Transformations of 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one under various conditions of cyclopropyldiazonium generation

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Cyclopropyldiazonium generated by basic decomposition of *N*-cyclopropyl-*N*-nitrosourea easily entered into an azo coupling reaction with 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2**) to give the corresponding cyclopropylhydrazone in up to 90% yield. Competitive processes occurring under the conditions of cyclopropyldiazonium generation by nitrosation of cyclopropylamine with butyl nitrite mainly include nitrosation of the starting pyrazolone **2**. Subsequent transformations of the resulting heterocyclic 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dione 4-oxime yield 4-[cyclopropyl(oxido)imino]-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one.

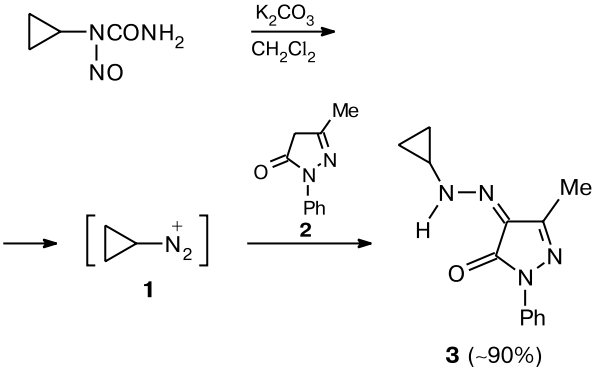
Key words: cyclopropyldiazonium, cyclopropylhydrazone, *N*-cyclopropylnitrone, spiro[isoxazolidine-3,4′-pyrazoline], azo coupling, nitrosation, 1,3-dipolar addition.

It is known[1,2] that diazotization of aliphatic amines gives extremely unstable diazonium ions, which are easily converted, through the loss of nitrogen, into carbocations and products of their subsequent transformations. Nevertheless, some alkyldiazonium ions can enter into azo coupling reactions, which successfully compete with dediazotization processes.[3] In particular, azo coupling is possible for the cyclopropyldiazonium ion (**1**) generated by basic hydrolysis of *N*-cyclopropyl-*N*-nitrosourea or by direct nitrosation of cyclopropylamine with alkyl nitrites. For instance, scavenging of diazonium **1** by reactive aromatic compounds (*e.g.*, hydroxy derivatives of naphthalene) gives cyclopropylazoarenes[4,5] and that by aliphatic CH acids (compounds with an active methylene group) yields the corresponding cyclopropylhydrazones.[6]

Here we extensively studied transformations of 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2**) under conditions of cyclopropyldiazonium generation by both basic hydrolysis of *N*-cyclopropyl-*N*-nitrosourea and nitrosation of cyclopropylamine with butyl nitrite. The reaction outcomes were found to be largely dependent on the way of generation of diazonium **1** and, first of all, on the presence or the absence of a nitrosating reagent in the reaction mixture.

For instance, when cyclopropyldiazonium **1** was generated by decomposition of *N*-cyclopropyl-*N*-nitrosourea with solid K_2CO_3 containing ~20% H_2O at 5—7 °C in the presence of pyrazolone **2**, the major reaction was azo coupling leading to low-melting crystalline 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dione 4-cyclopropylhydrazone **3** in ~90% yield (Scheme 1). This process is analogous to azo coupling of arenediazonium salts with pyrazolone **2**, in which the initially formed azo compound isomerizes into 1*H*-pyrazole-4,5-dione monohydrazone.[7]

Scheme 1



The ^{1}H NMR spectrum of compound **3** in $CDCl_3$ shows a signal for the methine proton of the cyclopropyl substituent at δ 3.20, which agrees with data for the earlier obtained cyclopropylhydrazones.[4,5] The signal of the NH proton is shifted downfield (δ 12.2) because of intramolecular hydrogen bonding to the carbonyl O atom.

When diazonium **1** was generated by nitrosation of cyclopropylamine with butyl nitrite in $CHCl_3$ at 5 °C in the presence of pyrazolone **2**, the yield of the expected cyclopropylhydrazone **3** was only 11—12%. After removal of the solvent and the resulting butanol *in vacuo* (1—2 Torr) and treatment of the residue with benzene, we

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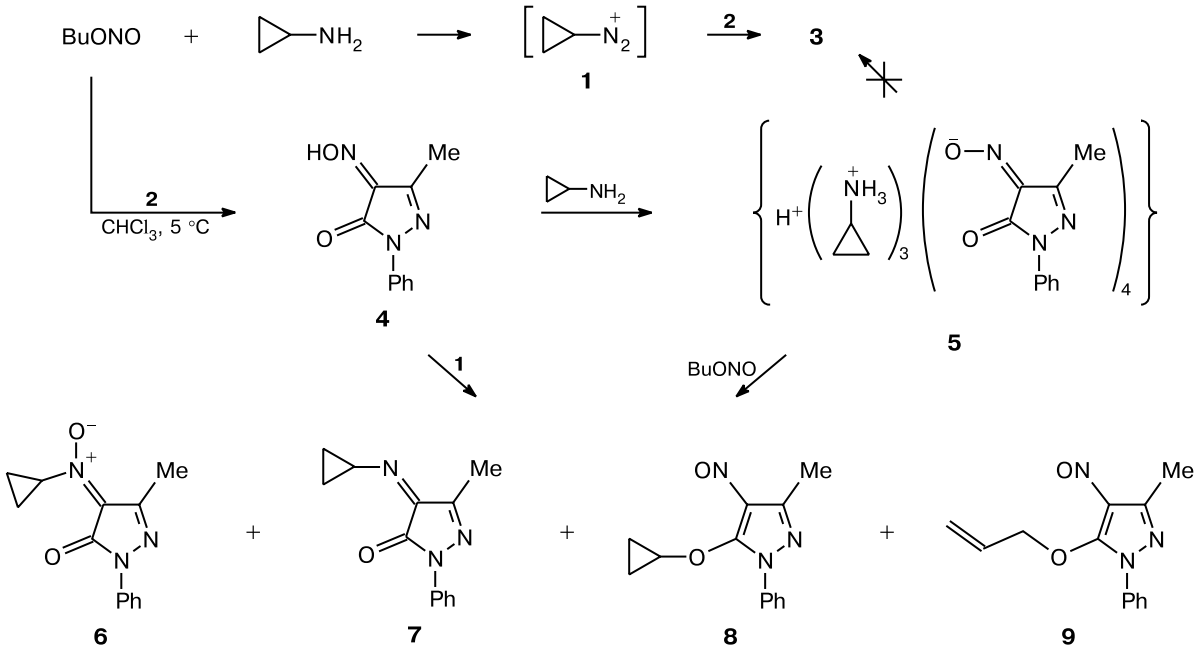
Scheme 2



isolated a finely crystalline yellow powder. According to elemental analysis data and ^{1}H and ^{13}C NMR spectra, this product was a complex salt of oxime **4** with cyclopropylamine in the ratio 4 : 3 (product **5**, ~35% yield) (Scheme 2).

Using column chromatography on SiO_2, we isolated from the benzene solution and identified some other compounds: cyclopropylnitrone **6** (11.5% yield), dihydro-3*H*-pyrazol-3-one **7** (4.5%), and 5-cyclopropyloxy- (**8**) and 5-allyloxy-3-methyl-4-nitroso-1-phenyl-1*H*-pyrazole (**9**) (6.5 and 4%, respectively).

The low yield of hydrazone **3** and the nonselectivity of the reaction are due to nitrosation of the starting pyrazolone **2** with butyl nitrite (which we confirmed experimentally) and subsequent transformations of the corresponding 4-nitroso-2,4-dihydro-3*H*-pyrazol-3-one, which exists in solution mainly as *E*- and *Z*-oximes **4** (see Ref. 8). For instance, when diazonium **1** generated by nitrosation of cyclopropylamine is scavenged by naphthols, azo coupling successfully competes with nitrosation of naphthols themselves,[9] and when 8-hydroxyquinoline is used, no nitroso derivative is detected at all.[6] In contrast, pyrazolone **2** is readily nitrosated by butyl nitrite. Indeed, a reaction of cyclopropylamine with preliminarily prepared sample of isomeric oximes **4** [10] gave the same associate **5** as in the aforementioned reactions in ~60% yield.

It should be noted that the compound obtained is stable, decomposing only above 138 °C. The ratio of the integral intensities of the signals for the protons of the heterocyclic and cyclopropane fragments in the ^{1}H NMR spectra of different samples is 4 : 3; the signal for the methyl group appears as two singlets, which indicates the presence of the *E*- and *Z*-isomers of the oximes. The ^{13}C NMR spectrum of associate **5** also shows the double set of signals for all the C atoms of the methyl-2,4-dihydro-3*H*-pyrazol-3-one fragment (see Experimental). On acidification of associate **5** with an equivalent amount of HCl, an exchange reaction occurred and free *E*- and *Z*-oximes **4** were detected in the organic phase (^{1}H NMR data).

The action of BuONO on associate **5** in $CHCl_3$ at 5 °C gave rise to a mixture of nitrone **6**, imine **7**, and ethers **8** and **9** (see Scheme 2) in a total yield of 82%. The ratio of the products was comparable with that in the reaction between pyrazolone **2**, cyclopropylamine, and butyl nitrite (see Experimental). Therefore, the formation of compounds **6**—**9** results from the action of BuONO on associate **5**; in this case, the generation of cyclopropyldiazonium **1** is also possible, because the formation of nitrone **6** and ethers **8** and **9** is most likely due to its dediazotization and alkylation of the anion in complex salt **5**. Note that the formation of *O*-allyl derivative **9** is quite characteristic of processes involving cyclopropyldiazonium.[11] Apparently, the formation of imine **7** in the reaction mixture is preceded by the formation of 1*H*-pyrazole-4,5-dione **10**; however, we did not investigate a particular way of its formation.

Column chromatography on SiO_2 gave hydrazone **3**, nitrone **6**, and imine **7** in the individual state and compounds **8** and **9** as a mixture of the isomers in the ratio 1.6 : 1 (^{1}H NMR data).

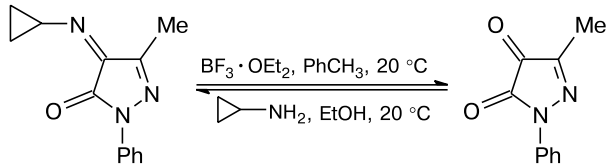
The structures of nitrone **6** and imine **7** were proved by elemental analysis, NMR spectroscopy, mass spectrometry, and chemical transformations.

In the ^{1}H and ^{13}C NMR spectra of compounds **6** and **7**, the signals for the methine fragment of the cyclopropyl substituent are shifted downfield (δ 6.19 and 5.30 (^{1}H) and 44.07 and 38.03 (^{13}C), respectively); this is due to the deshielding effect of the C=N bond, especially pronounced for nitrone **6**. It should be noted that the ^{14}N NMR spectrum of nitrone **6** (δ −51.3; $\Delta\nu_{1/2}$ = 217 Hz) agrees with the literature data for nitrones.[12]

We carried out reactions typical of compounds of these two classes. It is known[13] that 4-(arylimino)-2,4-dihydro-3*H*-pyrazol-3-ones easily undergo acid hydrolysis to give 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dione (**10**). The latter reacts with arylamine in EtOH to produce the corresponding imine.

Analogously, under the action of $BF_3 \cdot Et_2O$, compound **7** was converted into 1*H*-pyrazole-4,5-dione **10**, which was identical with a product reported earlier[13] (Scheme 3). Addition of cyclopropylamine to compound **10** in EtOH at 20 °C gave imine **7** in 90% yield; its spectroscopic and physicochemical characteristics match the product described above.

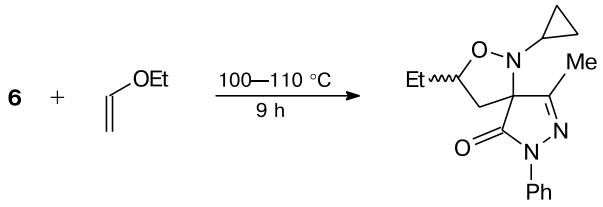
Scheme 3



7 **10**

Reactions with alkenes are characteristic transformations of nitrones.[14] In particular, 5-methyl-2-phenyl-4-[phenyl(oxido)imino]-2,4-dihydro-3*H*-pyrazol-3-one (**11**), which is similar to cyclopropylnitrone **6**, reacts regio- and stereoselectively with ethyl vinyl ether (20 °C, 48 h) to give 1,3-dipolar cycloadduct, namely, the corresponding ethoxyisoxazolidine derivative.[15] However, in contrast to phenylnitrone **11**, cyclopropylnitrone **6** was less reactive and its reaction with ethyl vinyl ether was successfully completed only on heating in a sealed tube (100—110 °C, 9 h) with a 50-fold excess of the unsaturated compound (Scheme 4). In this case, the reaction was also highly regioselective (the yield of spiroisoxazolidine **12** was high) but noticeably less stereoselective (the ratio of the isomers was ~4 : 1). The stereoisomers were separated off by preparative TLC on SiO_2. The ^{1}H NMR spectrum of the major isomer is in best agreement with the spectroscopic data for the adduct of phenylnitrone **11** with ethyl vinyl ether,[15] which suggests that their spatial structures are close.

Scheme 4



12 (~4 : 1)

The results obtained show that pyrazolone (**2**) is a good scavenger for the cyclopropyldiazonium ion generated by basic decomposition of *N*-cyclopropyl-*N*-nitrosourea, producing the corresponding cyclopropylhydrazone **3** in up to 90% yield. However, under the conditions of nitrosation of cyclopropylamine with butyl nitrite, several competitive processes occur. The main parallel process is nitrosation of the starting pyrazolone **2** followed by transformations of the resulting heterocyclic oxime **4**. It is worth noting that one of the reaction products is nitrone **6** with the cyclopropyl substituent at the electron-deficient N atom. Its regioselective 1,3-dipolar addition to ethyl vinyl ether gives the corresponding spiro[isoxazolidine-3,4′-pyrazoline] in high yield.

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 $CDCl_3$, $(CD_3)_2SO$, or THF-d_8 containing 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 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2**) was used as purchased. 3-Methyl-1-phenyl-1*H*-pyrazole-4,5-dione 4-oxime (**4**) was prepared according to a known procedure.[13] Butyl nitrite was distilled before use. Chromatography was carried out on silica gel 60 (0.040—0.063 mm, Merck).

3-Methyl-1-phenyl-1*H*-pyrazole-4,5-dione 4-cyclopropylhydrazone (3). Potassium carbonate (1.65 g) containing ~20 wt.% H_2O was added at 5—7 °C to a solution of pyrazolone **2** (0.58 g, 3.3 mmol) and *N*-cyclopropyl-*N*-nitrosourea (0.62 g, 4.8 mmol) in CH_2Cl_2 (12 mL) and methanol (0.2 mL). The reaction mixture was vigorously stirred at this temperature for 3 h and filtered. The solvent was removed *in vacuo* and the residue was crystallized from hexane at −15 °C. The yield of hydrazone **3** was 0.72 g (90%), yellow crystals, m.p. 44—46 °C. Found (%): C, 64.68; H, 6.00; N, 22.92. $C_{13}H_{14}N_4O$. Calculated (%): C, 64.45; H, 5.82; N, 23.13. ^{1}H NMR ($CDCl_3$), δ: 0.98 (m, 4 H, CH_2CH_2); 2.29 (s, 3 H, Me); 3.20 (ddt, 1 H, CH, $J_{cis} \approx 11.0$ Hz and 7.1 Hz, $J_{trans} \approx 4.0$ Hz); 7.18, 7.41, 7.92 (m, 1 H + 2 H + 2 H, Ph); 12.16 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 6.7 (CH_2CH_2); 11.8 (Me); 33.6 (CH); 118.5 (C(2′)); 124.8 (C(4′)); 127.0 (C(5)); 128.8 (C(3′)); 138.3 (C(1′)); 148.2 (C(4)); 157.9 (C(3)). Partial MS, *m/z* (I_{rel} (%)): 242 $[M]^+$ (100), 213 (8), 172 (5), 77 (68).

Reaction between pyrazolone 2, cyclopropylamine, and butyl nitrite. Cyclopropylamine (0.22 g, 3.7 mmol) and *n*-butyl nitrite (0.38 g, 3.7 mmol) were added at 5 °C to a stirred solution of pyrazolone **2** (0.44 g, 2.5 mmol) in $CHCl_3$ (40 mL). The reaction mixture was stirred at 5 °C for 3 h and concentrated. Butanol was removed *in vacuo*. The residue was diluted with benzene (10 mL) and the precipitate that formed was filtered off. The yield of product **5** was 0.22 g (~35%), yellow crystals, decomp. at ~138 °C (from MeCN). Its composition matches a 4 : 3 associate of 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dione 4-oxime (**4**) with cyclopropylamine. Found (%): C, 59.53; H, 6.28; N, 21.05. $C_{49}H_{57}N_{15}O_8$. Calculated (%): C, 59.81; H, 5.84; N, 21.35. ^{1}H NMR ($(CD_3)_2SO$), δ: 0.67 (m, 4 H, CH_2CH_2); 2.19, 2.40 (both s, 1.5 H + 2.5 H, Me); 2.56 (m, 1 H, CH); 7.0 (br.s, 3.3 H, NH_2 + OH); 7.08, 7.34, 7.93 (all m, 1.3 H + 2.6 H + 2.6 H, Ph). ^{13}C NMR ($(CD_3)_2SO$), δ: 3.11 (CH_2CH_2); 12.39, 16.26 (~1 : 1.6, Me of two isomers); 21.90 (CH); 117.02, 117.34 (~1.6 : 1, C_o of two isomers); 122.73, 122.84 (~1.6 : 1, C_p of two isomers); 127.99, 128.06 (~1 : 1.6, C_m of two isomers); 137.22, 149.75 (~1.6 : 1, C(3) of two isomers); 138.84, 139.03 (~1 : 1.6, C_{ipso} of two isomers); 148.38, 149.11 (~1.6 : 1, C(4) of two isomers); 149.05, 163.57 (~1 : 1.6, C(5) of two isomers).

The filtrate was concentrated and chromatographed on SiO_2 with benzene—light petroleum (1 : 1) as an eluent. Four fractions were collected.

Fraction 1: **4-(cyclopropylimino)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one** (**7**). The yield was 25.5 mg (4.5%), yellow crystals, m.p. 118—119 °C. Found (%): C, 68.97; H, 5.76; N, 18.40. $C_{13}H_{13}N_3O$. Calculated (%): C, 68.72; H, 5.73; N, 18.50. ^{1}H NMR ($CDCl_3$), δ: 1.32, 1.48 (both m, 2 H each, CH_2CH_2); 2.20 (s, 3 H, Me); 5.30 (m, 1 H, CH); 7.20, 7.42, 7.90 (all m, 1 H + 2 H + 2 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 11.97 (Me); 16.09 (CH_2CH_2); 38.03 (CH); 118.55 (C_o); 125.36 (C_p); 128.95 (C_m); 137.82 (C_{ipso}); 150.08 (C(5)); 153.42 (C(4)); 154.00 (C(3)). Partial MS, *m/z* (I_{rel} (%)): 227 $[M]^+$ (80), 199 (18), 129 (35), 103 (78), 91 (80), 77 (100).

Fraction 2: **4-[cyclopropyl(oxido)imino]-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one** (**6**). The yield was 69.8 mg (11.5%), red crystals, m.p. 148—149 °C. Found (%): C, 63.85; H, 5.29; N, 17.33. $C_{13}H_{13}N_3O_2$. Calculated (%): C, 64.20; H, 5.35; N, 17.28. ^{1}H NMR ($CDCl_3$), δ: 1.19, 1.60 (both m, 2 H each, CH_2CH_2); 2.43 (s, 3 H, Me); 6.19 (m, 1 H, CH); 7.20, 7.42, 7.90 (all m, 1 H + 2 H + 2 H, Ph). ^{13}C NMR (THF-d_8), δ: 10.52 (CH_2CH_2); 16.88 (Me); 44.07 (CH); 118.83 (C_o); 125.13 (C_p); 129.05 (C_m); 136.41 (C_{ipso}); 139.20, 144.80 (C(5), C(4)); 157.65 (C(3)). ^{14}N NMR (21.69 MHz, $CDCl_3$), δ (*vs.* $MeNO_2$): −51.25 ($\Delta\nu_{1/2}$ = 217 Hz). Partial MS, *m/z* (I_{rel} (%)): 243 $[M]^+$ (25), 159 (20), 119 (45), 103 (18), 91 (70), 77 (100).

Fraction 3: compound **3** (65 mg, 11%) was identical with that obtained in the preceding experiment.

Fraction 4: a mixture of **5-cyclopropyloxy-** (**8**) and **5-allyloxy-3-methyl-4-nitroso-1-phenyl-4,5-dihydro-1*H*-pyrazoles** (**9**) in the ratio 1.6 : 1. The yield was 63.7 mg (10.5%). Compound **8**. ^{1}H NMR ($CDCl_3$), δ: 0.85, 1.05 (both m, CH_2CH_2); 2.28 (s, Me); 4.50 (m, OCH); 7.18, 7.38, 7.90 (all m, Ph). ^{13}C NMR ($CDCl_3$), δ: 6.10 (CH_2CH_2); 12.65 (Me); 61.29 (OCH); 118.49 (C_o); 125.32 (C_p); 128.89 (C_m); 137.62 (C_{ipso}); 144.71 (C(4)); 147.49 (C(3)); 151.76 (C(5)). Compound **9**. ^{1}H NMR ($CDCl_3$), δ: 2.27 (s, Me); 5.00 (br.t, OCH_2, ^3J = 6.2 Hz, ^4J = 1.2 Hz); 5.36, 5.45 (both ddt, $=CH_2$, $^3J_{cis}$ = 10.5 Hz, $^3J_{trans}$ = 17.0 Hz, ^4J = 1.2 Hz); 6.08 (ddt, =CH, ^3J = 6.2 Hz, $^3J_{cis}$ = 10.5 Hz, $^3J_{trans}$ = 17.0 Hz); 7.18, 7.38, 7.90 (all m, Ph). ^{13}C NMR ($CDCl_3$), δ: 12.59 (Me); 79.72 (OCH_2); 118.49 (C_o); 120.22 ($=CH_2$); 125.32 (C_p); 128.89 (C_m); 131.98 (=CH); 137.63 (C_{ipso}); 144.33 (C(4)); 147.48 (C(3)); 151.55 (C(5)).

Reaction of oxime 4 with cyclopropylamine. A mixture of 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dione 4-oxime (**4**) (2.02 g, 10 mmol) and cyclopropylamine (0.69 g, 12 mmol) in MeOH (30 mL) was stirred at 5 °C for 3 h. The nonconsumed oxime **4** (~0.18 g) was filtered off and the filtrate was concentrated and diluted with benzene (~20 mL). The precipitate that formed was filtered off and dried *in vacuo*. The yield of associate **5** was 1.53 g (~60%). According to ^{1}H and ^{13}C NMR data, associate **5** was identical with the product obtained in the preceding experiment. To a vigorously stirred suspension of complex **5** (45 mg; the theoretical content of cyclopropylamine ~0.14 mmol) in CH_2Cl_2 (2 mL), 1 *M* HCl (0.14 mL) was added at 5 °C. The reaction mixture was stirred for 30 min and diluted with water (1 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated. The solid residue (35 mg) was a ~1 : 1.5 mixture of *E*- and *Z*-oximes **4** (for the ^{13}C NMR spectra, see Ref. 8).

Reaction of associate 5 with butyl nitrite. Butyl nitrite (0.54 g, 5.2 mmol) was added at 3 °C to vigorously stirred compound **5** (1.27 g, 3.9 mmol with respect to cyclopropylamine) in $CHCl_3$ (45 mL). The reaction mixture was stirred for 3 h (gas evolution was observed during the reaction), left for ~14 h, and concentrated *in vacuo*. The solid residue was separated by column chromatography on SiO_2 eluted with benzene—light petroleum (1 : 1) as described above to give imine **7** (158 mg, 14%), nitrone **6** (473 mg, 41%), and a 1.6 : 1 mixture of ethers **8** and **9** (316 mg, 27%).

3-Methyl-1-phenyl-1*H*-pyrazole-4,5-dione (10). To a solution of imine **7** (100 mg, 0.44 mmol) in toluene (4 mL), $BF_3 \cdot Et_2O$ (0.1 mL) was added and the reaction mixture was stirred at 20 °C for 24 h until the starting imine was completely consumed (^{1}H NMR data). The solvent was removed *in vacuo*. Pyrazoledione **10** (30 mg, 36%) was isolated by preparative TLC (SiO_2, benzene—ether (1 : 1)) as red crystals, m.p. 117—118 °C (*cf.* Ref. 13: m.p. 118 °C). The product (30 mg, 0.16 mmol) was dissolved in EtOH (8 mL) and kept with cyclopropylamine (20 mg, 0.35 mmol) at 20 °C for 4 h. Concentration gave a solid residue (30 mg) containing imine **7** (~90%) (MS and ^{1}H NMR data).

1-Cyclopropyl-3-ethoxy-6-methyl-8-phenyl-2-oxa-1,7,8-triazaspiro[4,4]non-6-en-9-one (12). A mixture of nitrone **6** (29 mg, 0.12 mmol) and ethyl vinyl ether (430 mg, 6 mmol) was heated in a sealed tube at 100—110 °C for 9 h. The excess of ethyl vinyl ether was removed. According to ^{1}H NMR data, the residue (36 mg) was a ~4 : 1 mixture of isomeric spiro[isoxazolidine-3,4′-pyrazolines] **12**. The isomers were separated off by preparative TLC (SiO_2, benzene—ether (5 : 1)). The yields of compounds **12a** and **12b** were 27 mg (72%) and 7 mg (19%), respectively. Compound **12a**. IR, ν/cm^{-1}: 1716 (C=O). ^{1}H NMR ($CDCl_3$), δ: 0.42, 0.66 (both m, 2 H each, CH_2CH_2); 1.21 (t, 3 H, Me, ^3J = 7.0 Hz); 2.21 (s, 3 H, Me); 2.44 (dd, 1 H, H_a(4), ^2J = 13.5 Hz, ^3J = 1.5 Hz); 2.74 (m, 1 H, CH in *cyclo*-C_3H_5); 2.82 (dd, 1 H, H_b(4), ^2J = 13.5 Hz, ^3J = 5.5 Hz); 3.52, 3.81 (both dq, 1 H each, OCH_2, ^2J = 10.1 Hz, ^3J = 7.0 Hz); 5.38 (dd, 1 H, H(3), ^3J = 5.5 Hz, ^3J = 1.5 Hz); 7.20, 7.41, 7.88 (all m,

1 H + 2 H + 2 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 4.65, 6.66 (CH_2CH_2); 13.65 (Me at C(6)); 15.20 (Me); 32.66 (CH in *cyclo*-C_3H_5); 45.02 (C(4)); 63.30 (OCH_2); 74.67 (C(5)); 100.56 (C(3)); 118.70 (C_o); 125.19 (C_p); 128.95 (C_m); 137.91 (C_{ipso}); 160.48 (C(6)); 171.34 (C(9)). Partial MS, m/z (I_{rel} (%)): 315 $[M]^+$ (13), 244 (15), 215 (35), 201 (13), 187 (55), 91 (25), 77 (100). Compound **12b**. ^{1}H NMR ($CDCl_3$), δ: 0.57, 0.88 (both m, 2 H each, CH_2CH_2); 1.27 (t, 3 H, Me, ^3J = 7.0 Hz); 2.21 (s, 3 H, Me); 2.58 (m, 1 H, CH in *cyclo*-C_3H_5); 2.68 (dd, 1 H, H_a(4), ^2J = 13.5 Hz, ^3J = 6.0 Hz); 2.75 (dd, 1 H, H_b(4), ^2J = 13.5 Hz, ^3J = 2.9 Hz); 3.53, 3.88 (both dq, 1 H each, OCH_2, ^2J = 10.0 Hz, ^3J = 7.0 Hz); 5.30 (dd, 1 H, H(3), ^3J = 6.0 Hz, ^3J = 2.9 Hz); 7.20, 7.41, 7.88 (all m, 1 H + 2 H + 2 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 5.75, 6.79 (CH_2CH_2); 15.13, 15.74 (both Me); 33.02 (CH in *cyclo*-C_3H_5); 44.65 (C(4)); 64.48 (OCH_2); 75.73 (C(5)); 101.62 (C(3)); 118.84 (C_o); 125.30 (C_p); 129.00 (C_m); 137.94 (C_{ipso}); 160.95 (C(6)); 168.63 (C(9)). Partial MS, m/z (I_{rel} (%)): 315 $[M]^+$ (3), 244 (5), 215 (12), 201 (3); 187 (16), 119 (5), 84 (100).

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