Unusual formation of hydroperoxides in the reactions of substituted spiro[pyrazolinecyclopropanes]

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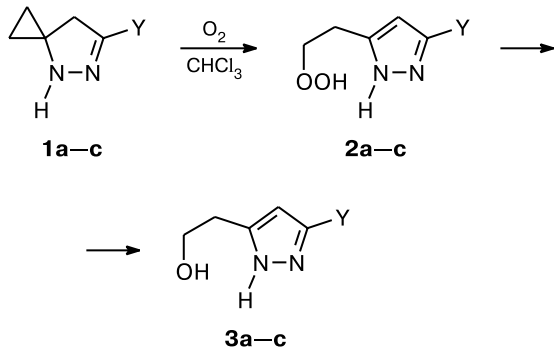
3-Cyano- and 3-(alkoxycarbonyl)spiro[2-pyrazoline-5,1′-cyclopropane] and 5-phenylspiro[1-pyrazoline-3,1′-cyclopropane] undergo unusual transformations into 3(5)-substituted 5(3)-(2-hydroperoxyethyl)pyrazoles in the presence of atmospheric oxygen. The conditions for the formation of hydroperoxides (*e.g.*, in oxygen-saturated solutions of spiro[2-pyrazoline-5,1′-cyclopropanes] in $CHCl_3$) and their conversion into (2-hydroxyethyl)pyrazoles or the corresponding nitrates under the action of nitrosating reagents were considered.

Key words: spiro[1- and 2-pyrazolinecyclopropanes], hydroperoxides, opening of the cyclopropane ring, organic nitrates.

Earlier, we showed[1,2] that the generation and [3+2] cycloaddition of diazocyclopropane to acrylonitrile or methyl acrylate affords 3-cyano- (**1a**) or 3-methoxycarbonylspiro[2-pyrazoline-5,1′-cyclopropanes] (**1b**). It turned out that these pyrazolines are most conveniently obtained from diazocyclopropane generated by decomposition of *N*-cyclopropyl-*N*-nitrosourea at 5 to 10 °C in the presence of K_2CO_3 containing water (~20%). The yields of pyrazolines **1a,b** were 70 to 75%. However, in some cases, by-products were obtained as a result of the opening of the cyclopropane ring (*e.g.*, in the synthesis of pyrazoline **1a** with access for air or when keeping pyrazolines **1a,b** in $CDCl_3$ for several hours). The ^1H NMR spectra of these compounds in $CDCl_3$ contain characteristic sets of signals: two triplets at δ 4.1 and 2.9 (J = 6.9 Hz) and a singlet at δ 6.5. Tentatively, these spectra could belong to 4-unsubstituted pyrazoles with an OCH_2CH_2 fragment formed as a result of the opening of the cyclopropane ring.

With the aim of studying possible ways of formation of suggested β-oxyethylpyrazoles and determining their structures, we investigated some chemical transformations of 2-pyrazolines **1a**—**c** and 5-phenylspiro[1-pyrazoline-3,1′-cyclopropane],[3] which can yield, under certain conditions, products with the above characteristic set of signals in their ^1H NMR spectra.

Prolonged (48 h) stirring of pyrazoline **1a** in CH_2Cl_2 in the presence of 10 mol. % LiCl in air gave a compound containing no cyclopropane fragment. The major product isolated with a satisfactory purity by preparative TLC on silica gel was identified as 3-cyano-5-(2-hydroperoxyethyl)pyrazole (**2a**) (~55% yield). This compound is poorly soluble in $CDCl_3$ but well soluble in CD_3OD. Its ^1H NMR spectrum in CD_3OD contains two triplets at δ 4.16 and 3.09 and a broadened low-field singlet at δ 6.69. Note that without access for atmospheric oxygen, LiCl has no noticeable effect on cyanopyrazoline **1a**. Nor did attempts at oxidation of pyrazoline **1a** with such reagents as *m*-chloroperbenzoic acid or lead tetraacetate afford hydroperoxide **2a**.



1a—c **2a—c** **3a—c**

Y = CN (**a**), COOMe (**b**), $COOBu^t$ (**c**)

Later, we found that pyrazoline **1a** can be efficiently oxidized in oxygen-saturated $CHCl_3$ (5 °C, 12 h) to give pure hydroperoxide **2a** in virtually stoichiometric yield. Its ^1H NMR spectrum in $(CD_3)_2SO$ shows, along with the aforementioned two triplets and singlet, distinct separate signals for the NH and OH protons at δ 11.8 and 13.7, respectively. ^{13}C NMR spectroscopy revealed the presence of the pyrazole ring containing two quaternary C atoms and two CH_2 groups. One of them is manifested as a low-field signal (δ_C 75.4) because of its bond to the hydroperoxide fragment. The composition of compound **2a** was also confirmed by MS and elemental analysis data.

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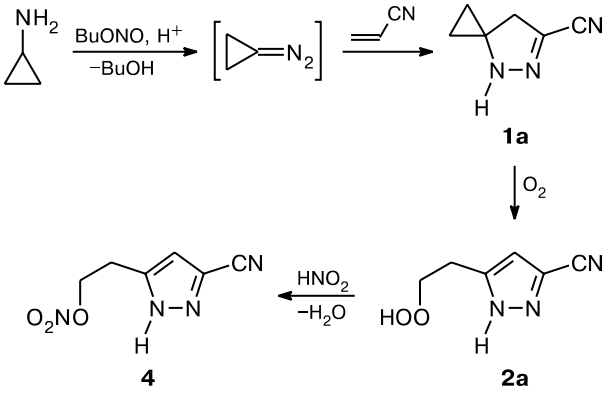
It should be noted that iodometric titration gave an acceptable result (~96%) for a sample refluxed in $CHCl_3$ for 5 min.

The relatively high chemical and thermal stability of (peroxyethyl)pyrazole **2a** (m.p. 56—58 °C, without decomp.) can be associated with intramolecular hydrogen bonding, which prevents its radical decomposition.

Under analogous conditions (oxygen-saturated $CHCl_3$, 5 °C, 12 h), pyrazoline **1b** oxidizes nonselectively to give a mixture of compounds (^{1}H NMR spectrum contains several signals for methoxy groups). According to the integral intensities of the characteristic signals for the 2-hydroperoxyethyl substituent, the yield of hydroperoxide **2b** does not exceed 20%; compound **2b** was not isolated in the individual state. Unlike methoxycarbonylpyrazoline **1b**, its *tert*-butyl analog **1c** was converted under the same conditions into the corresponding hydroperoxide **2c** in up to 85% yield.

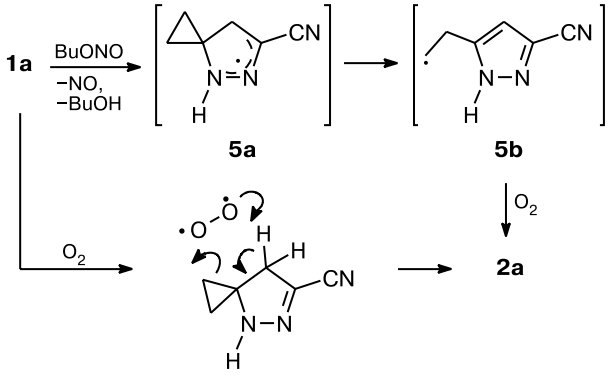
When stored for several days, hydroperoxides **2a,c** slowly decompose, which is evident from a second set of signals in their ^{1}H NMR spectra (in particular, two triplets appear at $\delta \approx 3.8$ and 2.9). As expected, the decomposition products are substituted (2-hydroxyethyl)pyrazoles **3a,c** (^{13}C NMR and MS data). Treatment of hydroperoxide **2a** with $Na_2S_2O_5$ in aqueous methanol for 40 h affords 3-cyano-5-(2-hydroxyethyl)pyrazole (**3a**) in 84% yield.

As noted above, hydroperoxide **2a** can also form during the synthesis of pyrazoline **1a** itself in air. By-product **2a** is obtained not only when diazocyclopropane is generated from *N*-cyclopropyl-*N*-nitrosourea in the presence of K_2CO_3, but also in the direct nitrosation of cyclopropylamine with alkyl nitrites.[4] For instance, when kept in air at 5 °C for 5 days, equimolar amounts of acrylonitrile, cyclopropylamine, and butyl nitrite in the presence of 10 mol. % PhCOOH give a mixture of pyrazoline **1a**, hydroperoxide **2a**, and 2-(3-cyanopyrazol-5-yl)ethyl nitrate (**4**) in a molar ratio of 1 : 6.8 : 2.2, respectively (^{1}H NMR data). Only nitrate **4** was isolated in the pure state (18%) from the final reaction mixture by preparative TLC (SiO_2, hexane—Et_2O, 3 : 1). Under analogous conditions, the direct reaction of butyl nitrite with pyrazoline **1a** in air affords nitrate **4** in 42% yield. Its ^{1}H NMR spectrum, as well as the spectrum of hydroperoxide **2a**, contains two triplets at δ 4.70 and 3.23 and a singlet at δ 6.65; its mass spectrum shows the molecular ion peak with m/z 182.



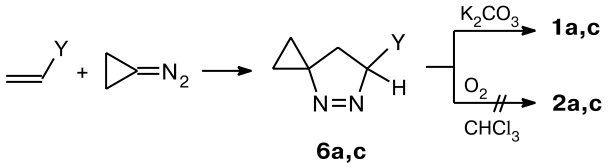
Obviously,[5] nitrate **4** is formed in the reaction of hydroperoxide **2a** (obtained through the oxidation of pyrazoline **1a** with atmospheric oxygen) with alkyl nitrite used to nitrosate cyclopropylamine. Indeed, the same reaction of acrylonitrile, cyclopropylamine, and isoamyl nitrite in the presence of 10 mol. % PhCOOH (see Ref. 4) without access for atmospheric oxygen yields only pyrazoline **1a** and no hydroperoxide **2a** and, accordingly, nitrate **4**.

So far, we cannot unambiguously judge the reaction of cyanopyrazoline **1a** with an oxygen molecule. However, the easy formation of hydroperoxide **2a** in some cases suggests a possible pre-initiation of the pyrazoline molecule and a generation of radical intermediates (*e.g.*, compounds **5a,b**). At the same time, it was experimentally found that hydroperoxide obtained by the oxidation of pyrazoline **1a** with atmospheric oxygen in $CDCl_3$ contains no deuterium. For instance, the ^{1}H NMR spectrum of the product in $(CD_3)_2SO$ after the removal of the chloroform retains the full-proton signals for the NH and OH groups at δ 11.8 and 13.7, which suggests a concerted rather than free-radical mechanism of the formation of hydroperoxides **2**.



It is also worth noting that the formation of hydroperoxides **2** under the aforesaid conditions is characteristic of 2-pyrazolines rather than isomeric 1-pyrazolines **6**, which can be identified under certain conditions, despite the presence of electron-withdrawing substituents and a reactive α-H atom, from the ^{1}H and ^{13}C NMR spectra of the reaction mixtures obtained by addition of *in situ* generated diazocyclopropane to acrylonitrile or *tert*-butyl acrylate. For instance, a reduction in K_2CO_3 from its double excess to an equimolar amount, as well as a reduction in the reaction time from 2.5 to 1.5 h (when *N*-cyclopropyl-*N*-nitrosourea is not yet decomposed completely), gives both 2- (**1a,c**) and 1-pyrazolines **6a,c**. In the case of

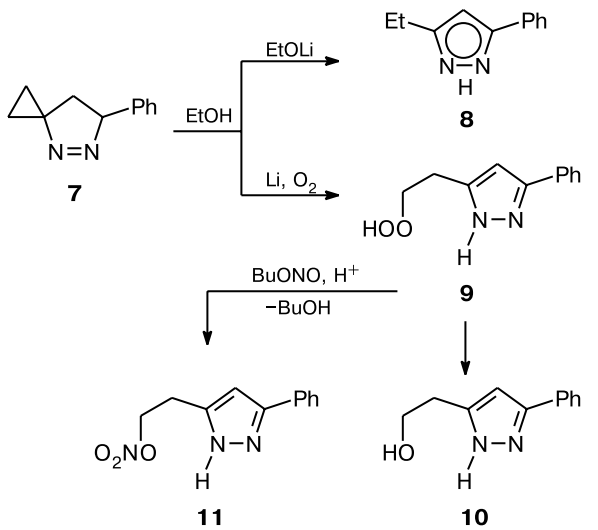
acrylonitrile, 2-pyrazoline **1a** is dominant (isomer ratio ~4 : 1); in contrast, in the reaction of *tert*-butyl acrylate with diazocyclopropane under these conditions, the major product is 1-pyrazoline (ratio between isomers **1c** and **6c** is ~1 : 3; total yield is ~70%). The ^{1}H NMR spectra of 1-pyrazolines **6a,c** show a characteristic ABX system, the X part of which (δ ~5.2, dd) corresponds to the proton of the CH—N=N fragment. In the absence of acids or bases, 1-pyrazolines are rather stable; however, attempts at their isolation by TLC on SiO_2 or neutral Al_2O_3, as well as the treatment of K_2CO_3 in CH_2Cl_2 in an inert atmosphere, causes complete isomerization of 1-pyrazolines **6a,c** into 2-pyrazolines **1a,c**. For instance, in oxygen-saturated solutions of the resulting 1- and 2-pyrazolines in $CHCl_3$ (5 °C, 12 h), 2-pyrazolines **1a,c** are converted into the corresponding hydroperoxides **2a,c**, while 1-pyrazolines **6a,c** remain virtually unchanged (^{1}H NMR data).



6a,c

Y = CN (**a**), COOBu^t (**c**)

Unexpectedly, a structurally analogous hydroperoxide was obtained on attempted reduction of 5-phenylspiro[1-pyrazoline-3,1′-cyclopropane] (**7**) with lithium in EtOH in air. The previously described 5(3)-ethyl-3(5)-phenylpyrazole (**8**)[6] was also identified (~18%) among the reaction products. This compound is formed as a result of base-induced partial isomerization of the starting pyrazoline **7**. A second compound, which is poorly soluble in $CHCl_3$, was isolated in ~60% yield as a colorless finely crystalline powder (m.p. 110—113 °C). According to MS, ^{1}H and ^{13}C NMR, elemental analysis, and iodometric titration data, this compound was assigned the structure



of 5-(2-hydroperoxyethyl)-3-phenylpyrazole (**9**). The ^{1}H NMR spectrum of compound **9** contains two triplets at δ 4.08 and 2.92 (J = 6.9 Hz) and a singlet at δ 6.51, while its ^{13}C NMR spectrum shows signals characteristic of an oxyethyl (δ 79.0 and 29.0), phenyl, and 3,5-disubstituted pyrazole fragments. Of course, the same reaction in an argon atmosphere yields no noticeable amounts of peroxyethylpyrazole **9**.

Hydroperoxide **9** decomposes with time to give a complex mixture of compounds; however, in the presence of KOH (~50 h), the major decomposition product is 5(3)-(2-hydroxyethyl)-3(5)-phenylpyrazole (**10**). Its ^{1}H NMR spectrum also contains two triplets at δ 3.84 and 2.88 and a singlet at δ 6.48. As expected, the triplet signals are slightly shifted upfield compared to those for hydroperoxide **9**.

The reaction of hydroperoxide **9** with butyl nitrite in $CHCl_3$ in the presence of 10 mol. % PhCOOH (5 °C, 40 h) gave, as in the case of hydroperoxide **2a**, the corresponding 2-pyrazolylethyl nitrate **11** in ~80% yield.

In our opinion, the unexpected formation of hydroperoxide **9** from 1-pyrazoline **7** in the reaction in air is difficult to imagine without generation of radical intermediates similar to structures **5a,b**, which seem to be highly reactive toward atmospheric oxygen.

Thus, we discovered the selective formation of (2-hydroxyethyl)pyrazoles in the oxidation of some spiro[pyrazolinecyclopropanes] with molecular oxygen. Their sensitivity to atmospheric oxygen under certain conditions points to a possible generation of radical intermediates responsible for the formation of the corresponding hydroperoxides, which is favored by the opening of the spiro-connected cyclopropane ring.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker AM-300 spectrometers (300 and 75.5 MHz) in $CDCl_3$, CD_3OD, or $(CD_3)_2SO$ with 0.05% Me_4Si as the internal standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet probe). IR spectra were recorded on a Bruker IFS-113v spectrometer in CCl_4. The starting pyrazolines **1a,b** and **7** were prepared according to known procedures.[1–3] *n*-Butyl nitrite (97%, Merck) and *tert*-butyl acrylate (98%, Aldrich) were used without additional purification. Thin-layer chromatography was carried out on Merck silica gel 60 (0.040—0.063 mm).

6-*tert*-Butoxycarbonyl-4,5-diazaspiro[2.4]hept-5-ene (1c) was synthesized as described for pyrazolines **1a,b** [1,2] by the reaction of *N*-cyclopropyl-*N*-nitrosourea[7] (130 mg, 1 mmol) with K_2CO_3 (400 mg, 2.3 mmol) containing water (~20%) and *tert*-butyl acrylate (280 mg, 2.2 mmol) in CH_2Cl_2 at 5 °C. The reaction mixture was stirred for 2 h, filtered through a dense filter, and concentrated *in vacuo* to give pyrazoline **1c** (190 mg, 75%) as a viscous liquid. ^{1}H NMR ($CDCl_3$), δ: 0.80 and 0.88 (both m, 2 H each, CH_2CH_2); 1.55 (s, 9 H, CMe_3); 2.98 (s, 2 H,

CH_2); 5.75 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.0 (CH_2CH_2); 28.2 (3 Me); 38.2 (C(4)); 45.5 (C(5)); 81.7 (C—O); 143.8 (C(3)); 162.2 (C=O). Partial MS, *m/z* (I_{rel} (%)): 196 (15) $[M]^+$, 140 (15), 95 (50) $[M—COOBu^t]^+$, 57 (100) $[Bu^t]^+$.

3(5)-Cyano-5(3)-(2-hydroperoxyethyl)pyrazole (2a). ***A.*** Oxygen was passed at 5 °C for 40 min through a solution of cyanopyrazoline **1a** (0.18 g, 1.5 mmol) in 4 mL of $CHCl_3$ at a rate of no higher than 1 mL min^{-1}. The solution was kept at this temperature for 16 h. The layer of peroxide was separated and washed with 1 mL of $CHCl_3$. The residual solvent was removed *in vacuo*. The yield of compound **2a** was 0.22 g (96%), colorless crystals, m.p. 56—58 °C. Found (%): C, 46.72; H, 4.58; N, 27.22. $C_8H_{12}N_2O_2$. Calculated (%): C, 47.06; H, 4.61; N, 27.44. ^1H NMR (DMSO-d_6), δ: 2.98 (t, 2 H, ^3J = 6.5 Hz); 4.08 (t, 2 H, ^3J = 6.5 Hz); 6.75 (s, 1 H); 11.75 and 13.69 (both br.s, 1 H each, NH and OH). ^1H NMR (CD_3OD), δ: 3.09 (t, 2 H, *J* = 6.6 Hz); 4.16 (t, 2 H, *J* = 6.6 Hz); 6.69 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 24.9 (CH_2); 75.4 (CH_2O); 110.3 (C(4)); 115.3 (CN); 126.2 and 143.6 (C(3) and C(5)). Partial MS, *m/z* (I_{rel} (%)): 153 (15) $[M]^+$, 135 (18) $[M - H_2O]^+$, 106 (100). IR, ν/cm^{-1}: 3500—3150 (OH, NH), 2923 s (CH_2), 2854 m (CH_2), 2243 m (CN), 994 m (OO).

B. Lithium chloride (4 mg, 0.094 mmol) was added at 20 °C to a solution of pyrazoline **1a** (68 mg, 0.56 mmol) in 3 mL of CH_2Cl_2. The reaction mixture was stirred with free access for air for 4 days and concentrated *in vacuo*. Hydroperoxide **2a** (49 mg, 49%) was isolated as colorless crystals from the residue by preparative TLC (SiO_2, benzene—AcOEt, 1 : 1), R_f 0.54. The compound obtained was identical with hydroperoxide **2a** in procedure ***A***.

3(5)-*tert*-Butoxycarbonyl-5(3)-(2-hydroperoxyethyl)pyrazole (2c) was obtained as described for hydroperoxide **2a** (see procedure ***A***) from 6-*tert*-butoxycarbonyl-4,5-diazaspiro[2.4]hept-5-ene (**1c**) (0.29 g, 1.5 mmol). The yield of compound **2c** was 0.29 g (85%). ^1H NMR (DMSO-d_6), δ: 1.48 (s, 9 H, CMe_3); 2.91 (br.t, 2 H, ^3J = 6.5 Hz); 4.09 (t, 2 H, ^3J = 6.5 Hz); 6.50 (s, 1 H); 11.70 and 13.10 (both br.s, 1 H each, NH and OH). ^{13}C NMR (CD_2Cl_2), δ: 24.9 (CH_2); 27.4 ($C\underline{Me}_3$); 74.5 (CH_2O); 81.7 ($\underline{C}Me_3$); 106.4 (C(4)); 140.0 and 146.2 (C(3) and C(5)); 160.0 (C=O).

3(5)-Cyano-5(3)-(2-hydroxyethyl)pyrazole (3a). Sodium pyrosulfite (40 mg, 0.21 mmol) in 4 mL of water was added to a solution of hydroperoxide **2a** (54 mg, 0.35 mmol) in 5 mL of MeOH. The reaction mixture was kept for ~40 h and concentrated. The residue was treated with MeOH and the solution was filtered and concentrated. Alcohol **3a** (40 mg, 84%) was isolated as a low-melting waxy mass from the residue by preparative TLC (SiO_2, benzene—AcOEt, 1.3 : 1), R_f 0.55. ^1H NMR (CD_3OD), δ: 2.94 (t, 2 H, CH_2, *J* = 6.5 Hz); 3.82 (t, 2 H, CH_2O, *J* = 6.5 Hz); 6.67 (s, 1 H). Partial MS, *m/z* (I_{rel} (%)): 137 (36) $[M]^+$, 119 (6) $[M - H_2O]^+$, 107 (100).

3(5)-Cyano-5(3)-(2-nitrooxyethyl)pyrazole (4). ***A.*** Benzoic acid (0.10 g, 0.89 mmol) and then Bu^nONO (0.92 g, 8.9 mmol) were added at 5 °C to a stirred solution of pyrazoline **1a** (0.90 g, 7.4 mmol) in 15 mL of $CHCl_3$. The reaction mixture was stirred at 5 °C for 3 h, filtered through a dense porous filter, and concentrated *in vacuo*. Nitrate **4** (0.55 g, 42%) was isolated from the residue by preparative TLC on silica gel (benzene—AcOEt, 3 : 1), R_f 0.70. IR, ν/cm^{-1}: 3430 (NH); 2252 (CN); 1648, 1280 (NO_2). ^1H NMR ($CDCl_3$), δ: 3.23 (t, 2 H, CH_2, *J* = 6.4 Hz); 4.70 (t, 2 H, CH_2O, *J* = 6.4 Hz); 6.65 (s, 1 H, CH); 12.0 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 23.7 (CH_2); 70.5 (CH_2O); 110.4 (C(4)); 113.7 (CN); 125.1 and 141.0 (C(3) and C(5)). Partial MS, *m/z* (I_{rel} (%)): 182 (10) $[M]^+$, 136 (5) $[M - NO_2]^+$, 119 (8), 106 (100), 76 (25), 46 (55).

B. *n*-Butyl nitrite (36 mg, 0.35 mmol) and then PhCOOH (4.3 mg, 0.035 mmol) and cyclopropylamine (20 mg, 0.35 mmol) were added at 5 °C to a stirred solution of acrylonitrile (19 mg, 0.35 mmol) in 4 mL of $CHCl_3$. The reaction mixture was kept at 5 °C for 5 days. The final mixture contained pyrazoline **1a**, hydroperoxide **2a**, and nitrate **4** in a molar ratio of 1 : 6.8 : 2.2 (^1H NMR data). The solvent was removed *in vacuo* and nitrate **4** (11.5 mg, 18%) was isolated from the residue by TLC.

5(3)-(2-Hydroperoxyethyl)-3(5)-phenylpyrazole (9). Lithium metal (56 mg, 8.0 mmol) was added in two portions to a solution of pyrazoline **7** (0.95 g, 5.5 mmol) in 10 mL of EtOH with free access for air. Thirty minutes after the metal was dissolved, the solution was diluted with water (20 mL) and organic material was extracted with CH_2Cl_2 (35 mL). The organic layer was separated, dried with anhydrous Na_2SO_4 and concentrated *in vacuo* to give a compound (0.17 g, 18%) identical with 5(3)-ethyl-3(5)-phenylpyrazole (**8**) [6] (^1H and ^{13}C NMR data). The aqueous layer was acidified with 3% HCl (~15 mL) to pH 2 and organic material was extracted with CH_2Cl_2. The extract was dried with anhydrous Na_2SO_4 and concentrated *in vacuo* to give hydroperoxide **9** (0.67 g, 60%) as colorless crystals, m.p. 110—113 °C. Found (%): C, 64.15; H, 5.58; N, 13.27. $C_8H_{12}N_2O_2$. Calculated (%): C, 64.69; H, 5.92; N, 13.72. ^1H NMR (DMSO-d_6), δ: 2.92 (t, 2 H, CH_2, *J* = 6.9 Hz); 4.08 (t, 2 H, CH_2O, *J* = 6.9 Hz); 6.51 (s, 1 H, H(4)); 7.38 and 7.71 (both m, 3+2 H, Ph); 11.71 (s, OOH); 12.62 (br.s, NH). ^{13}C NMR (DMSO-d_6), δ: 29.0 (CH_2); 79.00 (CH_2O); 105.2 (C(4)); 129.1, 131.5, 132.3 (Ph); 136.1 and 149.6 (C(3) and C(5)). Partial MS, *m/z* (I_{rel} (%)): 204 (16) $[M]^+$, 186 (19) $[M - H_2O]^+$, 157 (100). IR, ν/cm^{-1}: 3256 (OH), 2935 s (CH_2), 2764 m (CH_2), 968 m (OO).

5(3)-(2-Hydroxyethyl)-3(5)-phenylpyrazole (10). A solution of KOH (28 mg, 0.5 mmol) in 0.3 mL of water was added to a solution of hydroperoxide **2d** (98 mg, 0.48 mmol) in 3 mL of EtOH. The reaction mixture was stirred at 20 °C for 50 h and then neutralized with 3% HCl and concentrated to a half volume *in vacuo*. The product was extracted with CH_2Cl_2. The organic layer was dried with anhydrous Na_2SO_4 and concentrated. (Hydroxyethyl)pyrazole **10** (57 mg, 63%) as colorless crystals was isolated from the residue by TLC on silica gel (benzene—AcOEt, 4 : 1), m.p. 158—160 °C, R_f 0.65. Found (%): C, 70.58; H, 6.18; N, 15.06. $C_{11}H_{12}N_2O$. Calculated (%): C, 70.19; H, 6.43; N, 14.88. ^1H NMR (DMSO-d_6), δ: 2.81 (t, 2 H, CH_2, *J* = 6.7 Hz); 3.69 (t, 2 H, CH_2O, *J* = 6.7 Hz); 4.82 (br.s, OH); 6.51 (s, 1 H, H(4)); 7.32 and 7.76 (both m, 2+3 H, Ph); 12.62 (br.s, NH). ^{13}C NMR (DMSO-d_6), δ: 28.7 (CH_2); 60.0 (CH_2O); 100.3 (C(4)); 124.5, 126.7, 128.1 and 133.7 (Ph), 141.5 and 149.8 (C(3) and C(5)). Partial MS, *m/z* (I_{rel} (%)): 188 (88) $[M]^+$, 171 (25) $[M - H_2O]^+$, 158 (100).

5(3)-(2-Nitrooxyethyl)-3(5)-phenylpyrazole (11). A solution of Bu^nONO (10 mg, 0.1 mmol) in 0.1 mL of $CHCl_3$ was added to a suspension of hydroperoxide **9** (20 mg, 0.1 mmol) in 0.5 mL of $CHCl_3$. The reaction mixture was stirred at 5 °C for 40 h and then concentrated *in vacuo*. Nitrate **11** (18 mg, 80%) was isolated from the residue by TLC on silica gel (benzene—AcOEt, 3 : 1), R_f 0.62. ^1H NMR ($CDCl_3$), δ: 3.05 (t, 2 H, CH_2, *J* = 6.2 Hz); 4.65 (t, 2 H, CH_2O, *J* = 6.2 Hz); 6.42 (s, 1 H, H(4)); 7.35 and 7.65 (both m, 2+3 H, Ph); 9.18 (br.s, 1 H, NH).

^{13}C NMR ($CDCl_3$), δ: 25.1 (CH_2); 71.5 (OCH_2); 102.5 (C(4)); 125.8 (*o*-Ph); 128.3 (*p*-Ph); 128.8 (*m*-Ph); 130.1 (*i*-Ph); 145.4 and 147.6 (C(3) and C(5)). Partial MS, *m*/*z* (I_{rel} (%)): 233 $[M]^+$ (19), 157 $[M - CH_2ONO_2]^+$ (100).

Spectroscopic detection of 1-pyrazolines 6a,c (general procedure). *N*-Cyclopropyl-*N*-nitrosourea (64 mg, 0.5 mmol) and K_2CO_3 (69 mg, 0.4 mmol) containing water (~20%) were added at 5 °C in an argon atmosphere to a solution of acrylonitrile or *tert*-butyl acrylate (1 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred at 5 °C for 1.5 h and filtered. The filtrate was concentrated, and C_6H_6 (2 mL) was added. The unreacted *N*-cyclopropyl-*N*-nitrosourea was filtered off. The filtrate was concentrated to give a residue (45—55 mg) containing compounds **1a** and **6a** (molar ratio ~4 : 1) or compounds **1c** and **6c** (ratio ~1 : 3) in a total yield of ~70% (^{1}H NMR data).

6-Cyano-4,5-diazaspiro[2.4]hept-4-ene (6a). ^{1}H NMR ($CDCl_3$), δ: 1.27 (m, 2 H, H(1) and H(2), directed from the N atom of the heterocycle); 1.82—1.95 (m, 2 H, H(1) and H(2), directed toward the N atom of the heterocycle); 2.11 (dd, 1 H, H_a(7), ^2J = 12.6 Hz, ^3J = 8.0 Hz); 2.21 (dd, 1 H, H_b(7), ^2J = 12.6 Hz, ^3J = 10.5 Hz); 5.22 (dd, 1 H, H(6), ^3J = 10.5 Hz, ^3J = 8.0 Hz).

6-*tert*-Butoxycarbonyl-4,5-diazaspiro[2.4]hept-5-ene (6c). ^{1}H NMR (CD_2Cl_2), δ: 1.15 (m, 2 H, H(1) and H(2), directed from the N atom of the heterocycle); 1,48 (s, 9 H, CMe_3); 1.63—1.81 (m, 2 H, H(1) and H(2), directed toward the N atom of the heterocycle); 1.89 (dd, 1 H, H_a(7), ^2J = 12.5 Hz, ^3J = 7.8 Hz); 2.02 (dd, 1 H, H_b(7), ^2J = 12.5 Hz, ^3J = 10.3 Hz); 5.18 (dd, 1 H, H(6), ^3J = 10.3 Hz, ^3J = 7.8 Hz). ^{13}C NMR (CD_2Cl_2), δ: 13.6 and 13.8 (CH_2CH_2); 26.9 (C(7)); 37.3 ($\underline{Me}_3C$); 69.8 (C(3)); 81.7 ($Me_3\underline{C}$); 89.5 (C(6)); 167.4 (C=O).

Isomerization of 1-pyrazoline 6c into 2-pyrazoline 1c. Potassium carbonate (17 mg, 0.1 mmol) containing water (~20%) was added at 5 °C in an argon atmosphere to a solution of the above mixture of pyrazolines **1c** and **6c** ((20 mg, 0.1 mmol, ratio 1 : 3) in 0.5 mL of CH_2Cl_2. The reaction mixture was stirred for 4 h, filtered, and concentrated to give pure pyrazoline **1c** (^{1}H NMR data).

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