Generation of diazo-2-methylenecyclopropane and its 1,3-dipolar cycloaddition to acrylates

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N-(2-Methylenecyclopropyl)-*N*-nitrosourea (**2**) was synthesized for the first time (yield 70%) and its decomposition induced by bases was studied. In particular, treatment with MeONa/MeOH at −30 °C in the presence of methyl methacrylate gives the corresponding 1-pyrazoline stereoisomers, the products of [3+2]-cycloaddition of diazo-2-methylenecyclopropane (**1**) generated *in situ*. Decomposition of **2** on treatment with K_2CO_3 at 0—5 °C in the presence of acrylonitrile also proceeds as [3+2]-cycloaddition; however, the expected 2-pyrazoline easily isomerizes into 5(3)-isopropenyl-3(5)-cyanopyrazole. Buta-1,2,3-triene is the main product of base-induced decomposition of **2** in the absence of unsaturated substrates.

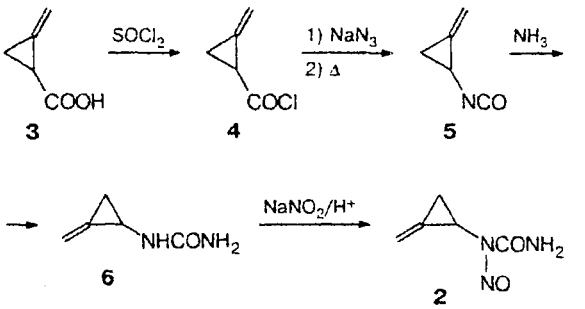
Key words: diazo-2-methylenecyclopropane, spiro(1- and 2-pyrazoline-5,1′-cyclopropanes), cyanopyrazoles, buta-1,2,3-triene, cyclopropylidenes, 1,3-dipolar cycloaddition, NMR spectra.

Unlike most known cyclic diazo compounds, diazocyclopropanes are exceptionally unstable and have not yet been detected in the individual state. Nevertheless, the possible generation of diazocyclopropanes *in situ* is indicated by the formation of products of their trapping by various substrates, for example, olefins. The [3+2]-cycloaddition reactions occurring in this case result in pyrazolines containing a spiro cyclopropane fragment.

Trapping of unsubstituted diazocyclopropane *in situ* by various unsaturated compounds has been comprehensively studied by now; however, examples of generation and capture of substituted diazocyclopropanes are very few. Thus the addition of 2,2-diphenyldiazocyclopropane generated *in situ* to diethyl fumarate,[1,2] 2,2-dimethyl- and 2,2-dichlorodiazocyclopropanes to 3,3-dimethylcyclopropene,[3] and diazospiropentane to methyl methacrylate and 3,3-dimethylcyclopropene[4] have been reported. In all cases, the appropriate *N*-cyclopropyl-*N*-nitrosourea (CNU) was used as the source for generation of diazocyclopropanes.

As a continuation of studies of reactions between diazocyclopropanes generated *in situ* and unsaturated compounds, we studied reactions of diazo-2-methylenecyclopropane (**1**), synthesized by base-induced decomposition of *N*-(2-methylenecyclopropyl)-*N*-nitrosourea (**2**), with methyl methacrylate and acrylonitrile, which are active dipolarophiles in [3+2]-cycloaddition reactions.

The previously unknown nitrosourea **2**, a potential source of **1**, was synthesized in several steps similarly to other *N*-cyclopropyl-*N*-nitrosoureas[3,4] starting from the known 2-methylenecyclopropanecarboxylic acid (**3**).[5] Acid chloride **4** was prepared in 83% yield by the reaction of **3** with a 20% molar excess of $SOCl_2$ at 15—20 °C (in a previous study,[6] compound **4** was prepared from the same acid on treatment with a fivefold excess of oxalyl chloride). Subsequently, chloride **4** was treated with NaN_3 in an aqueous acetone solution at 0 °C, the product was extracted with benzene, and the resulting solution of azide was decomposed at 70—77 °C. Then the reaction mixture was treated with excess dry NH_3, without isolation of isocyanate **5**, and the resulting cyclopropylurea **6** (yield ~55% based on **4**) was nitrosated by a standard procedure.[7]



In the presence of methyl methacrylate, decomposition of nitrosourea **2** on treatment with MeONa in a CH_2Cl_2—MeOH (3 : 1) mixture at −30 °C proceeds virtually without nitrogen evolution and, after the usual workup, results in isomeric 6-methoxycarbonyl-6-methyl-1-methylene-4,5-diazaspiro[2.4]hept-4-enes (**7**) in an overall yield of ~70% (isomer ratio ~1 : 1). How-

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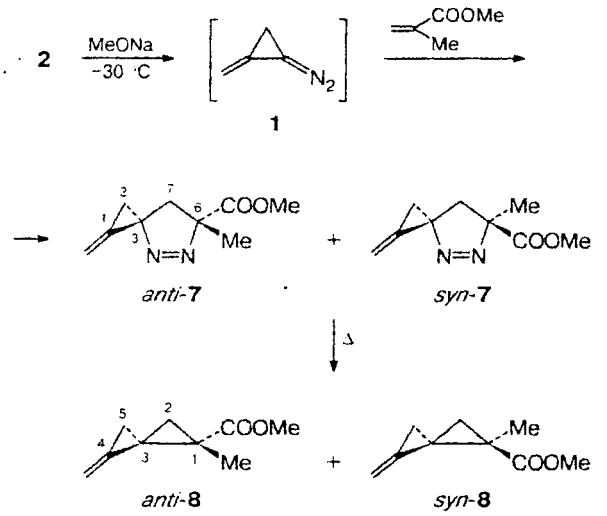
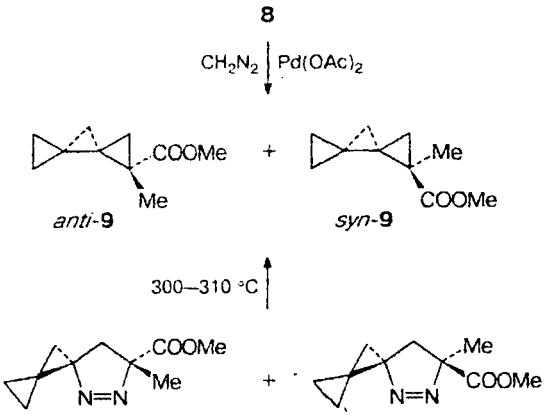
ever, we were unable to isolate these isomers in a pure state or, at least, to enrich markedly the mixture in either of the isomers by TLC. Nevertheless, the structure of compounds 7 as products of 1,3-dipolar cycloaddition of **1** to methyl methacrylate was confirmed by the ^1H and ^{13}C NMR spectra, in particular, by rather typical positions and multiplicities of all signals. Thus the signals of the nonequivalent geminal protons at C(7) are manifested as two doublets with a spin-spin coupling constant, J = 13.0 Hz, typical of an 1-pyrazoline ring[8]; $\Delta\delta$ is equal to ~0.7 ppm, whereas for the two isomers considered, these signals overlap. The signals of geminal protons at C(2) are displayed in different spectral regions (δ 2.5 and 1.8); however, for *anti*- and *syn*-isomers, they partially overlap. Apart from the coupling constant ^2J = 10.4 Hz, an additional triplet splitting due to coupling with olefinic protons is observed for each signal.



It was found that thermal deazotization of the resulting pyrazolines, carried out by passing a mixture of *anti*- and *syn*-7 with benzene through a quartz tube at atmospheric pressure and a temperature of ~300 °C, proceeds highly selectively to give methyl 1-methyl-4-methylenespiropentane-1-carboxylate isomers (**8**) in a total yield of 71%. According to the ^1H and ^{13}C NMR spectra, spiropentane esters **8**, like their precursors, esters **7**, are *anti*- and *syn*-isomers in ~1 : 1 ratio. However, in this case, all protons in the ^1H NMR spectrum (500 MHz, C_6D_6 as the solvent) were exhibited as nonoverlapping signals. This fact, together with the effect of spatial proximity of the *exo*-methylene group and the COOMe and Me substituents on passing from five- to the three-membered ring, permitted efficient use of the {C,H}-correlation and NOESY techniques for the assignment of signals to either *anti*- or *syn*-isomer. Owing to the deshielding influence of the ester group, the olefinic protons of *syn*-**8** are manifested in the lowest field (δ 5.55 and 5.38). The corresponding protons in the *anti*-isomer of ester **8** occur at δ 5.31 and 5.18; weak coupling of the proton at δ 5.18 with the proton of the methyl group (δ 1.32), brought close in space to one olefinic proton, can be observed in the NOESY spectrum of the *anti*-isomer (in both isomers, the geminal coupling of olefinic protons shows itself with $J \leq 1$ Hz). It is noteworthy that olefinic protons of unsubstituted methylenespiropentane are exhibited in nearly the same region and have the same $\Delta\delta$ (δ 5.21 and 5.08[9]) as those in the case of *anti*-**8**. The methylene protons at C(2) and C(5) differ both in the spin—spin coupling constant (^2J = 3.6 and 8.3 Hz, respectively) and by the fact that the signals for H(5) undergo additional allylic splitting.

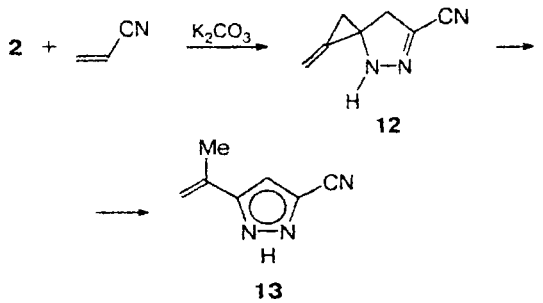
Cyclopropanation of isomeric methylenecyclopropanes **8** on treatment with a solution of diazomethane in ether in the presence of $Pd(OAc)_2$ at 15 °C affords isomeric methyl 1-methyldispiro[2.0.2.1]heptane-1-carboxylates (**9**) in ~90% yield; the *anti* to *syn* ratio is the same (~1 : 1) as that in the starting olefin **8**. Dispirane esters **9** are identical (GLC, ^1H and ^{13}C spectra) to the products of pyrolysis of the dispirane 1-pyrazolines prepared in our previous study by the addition of diazospiropentane generated *in situ* to methyl methacrylate.[4]



We have shown previously[10] that reactions of diazocyclopropane, generated by decomposition of *N*-cyclopropyl-*N*-nitrosourea (**10**) on treatment with MeONa, with electron-deficient unsaturated compounds such as acrylonitrile containing no additional substituents at the α-position are complicated by the Michael addition of MeOH to the double bond of the substrate. This undesirable reaction can be largely suppressed by changing the order in which the reactants are mixed, namely, by slow addition of a solution of MeONa in MeOH to a mixture of nitrosourea **10** and acrylonitrile stirred in CH_2Cl_2 at –15 to –25 °C.[10] Moreover, we have shown in this study that trapping of diazocyclopropane by acrylonitrile occurs with equal success when excess K_2CO_3 in CH_2Cl_2 is employed as the base to decompose **10** at 0—5 °C. In this case, the yield of 3-cyanospiro(2-pyrazoline-5,1′-cyclopropane) (**11**), resulting from 1,3-dipolar addition of diazocyclopropane

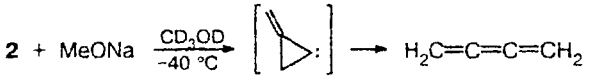
to acrylonitrile accompanied by isomerization of the resulting 1-pyrazoline to 2-pyrazoline, is equal to ~70%.

The same procedure proved to be efficient for generation and trapping of **1** when acrylonitrile is used as the unsaturated substrate. However, the spirocyclopropane-containing 2-pyrazoline **12**, expected in this case, was found to be less stable than pyrazoline **11** with an unsubstituted cyclopropane ring; under the reaction conditions, it isomerized to 5(3)-isopropenyl-3(5)-cyanopyrazole (**13**). Thus the reaction of a mixture of acrylonitrile, K_2CO_3, and nitrosourea **2** in CH_2Cl_2 performed at a reactant molar ratio of 1.1 : 2 : 1 at ~0 °C for 3 h gives mainly two new compounds. According to the ^1H NMR spectrum, they were identified as pyrazoline **12** and pyrazole **13** present in ~2.5 : 1 molar ratio. However, the ^1H NMR spectrum recorded for the same reaction mixture after three days no longer exhibited signals corresponding to pyrazoline **12** (an AB-spectrum for the protons of the pyrazoline ring at δ 3.10, a broadened singlet for the protons of the cyclopropane ring at δ 1.50, and signals for olefinic protons at δ 5.61 and 5.80). Pyrazole **13** was isolated in 63% yield as colorless crystals by TLC on neutral Al_2O_3; the composition and structure of the product were confirmed by data of elemental analysis and ^1H and ^{13}C NMR. The ^{13}C NMR spectrum contains only one set of signals, which may be due to a fast exchange process in the heteroaromatic structure in solution or, which is less probable, to a fixed position of the proton at either N(1) or N(2). Our results do not allow an unambiguous decision concerning the position of the proton in the molecule (without additional investigation).



The isomerization of pyrazoline **12** to pyrazole **13** is apparently facilitated by the easy cleavage of the σ-bond opposing the exo-methylene unit in the cyclopropane ring; the reaction is selective.

As a rule, base-induced decomposition of CNU under the same conditions (−20 to 0 °C) makes it possible to generate not only diazocyclopropane but also cyclopropylidene, which isomerizes spontaneously to allene or is partially trapped by an olefin such as bicyclopropylidene[11] or bicyclobutylidene.[12] To identify the products of the possible deazotization of **1**, we studied decomposition of nitrosourea **2** both in the absence of unsaturated trapping agents and in the presence of bicyclobutylidene. In the former case, decomposition of **2** induced by MeONa in MeOD at −40 to −20 °C was found to be accompanied by evolution of N_2 and to give buta-1,2,3-triene, which is the product of the cyclopropylidene–allene rearrangement (the ^1H NMR spectrum exhibits mainly a singlet at δ 5.35 corresponding to buta-1,2,3-triene in accordance with the published data[13]). No noticeable amounts of the products of addition of 2-methylenecyclopropylidene to the double bond of the starting nitrosourea **2** or of the butatriene formed were detected in the ^1H NMR spectrum. It is worth noting that no [1+2]-cycloadduct formed from 2-methylenecyclopropylidene and bicyclobutylidene added preliminarily to the reaction mixture as an unsaturated substrate was detected either. In this case, too, according to the ^1H NMR spectrum, buta-1,2,3-triene was the major product of decomposition of nitrosourea **2**.



The absence of the products of cyclopropanation of olefins with 2-methylenecyclopropylidene is apparently due to the facts that it is much less stable and more easily undergoes intramolecular isomerization to cumulene than cyclopropylidene. In turn, diazo-2-methylenecyclopropane is successfully captured by unsaturated compounds containing electron-withdrawing substituents to give 1,3-dipolar cycloadducts.

Thus, we synthesized previously unknown *N*-(2-methylenecyclopropyl)-*N*-nitrosourea and showed that its decomposition induced by sodium methoxide affords new unstable cyclic diazo compound diazomethylenecyclopropane. In the presence of methyl methacrylate or acrylonitrile, this compound is converted into the corresponding pyrazolines, [3+2]-cycloaddition products, in good yields. In the absence of unsaturated substrates, buta-1,2,3-triene is produced.

Experimental

The compounds obtained and their mixtures were analyzed by GLC (a 30-m long RSL-200 capillary column) or TLC on neutral Al_2O_3. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker DRX-500 (500 MHz) spectrometers for solutions in $CDCl_3$ (unless otherwise specified) containing 0.05% Me_4Si as the internal standard. Mass spectra were run on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct injection). 2-Methylenecyclopropanecarboxylic acid (**3**) was prepared by a previously described procedure.[5]

The solvents used were purified by conventional procedures, methyl methacrylate (chemically pure grade) was distilled prior to use, and $Pd(OAc)_2$ (pure grade) was recrystallized.

Methylenecyclopropanecarboxylic acid chloride (4). Thionyl chloride (2.86 g, 24 mmol) was added with stirring over a period of ~40 min to acid **3** (1.98 g, 20 mmol); gas evolution and a slight exothermic effect were observed. The mixture was stirred for 30 min and distilled *in vacuo* to give 1.93 g (83%) of

chloride **4** as a colorless liquid, b.p. 65—66 °C (65 Torr) (Ref. 6: b.p. 48 °C (30 Torr)). ^{1}H NMR, δ: 5.67 (m, 2 H, $=CH_2$); 2.[illegible] (t, 1 H, H(1)); 2.15 and 1.92 (both m, each 1 H, H(3)). ^{13}C NMR, δ: 172.6 (CO); 129.0 (C(2)); 107.0 ($=CH_2$); 27.0 (C(1)); 15.3 (C(3)).

***N*-(Methylenecyclopropyl)urea (6).** A solution of NaN_3 (1.56 g, 24 mmol) in 4.7 mL of H_2O was added with vigorous stirring at ~0 °C to a solution of chloride **4** (1.88 g, 16 mmol) in 15 mL of dry acetone. The mixture was stirred for 30 min. Then 45 mL of water was added, the organic layer was separated, and the aqueous layer was extracted with benzene (2×5 mL). The organic solutions were combined and dried with Na_2SO_4. The resulting solution of azide in benzene was heated in a water bath at 70—77 °C; nitrogen evolution continued for ~4 h. Then the reaction mixture was cooled to 15—20 °C. Excess NH_3, dried over solid NaOH, was passed into the resulting solution of isocyanate **5**. The colorless precipitate was filtered off and the filtrate was concentrated to 1/4 of the initial volume in order to attain fuller precipitation. The yield of urea **6** was 0.98 g (~55%), m.p. 101—102 °C. Found (%): C, 53.32; H, 7.25; N, 24.81. $C_5H_8N_2O$. Calculated (%): C, 53.56; H, 7.19; N, 24.98. ^{1}H NMR (CD_3OD), δ: 5.73 (br.t, 1 H, $=CH_2$, J = 2.5 Hz); 5.55 (q, 1 H, $=CH_2$, J = 2.0 Hz); 4.92 (br.s, 3 H, NH + NH_2, partially overlapped by the signal of the residual protons of the solvent); 3.12 (m, 1 H, H(1)); 1.60 and 1.18 (both m, 1 H each, H(3)). ^{13}C NMR ($CDCl_3$), δ: 160.4 (CO); 131.4 (C(2)); 107.0 ($=CH_2$); 24.8 (C(1)); 13.3 (C(3)).

***N*-(Methylenecyclopropyl)-*N*-nitrosourea (2).** A mixture of $NaNO_2$ (0.62 g, 9 mmol) and urea **6** (0.90 g, 8 mmol) in 20 mL of H_2O was added with stirring over a period of 1 h to a solution of H_2SO_4 (0.98 g, 10 mmol) in 5.2 mL of H_2O; a temperature of 0—5 °C was maintained during this period. The mixture was stirred for 15 min, and the resulting precipitate was filtered off, washed with 2 mL of ice water to which 1 drop of 20% H_2SO_4 had been added, and dried in a vacuum desiccator. The filtrate was extracted with CH_2Cl_2 (2×10 mL), the organic layer was separated and dried with Na_2SO_4. After removal of the solvent, this gave an additional 0.11 g of a solid identical to the above precipitate. The total yield of nitrosourea **2**, which consisted of fine yellow crystals decomposing at 72—75 °C, was 0.81 g (72%). Found (%): C, 42.31; H, 5.12; N, 29.52. $C_5H_7N_3O_2$. Calculated (%): C, 42.55; H, 5.00; N, 29.77. ^{1}H NMR (CD_3OD), δ: 5.85 (t, 1 H, $=CH_2$, J = 3.0 Hz); 5.58 (q, 1 H, $=CH_2$, J = 2.1 Hz); 4.86 (s, 2 H, NH_2, partially overlapped by the solvent signal); 3.00 (m, 1 H, H(1)); 1.86 and 1.26 (both m, 1 H each, H(3)). ^{13}C NMR (CD_3OD), δ: 156.9 (CO); 130.1 (C(2)); 109.9 ($=CH_2$); 25.7 (C(1)); 12.9 (C(3)).

Buta-1,2,3-triene. Sodium methoxide (9.8 mg, 0.18 mmol) was added at −60 °C to a solution of nitrosourea **2** (8.4 mg, 0.06 mmol) in 0.36 mL of CD_3OD in an NMR tube. Slow warming of the solution was accompanied by gas evolution, which started at −50 °C. The mixture was kept at −40 °C until yellow color completely disappeared; after that, the ^{1}H NMR spectrum was recorded. The spectrum contained only a singlet at δ 5.35, which corresponded to buta-1,2,3-triene (see Ref. 13).

6-Methoxycarbonyl-6-methyl-1-methylene-4,5-diazaspiro-[2.4]hept-4-ene (7). At −30 °C, sodium methoxide (0.15 g, 2.8 mmol) was added with stirring to a solution of methyl methacrylate (0.20 g, 2 mmol) in 1.5 mL of CH_2Cl_2 and 0.5 mL MeOH. Then nitrosourea **2** (0.20 g, 1.4 mmol) was added in portions over a period of 20 min. After 5 min, 3 mL of H_2O was added to the reaction mixture, the aqueous layer was extracted with 2 mL of CH_2Cl_2, and the organic fractions were combined and dried with Na_2SO_4. Evaporation of the solvent gave 0.17 g (~70%) of compound **7** as a mixture of two isomers in ~1 : 1 ratio. Found (%): C, 60.02; H, 6.65; N, 15.61. $C_9H_{12}N_2O_2$. Calculated (%): C, 59.99; H, 6.71; N, 15.55. ^{1}H NMR, δ (one unit of integral intensity corresponds to 1 H of one isomer): 5.65 (m, 3 H, $=CH_2$, ^4J ≈ 2.8 Hz); 5.58 (t, 1 H, $=CH_2$, ^4J ≈ 2.9 Hz); 3.82 (s, 3 H, OMe); 3.79 (s, 3 H, OMe); 2.52 (m, 2 H, H(2), ^2J ≈ 10.5 Hz, ^4J ≈ 2.8 Hz); 2.41 and 2.38 (both d, 2 H, H(7), ^2J = 13.0 Hz); 1.84 (m, 2 H, H(2), ^2J ≈ 10.5 Hz, ^4J ≈ 2.8 Hz); 1.72 and 1.70 (both d, 2 H, H(7), ^2J = 13.0 Hz); 1.67 (s, 3 H, Me); 1.60 (s, 3 H, Me). ^{13}C NMR, δ: 171.5 and 171.1 (CO); 133.4 and 132.8 (C(1)); 106.7 and 106.3 ($=CH_2$); 93.5 and 93.2 (C(6)); 70.8 and 70.5 (C(3)); 52.9 (OMe of both isomers); 35.6 and 35.3 (C(7)); 22.3 and 22.5 (Me); 18.3 and 17.8 (C(2)).

Methyl 1-methyl-4-methylenespiropentane-1-carboxylate (8). A solution of pyrazoline **7** (63 mg, 0.35 mmol) in 1.2 mL of benzene was passed through a quartz tube with an inner diameter of 3.5 mm, preheated to 300 °C and filled to 12 cm with fine quartz. Simultaneously, the tube was blown with an argon stream (~8 mL min^{-1}). When the reaction had been completed, 0.4 mL of benzene was passed through the tube. The pyrolyzate was concentrated. Vacuum microdistillation (bath temperature 85—90 °C, 30 Torr) gave 38 mg (71%) of **8** as a colorless liquid, which was a mixture of two isomers in ~1 : 1 ratio. ^{1}H NMR (C_6D_6), δ: (**8**, *anti*-isomer) 5.31 and 5.18 (both br.t, each 1 H, $=CH_2$, ^4J = 2.2 Hz); 3.32 (s, 3 H, OMe); 2.01 (d, 1 H, H(2), ^2J = 3.6 Hz); 1.50 (dt, 1 H, H(5), ^2J = 8.4 Hz, ^4J = 2.2 Hz); 1.39 (m, 1 H, H(5), ^2J = 8.4 Hz); 1.32 (s, 3 H, Me); 0.94 (d, 1 H, H(2), ^2J = 3.6 Hz); (**8**, *syn*-isomer) 5.55 (dt, 1 H, $=CH_2$, ^4J = 2.2 Hz, ^2J = 1.0 Hz); 5.38 (m, 1 H, $=CH_2$); 3.33 (s, 3 H, OMe); 1.94 (br.d, 1 H, H(2), ^2J = 3.6 Hz); 1.27 (s, 3 H, Me); 1.20 (m, 1 H, H(5), ^2J = 8.3 Hz); 1.11 (br.dt, 1 H, H(5), ^2J = 8.3 Hz, ^4J = 2.2 Hz); 0.99 (d, 1 H, H(2), ^2J = 3.6 Hz). ^{13}C NMR (C_6D_6), δ: 173.6 and 173.5 (CO); 134.3 and 133.7 (C(4)); 100.5 and 100.4 ($=CH_2$); 51.4 and 51.2 (OMe); 49.9 and 48.6 (C(1)); 28.3 and 25.3 (C(3)); 24.1 and 23.8 (C(2) in the *syn*- and *anti*-isomers, respectively); 17.4 and 17.1 (Me in the *anti*- and *syn*-isomers); 10.7 and 8.1 (C(5) in the *anti*- and *syn*-isomers).

Methyl 1-methyldispiro[2.0.2.1]heptane-1-carboxylate (9). Methylenespiropentane **8** (28 mg, 0.18 mmol) in 0.4 mL of CH_2Cl_2 and ~6 mg of $Pd(OAc)_2$ were added successively at 5—10 °C to 1.3 mL of an ethereal solution of diazomethane (~0.85 mmol) and the mixture was stirred at 5—10 °C until nitrogen evolution ceased. The solvents were evaporated *in vacuo* and the residue (~28 mg) was analyzed by ^{1}H and ^{13}C NMR spectroscopy; according to spectroscopic data, the mixture contained ~10% starting olefins **8** and ~90% isomeric dispiroheptanecarboxylates **9** (isomer ratio ~1 : 1); all signals fully conformed to published data.[4]

5(3)-Isopropenyl-3(5)-cyanopyrazole (13). Potassium carbonate (0.20 g, 1.4 mmol) was added at 0 °C to a mixture of nitrosourea **2** (0.10 g, 0.71 mmol), acrylonitrile (50 mg, 0.77 mmol), and 1.3 mL of CH_2Cl_2 and the mixture was vigorously stirred for 3 h, the temperature being maintained at 0—5 °C. A small portion of the solution was concentrated *in vacuo* without heating and its ^{1}H NMR spectrum was recorded; the remainder of the solution was kept for 24 h at 10 °C. According to spectral data, the reaction mixture contained 6-cyano-1-methylene-4,5-diazaspiro[2.4]hept-5-ene (**12**) (20—25%) and pyrazole **13** (~70%). ^{1}H NMR (for **12**, $CDCl_3$), δ: 5.79 and 5.63 (both br.s, each 1 H, $=CH_2$); 3.10 (AB-spectrum, 2 H, H(7), ^2J = 17.1 Hz); 1.51 (br.s, 2 H, H(2)); a signal for the NH group was not identified unambiguously. The sample obtained after 3 days displayed no signals corresponding to pyrazoline **12**. The reaction mixture was concentrated *in vacuo* and the thick yellowish residue was

separated by preparative TLC (neutral Al_2O_3, AcOEt—benzene (2 : 1) as the eluent) to give 69 mg (~73%) of isopropenylcyanopyrazole **13** as colorless crystals, R_f 0.83, m.p. 94–95 °C. Found (%): C, 63.28; H, 5.25; N, 31.44. $C_7H_7N_3$. Calculated (%): C, 63.14; H, 5.30; N, 31.56. ^{1}H NMR, δ: 7.25 (br.s, 1 H, NH); 6.68 (s, 1 H, H(4)); 5.52 (q, 1 H, $=CH_2$, ^4J = 1.1 Hz); 5.28 (q, 1 H, $=CH_2$, ^4J = 1.6 Hz); 2.12 (dd, 3 H, CH_3, ^4J = 1.6 Hz, ^4J = 1.1 Hz). ^{13}C NMR, δ: 145.7 (C(5)); 130.9 ($\underline{C}=CH_2$); 125.6 (C(3)); 115.4 ($=CH_2$); 113.9 (CN); 108.0 (C(4)); 20.5 (Me).

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