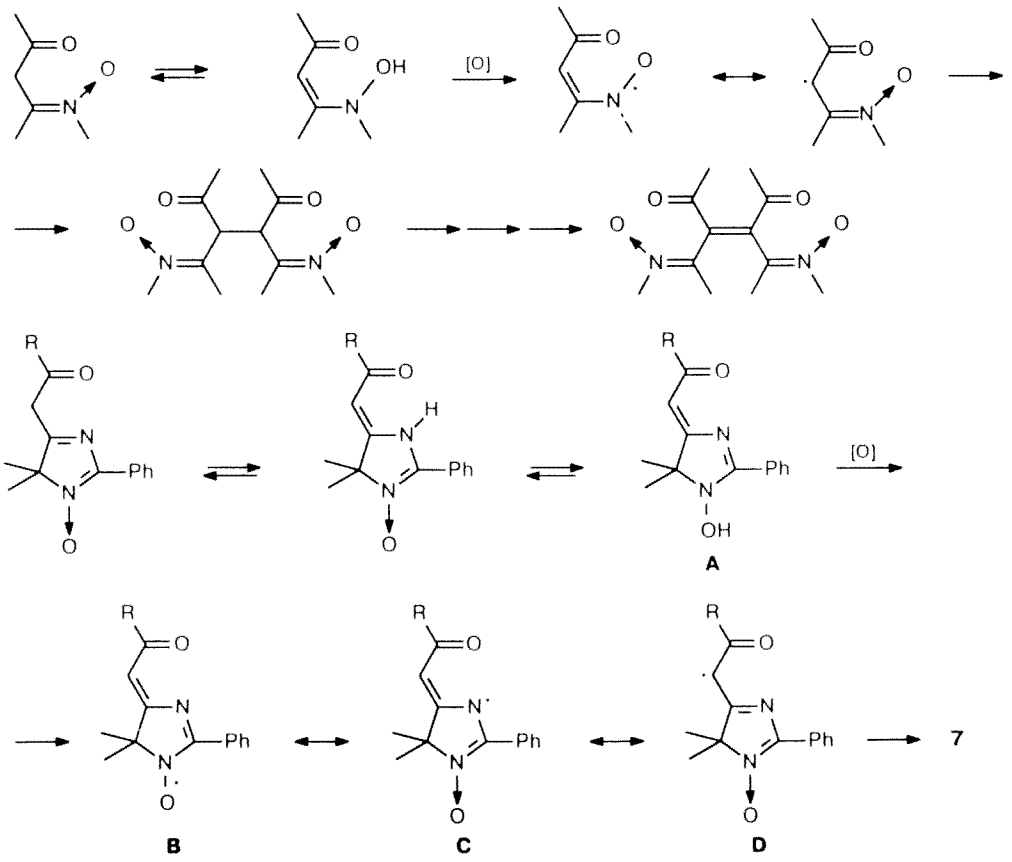
Scheme 2



that β-oxonitrones are capable of existing in the enehydroxylaminoketone tautomeric form,[9] in which the hydroxylamino group is readily oxidized to a nitroxyl group, and then recombination occurs. Conversely, the amino group incorporated in an enaminone group cannot be oxidized to a nitroxyl group under these condi-

Scheme 3



tions. The oxidation of compound **6a** to give dimer **7** obviously occurs through tautomeric form **A**, which incorporates a hydroxylamino group susceptible to oxidation. The resulting nitroxyl radical **B** is unstable, probably, due to effective delocalization of spin density. This is why radicals **D** undergo recombination, which ends with the formation of dimer **7** (Scheme 3).

We were not able to oxidize compound **6b** to the corresponding dimer **7b**. It should be noted that oxidation of β-oxonitrones can yield at least two different dimers: ethane and ethylene type compounds. Compound **7** is a dimer of the ethane type. The oxidation of enaminoester **5c** afforded neither monomer **6c** nor ethane type dimer **7c**. In this case, the reaction gave dimer **8** of the ethylene type. Nitroenamine **9**, formed in the reaction of imidazoline **4** with methyl nitrate under the conditions described previously,[10] is readily oxidized by MnO_2; however, we were not able to isolate any reaction products.

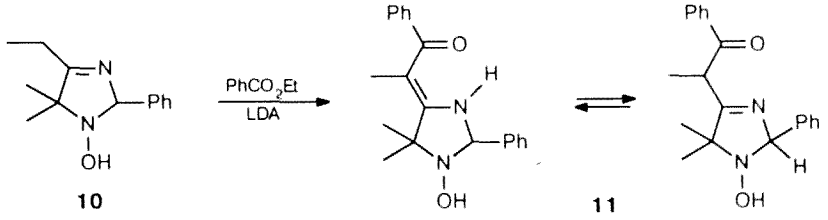
It could be expected that the presence of a substituent at the enamine carbon atom in the enaminone molecule would prevent recombination, and the corresponding nitroxyl radicals (**B**) would be stable. In order to verify this suggestion, we prepared enaminone **11** by the reaction of imidazoline **10** with ethyl benzoate (Scheme 4); however, in this case, too, no oxidation product was isolated.

It is of interest that unlike enaminones **4**, compound **11** exists in $CDCl_3$ solution as a mixture of an enaminone form and two diastereomeric oxoimine tautomeric forms, which is indicated by the complex multiplet at 4.4 ppm corresponding to the methylene proton and the doublet at 1.51 ppm due to the methyl group. The ratio between the enolized and nonenolized forms is ~ 2 : 1.

It may have been expected that nitronylnitroxyl radicals could be obtained by the oxidation of the products of the condensation of hydroxy-3-imidazoline 3-oxide **12** with esters. However, instead of the expected β-oxonitrone **13**, the reaction of **12** with ethyl benzoate gave a small amount of the product of its dehydration, 4*H*-imidazole **14**, in which the oxo group is also enolized, according to the NMR spectral data (Scheme 5).

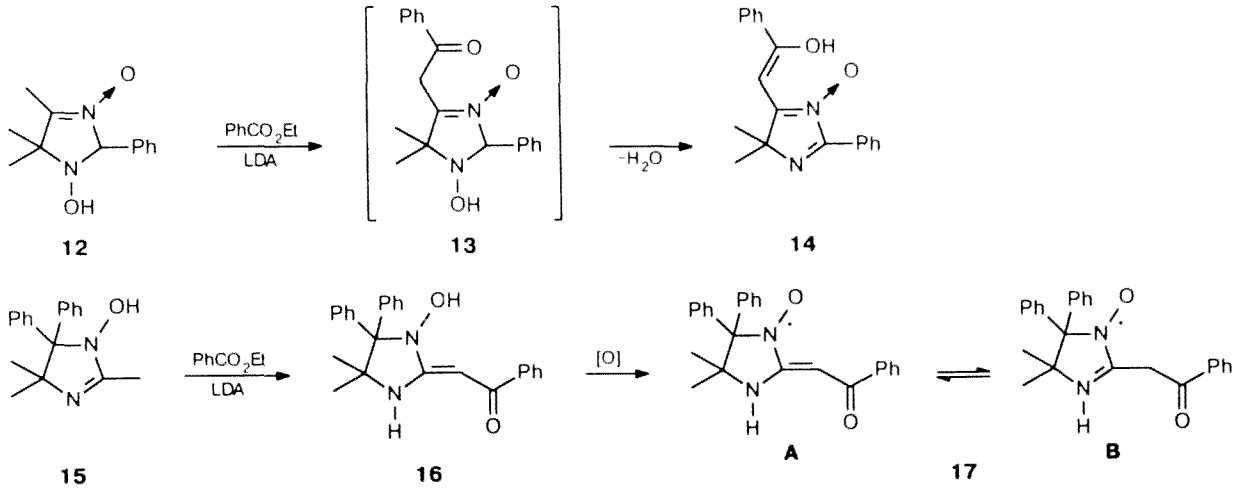
The condensation of 1-hydroxy-2-imidazoline **15** with ethyl benzoate results in compound **16**, which can be regarded as a β-oxonitrone or enaminone. According to ^1H and ^{13}C NMR spectral data, in a DMSO solution, compound **16** exists exclusively as the tautomeric form with an exocyclic double bond, as shown in Scheme 5. Oxidation of **16** leads to nitroxyl radical **17**, which was obtained and characterized as an individual compound, although it readily decomposes on attempted isolation or during chromatography. The IR and UV spectra of compounds **16** and **17** are similar. Based on this fact, one could have assumed that they exist in the same

Scheme 4



10 11

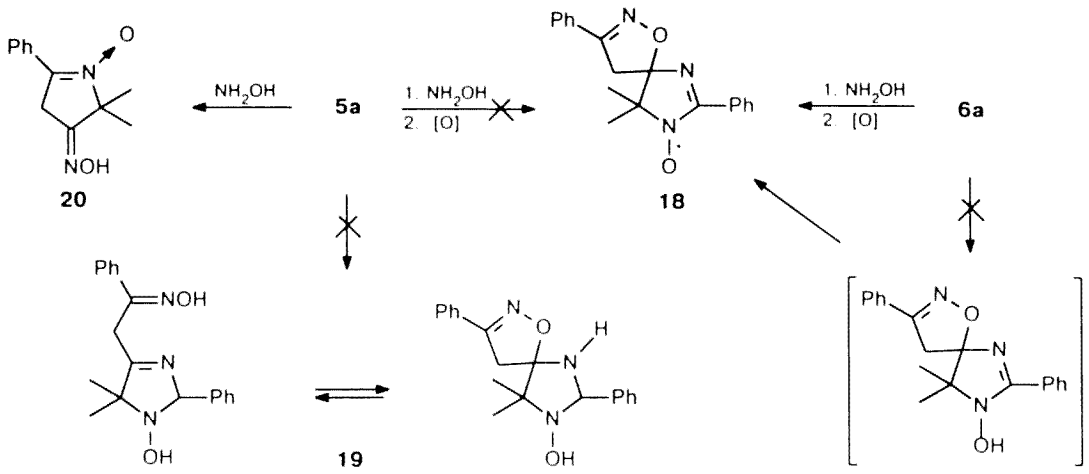
Scheme 5



12 13 14

15 16 A 17 B

Scheme 6



tautomeric form; however, the ESR spectrum of radical **17** (EtOH) is a triplet of triplets with HFC constants $a_{(N1)} = 9.0$ Gs and $a_{(N3)} = 4.4$ Gs, which largely corresponds to the structure of iminonitroxyl radical (**B**) (*cf.* Ref. 3).

Another stable iminonitroxyl radical, **18**, could be obtained by the interaction of enaminone **5a** with hydroxylamine followed by oxidation. However, the interaction of compound **5a** with hydroxylamine yields pyrroline **20** rather than oxime **19** (*cf.* Ref. 11). Iminonitroxyl radical **18** was obtained by the reaction of 4*H*-imidazole **6a** with hydroxylamine followed by oxidation (Scheme 6).

Experimental

IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets (at a concentration of 0.25 %) or in CCl_4 and $CHCl_3$ solutions (at a concentration of 5 %). UV spectra were measured on a Specord UV-VIS spectrometer in ethanol, ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-200 instrument at 300 K (in 5 % solutions). Chemical shifts were obtained relative to the signal of the solvent. Characteristics of the compounds synthesized are presented in Table 1, and NMR spectral data are listed in Tables 2—4. 3-Imidazoline **10** was obtained by a known procedure,[12] and 3-imidazoline-3-oxide **12** was prepared by a previously reported procedure.[13]

1-Hydroxy-4,5,5-trimethyl-2-phenyl-3-imidazoline (4). A 25% aqueous solution of ammonia (4 mL) was added to a solution of 2-hydroxyamino-2-methylbutan-3-one hydrochloride (3.1 g, 20 mmol) and benzaldehyde (2.4 mL, 24 mmol) in methanol (15 mL). After 2 h, the reaction mixture was diluted with water (20 mL). The precipitate of imidazoline **5** was filtered off and washed with water and hexane. ^1H NMR (CD_3OD), δ: 1.27 (s, 6 H, 5-CH_3), 1.34 (s, 6 H, 5-CH_3), 2.06 (d, 3 H, 4-CH_3, J = 2 Hz), 5.38 (q, 1 H, 2-H, J = 2 Hz), 7.4 (5 H, 2 Ph).

1-Hydroxy-5,5-dimethyl-4-phenacylidene-2-phenylimidazolidine (5a). Thoroughly pulverized imidazoline **5** (1 g, 5 mmol) was added with stirring under argon to a solution of lithium diisopropylamide prepared from lithium (0.28 g, 40 mmol), bromobenzene (2.1 mL, 20 mmol), and diisopropylamine (2.5 mL) in 30 mL of ether. The mixture was stirred for 2 h at 20 °C and cooled to 0 °C, and a solution of ethyl benzoate (2.1 mL, 15 mmol) in 5 mL of ether was added. The mixture was stirred for an additional 15 min at 20 °C, and 15 mL of water was added. The ethereal layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2×20 mL). The combined extracts were dried with $MgSO_4$, the solvent was evaporated, and enaminone **5a** was isolated by chromatography on a column with silica gel using $CHCl_3$ as the eluent.

The reaction of imidazoline **10** with ethyl benzoate under similar conditions gave enaminone **11**, which was isolated by chromatography on a column with silica gel using a 4 : 1 hexane—ethyl acetate mixture as the eluent.

1-Hydroxy-5,5-dimethyl-4-(3,3,3-trifluoroacetonilidene)-2-phenylimidazolidine (5b) was prepared by the reaction of imidazoline **4** with ethyl trifluoroacetate under the conditions described above. The combined extracts were concentrated without drying, the residue was washed with hexane, and the precipitate of enaminone **5b** was filtered off and washed with a 2 : 1 hexane—$CHCl_3$ mixture.

4-Ethoxycarbonylmethylidene-1-hydroxy-5,5-dimethyl-2-phenylimidazolidine (5c) was prepared by the reaction of compound **4** with diethyl carbonate under the conditions described for enaminone **5a** and isolated by chromatography on a column with silica gel using a 4 : 1 hexane—ethyl acetate mixture as the eluent.

5-(2-Hydroxy-2-phenylethenyl)-4,4-dimethyl-2-phenyl-4*H*-imidazole 3-oxide (6a). A solution of enaminone **4a** (0.3 g) in 10 mL of $CHCl_3$ was stirred with MnO_2 (1 g) for 1 min, the excess oxidant was filtered off, and the solvent was evaporated. Compound **6a** was isolated by chromatography on a column with silica gel using a $CHCl_3$—methanol mixture (30 : 1) as the eluent. Thirty minutes of oxidation afforded **bis[4,4-dimethyl-5-(phenacyl-2-yl)-2-phenyl-4*H*-imidazole 3-oxide] (7)**, which crystallized after the $CHCl_3$ was evaporated and the residue was triturated with hexane.

When enaminone **4b** was oxidized with MnO_2 for 15 min, 4*H*-imidazole **6b** was obtained and isolated as described above for compound **6a**. To obtain dimer **8**, oxidation of enaminoester **4c** was carried out for 20 h at 20 °C, and the target product was isolated by chromatography on a column with silica gel using $CHCl_3$ as the eluent.

1-Hydroxy-5,5-dimethyl-4-nitromethylidene-2-phenylimidazolidine (9). Thoroughly pulverized imidazoline **4** (1 g, 5 mmol) was added with stirring to a solution of phenyllithium prepared from lithium (0.28 g, 40 mmol) and bromobenzene (2.1 mL, 20 mmol) in 25 mL of ether. The reaction was carried out under argon. The reaction mixture was stirred for 2 h and cooled to −10 °C, and a solution of methyl nitrate (0.95 mL, 15 mmol) in 3 mL of ether was added to it. The mixture was stirred for an additional 30 min at 20 °C, and water (5 mL) was added. The mixture was kept for 1 h at 0 °C, and the precipitate of the Na salt of the aci-form of compound **9** was filtered off and washed with a small amount of ice water and with ether. The precipitate was dissolved in 5 mL of water at 50–60 °C, the solution was cooled to 10 °C and acidified with 5% HCl to pH 3, and the precipitate of nitroenamine **9** was filtered off and dried.

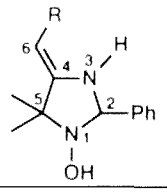
5-(2-Hydroxy-2-phenylethenyl)-4,4-dimethyl-2-phenyl-4*H*-imidazole 1-oxide (14). Thoroughly pulverized imidazoline **12** (1.5 g, 6.84 mmol) was added portionwise with stirring to a solution of lithium diisopropylamide prepared from lithium (0.38 g, 54.8 mmol), bromobenzene (2.9 mL, 27.4 mmol), and diisopropylamine (3.5 mL, 25 mmol) in 40 mL of ether. The reaction was carried out under argon. The mixture was stirred for 2 h at 20 °C, ethyl benzoate (2.4 mL, 17.1 mmol) was added, and stirring was continued for an additional 1 h. The reaction mixture was quenched by adding water (15 mL),

Table 1. Characteristics of the compounds synthesized

Compound	Yield (%)	M.p.[a] /°C	Found / Calculated (%) C	H	N	Molecular formula	IR, (KBr), ν/cm^{-1}	UV, λ_{max}/nm (log e)
4	≈100	186–188	70.5 / 70.6	7.8 / 7.9	13.7 / 13.7	$C_{12}H_{16}N_2O$	1645 (C=N)	—
5a	75	193–195	73.9 / 74.0	6.5 / 6.5	9.1 / 9.1	$C_{19}H_{20}N_2O_2$	1525, 1580, 1620 (O=C–C=C–N)	243 (3.93), 348 (4.28)
5b	90	244–246	55.8 / 56.1	5.2 / 5.0	9.4 / 9.3	$C_{14}H_{15}F_3N_2O_2$	1540, 1600 (O=C–C=C–N)	316 (4.32)
5c	60	175–178	65.4 / 65.2	7.2 / 7.2	10.4 / 10.1	$C_{15}H_{20}N_2O_3$	1605, 1665 (O=C–C=C–N)	280 (4.42)
6a	90	166–167	74.3 / 74.5	5.9 / 5.9	9.0 / 9.2	$C_{19}H_{18}N_2O_2$[b]	1545, 1580, 1620 (O=C, C=N)	243 (4.22), 298 (4.26), 402 (4.26)
6b	60	128–131	56.1 / 56.4	4.1 / 4.4	9.4 / 9.4	$C_{14}H_{13}F_3N_2O_2$	1550, 1575, 1640 (O=C, C=N)	235 (4.04), 242 (4.03), 299 (4.23), 402 (4.05)
7	90[c]	214–216	73.6 / 73.3	5.6 / 5.6	8.9 / 9.0	$C_{38}H_{34}N_4O_4 \cdot H_2O$[b]	1670, 1595 (C=N), 1680 (C=O)	261 (4.58), 348 (4.06)
8	45	229–230	66.1 / 66.2	6.1 / 5.9	10.1 / 10.3	$C_{30}H_{32}N_2O_6$	1740 (C=O)	233 (4.26), 252 (4.23), 304 (4.34), 470 (4.02)
9	45	198–201	57.7 / 57.8	6.0 / 6.0	16.7 / 16.9	$C_{12}H_{15}N_3O_3$	1620, 1590 (N–C=C–NO_2)	336 (4.33)
11	25	175–177	74.8 / 74.5	7.0 / 6.8	8.7 / 8.9	$C_{20}H_{22}N_2O_2$	1575, 1600 (O=C–C=C–N)	344 (4.40)
14	25	142–145	74.8 / 74.5	5.9 / 5.9	9.2 / 9.2	$C_{19}H_{18}N_2O_2$	1635 (C=C, C=N)	229 (4.15), 264 (4.19), 398 (4.16)
15	65	255–257	77.1 / 77.2	7.3 / 7.1	10.0 / 10.0	$C_{18}H_{20}N_2O$	1620 (C=N)	250 (3.10)
16	40	224–226	75.0 / 74.7	6.5 / 6.5	6.8 / 7.0	$C_{25}H_{24}N_2O_2 \cdot H_2O$	1520, 1575, 1605 (O=C–C=C–N)	238 (4.06), 334 (4.39)
17	90	124–127	—	—	7.0 / 7.3	$C_{25}H_{23}N_2O_2$	1520, 1585, 1600, 1615 (O=C–C=C–N)	247 (4.03), 343 (4.04)
18	50	140–142	70.6 / 70.4	5.8 / 5.6	13.0 / 13.0	$C_{19}H_{18}N_3O_2$	1535 (C=N), 1600 (C=C)	259 (4.33), 442 (3.11)

[a] Compounds **5a**, **7**, and **9** were purified by recrystallization from ethanol, compounds **5b,c**, **6a**, **11**, and **16** were recrystallized from a hexane–ethyl acetate mixture, **6b** was recrystallized from hexane, **14**, **18** from heptane, and **4** from ethyl acetate.
[b] Molecular weight in $CHCl_3$, found/calculated: 308/306 (**6a**), 611/610 (**7**).
[c] The yield is based on enaminone **5a**.

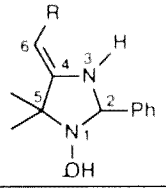
Table 2. The ^{13}C NMR spectra of 1-hydroxyimidazolidines



Compound	δ, J/Hz							Solvent
	C-2	C-4	C-5	C-6	$(CH_3)_2$	2-Ph	R	
5a	79.55	170.30	67.85	83.53	18.82, 24.37	140.0, 138.85 (Ph_{ipso}), 126.86—130.12 (m, 2 Ph)	188.60 (C=O)	DMSO-d_6
5b	83.73	166.47	71.56	90.42	17.56, 25.11	142.44 (Ph_{ipso}), 128.84, 128.93, 129.50	178.34 (C=O) 121.65 (CF_3, q, J = 285)	DMSO-d_6
5c	76.26	166.99	67.60	78.93	19.01, 23.73	137.54 (Ph_{ipso}), 128.19, 128.43, 129.35	170.52 (C=O) 58.68, 14.38 (OC_2H_5)	
9	81.04	163.57	67.96	105.34	18.87, 24.20	137.82 (Ph_{ipso}), 128.14, 128.36, 128.90	—	DMSO-d_6
11	79.44 91.78* 91.07*	179.54 167.15*	69.17 72.75*	93.65 45.25* 44.15*	16.06, 24.73, 16.92,* 23.61*	126.88—142.40 (m, 2 Ph),	196.61, 197.60* (C=O), 14.38 15.46*, 23.92 *(CH_3)	$CDCl_3$

* Signals of the keto-form.

Table 3. ^1H NMR spectra of 1-hydroxyimidazolidines



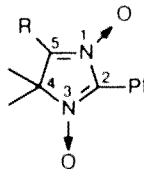
Compound	δ, J/Hz						Solvent
	$(CH_3)_2$	—CH=	2-H	Ph	R	Other signals	
5a	1.34 (3 H), 1.40 (3 H)	5.97	5.33	7.4 m, 7.9 m	—	8.09 (OH) 10.05 (NH)	DMSO-d_6
5b	1.23 (3 H), 1.34 (3 H)	5.35	5.13	7.3—7.6 m	—	—	DMSO-d_6
5c	1.01 (3 H), 1.21 (3 H)	5.11	4.49	7.35 m	1.21 (t, 3 H, J = 7.5), 4.03 (q, 2 H, J = 7.5)	5.61 (br.s, 1 H, OH), 7.75 (br.s, 1 H, OH)	$CDCl_3$
9	1.31 (3 H), 1.33 (3 H)	6.79	5.37	7.46 m	—	8.21 (OH), 9.84 (NH)	DMSO-d_6
11	1.38 (6 H), 0.93*, 0.95,* 1.09*, 1.07	4.4 (m, 1 H)*	5.37	7.4 m, 7.9 m*	—	1.88 (s, 3 H, CH_3), 1.51 (d, 3 H, J = 5) 11.3 (NH)	$CDCl_3$

* Signals of the keto-form.

and the ethereal layer was separated and extracted with a 1% aqueous solution of KOH. The combined aqueous solutions were washed with ether (2×10 mL), acidified with 5% HCl to pH 3, and extracted with $CHCl_3$ (4×20 mL). The extract was dried with $MgSO_4$, the solvent was evaporated, the residue was diluted with a 1 : 1 mixture of ether with hexane, and the precipitate of the starting imidazoline 3-oxide **12** (weight 0.8 g) was filtered off and washed with ether. Compound **14** was isolated from the filtrate by chromatography on a column with silica gel using $CHCl_3$ as the eluent.

1-Hydroxy-2,4,4-trimethyl-5,5-diphenyl-2-imidazoline (15). Thoroughly pulverized 2,4,4-trimethyl-5-phenyl-4*H*-imidazole 1-oxide[14] (0.6 g, 3 mmol) was added under argon to a solution of phenyllithium prepared from lithium (0.13 g, 18 mmol) and bromobenzene (0.95 mL, 9 mmol) in 25 mL of ether. The reaction mixture was stirred for 3 h and quenched with 10 mL of water. The precipitate of imidazoline **15** was filtered off and washed with water and hexane.

1-Hydroxy-4,4-dimethyl-2-phenacylidene-5,5-diphenylimidazolidine (16). Thoroughly pulverized imidazoline **15** (1.12 g, 4 mmol) was added with stirring under argon to a solution prepared from lithium (0.22 g, 32 mmol), bromobenzene (1.7 mL, 16 mmol), and diisopropylamine (2 mL, 14 mmol) in 20 mL of ether. The mixture was stirred for 2 h at 20 °C, and ethyl benzoate (0.86 mL, 6 mmol) was added. The mixture was stirred for an additional 2 h, water (10 mL) was

Table 4. ^{13}C and ^{1}H NMR spectra of 4*H*-imidazole oxide derivatives  (δ, *J*/Hz)

Compound	^{13}C						^{1}H		Solvent
	C-2	C-4	C-5	Ph	$(CH_3)_2$	R	$(CH_3)_2$	R	
6a	137.53	76.31	165.49	123.29—137.03 m	24.91	89.58 (CH=), 186.96 (CH=C—OH)	1.69	6.15 (s, 1 H, CH=), 7.5 m, 7.9 m, 8.4 m	$CDCl_3$
6b	134.74	77.04	167.65	125.24, 125.93, 129.05, 131.78	24.78	86.26 (CH=), 178.81 (q, CH=C—OH, *J* = 35), 118.08 (q, CF_3, *J* = 145)	1.68	5.79 (s, 1 H, CH=), 7.5, 8.3 (both m, Ph), 11.23 (br.s, 1 H, OH)	$CDCl_3$
7	143.60	82.70	175.48	126.69—136.14 m (4 Ph)	21.58 22.44	195.19 (C=O), 49.19 (CH)	1.00 (s, 6 H), 1.56 (s, 6 H)	6.46 (s, 2 H), 7.5 m, 8.1 m (4 Ph)	DMSO-d_6
8	145.81	62.44	164.97	126.67, 128.23, 128.47, 130.68	22.31	13.67 (CH_3), 83.00 (CH_2O), 131.39 (C=), 169.14 (C=O)	1.59	1.14 (t, 3 H, $\underline{CH_3}CH_2$, *J* = 7), 4.22 (q, 2 H, $\underline{CH_3}CH_2$ *J* = 7), 7.45, 8.55 (both m, Ph)	$CDCl_3$
14	172.30	70.73	157.17	126.64—131.63 m	26.18	85.28 (CH=), 182.98 (CH=C—OH)	1.50	5.80 (s, 1 H, CH=), 7.38—8.25 (10 H, Ph_2), 16.10 (br.s, 1 H, OH)	$CDCl_3$

added, the ethereal layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3×20 mL). The combined extracts were dried with $MgSO_4$, the solvent was evaporated, the residue was washed with hexane, and the precipitate was filtered off. Compound **16** was isolated by chromatography on a column with silica gel using $CHCl_3$ as the eluent. ^{1}H NMR (DMSO-d_6), δ: 1.17 (s, 6 H, $(CH_3)_2$), 5.70 (s, 1 H, CH=), 7.4 (m, 13 H), 7.85 (m, 2 H, $(C_6H_5)_3$), 9.35 (br.s, 1 H), 9.68 (br.s, 1 H, OH, NH). ^{13}C NMR (DMSO-d_6), δ: 25.82 $(CH_3)_2$, 63.27, 80.31 (C-4, C-5), 75.21 (CH=), 126.30—140.55 (m, $(C_6H_5)_3$), 164.71 (C-2), 184.04 (C=O).

4,4-Dimethyl-2-phenacylidene-5,5-diphenylimidazolidine-1-oxyl (17). A solution of imidazoline **16** (0.1 g) in 5 mL of $CHCl_3$ was stirred with MnO_2 (0.2 g) for 15 min, the excess oxidant was filtered off, and the solvent was evaporated to give nitroxyl radical **17**.

4-Hydroxyimino-5,5-dimethyl-2-phenylpyrroline 1-oxide (20). A solution of enaminone **4a** (0.5 g, 1.6 mmol), hydroxylamine hydrochloride (0.51 g, 7.3 mmol), and CH_3ONa (0.28 g, 5.2 mmol) in 20 mL of methanol was kept for 48 h at 20 °C and then evaporated. A saturated aqueous solution of NaCl (10 mL) and then hexane (10 mL) were added to the residue, and the precipitate of oxime **20** was filtered off and washed with a mixture of ether and hexane (1 : 2), yield 0.27 g (75 %), m.p. 168—170 °C (ethyl acetate), see Ref. 15: 168—170 °C.

5,5-Dimethyl-2-phenyl-1-oxyl-2-imidazoline-4-spiro-5′-(3′-phenyl-2′-isoxazoline) (18). A solution of imidazole **6a** (0.33 g, 1.08 mmol), hydroxylamine hydrochloride (0.38 g, 5.4 mmol), and CH_3ONa (0.18 g, 3.2 mmol) in methanol (10 mL) was kept for 21 days at 20 °C and then evaporated. The residue was diluted with 10 mL of water, and the precipitate of compound **19** was filtered off, dried, and dissolved in $CHCl_3$ (10 mL). The solution was stirred for 15 min with MnO_2 (1 g). The excess oxidant was filtered off, the solvent was evaporated, and radical **18** was isolated by chromatography on a column with silica gel using a mixture of hexane with ethyl acetate (3 : 1) as the eluent.

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