Formation of *N*-cyclopropylhydrazones by azo coupling of cyclopropyldiazonium with aliphatic CH acids

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Decomposition of *N*-cyclopropyl-*N*-nitrosourea under the action of K_2CO_3 or KOH containing 15—20% of H_2O at 0—7 °C gives rise to cyclopropyldiazonium, which reacts with some β-diketones, methyl cyanoacetate, or malonodinitrile to form the corresponding cyclopropylhydrazones. The latter compounds are analogous to products of azo coupling and isomerization of aryldiazonium ions with the above-mentioned substrates. These transformations provide the first example of azo coupling of the cyclopropyldiazonium ion in the series of activated aliphatic CH acids.

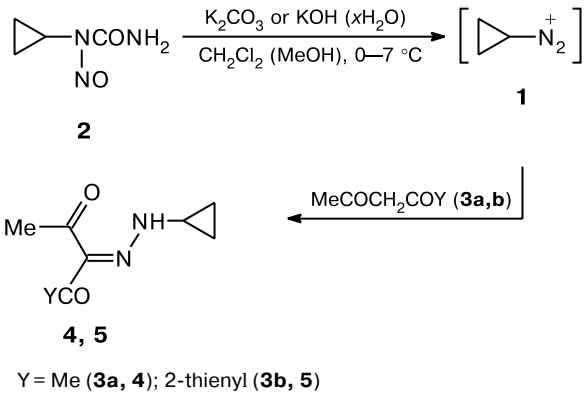
Key words: cyclopropylnitrosourea, diazocyclopropane, cyclopropyldiazonium, functionalized *N*-cyclopropylhydrazones, competitive reactions.

Decomposition of *N*-alkyl-*N*-nitrosoamides under the action of bases is one of the methods, which are most generally used for the synthesis of aliphatic diazo compounds.[1] The generation of diazocyclopropanes from the corresponding *N*-cyclopropyl-*N*-nitrosoureas or *N*-cyclopropyl-*N*-nitrosocarbamates follows the same pathway. In spite of the fact that all diazocyclopropanes are very unstable, their *in situ* formation can be judged by chemical trapping techniques, in particular, by the 1,3-dipolar cycloaddition to some unsaturated compounds.[2] The reactions of aliphatic diazo compounds assuming generation of diazonium ions are generally accompanied by elimination of the nitrogen molecule followed by transformations of the resulting carbocations.[3,4] Nevertheless, it appeared that the cyclopropyldiazonium ions can undergo transformations, which are highly competitive with deazotization. Thus, the intermediate formation of the cyclopropyldiazonium ion (**1**) is evidenced from the reactions of *N*-cyclopropyl-*N*-nitrosourea (**2**) with dimethylamine or ethylamine, which give cyclopropyltriazenes[5] and typical azo coupling products in reactions involving certain hydroxynaphthalenes,[6,7] spiro(2-pyrazoline-5,1′-cyclopropanes),[8] or 8-hydroxyquinoline[7] as azo components.

With the aim of extending the range of compounds, which can trap the cyclopropyldiazonium ion (**1**), we examined alkaline decomposition of nitrosourea **2** in the presence of selected aliphatic CH acids, *viz.*, β-diketones, methyl cyanoacetate, or malonodinitrile, which exhibit properties of typical azo components in reactions with aromatic diazo compounds.[9,10] It should be noted that the latter, when reacting at the activated C—H bond of the methyl or methylene fragment (for example, in the reactions of phenyldiazonium chloride with nitromethane or acetylacetone), generally produce isomeric arylhydrazones rather than azo compounds. Hence, in the case of trapping of ion **1** by compounds containing an activated methylene group, the reactions would also be expected to afford the corresponding cyclopropylhydrazones.

Actually, the reaction of nitrosourea **2** with solid K_2CO_3 containing ~20% of H_2O in the presence of pentane-2,4-dione (**3a**) in CH_2Cl_2 at 0—7 °C gave rise to low-melting crystalline 3-cyclopropylhydrazonopentane-2,4-dione (**4**) in 84% yield (Scheme 1). The yield of cyclopropylhydrazone substantially decreased in the reactions with the use of either anhydrous K_2CO_3 or aqueous

Scheme 1



Y = Me (**3a, 4**); 2-thienyl (**3b, 5**)

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Table 1. Yields of cyclopropylhydrazone **4** upon decomposition of nitrosourea **2** under different conditions (5 °C)

Base (**B**)	Solvent	**2** : **3a** : **B**	*t*/h	*Y** (%)
K_2CO_3 + H_2O (20%)	CH_2Cl_2	1.2 : 1 : 2.5	2.5	84
KOH + H_2O (15%)	CH_2Cl_2—MeOH (4 : 1)	1.2 : 1 : 2.5	0.5	82
$LiOH \cdot H_2O$	CH_2Cl_2	1 : 1 : 3	1	78
K_2CO_3 + H_2O (50%)	CH_2Cl_2	1 : 1 : 3	1	40
K_2CO_3 (anhydrous)	CH_2Cl_2	1 : 1 : 2	5	38
K_2CO_3 + H_2O (20%)	MeCN	1 : 1 : 2	3	10

* The yield with respect to the isolated product.

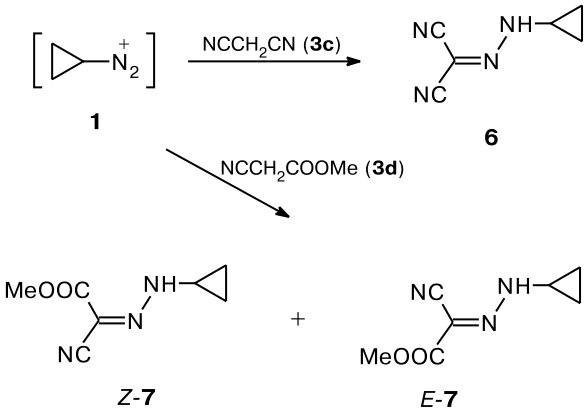
solutions of K_2CO_3 or KOH (Table 1). A decrease in the yield of compound **4** is attributable to the fact that decomposition of nitrosourea **2** in the presence of anhydrous K_2CO_3 proceeded very slowly, whereas decomposition with the use of aqueous solutions of the base proceeded, on the contrary, vigorously, which was characterized by substantial deazotization of intermediate diazonium ion **1** under the action of H_2O.

In the ^1H and ^{13}C NMR spectra of compound **4** in $CDCl_3$, the signals of the protons of the methyl groups differ by 0.19 and 4.9 ppm, respectively, which is indicative of their nonequivalence due to a fixed position of the cyclopropylamine substituent with respect to the C=N bond. The signal of the proton of the NH fragment is observed at low field (δ 13.6) due to the formation of an intramolecular hydrogen bond with the carbonyl O atom.

Decomposition of nitrosourea **2** under the action of K_2CO_3 in CH_2Cl_2 in the presence of diketone **3b** using the reagent molar ratio of 1.2 : 2.5 : 1 also proceeded rather efficiently to give 2-cyclopropyl-1-(2-thienyl)hydrazonobutane-1,3-dione (**5**) in ~75% yield with respect to the isolated product (see Scheme 1), ~20% of the starting diketone **3b** remaining unconsumed. The ^1H and ^{13}C NMR spectra of the reaction product have one set of signals corresponding to one of the possible isomers (presumably, to isomer **5** in which the cyclopropylamino fragment forms an intramolecular hydrogen bond with the acetyl group).

Under analogous conditions, cyclopropyldiazonium **1** generated *in situ* reacted with malonodinitrile (**3c**) or methyl cyanoacetate (**3d**) to give the corresponding cyclopropylhydrazones **6** or **7** in 56—60% yields (Scheme 2). The latter reaction afforded a mixture of isomeric hydrazones *Z*-**7** and *E*-**7** in a ratio of ~5 : 1 (according to the data on the integral intensities of the signals of the methoxy groups in the ^1H NMR spectrum). In addition, the spectrum has two broadened signals of the NH group at δ 11.7 and 8.3 corresponding to two different isomers. Since the spectrum of symmetrically substituted hydrazone **6** has a signal of the NH group at δ 8.5, it can be assumed that the cyclopropylamino substituent in minor isomer *E*-**7** is also oriented toward the CN group.

Scheme 2



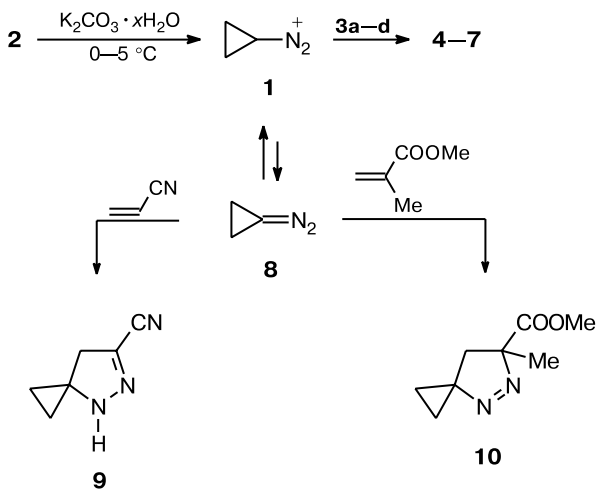
Under the action of a methanolic solution of KOH, the percentage of isomer *E*-**7** in the resulting mixture of hydrazones *Z*-**7** and *E*-**7** in CH_2Cl_2 increased. According to the ^1H NMR spectroscopic data, the ratio between isomers *Z*-**7** and *E*-**7** changed from ~5 : 1 to ~1 : 3.3 after stirring for 36 h. After treatment of the reaction mixture with diethyl ether, isomer *E*-**7** was isolated in the individual form as beige needle-like crystals. The repeated treatment of a solution of isomer *E*-**7** in CH_2Cl_2 with a methanolic solution of KOH again gave rise to isomer *Z*-**7**, but isomer *E*-**7** did remain the major product. After storage of the reaction mixture for 4 days, the ratio between isomers *Z*-**7** and *E*-**7** was ~1 : 6, which is, apparently, most close to the equilibrium state under the reaction conditions used. Therefore, isomer *E*-**7** is the most stable product in the presence of strong bases, whereas azo coupling gives rise to isomer *Z*-**7** as the major product irrespective of whether K_2CO_3 or KOH in a ~4 : 1 CH_2Cl_2—MeOH mixture is used for the generation of cyclopropyldiazonium **1** from nitrosourea **2**.

Unlike CH acids **3a—d**, dimethyl malonate and acetoacetic ester were not involved in azo coupling with cyclopropyldiazonium **1** under the same reaction conditions. In the last two cases, nitrosourea **2** decomposed, but dimethyl malonate or acetoacetic ester used as trapping agents were recovered.

Taking into account that the formation of products of azo coupling of cyclopropyldiazonium **1** with activated CH acids, in particular, with compounds **3a—d**, and the formation of the products of 1,3-dipolar cycloaddition of diazocyclopropane (**8**), for example, with acrylonitrile or methyl methacrylate,[11] proceeded under the same conditions of decomposition of nitrosourea **2**, it was of interest to examine the possibility of the simultaneous trapping of intermediates **1** and **8** by the corresponding substrates.

For this purpose, we studied decomposition of nitrosourea **2** in the presence of pentanedione **3a** and acrylonitrile or methyl methacrylate using **2**, **3a**, and the unsaturated compound in a molar ratio of 1 : 4 : 4. The reaction was carried out in CH_2Cl_2 by adding 2 equiv. of K_2CO_3 containing ~20% of H_2O at 5 °C for 2 h. After the removal of an excess of **3a** and unsaturated compounds from the mixtures obtained in both reactions, the residues contained (according to ^1H NMR spectroscopy) both hydrazone **4** and a 1,3-dipolar cycloaddition product, *viz.*, pyrazoline **9** or pyrazoline **10** in the case of acrylonitrile (**4** : **9** ≈ 1 : 2.4) or methyl methacrylate (**4** : **10** ≈ 1 : 2.2), respectively (Scheme 3). However, the examination of the competitive reactions of diazocyclopropane **8** with an equimolar mixture of acrylonitrile and methyl methacrylate performed under the same conditions demonstrated that acrylonitrile is ~18 times more active than methyl methacrylate. Apparently, these results are attributed, on the one hand, to a low current concentration of diazo compound **8** under the reaction conditions used (*i.e.*, to the shift of equilibrium to diazonium ion **1**)[12] and, on the other hand, to a substantially lower rate of azo coupling of diazonium **1** with pentanedione **3a** compared to the rate of 1,3-dipolar cycloaddition of diazocyclopropane to the above-mentioned acrylates.

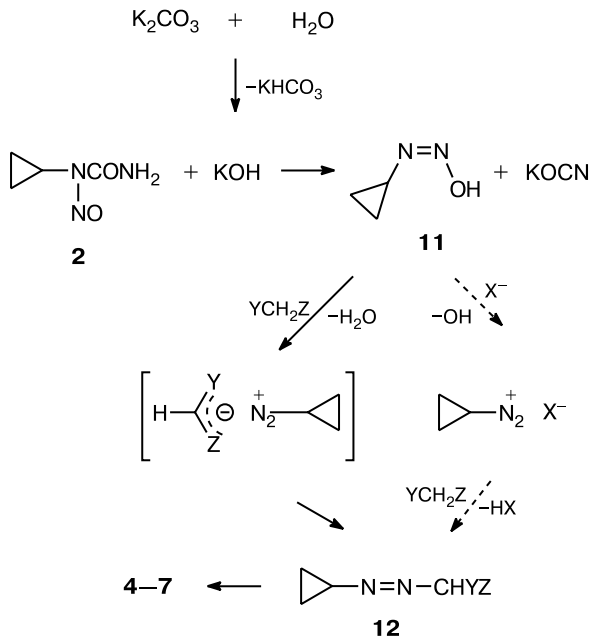
Scheme 3



It should be emphasized that intermediates **1** and **8** are very unstable species and their successful trapping depends substantially on the nature of the substrates used. In particular, the low reactivity of the trapping agent is, apparently, responsible for the absence of azo coupling products in the case of acetoacetic ester or dimethyl malonate as well as for the absence of 1,3-dipolar cycloaddition products upon decomposition of nitrosourea **2** with potassium carbonate in the presence of such unsaturated compounds as norbornene, styrene, or vinyl bromide, although the latter readily gave the corresponding spiro(1-pyrazoline-3,1′-cyclopropanes)[13—15] upon decomposition of nitrosourea **2** with sodium methoxide. These results are in agreement with the earlier explanation[12] provided for the substantial shift of the equilibrium to diazocyclopropane **8** in the presence of strong bases, which is responsible for an increase in the rate of 1,3-dipolar cycloaddition dependent on the concentrations of the starting reagents.

In the above discussion of the possibility of azo-coupling, we considered cyclopropyldiazonium ion **1** as an intermediate. However, it is not inconceivable that cyclopropyldiazohydrate (**11**) serves as the reactive species in this process, because only anions of weak acids, *viz.*, HCO_3^- and NCO^-, or the hydroxide ion itself can serve as counterions for cyclopropyldiazonium **1** (unlike direct diazotization of aromatic amines). In addition, the anions of aliphatic CH acids **3a—d** can also be considered as counterions. For example, this can give rise to a tight ion pair, which is rapidly transformed into azo compounds **12** and then into more stable hydrazones **4—7** (Scheme 4).

Scheme 4



Therefore, decomposition of *N*-cyclopropyl-*N*-nitrosourea with bases makes it possible to generate cyclopropyldiazonium intermediates, which can be involved in azo coupling with some active CH acids analogously to the processes taking place in the series of aromatic diazo compounds. As a result, cyclopropylhydrazones, which cannot virtually be prepared according to other methods, become readily accessible. Depending on

the nature of the trapping agents, either diazocyclopropane or cyclopropyldiazonium and cyclopropyldiazohydrate can be involved in the reactions performed under the same conditions to give 1,3-dipolar cycloaddition adducts with unsaturated compounds or azo coupling products, respectively. Hence, cyclopropyldiazonium intermediates are related to both aliphatic and aromatic diazo compounds.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz, respectively) and Bruker AM-300 (300 and 75.5 MHz) spectrometers for solutions in $CDCl_3$ containing 0.05% of Me_4Si as the internal standard. The mass spectra were obtained on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet). The IR spectra were measured on a Bruker IFS-113v spectrometer in CCl_4. The starting CH acids **3a**,**c**,**d** (high-purity grade) were used without additional purification. β-Diketone **3b** (see Ref. 16) and *N*-cyclopropyl-*N*-nitrosourea[12,13] were synthesized according to known procedures. Potassium carbonate (reagent grade) used in the experiments contained (according to the results of drying) ~20% of H_2O. The TLC analysis was carried out on silica gel (0.040—0.063 mm, Merck).

3-Cyclopropylhydrazonopentane-2,4-dione (4). Potassium carbonate (1.65 g) was added to a mixture of pentanedione **3a** (0.40 g, 4 mmol) and *N*-cyclopropyl-*N*-nitrosourea (**2**) (0.62 g, 4.8 mmol) in CH_2Cl_2 (15 mL) at 5—7 °C and the reaction mixture was vigorously stirred at this temperature for 2.5 h. Then the reaction mixtue was filtered, the solvent was removed *in vacuo*, and the residue was crystallized from hexane at −15 °C. Hydrazone **4** was obtained in a yield of 0.56 g (84%) as yellow crystals, m.p. 32—34 °C. Found (%): C, 57.42; H, 7.48; N, 16.52. $C_8H_{12}N_2O_2$. Calculated (%): C, 57.13; H, 7.19; N, 16.66. ^1H NMR ($CDCl_3$), δ: 0.98 (m, 4 H, CH_2CH_2); 2.30 and 2.49 (both s, 2×3 H, 2 Me); 3.20 (br.ddt, 1 H, CH, $J_{cis} \approx 10.2$ and 7.5 Hz, $J_{trans} \approx 4.0$ Hz); 13.6 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 6.5 (CH_2CH_2); 26.4 (C(1)); 31.3 (C(5)); 33.9 (CH); 133.2 (C(3)); 196.7 and 196.8 (C(2) and C(4)). Partial MS, m/z (I_{rel} (%)): 168 (1.5) $[M]^+$, 167 (1.5) $[M - H]^+$, 125 (38) $[M - COMe]^+$, 43 (100) $[COMe]^+$.

2-Cyclopropylhydrazono-1-(2-thienyl)butane-1,3-dione (5). Hydrazone **5** was prepared according to the above-described procedure from 1-(2-thienyl)butane-1,3-dione (0.67 g, 4 mmol) (**3b**), nitrosourea **2** (0.62 g, 4.8 mmol), and K_2CO_3 (1.65 g). After recrystallization from hexane, hydrazone **5** was obtained in a yield of 0.71 g (75%) as orange crystals, m.p. 45—47 °C. Found (%): C, 55.64; H, 5.27. $C_{11}H_{12}N_2O_2S$. Calculated (%): C, 55.92; H, 5.12. ^1H NMR ($CDCl_3$), δ: 0.97 and 1.04 (both m, 2×2 H, CH_2CH_2); 2.57 (s, 3 H, Me); 3.28 (m, 1 H, CH); 7.12 (dd, 1 H, H(4), J = 4.9 Hz, J = 3.7 Hz); 7.60 (dd, 1 H, H(5), J = 4.9 Hz, J = 1.2 Hz); 7.94 (dd, 1 H, H(3), J = 3.7 Hz, J = 1.2 Hz); 13.6 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 6.9 (CH_2CH_2); 30.8 (Me); 33.8 (CH); 127.0 (C(4′)); 132.3 (C(2)); 134.1 and 134.2 (C(3′) and C(5′)); 141.0 (C(2′)); 181.7 (C(1)); 197.5 (C(3)). Partial MS, m/z (I_{rel} (%)): 236 (1.5) $[M]^+$, 235 (1) $[M - H]^+$, 193 (19) $[M - COMe]^+$, 111 (100) $[(C_4H_3S)CO]^+$.

2-(Cyclopropylhydrazono)malonodinitrile (6). Hydrazone **6** was prepared according to the above-described procedure from malonodinitrile (**3c**) (0.27 g, 4 mmol), nitrosourea **2** (0.62 g, 4.8 mmol), and K_2CO_3 (1.65 g). After separation of the reaction mixture by preparative TLC (SiO_2, Et_2O—benzene, 1 : 3), hydrazone **6** was obtained in a yield of 0.30 g (56%) as yellow crystals, m.p. 67—69 °C, R_f 0.80. Found (%): C, 53.98; H, 4.74; N, 41.29. $C_6H_6N_4$. Calculated (%): C, 53.72; H, 4.51; N, 41.77. ^1H NMR ($CDCl_3$), δ: 0.95 (m, 4 H, CH_2CH_2); 3.20 (m, 1 H, CH); 8.6 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 6.8 (CH_2CH_2); 33.8 (CH); 84.5 (C(2)); 108.3 and 112.3 (2 CN). Partial MS, m/z (I_{rel} (%)): 134 (4) $[M]^+$, 133 (4) $[M - H]^+$, 106 (30), 86 (57), 84 (92), 41 (100) $[C_3H_5]^+$.

Methyl (cyclopropylhydrazono)cyanoacetate (7). Potassium carbonate (1.65 g) was added to a mixture of methyl cyanoacetate (**3d**) (0.40 g, 4 mmol) and nitrosourea **2** (0.62 g, 4.8 mmol) in CH_2Cl_2 (12 mL) at 5—7 °C. The reaction mixture was vigorously stirred for 2 h and then filtered. To remove unconsumed ester **3d**, the filtrate was treated with a 5% KOH solution (5 mL) and then the aqueous layer was neutralized with a 5% aqueous HCl solution and extracted with CH_2Cl_2 (3×5 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo* to obtain a viscous liquid as a mixture of isomeric hydrazones *Z*-**7** and *E*-**7** (~5 : 1) in a yield of 0.41 g (~60%). Found (%): C, 50.07; H, 5.58; N, 24.80. $C_7H_9N_3O_2$. Calculated (%): C, 50.29; H, 5.43; N, 25.14. ^1H NMR for *Z*-**7** ($CDCl_3$), δ: 0.92 (m, CH_2CH_2); 3.19 (m, CH); 3.81 (s, OMe); 11.7 (br.s, NH). ^{13}C NMR for *Z*-**7** ($CDCl_3$), δ: 6.3 (CH_2CH_2); 33.8 (CH); 52.2 (OMe); 101.9 (C(2)); 115.7 (CN); 162.9 (CO). Partial MS, m/z (I_{rel} (%)): 167 (4) $[M]^+$, 166 (4) $[M - H]^+$, 108 (100) $[M - COOMe]^+$.

Isomerization of hydrazones *Z*-7 and *E*-7. A 6% KOH solution in MeOH (3 mL) was added to a solution of hydrazones *Z*-**7** and *E*-**7** (~5 : 1) (0.30 g) in CH_2Cl_2 (5 mL) and the reaction mixture was stirred at 20 °C for 36 h. The solvents were evaporated *in vacuo*. The residue was washed with CH_2Cl_2 (5 mL), treated with a 5% HCl solution (5 mL), and extracted with CH_2Cl_2 (3×5 mL). The organic layer was dried with Na_2SO_4, the solvent was removed *in vacuo* (according to results of ^1H NMR spectroscopy of the residue, the ratio between isomers *Z*-**7** and *E*-**7** was ~1 : 3.3). The residue was treated with Et_2O (2 mL) at −15 °C to obtain hydrazone *E*-**7** in a yield of 0.14 g as beige needle-like crystals, m.p. 88—90 °C. Found (%): C, 50.51; H, 5.59; N, 25.02. $C_7H_9N_3O_2$. Calculated (%): C, 50.29; H, 5.43; N, 25.14. ^1H NMR ($CDCl_3$), δ: 0.92 (m, CH_2CH_2); 3.19 (m, CH); 3.88 (s, OMe); 8.3 (br.s, NH). ^{13}C NMR ($CDCl_3$), δ: 6.7 (CH_2CH_2); 33.1 (CH); 52.7 (OMe); 103.0 (C(2)); 110.7 (CN); 161.4 (CO). An analogous procedure was repeated for individual hydrazone *E*-**7**. After 4 days, the ratio between isomers *Z*-**7** and *E*-**7** (according to the ^1H NMR spectroscopic data) was ~1 : 6, signals of other compounds being virtually absent in the spectrum.

Competitive formation of cyclopropylhydrazone 4 and spiro(pyrazolinecyclopropanes). Potassium carbonate (165 mg) containing ~20% of H_2O was added in one portion to a mixture of acrylonitrile (106 mg, 2.0 mmol) or methyl methacrylate (200 mg, 2.0 mmol), acetylacetone (200 mg, 2.0 mmol), and nitrosourea **2** (70 mg, 0.5 mmol) in CH_2Cl_2 (7 mL) at 5 °C. The reaction mixture was stirred for 2 h and filtered. The solvent and the starting compounds, including acetylacetone, were removed *in vacuo*. The residues obtained in both cases were analyzed by ^1H NMR spectroscopy. In the case of acrylonitrile, compound **4** and pyrazoline **9** were generated in a ratio of ~1 : 2.4. In the case

of methyl methacrylate, the ratio between compound **4** and pyrazoline **10** was ~1 : 2.2.

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