Stable vinylnitroxyl radicals, pyrroline derivatives

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The first representatives of stable vinyl nitroxides, *viz.*, radicals of the pyrroline series, were synthesized.

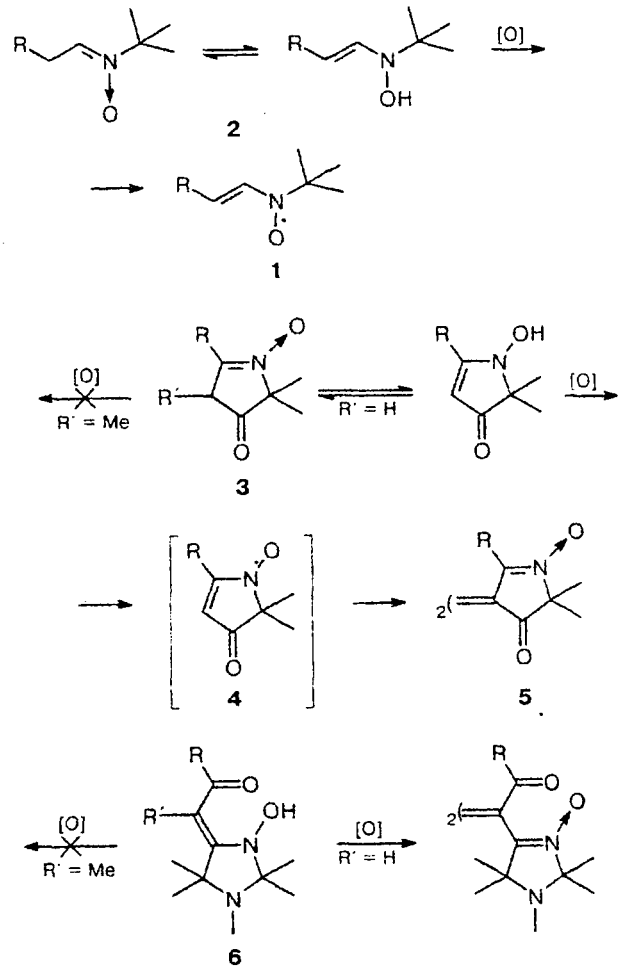
Key words: β-oxonitrones, pyrroline oxides, 3-imidazoline 3-oxides, nitroxyl radicals, vinyl nitroxides.

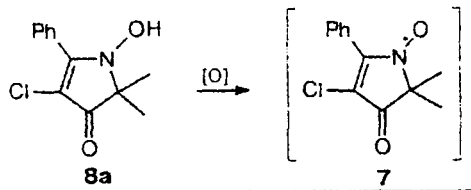
Compounds with structure **1** are called vinylnitroxyl radicals (vinyl nitroxides). These compounds are generated by oxidation of the corresponding nitrones **2**, which can readily undergo tautomerization to the enhydroxylamine form due to the presence of an R substituent possessing the $-M$ effect. Owing to the high degree of delocalization of the spin density over the π system, vinyl nitroxides are extremely highly reactive and, as a rule, immediately enter into recombination reactions to form dimers of the C—C or C—O type. Therefore, these radicals cannot be separated in individual form and they are not necessarily even detected by ESR spectroscopy. In these cases, their formation is judged from ESR spectra of spin adducts using traps for short-lived radicals. The initial nitrones can often serve as such traps.[1,2]

Previously, we have demonstrated that vinylnitroxyl radicals **4**, which were formed upon oxidation of endocyclic β-oxonitrones, *viz.*, pyrroline derivatives **3** (R′ = H), immediate enter into recombination reactions to form dehydrodimers **5**. Exocyclic β-oxonitrones **6** (R = H)[3] as well as exocyclic β-oxonitrones of the pyrrolidine series[4] behave analogously. It is believed that the ease of dimerization is associated with the absence of steric hindrance at the C(3) atom located between the nitrone and carbonyl groups. When the methyl group is introduced at this position of the molecules of both endocyclic (**3**, R′ = Me) and exocyclic β-oxonitrones (**6**, R′ = Me), oxidative dimerization products as well as the corresponding nitroxyl radicals are not formed[5] (Scheme 1). Apparently, this is associated with the fact that methyl-substituted β-oxonitrones exist in the nonconjugated oxonitrone tautomeric form due to an unfavorable electronic effect.

Previously,[6] the formation of unstable vinylnitroxyl radical **7** containing Cl atoms as the substituent at the C(3) atom has been observed by ESR spectroscopy.

Scheme 1





One would expect that the replacement of the chlorine atom by another electron-withdrawing substituent would enhance the stability of radicals of this type. The reaction of pyrroline **8a** with NaCN in acetonitrile in the presence of 15-crown-5 ether afforded dimer **5a** (R = Ph) rather than the corresponding nitrile **9a**.

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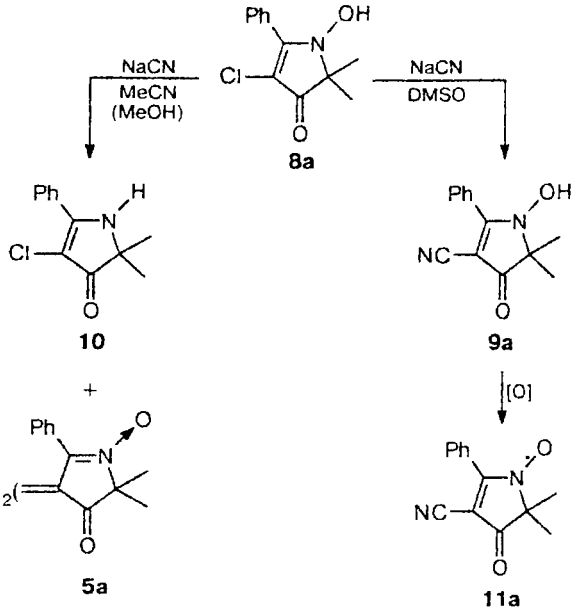
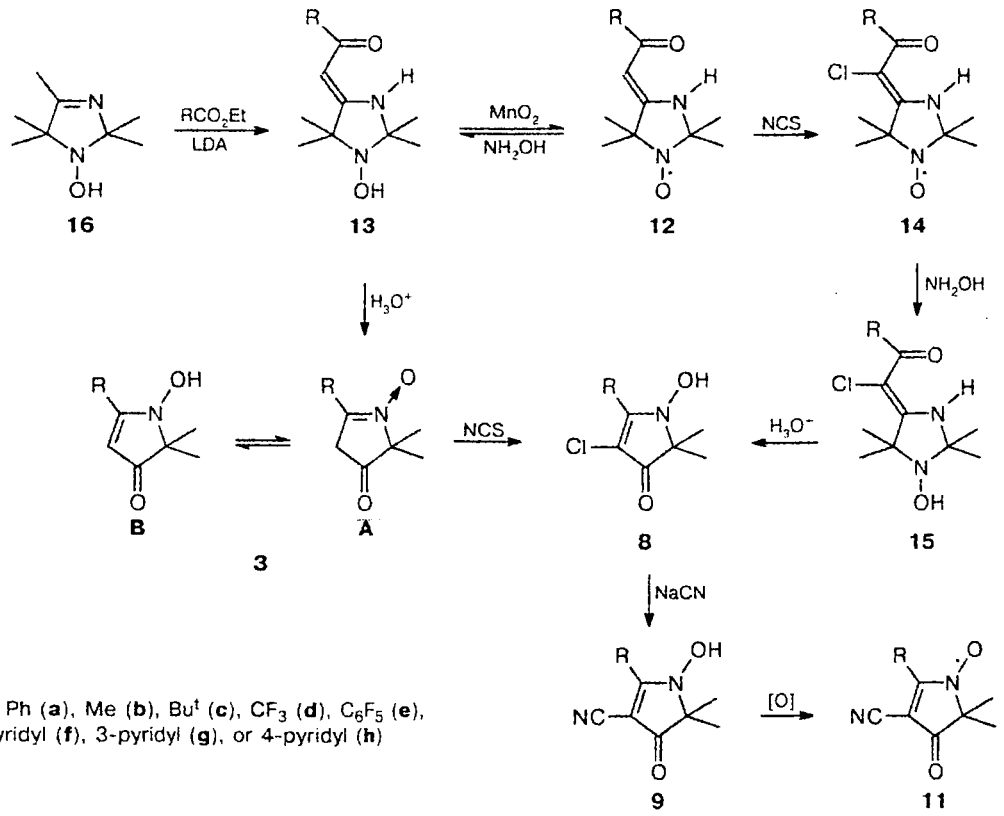
Scheme 2



Apparently, this is associated with a low concentration of the nucleophile and its high basicity, resulting in 1,1-elimination and generation of carbene, whose dimerization affords compound **5a**. The reaction of pyrroline **8a** with NaCN in methanol gave nitrile **9a** in low yield as well as dimer **5a** and enaminoketone **10** as by-products (*cf.* Ref. 6). Nitrile **9a** was obtained in high yield in a reaction performed in DMSO. Compound **9a** was oxidized to stable vinylnitroxyl radical **11a** under the action of MnO_2 in $CHCl_3$ (Scheme 2). The ESR spectrum of **11a** is a triplet with the hyperfine interaction constant a_N = 5.9 G ($CHCl_3$).

The range of radicals of this type can be extended by varying the substituent at position 2 of the pyrroline heterocycle, for which purpose it is necessary to synthesize analogs of chlorine-substituted pyrroline **8a**. These compounds can, in principle, be prepared from enaminoketones **12** according to two procedures. The first procedure involves reduction of nitroxyl radicals **12** to hydroxylamino derivatives **13**, their recyclization to pyrrolines **3**, and subsequent chlorination. An alternative procedure involves chlorination of enaminoketones **12**, reduction of chlorine-substituted enaminoketones

Scheme 3



R = Ph (**a**), Me (**b**), Bu^t (**c**), CF_3 (**d**), C_6F_5 (**e**), 2-pyridyl (**f**), 3-pyridyl (**g**), or 4-pyridyl (**h**)

14, and recyclization of hydroxylamino derivatives **15** (Scheme 3).

Enaminoketones **12** are prepared by the reactions of imidazoline **16** with esters in the presence of lithium diisopropylamide (LDA) followed by oxidation. In some cases, when the stage of oxidation is excluded, hydroxylamino derivatives **13** can be isolated (*cf.* Ref. 7). The reactions of compounds **12** with *N*-chlorosuccinimide (NCS) afford chlorine-substituted enaminoketones **14**. Reduction of the latter with hydroxylamine or hydrogen in the presence of Pd/C yields hydroxylamino derivatives **15b—h**. However, attempts to prepare pyrrolines **8** by their recyclization failed (except for compound **15e**, which was formed from pyrroline **8e** in high yield). Thus 2-pyridyl-substituted derivatives **8f—h** appeared to be unstable under isolation conditions. Since recyclization is performed in an acidic medium, neutralization of the reaction mixture is required for compounds **8f—h**, which exhibit basic properties. In the course of neutralization, these compounds are decomposed. Under conditions of recyclization, compounds **15c,d** are subjected to profound destruction, and pyrroline **8b** undergoes dehydrochlorination to form the corresponding dimer **5b**.

Attempts to prepare pyrroline **8b** by chlorination of compound **3b** failed due to the fact that the reaction proceeded nonselectively and afforded only a dichloro derivative (*cf.* Ref. 6). Apparently, the corresponding chloro derivative was formed upon chlorination of pyrroline **3c**. However, this compound could not be isolated due to its instability under conditions of chromatography. Chlorination of pyrroline **3d** afforded chloro derivative **8d**. An interesting characteristic feature of this compound is the fact that its UV spectrum in heptane changes with time (Fig. 1). Evidently, this is associated with the fact that in the crystalline state, pyrroline **8d** exists predominantly in the conjugated enolonitrone or enhydroxylaminoketone tautomeric form, while dissolution leads to an increase in the portion of the nonconjugated oxonitrone tautomeric form to which a shorter-wavelength absorption maximum corresponds. Noteworthy is a substantial difference in the UV spectra of compound **8d** in heptane and ethanol. Thus, a long-wavelength absorption maximum in heptane is observed at 295 nm, while this maximum in ethanol is observed at 394 nm due to deprotonation that occurs in an ethanolic solution, and, consequently, the observed UV spectrum belongs, apparently, to an equilibrium mixture of the conjugated tautomeric form and its anion. In DMSO, pyrroline **8d**, judging from the NMR spectra, exists exclusively in the conjugated enhydroxylaminoketone form (*cf.* Ref. 8).

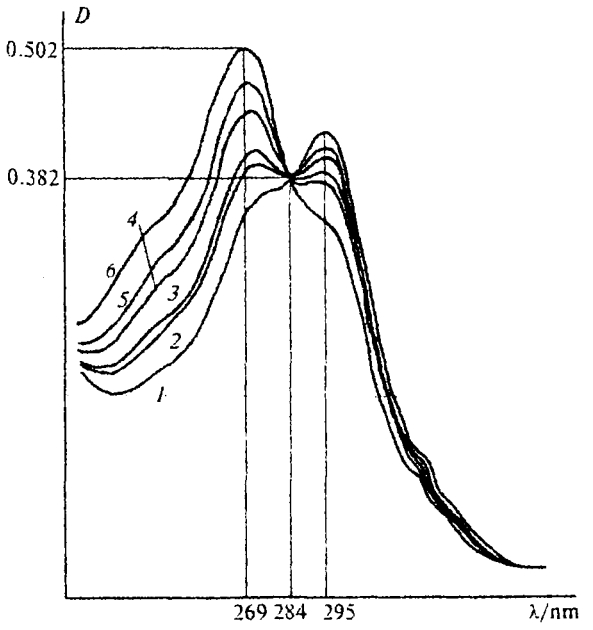


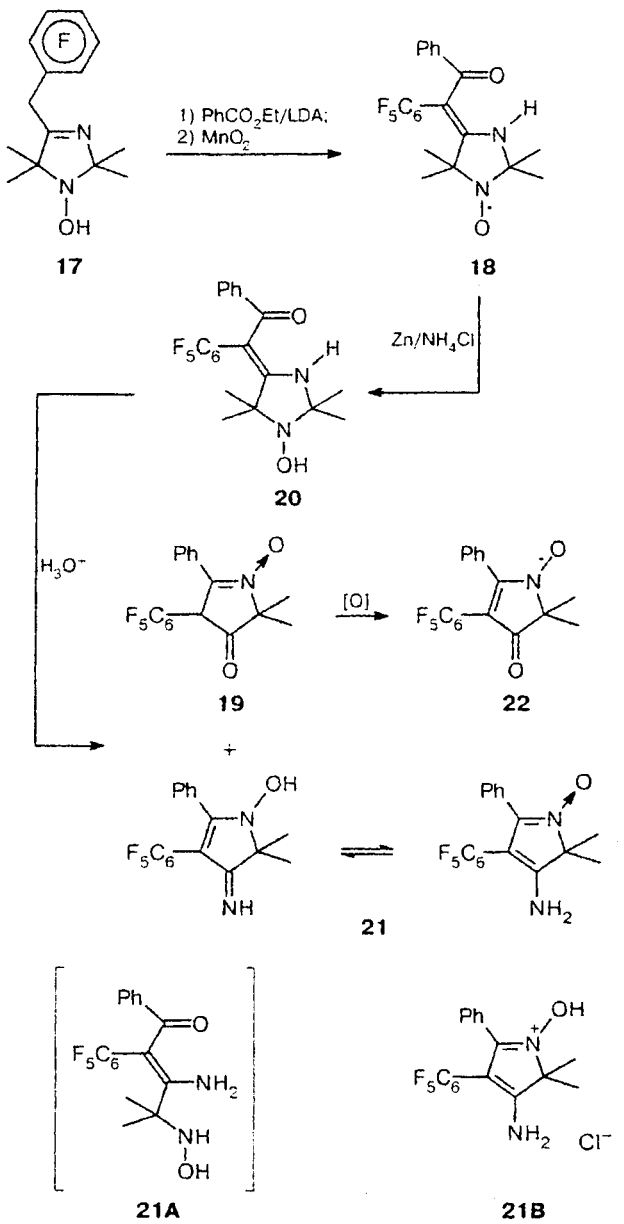
Fig. 1. UV spectrum of pyrroline **8d** in hexane at 20 °C immediately after preparation of the solution (*1*) and after 5 min (*2*), 10 min (*3*), 20 min (*4*), 30 min (*5*), and 12 h (*6*).

Chlorination of pyrrolines **3f—h** afforded chloro derivatives **8f—h**, which were not isolated in individual form. These compounds decomposed upon chromatography or even upon storage in an organic solvent due, apparently, to the presence of the pyridine ring, which can be alkylated at the nitrogen atom as well as induce dehydrochlorination. The reactions of chloro derivatives **8f—h** with NaCN followed by oxidation afforded the corresponding vinylnitroxyl radicals **11f—h** (according to the TLC data). However, these radicals rapidly decomposed upon chromatography and only radical **11g** was isolated in individual form.

Compounds **11a,g** are dark-violet crystals. Interestingly, radical **11a** exists in two crystal modifications, *viz.*, as violet and green modifications. Both these modifications are formed upon crystallization of compound **11a** from hexane. The predominance of a particular form depends on the concentration, the temperature, and the crystallization rate. It was found that these modifications possess different magnetic properties (in this work, these properties are not considered). When stored in a methanolic solution, radical **11a** was reduced to nitrile **9a**. This reaction proceeded much more rapidly under the action of an alkaline solution of hydrogen peroxide. In the course of the reaction, elimination of oxygen and decoloration of the radical were observed.

The range of stable vinylnitroxyl radicals of type **11** can also be extended by replacing the nitrile group at position 3 of the heterocycle by another electron-withdrawing group. We chose C_6F_5 groups as such an electron-withdrawing group. The method for the synthesis of pentafluorophenyl-substituted pyrroline **19** is shown in Scheme 4. Compound **20** appeared to be substantially more stable with respect to hydrolytic recyclization than enaminoketones **13** and **15**. We succeeded in splitting the imidazoline ring only upon boiling in a solution of a 1 : 3 concentrated HCl—MeOH mixture for 2 h. In this case, pyrroline **19** was formed only in low yield. Based on the data of elemental analysis and spectral character-

Scheme 4



istics, the structure of enaminoketone **21A** may be assigned to the major reaction product. However, we failed to perform hydrolysis of the resulting compound even upon prolonged boiling in a concentrated HCl—MeOH mixture, which cast doubt upon the validity of the structure assigned. Another intriguing feature of this compound is the fact that it is bright-yellow in color, while its hydrochloride **21B** is colorless.

In this connection, hydrochloride **21B** was studied by X-ray diffraction analysis. It was established that this compound is actually a 2*H*-pyrrole derivative and protonation occurs at the oxygen atom of the nitrone group. In the crystal structure, there is one water molecule per

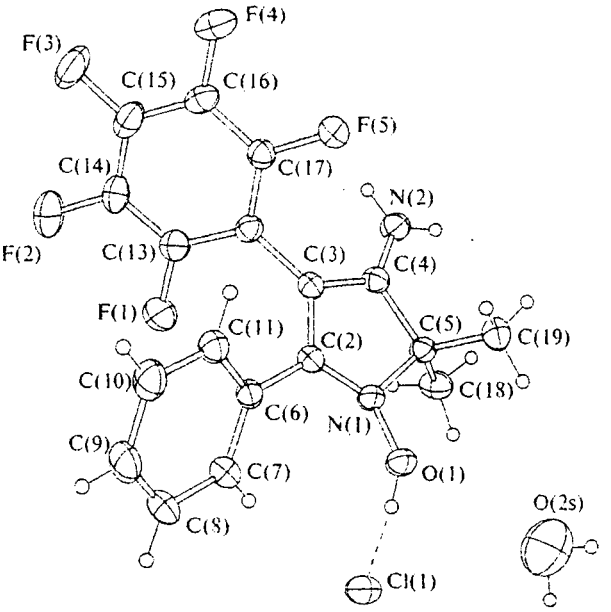


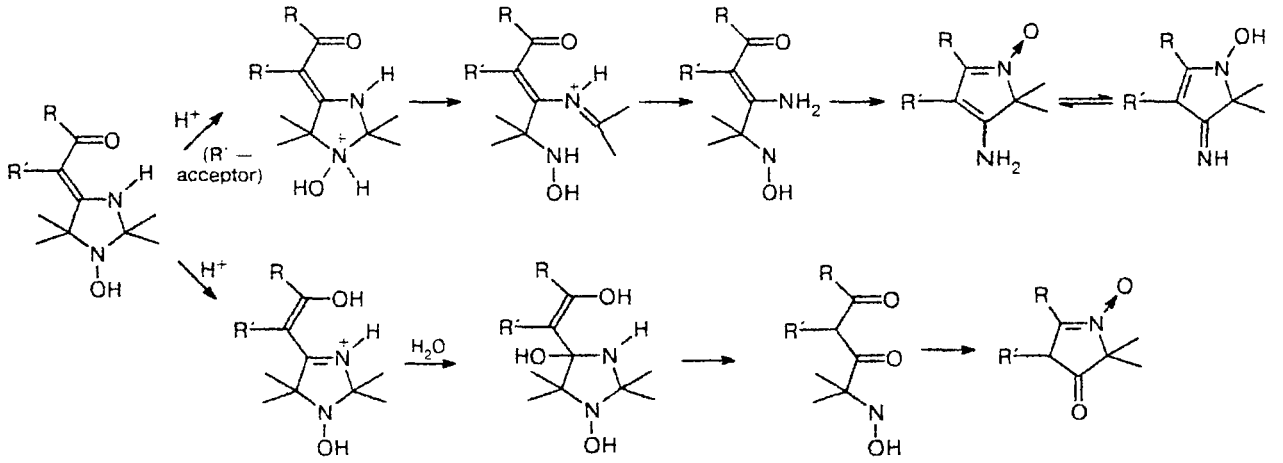
Fig. 2. Crystal structure of 3-amino-1-hydroxy-2,2-dimethyl-4-pentafluorophenyl-5-phenyl-2*H*-pyrrolium chloride (**21B**).

molecule **21B**, which agrees with the data of elemental analysis. Previously, these data would not allow us to assign the cyclic structure to the compound under consideration. The structure of molecule **21B** is shown in Fig. 2. Note equalization of the bond lengths in the C(4)=C(3)—C(2)=N(1) fragment (1.390(4), 1.412(4), and 1.326(4) Å, respectively). These bond lengths are close to the corresponding values in aromatic rings, for example, in pyridines.[9] According to the published data,[10] such equalization of the bond lengths was observed in 1-*tert*-butyl-3-hydroxy-1,2-dihydropyrrolium picrate.[11] The N^+—OH bond length (1.384(3) Å) coincides with the analogous bond length in 2-amino-1-hydroxy-5,5-dimethylpyrrolinium picrate.* The angles between the plane of the heterocycle and the planes of the Ph and C_6F_5 groups are 42.4(1)° and 55.6(1)°, respectively. In the crystal of compound **21B**, the cations and anions are linked through a network of OH...Cl^- and NH...Cl^- hydrogen bonds with the participation of water molecules of solvation. The parameters of the strongest OH...Cl hydrogen bond are as follows: H...Cl is 1.98(4) Å, O...Cl is 2.969(3) Å, and the O—H...Cl angle is 175(4)°.

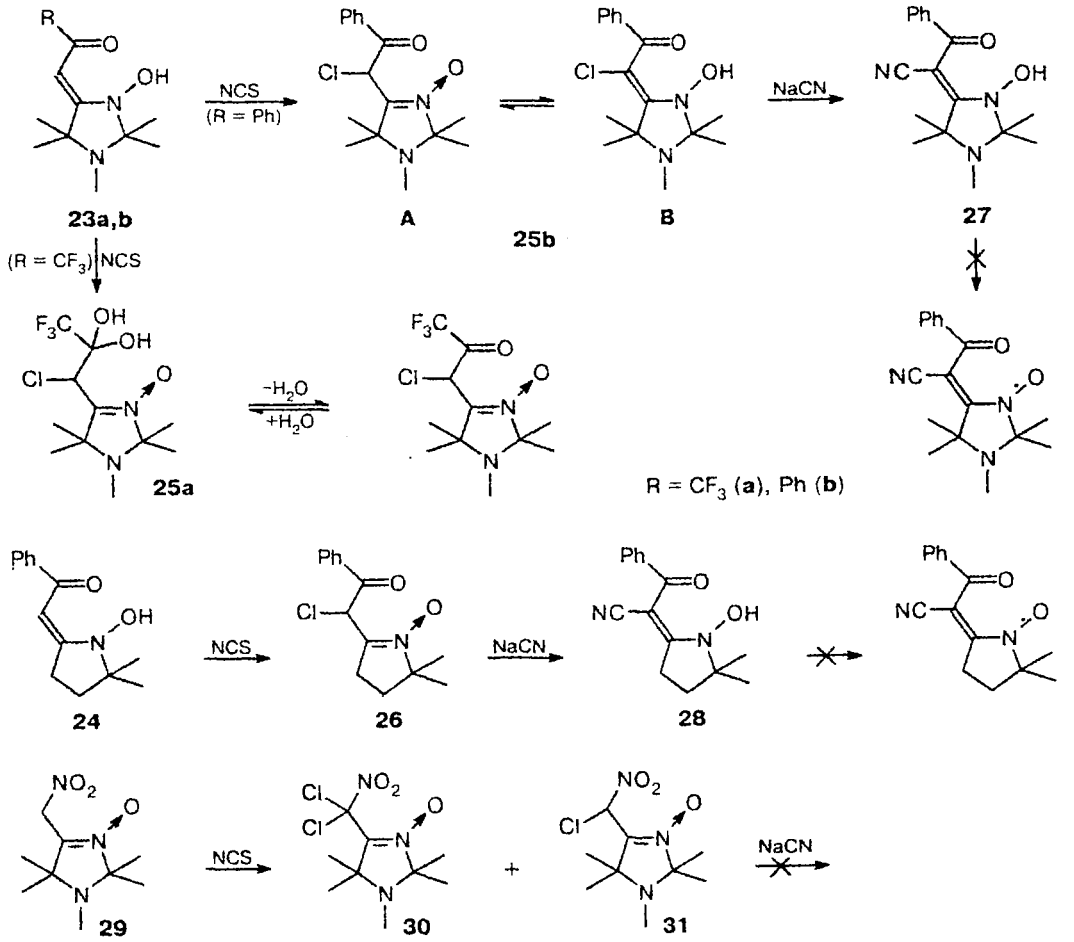
Evidently, protonation of the oxygen atom of the nitrone group is responsible for the unusually high stability of compound **21** to hydrolysis. Apparently, the yellow color of the crystals of **21** is associated with the fact that this compound exists, at least to some extent, in the enhydroxylaminoimine tautomeric form. Pyrroline **19** was oxidized to nitroxyl radical **22** under the action of MnO_2 in nearly quantitative yield.

* M. Hess, B. R. Vincen, and A. Linden, private communication, 1993.

Scheme 5



Scheme 6



Since compound **21** is not an intermediate in the course of preparation of pyrroline **19**, its formation is, apparently, determined by hydrolytic cleavage of the C(2)—N(1) bond (Scheme 5) rather than of the C(4)—N(2) bond, as is generally observed upon hydrolytic recyclization of enaminoketones of the imidazolidine series to pyrrolines. Apparently, this is associated with the electronic effect of the pentafluorophenyl group.

We also attempted to synthesize vinylnitroxyl radicals with another topology of the vinylnitroxyl group from exocyclic β-oxonitrones **23** and **24** (Scheme 6).

Chlorination of oxonitrones **23b** and **24** afforded the corresponding chloro derivatives **25b** and **26**, respectively. Judging from the NMR spectra in acetone, these derivatives, unlike the initial compounds, exist predominantly in the nonconjugated oxonitrone tautomeric form. On the contrary, the product of chlorination of oxonitrone **23a** in acetone exists predominantly as a hydrate (according to the NMR spectra). In the ^{13}C NMR spectrum of compound **25a**, a signal for the carbon atom of the carbonyl group is absent and a signal for the hydrated carbonyl carbon atom with slight splitting on the fluorine atoms of the trifluoromethyl group (q, J = 32 Hz) is observed at δ 99.10.

The reactions of chloro derivatives **25b** and **26** with NaCN afforded nitriles **27** and **28**, respectively. Apparently, the resulting compounds in DMSO solutions exist in the conjugated enhydroxylaminoketone or enolonitrone tautomeric form. In the ^{13}C NMR spectrum of compound **28**, signals for sp^2-hybridized carbon atoms are absent, except for signals for the C atoms of the phenyl group, due apparently to the exchange interaction between the conjugated tautomeric forms. In attempting to oxidize nitriles **27** and **28** with MnO_2 in $CHCl_3$, the characteristic blue color initially appeared and then rapidly disappeared. However, no products were chromatographically detected in the reaction mixture, and the solution contained only the initial nitrile. More prolonged storage of the reaction mixture resulted only in slow destruction of the initial nitrile. We failed to obtain nitrile by replacing the Cl atom in nitrochloro derivative **31**.

To summarize, we synthesized the first representatives of stable vinylnitroxyl radicals, *viz.*, pyrroline derivatives. Attempts to prepare analogous compounds with the exocyclic vinylnitroxyl group are as yet unsuccessful. It was found that nitroxyl radicals **11a,g** possess unusual magnetic properties, which will be described elsewhere.

Experimental

The IR spectra were recorded on a Specord M-80 instrument in KBr pellets (the concentration was 0.25%) and in CCl_4 (5% solutions). 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 (5% solutions). The chemical shifts were measured relative to the signal of the solvent. The characteristics of the synthesized compounds are given in Table 1.

Reaction of pyrroline 8a with NaCN in acetonitrile. A mixture of pyrroline **8a**[6] (0.3 g, 1.26 mmol), NaCN (0.15 g, 3 mmol), and 15-crown-5 ether (10 mg) in anhydrous MeCN (10 mL) was stirred at 20 °C for 2 h and then concentrated. The residue was chromatographed on a column with silica gel using $CHCl_3$ as the eluent. Dimer **5a** was obtained in a yield of 0.15 g (50%).

Reaction of pyrroline 8a with NaCN in methanol. A solution of pyrroline **8a** (0.25 g, 1 mmol) and NaCN (0.1 g, 2 mmol) in MeOH (10 mL) was kept at 20 °C for 2 h and then concentrated. Water (3 mL) was added to the residue, the mixture was acidified with 5% HCl to pH 4, and a 1 : 3 hexane—ether mixture was added. The precipitate of pyrroline **9a** was filtered off and washed with a small amount of ethyl acetate. Compound **9a** was obtained in a yield of 0.1 g (40%). According to the results of a comparison of the TLC data with those of the known samples, the organic phase of the filtrate contained dimer **5a** and pyrroline **10**.

3-Cyano-1-hydroxy-5,5-dimethyl-4-oxo-2-phenyl-2-pyrroline (9a). Pyrroline **8a** (0.5 g, 2 mmol) was added portionwise with stirring and cooling to a solution of NaCN (0.2 g, 4 mmol) in anhydrous DMSO (5 mL) over 15 min. Then the reaction mixture was stirred at 20 °C for 30 min, diluted with water (15 mL) upon cooling, and acidified with 5% HCl to pH 3. The precipitate of pyrroline **9a** was filtered off, washed with water and a 1 : 1 ethyl acetate—hexane mixture, and dried. ^1H NMR (DMSO-d_6), δ: 1.35 (s, 6 H, C(5)Me_2); 7.64 and 7.84 (both m, 3 H + 2 H, Ph). ^{13}C NMR (DMSO-d_6), δ: 20.75 (C(5)$\underline{Me}_2$); 71.08 (C(5)); 77.96 (C(3)); 115.41 (C≡N); 125.82, 128.45, 128.84, and 132.64 (Ph); 170.92 (C(2)); 194.96 (C(4)).

3-Cyano-5,5-dimethyl-4-oxo-2-phenyl-2-pyrroline-1-oxyl (11a). A suspension of nitrile **9a** (0.2 g) and MnO_2 (1 g) in $CHCl_3$ (10 mL) was stirred at 20 °C for 30 min. An excess of the oxidizing agent was filtered off, the reaction solution was concentrated, and compound **11a** was isolated by chromatography on a column with silica gel using $CHCl_3$ as the eluent.

3-Chloro-1-hydroxy-5,5-dimethyl-4-oxo-2-phenyl-2-pyrroline (8a). Enaminoketone **15a**[12] (1 g) was heated in a mixture of MeOH (3 mL) and 10% HCl (10 mL) until the initial compound was dissolved. Then the reaction mixture was kept at 20 °C for 10 h. The precipitate of pyrroline **8a** that formed was filtered off, washed with water, and dried. After evaporation of methanol, an additional amount of pyrroline **8a** was obtained from the filtrate. The yield was 0.7 g (83%), m.p. 110—112 °C; literature data[6]: m.p. 110—112 °C.

3-Chloro-1-hydroxy-5,5-dimethyl-4-oxo-2-pentafluorophenylpyrroline (8e) was prepared analogously. ^1H NMR (DMSO-d_6), δ: 1.31 (s). ^{13}C NMR (DMSO-d_6), δ: 21.70 (C(5)$\underline{Me}_2$); 72.44 (C(5)); 106.60 (C(3)); 135.0—145.8 (m, C_6F_5); 159.05 (C(2)); 194.36 (C(3)).

Enaminoketones 12g,h,[7] 13,[12] 15,[12] and 14[13] were prepared according to procedures reported previously. **Enaminoketones 13g,h** were prepared by the direct reactions of imidazoline **16** with ethyl nicotinate and isonicotinate, respectively, under conditions reported in the literature[5] excluding the stage of oxidation. The resulting compounds were purified by chromatography on a column with Al_2O_3 using $CHCl_3$ as the eluent. Compound **13g** was not obtained as an analytical sample and was converted into pyrroline as described below. **1-Hydroxy-4-isonicotinoylmethylene-2,2,5,5-tetramethylimidazolidine (13h).** ^1H NMR (DMSO-d_6), δ: 1.33 and 1.38 (both s, 6 H each, C(2)Me_2, C(5)Me_2); 5.82 (s, 1 H, —CH=); 7.90 (d, 2 H, H_m of pyridyl, J = 4.5 Hz); 8.12 (s, 1 H, OH); 8.67 (d, 2 H, H_o of pyridyl, J = 4.5 Hz); 10.93 (br.s, 1 H, NH).

Table 1. Characteristics of the synthesized compounds[a]

Compound	Yield (%)	M.p. /°C	IR (KBr), ν/cm^{-1}	UV, λ_{max}/nm (log ε)	Found / Calculated (%)			Molecular formula
					C	H	N	
3g	90	132—134	1540—1670 (C=C—C=O, C=N); 1760 (C=O)	242 (4.12), 308 (3.78), 360 (3.68)	64.5 64.8	5.9 5.9	13.5 13.7	$C_{11}H_{12}N_2O_2$
3h	60	130 (decomp.)	1760 (C=O); 1590, 1550 (C=C, C=N)	229 (4.24), 308 (3.99), 365 (3.67)	64.8 64.8	5.9 5.9	13.7 13.7	$C_{11}H_{12}N_2O_2$
8d	85	69—73	1670 (C=N); 1695 (C=O); 1530, 1595 (C=C)	312 (3.38), 394 (3.69)	36.6 36.6	3.0 3.0	6.2 6.1	$C_7H_7ClF_3O_2$
8e	60	120—122	1650 (C=C); 1715 (C=O)	240 (3.89), 318 (3.28), 362 (3.69)	44.1 44.0	2.0 2.1	4.5 4.3	$C_{12}H_7ClF_5NO_2$
9a	80	213—216	2200 (C≡N); 1675 (C=O)	245 (4.27), 346 (3.88)	68.3 68.4	5.3 5.3	12.2 12.3	$C_{13}H_{12}N_2O_2$
11a	60	143—145	2200 (C≡N); 1700 (C=O); 1540, 1600 (C=O)	250 (4.17), 270 (4.11), 313 (3.73), 334 (3.93), 397 (3.68), 578 (3.26)[b]	68.4 68.6	4.8 4.8	12.0 12.3	$C_{13}H_{11}N_2O_2$
11g	35	113—115	1705 (C=O); 1590 (C=C); 2200 (C≡N)	246 (4.14), 308 (3.48), 333 (3.67), 395 (3.48), 564 (3.05)[b]	63.2 63.2	4.6 4.4	18.2 18.4	$C_{12}H_{10}N_3O_2$
12g	60	167—169	3250 (NH); 1540, 1570, 1620 (C=C—C=O)	234 (3.76), 334 (4.03)	64.5 64.5	7.1 6.9	15.9 16.1	$C_{14}H_{18}N_3O_2$
12h	75	207—209	3290 (NH); 1540, 1570, 1620 (C=C—C=O)	229 (3.95), 340 (4.08)	64.5 64.5	6.9 6.9	16.1 16.1	$C_{14}H_{18}N_3O_2$
13h	70[c]	224—225	3260 (NH); 1530, 1555, 1595, 1610 (C=C—C=O)	227 (4.01), 346 (4.29)	64.8 64.4	7.6 7.3	16.1 16.1	$C_{14}H_{19}N_3O_2$
14b	65	139—141	3230 (NH); 1550, 1605 (C=C—C=O)	317 (4.20)	51.6 51.9	6.9 6.9	12.0 12.1	$C_{10}H_{16}ClN_2O_2$
14c	70	148—150	3170 (NH); 1530, 1600 (C=C—C=O)	318 (4.18)	57.4 57.2	8.1 8.1	10.1 10.2	$C_{13}H_{22}ClN_2O_2$
14e	90	188—189	3220 (NH); 1500—1650 (C=C, C=O)	238 (3.53), 335 (4.27)	57.4 57.2	8.1 8.1	10.1 10.2	$C_{15}H_{13}ClF_5N_2O_2$
14f	95	192—194	3200 (NH); 1540, 1580 1600 (C=C—C=O)	237 (3.96), 339 (4.11)	57.3 57.0	6.0 5.8	14.2 14.3	$C_{14}H_{17}ClN_3O_2$
14g	80	210—211	3210 (NH); 1545, 1570, 1605 (C=C—C=O)	235 (3.88), 343 (4.19)	57.3 57.0	5.8 5.8	14.5 14.3	$C_{14}H_{17}ClN_3O_2$
14h	70	193—194	3200 (NH); 1520, 1550, 1600 (C=C—C=O)	252 (3.78), 340 (4.18)	56.8 57.0	6.0 5.8	14.1 14.3	$C_{14}H_{17}ClN_3O_2$
15g	75	209—211	3215 (NH); 1525, 1570, 1590 (C=C—C=O)	346 (4.19)	57.2 56.9	6.4 6.1	14.3 14.2	$C_{14}H_{18}ClN_3O_2$
18	40	151—153	1605—1490 (N—C=C—C=O—Ph); 3200 (NH)	310 (4.15)	59.2 59.3	4.3 4.3	6.60 6.60	$C_{21}H_{18}F_5N_2O_2$
21	70	227—230	1650, 1595 (C=C—C=N); 3300, 3450 (NH, OH)	260 (4.16), 317 (3.58), 373 (3.58)	56.5 56.0	3.6 3.9	7.2 7.2	$C_{18}H_{13}F_5N_2O \cdot H_2O$
21B	100	260—261 (decomp.)	1570, 1590, 1660 (C=C—C=N)	259 (4.16), 358 (3.73)	50.9 51.1	3.9 3.8	6.6 6.6	$C_{18}H_{13}F_5N_2O \cdot HCl \cdot H_2O$
22	90	[d]	1700 (C=O)	251 (4.15), 327 (4.0), 381 (3.72), 551 (3.02)	58.3 58.7	3.2 3.0	3.6 3.8	$C_{18}H_{11}F_5NO_2$
25a	65	100—102	1690 (C=O); 1620 (C=N)	243 (3.81)	41.7 41.4	5.8 5.7	8.8 8.8	$C_{14}H_{18}ClF_3N_2O_3$
25b	90	121—123	1720 (C=O); 1590 (C=N)	245 (4.15)	62.5 62.2	7.1 6.8	9.3 9.1	$C_{16}H_{21}ClN_2O_2$
26	80	91—92	1700 (C=O); 1570, 1595 (C=C, C=N)	245 (4.19)	63.6 63.3	6.2 6.0	5.5 5.3	$C_{14}H_{16}ClNO_2$
27	90	140—142	1520—1600 (C=C—C=O); 2200 (C≡N)	240 (4.08), 328 (4.06)	68.1 68.3	7.1 7.0	14.0 14.0	$C_{17}H_{21}N_3O_2$
28	90	100—101	1520—1600 (C=C—C=O); 2200 (C≡N)	242 (4.06), 334 (4.08)	70.4 70.4	6.4 6.2	10.9 10.9	$C_{15}H_{16}N_2O_2$

(to be continued)

Table 1. (*continued*)

Compound	Yield (%)	M.p. /°C	IR (KBr), ν/cm^{-1}	UV, λ_{max}/nm (log ε)	Found / Calculated (%) C	H	N	Molecular formula
30	20	102—103	1600 (C=N); 1570, 1350 (NO_2)	244 (3.64)	38.0 / 38.1	5.1 / 5.3	14.6 / 14.8	$C_9H_{15}Cl_2N_3O_3$
31	50	115—117	1600 (C=N); 1570, 1350 (NO_2)	270 (3.59)	43.7 / 43.3	6.2 / 6.4	15.9 / 15.9	$C_9H_{16}ClN_3O_3$

[a] Compounds **8d**, **11a**, **14b,e**, **26**, and **30** were purified by recrystallization from hexane; compounds **9a** and **13h** were purified by recrystallization from an ethyl acetate—MeOH mixture; compounds **8e**, **12g,h**, **14b**, **18**, **25a,b**, **27**, **28**, and **31** were purified by recrystallization from a hexane—ethyl acetate mixture; compounds **13g**, **14f—h**, and **15g** were purified by recrystallization from ethyl acetate; and compounds **3g,h**, **11g**, and **21** were purified by chromatography on silica gel.
[b] The spectrum was recorded in hexane.
[c] From imidazoline **16**.
[d] Oil.

^{13}C NMR (DMSO-d_6), δ: 24.80 and 26.25 (C(2)$\underline{Me}_2$, C(5)$\underline{Me}_2$); 67.24 (C(5)); 80.25 (C(2)); 82.83 (CH=); 120.50 (C_m of pyridyl); 146.11 (C_p of pyridyl); 150.07 (C_o of pyridyl); 170.00 (C(4)); 184.59 (C=O).

5,5-Dimethyl-4-oxo-2-(3-pyridyl)-1-pyrroline 1-oxide (3g). A solution of enaminoketone **13g** (2 g) in 10% HCl (15 mL) was kept at 20 °C for 24 h, neutralized with Na_2CO_3, saturated with NaCl, and extracted with $CHCl_3$ (5×30 mL). The extract was dried with $MgSO_4$, the reaction solution was concentrated, and pyrroline **3g** was isolated by chromatography on a column with silica gel using a 25 : 1 $CHCl_3$—MeOH mixture as the eluent. ^{1}H NMR (DMSO-d_6), δ: 1.24 (s, 6 H, C(5)Me_2, **B**); 1.40 (s, 6 H, C(5)Me_2, **A**); 4.02 (s, 2 H, 2 H(3), **A**); 5.62 (s, 1 H, H(3), **B**); 7.53 (m, 1 H, H(5′) of pyridyl, **B**); 8.11 (m, 1 H, H(4′) of pyridyl, **B**); 8.68 (m, 1 H, H(6′) of pyridyl, **A** + **B**); 8.85 (m, 1 H, H(4′) of pyridyl, **A**); 8.94 (s, 1 H, H(2′) of pyridyl, **B**); 9.42 (s, 1 H, H(2′) of pyridyl, **A**); 9.79 (br.s, 1 H, OH, **B**). The **A** : **B** ratio was 1 : 4.5. All signals in the spectrum of compound **3g** are doubled, which is apparently associated with the slow (within the NMR time scale) exchange between the conformers with the different orientations of the pyridine ring. ^{13}C NMR (DMSO-d_6), δ: 20.94 (C(5)$\underline{Me}_2$, **A**); 21.73 (C(5)$\underline{Me}_2$, **B**); 71.04 (C(5), **B**); 76.85 (C(5), **A**); 100.41 (C(3), **B**); 123.54, 125.38, 136.18, 149.13, and 151.56 (pyridyl, **B**); 123.42, 125.38, 134.35, 148.50, and 150.31 (pyridyl, **A**); 135.72 (C(2), **A**); 172.91 (C(2), **B**); 201.02 (C(4), **B**); 208.04 (C(4), **A**).

Analogously, pyrroline **3h** was prepared from enaminoketone **13h**. ^{1}H NMR (DMSO-d_6), δ: 1.24 (s, 6 H, C(5)Me_2, **B**); 1.41 (s, 6 H, C(5)Me_2, **A**); 4.00 (s, 2 H, 2 H(3), **A**); 5.67 (s, 1 H, H(3), **B**); 7.68 (d, 2 H, H(β) of pyridyl, **B**, J = 5.5 Hz); 8.21 (d, 2 H, H(β) of pyridyl, **A**, J = 6 Hz); 8.73 (m, 4 H, H(α) of pyridyl, **A** + **B**); 9.80 (br.s, 1 H, OH, **B**); the **A** : **B** ratio was 1 : 2.5. ^{13}C NMR (DMSO-d_6), δ: 20.98 (C(5)$\underline{Me}_2$, **B**); 21.68 (C(5)$\underline{Me}_2$, **A**); 39.91 (C(3), **A**); 71.40 (C(5), **B**); 77.87 (C(5), **A**); 101.49 (C(3), **B**); 120.76 (C(β) of pyridyl, **A**); 122.59 (C(β) of pyridyl, **B**); 135.16 (C_i of pyridyl, **A**); 137.25 (C_i of pyridyl, **B**); 150.04 (C(α) of pyridyl, **B**); 150.19 (C(α) of pyridyl, **A**); 136.22 (C(2), **A**); 173.24 (C(2), **B**); 201.39 (C(4), **A**); 207.73 (C(4), **B**).

3-Chloro-1-hydroxy-5,5-dimethyl-4-oxo-2-trifluoromethyl-2-pyrroline (8d). NCS (0.54 g, 4 mmol) was added portionwise with stirring to a solution of pyrroline **3d** (0.8 g, 4 mmol) in $CHCl_3$ (20 mL) over 30 min. Then the reaction solution was stirred at 20 °C for 30 min and concentrated. The residue was treated with CCl_4 (10 mL). The precipitate of succinimide was filtered off and washed with a small amount of CCl_4. The filtrate was concentrated, hexane (5 mL) was added to the residue, and the mixture was kept at a temperature from 0 to −5 °C for 12 h. The precipitate of pyrroline **8d** that formed was filtered off. ^{1}H NMR (DMSO-d_6), δ: 1.26 (s, C(5)Me_2). ^{13}C NMR (DMSO-d_6), δ: 21.49 (C(5)$\underline{Me}_2$); 72.41 (C(5)); 108.92 (C(3)); 119.13 (q, CF_3, J_{C-F} = 185 Hz); 156.38 (q, C(2), J_{C-F} = 24 Hz); 196.03 (C(4)).

Pyrrolines **8f—h** were prepared analogously.

4-Chloro(nicotinoyl)methylene-1-hydroxy-2,2,5,5-tetramethylimidazolidine (15g) was prepared by reduction of the corresponding enaminoketone **14g** with hydroxylamine similarly to a procedure described previously.[12] ^{1}H NMR (DMSO-d_6), δ: 1.40 and 1.50 (both s, 6 H each, C(2)Me_2, C(5)Me_2); 7.45 (dd, 1 H, H(5′) of pyridyl, J_1 = 4 Hz, J_2 = 7 Hz); 7.89 (d, 1 H, H(4′) of pyridyl, J = 7 Hz); 8.10 (s, 1 H, OH); 8.60 (d, 1 H, H(6′) of pyridyl, J = 4 Hz); 8.68 (s, 1 H, H(2′) of pyridyl); 10.93 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 22.88 and 26.18 (C(2)$\underline{Me}_2$, C(5)$\underline{Me}_2$); 69.15 (C(5)); 79.94 (C(2)); 93.21 (C1C=); 122.80 (C(6′) of pyridyl); 134.88 (C(5′) of pyridyl); 136.15 (C(3′) of pyridyl); 147.82 (C(2′) of pyridyl); 149.94 (C(4′) of pyridyl); 165.43 (C(4)); 187.48 (C=O).

Diamagnetic derivatives 15f,h were prepared analogously by reduction of enaminoketones **14f,h**, respectively. The structures of compounds **15f,h** were confirmed by oxidation with MnO_2 to the initial compounds.

Enaminoketones 15b—d were prepared by hydrogenation of a solution of the corresponding enaminoketone **14b—d** (10 mmol) in ethyl acetate (50 mL) in the presence of 5% Pd/C (0.5 g) until ~120 mL of hydrogen was absorbed (approximately in 1 h under atmospheric pressure at 20 °C). The catalyst was filtered off and washed with ethyl acetate. The solution was concentrated, the residue was washed with hexane, and the precipitate of enaminoketone **15** was filtered off. The yield was ~80%.

3-Cyano-5,5-dimethyl-4-oxo-2-(3-pyridyl)-2-pyrroline-1-oxyl (11g). Crude pyrroline **8g** (1 g) was added portionwise with stirring and cooling to a solution of NaCN (0.4 g) in anhydrous DMSO (5 mL). Then the reaction mixture was stirred at 20 °C for 20 min and diluted with an ice saturated NaCl solution (15 mL). The resulting solution was acidified with 5% HCl to pH 6—7 upon cooling. The precipitate of nitrile **9g** was filtered off, washed with a small amount of ice water, hexane, and a 1 : 3 ethyl acetate—hexane mixture, and dried. Nitrile **9g** was oxidized to radical **11g** as described above for compound **9a**. Treatment of the filtrate obtained after isolation of nitrile **9g** afforded an additional amount of compound **11g**. For this purpose, the aqueous solution was saturated with NaCl and extracted with $CHCl_3$ (5×30 mL). The

extract was stirred with MnO_2 (2 g) for 30 min and excess oxidizing agent was filtered off. The solution was washed with water (5×30 mL), dried with $MgSO_4$, and concentrated. Radical **11g** was obtained and purified as described above. ESR ($CHCl_3$): a_N = 6.12 G.

2,2,5,5-Pentamethyl-4-(2-oxo-1-pentafluorophenyl-2-phenylethylidene)imidazolidine-1-oxyl (18). A solution of imidazoline **17**[5] (1.62 g, 5 mmol) was added dropwise with stirring to a solution of lithium diisopropylamide, which was prepared from lithium (0.28 g, 40 mmol), bromobenzene (2.1 mL, 20 mmol), and diisopropylamine (2.5 mL, 17.5 mmol) in ether (20 mL), over 5 min. The reaction was carried out under an argon atmosphere. The reaction mixture was stirred at 20 °C for 25 min. Then a solution of ethyl benzoate (1.8 mL, 12.5 mmol) in ether (2 mL) was immediately added to the reaction mixture with stirring upon cooling with an ice—salt mixture. The reaction mixture was stirred at ambient temperature for 30 min and decomposed with water (10 mL). The ethereal layer was separated and the aqueous layer was extracted with $CHCl_3$ (2×20 mL). The combined extracts were dried with $MgSO_4$. Then MnO_2 (5 g) was added to the solution and the reaction mixture was stirred for 20 min. An excess of the oxidizing agent was filtered off, the solution was concentrated, and compound **18** was isolated by chromatography on a column with silica gel using a 1 : 1 $CHCl_3$—hexane mixture as the eluent.

1-Hydroxy-2,2,5,5-tetramethyl-4-(2-oxo-1-pentafluorophenyl-2-phenylethylidene)imidazolidine (20). A zinc powder (1 g) and NH_4Cl (0.3 g) were added to a solution of enaminoketone **18** (0.5 g) in MeOH (15 mL) and the reaction mixture was stirred at 20 °C for 30 min. An excess of zinc and inorganic salts was filtered off and washed on a filter with ethyl acetate (4×5 mL). The reaction solution was concentrated, the residue was washed with hexane, and the precipitate of compound **20** was filtered off. The sample of compound **20** contained inorganic salts as impurities, which did not hinder subsequent conversions. The structure of compound **20** was established by oxidation with MnO_2 to the initial nitroxyl radical.

5,5-Dimethyl-4-oxo-3-pentafluorophenyl-2-phenyl-1-pyrroline 1-oxide (19) and 4-imino-1-hydroxy-5,5-dimethyl-3-pentafluorophenyl-2-phenyl-2-pyrroline (21). A solution of imidazolidine **20** (1 g) in a mixture of concentrated HCl (5 mL) and MeOH (15 mL) was refluxed for 2 h. The major portion of MeOH was evaporated and the precipitate was filtered off, washed with 3% HCl, and dried. The resulting substance, which was a mixture of hydrochloride **21B** and pyrroline **19**, was dissolved in MeOH (20 mL) and the solution was alkalized with sodium methylate to pH 8. The reaction solution was concentrated and the residue was chromatographed on a column with silica gel using a 10 : 1 $CHCl_3$—MeOH mixture as the eluent. Colorless pyrroline **19** (0.15 g) and compound **21** (0.5 g; a yellow band) were successively eluted. **Compound 21**, ^{1}H NMR (CD_3OD), δ: 1.65 (s, 6 H); 7.5 (m, 5 H). ^{13}C NMR (CD_3OD), δ: 21.66 (Me_2); 73.65 ($\underline{C}Me_2$); 84.43 (C(3)); 126.52, 127.35, 127.57, and 129.43 (Ph); 139.4—146.67 (m, C_6F_5); 149.74 (C(4)); 162.59 (C(2)).

Hydrochloride **21B** was prepared by dissolving free base **21** in a minimum amount of MeOH and an excess of concentrated HCl was added. The precipitate was filtered off, washed with a 5% HCl solution, and dried. Compound **21B** was obtained in quantitative yield. Crystals suitable for X-ray diffraction study were obtained by crystallization of hydrochloride **21B** from a concentrated HCl—MeOH mixture with slow evaporation of the latter.

5,5-Dimethyl-4-oxo-3-pentafluorophenyl-2-phenyl-2-pyrroline-1-oxyl (22) was prepared by oxidation of compound **19** with MnO_2 as described above for compound **11a**. ESR ($CHCl_3$): t, a_N = 7.02 G.

4-(1-Chloropropyl-3,3,3-trifluoro-2,2-dihydroxy)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide (25a). NCS (0.27 g, 2 mmol) was added to a solution of oxonitrone **23a** (0.53 g, 2 mmol) in CCl_4 (20 mL) and the reaction mixture was stirred at 20 °C for 48 h. The precipitate of succinimide was filtered off, the solution was concentrated, and compound **25a** was isolated by chromatography on a column with silica gel using methyl *tert*-butyl ether as the eluent. The product contained ~5% of the keto form. ^{1}H NMR (acetone-d_6), δ: 1.32, 1.41, 1.426, and 1.43 (all s, 3 H each, C(2)Me_2, C(5)Me_2); 2.40 (s, 3 H, N—Me); 2.67 (s, 3 H, N—Me, keto form); 4.88 (s, 1 H, CHCl); 5.42 (s, keto form); 7.56 (br.s, 1 H, OH); 9.56 (br.s, 1 H, OH). ^{13}C NMR (acetone-d_6), δ: 23.55, 23.77, 24.28, and 24.46 (C(2)$\underline{Me}_2$, C(5)$\underline{Me}_2$); 27.25 (N—Me); 52.62 (CHCl); 65.32 (C(5)); 91.42 (C(2)); 99.10 (q, $C(OH)_2$, J_{C-F} = 32 Hz); 128.19 (q, CF_3, J_{C-F} = 280 Hz); 149.45 (C(4)).

4-(1-Chloroethyl-2-oxo-2-phenyl)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide (25b). NCS (0.27 g, 2 mmol) was added portionwise with stirring to a solution of oxonitrone **23b** (0.55 g, 2 mmol) in CCl_4 (20 mL) over 20 min. The precipitate of succinimide was filtered off and the solution was concentrated. The residue was washed with a small amount of hexane and the precipitate of compound **25b** was filtered off. ^{1}H NMR (acetone-d_6), δ: 1.08, 1.22, 1.28, and 1.44 (all s, 3 H each, C(2)Me_2, C(5)Me_2, **A**); 1.05, 1.20, 1.25, and 1.42 (all s, 3 H each, C(2)Me_2, C(5)Me_2, **B**); 2.28 (s, 3 H, N—Me, **A**); 2.67 (s, 3 H, N—Me, **B**); 6.74 (s, CHCl, **A**); 7.4—7.9 (m, Ph). The **A** : **B** ratio was 15 : 1. ^{13}C NMR (acetone-d_6), δ: 23.67, 23.76, 24.41, and 25.05 (C(2)$\underline{Me}_2$, C(5)$\underline{Me}_2$); 26.53 (N—Me); 56.37 (CHCl); 64.31 (C(5)); 90.07 (C(2)); 128.40, 129.10, 134.13, and 139.81 (Ph); 136.26 (C(4)); 189.77 (C=O). Signals of form **B** are not observed.

Analogously, chlorination of oxonitrone **24** afforded chloro derivative **26**, which was isolated by chromatography on a column with silica gel using $CHCl_3$ as the eluent. ^{1}H NMR (DMSO-d_6), δ: 1.07 and 1.17 (both s, 3 H each, C(5)Me_2, **A**); 1.40 (s, 6 H, C(5)Me_2, **B**); 1.90—3.05 ($-CH_2CH_2-$, **A** + **B**); 6.76 (s, 1 H, CHCl, **A**); 7.4—7.9 (m, Ph). The **A** : **B** ratio was 4 : 1. ^{13}C NMR (DMSO-d_6), δ: 23.62 (C(4), **A**); 24.14 and 24.40 (C(5)$\underline{Me}_2$, **A**); 25.13 (C(5)$\underline{Me}_2$, **B**); 29.04 (C(4), **B**); 31.27 (C(3), **A**); 32.23 (C(3), **B**); 56.79 (CHCl, **A**); 73.13 (C(5), **B**); 74.03 (C(5), **A**); 127.72, 127.86, 128.41, 128.66, 129.47, 134.06, and 136.05 (Ph); 133.77 (C(2), **A**); 188.85 (C=O, **A**).

Chlorination of nitrone **29** under analogous conditions afforded a mixture of the mono- (**31**) and dichloro derivatives (**30**), which were separated by chromatography on a column with silica gel using chloroform as the eluent. **2,2,3,4,4-Pentamethyl-5-nitrochloromethyl-1-pyrroline 1-oxide (31).** ^{1}H NMR (acetone-d_6), δ: 1.37, 1.405, 1.41, and 1.48 (all s, 3 H each, C(2)Me_2, C(5)Me_2); 2.45 (s, 3 H, N—Me); 7.15 (s, 1 H, $CHNO_2$). ^{13}C NMR (DMSO-d_6), δ: 23.35, 23.39, 24.48, and 24.53 (C(2)$\underline{Me}_2$, C(5)$\underline{Me}_2$); 63.87 (C(5)); 82.51 ($CHNO_2$); 91.96 (C(2)).

Nitriles **27** and **28** were prepared analogously to pyrroline **9a**. **5-Benzoylcyanomethylene-1-hydroxy-2,2,3,4,4-penta-**

methylpyrrolidine (27). ^{1}H NMR (acetone-d_6), δ: 1.54 and 1.59 (both s, 6 H each, C(2)Me_2, C(5)Me_2); 2.45 (s, 3 H, N—Me); 7.45—7.83 (m, Ph). **5-Benzoylcyanomethylene-1-hydroxy-2,2-dimethylpyrrolidine (28).** ^{1}H NMR (acetone-d_6), δ: 1.48 (s, 6 H, C(5)Me_2); 2.22 (t, 2 H, 2 H(4), J = 7.5 Hz); 3.07 (t, 2 H, 2 H(3), J = 7.5 Hz); 7.42—7.85 (m, Ph). ^{13}C NMR (acetone-d_6), δ: 25.36 (C(5)$\underline{Me}_2$); 30.92 (C(4)); 33.36 (C(3)); 74.14 (C(5)); 120.16 (C≡N); 128.77, 129.08, 132.20, and 138.88 (Ph).

X-ray diffraction analysis of compound 21B was performed on a Syntex $P2_1$ diffractometer (Cu-Kα radiation, graphite monochromator, θ/2θ scanning, 2θ < 120°). The crystals of $[C_{18}H_{14}F_5N_2O]^+Cl^- \cdot H_2O$ (**21B**) belong to the monoclinic system: a = 30.397(10) Å, b = 8.653(1) Å, c = 18.278(5) Å, β = 125.56(2)°, V = 3911(2) Å^3, space group $C2/c$, Z = 8, d_{calc} = 1.436 g cm^{-3}, μ = 2.314 mm^{-1}. For a crystal of dimensions 0.25×0.4×0.6 mm, the intensities of 2904 independent reflections were measured. Corrections for absorption from the crystal habit were applied (transmission was 0.402—0.740). The structure was solved by the direct method using the SHELXS-86 program package and refined by the least-squares method in the anisotropic-isotropic approximation using the SHELXL-97 program package to wR_2 = 0.1410, S = 1.035 with the use of all reflections (R = 0.0495 for 2101 $F > 4\sigma$). The positions of the hydrogen atoms were located from the difference electron density synthesis and refined isotropically. Tables of the bond lengths, bond angles, and atomic coordinates for the structure of **21** were deposited with the Cambridge Structural Database.

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