Formation and reactions of substituted diazocyclopropanes and cyclopropyldiazonium ions

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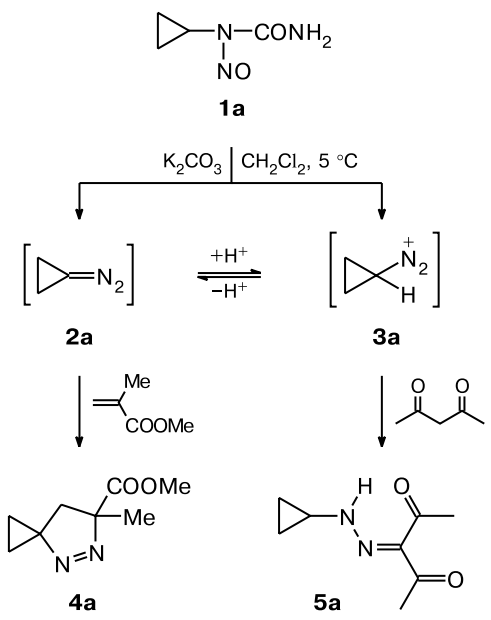
Decomposition of *N*-nitroso-*N*-cyclopropylureas at 5—7 °C on treatment with K_2CO_3 containing 15—20% H_2O allows simultaneous generation of both substituted diazocyclopropanes and cyclopropyldiazonium ions, which can react according to 1,3-dipolar cycloaddition or azo-coupling pattern with appropriate substrates. The nature of substituents in the cyclopropyl ring have a pronounced influence on the product ratio (and, probably, on the equilibrium between the diazo compound and the diazonium ion). Thus, on treatment with a base in the presence of equimolar amounts of methyl metacrylate as a trap for the diazo compound and 2-naphthol as a trap for the diazonium ion, *N*-cyclopropyl- and *N*-(2,2-dimethylcyclopropyl)-*N*-nitrosourea azo coupling products predominate. Conversely, *N*-(2,2-dichlorocyclopropyl)-*N*-nitrosourea is transformed predominantly into 1,3-cycloaddition products. A rationalization for the experimental data is proposed.

Key words: nitrosocyclopropylureas, diazocyclopropanes, cyclopropyldiazonium ions, azo compounds, spiro[4,5-dihydropyrazole-5,1′-cyclopropanes], competitive reactions.

Base-induced decomposition of *N*-cyclopropyl-*N*-nitrosourea (**1a**) is a convenient method for generation of diazocyclopropane (**2a**), which enters into 1,3-dipolar cycloaddition with some unsaturated compounds, giving rise to spirocyclopropane-containing 1- and 2-pyrazolines.[1] Recently, we have shown[2,3] that by using active aromatic compounds and aliphatic CH-acids as substrates, it is possible to trap also the cyclopropyldiazonium ion (**3a**) with the formation of azo coupling products. Moreover, both intermediates, **2a** and **3a**, can be trapped simultaneously under the same conditions. Decomposition of nitrosourea **1a** induced by K_2CO_3 carried out at +5 °C in the presence of equimolar amounts of methyl methacrylate and pentane-2,4-dione yields both pyrazoline **4a**, formed upon 1,3-dipolar cycloaddition of **2a** to methyl methacrylate, and cyclopropylhydrazone **5a**, resulting from the addition of ion **3a** to the reactive methylene group of the diketone. The **4a** to **5a** ratio equals[3] 2.2 : 1 (Scheme 1).

Scheme 1



This study deals with reactions of substituted diazocyclopropanes and the related cyclopropyldiazonium ions, formed from *N*-(2,2-dichlorocyclopropyl)- (**1b**) and *N*-(2,2-dimethylcyclopropyl)-*N*-nitrosourea (**1c**).[4] The influence of substituents in the cyclopropane ring on the equilibrium between diazocyclopropanes and the cyclopropyldiazonium ions was studied. In addition, the procedure for the preparation of nitrosourea **1b** was considerably improved. First, the nitrosation of starting *N*-(2,2-dichlorocyclopropyl)urea with N_2O_3 was carried out in the presence of AcONa for binding HNO_2. Second, after the reaction, the product was precipitated by diluting the reaction mixture with light petroleum, the precipitate was extracted with $CHCl_3$, and the resulting

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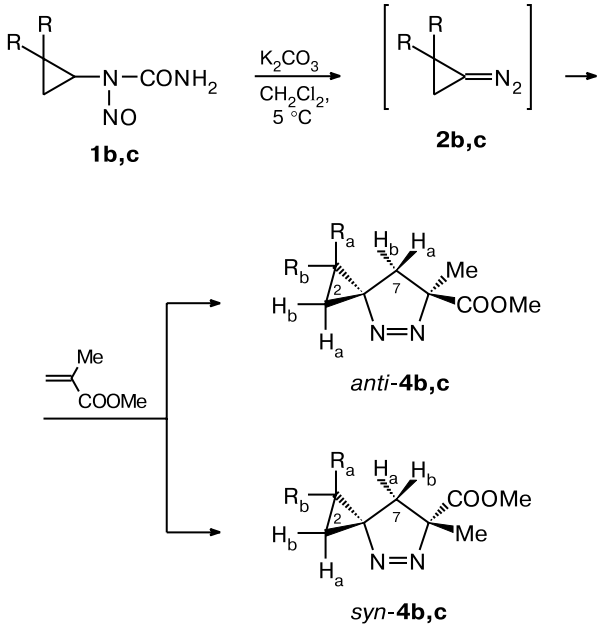
solution of nitrosourea **1b** was washed with a 1% solution of $NaHCO_3$ (see Experimental). All work-up was carried out rather rapidly at a temperature of 0—5 °C. This allowed us to prepare pure nitrosourea **1b** (yield ~30%), formed as pale yellow crystals slowly decomposing at 110 °C (previously,[4] it was reported that this nitrosourea decomposes above 35 °C). The relatively low yield of product **1b** can be due to either partial nitrosation of the starting urea at the NH_2 group or to the fact that a substantial portion of nitrosourea decomposes in the acid medium to give 2,2-dichlorocyclopropyl isocyanate. Unlike nitrosourea **1b**, this compound is soluble in a CH_2Cl_2—light petroleum mixture and, thus, it can be separated. The formation of the isocyanate on decomposition of **1b** is confirmed by the fact that treatment with an excess of dry NH_3 of the filtrate obtained after precipitation of nitrosourea **1b** with light petroleum affords the starting *N*-(2,2-dichlorocyclopropyl)urea in a yield of up to 25%. In another run, the treatment of this filtrate with MeOH gave rise to methyl *N*-(2,2-dichlorocyclopropyl)carbamate (yield 20%). The formation of isocyanates on decomposition of nitrosoureas has been noted previously, for example, for *N*-methyl-*N*-nitrosourea.[5] However, in this case, decomposition proceeds apparently even at −10 °C and is catalyzed by the acid present, because nitrosourea **1b** that has been isolated from the reaction mixture is quite stable.

Base-induced decomposition of nitrosoureas **1b,c** allowed us to generate diazocyclopropanes **2b,c** and diazonium ions **3b,c** both with donor and with acceptor substituents in the cyclopropane ring and to compare their reactivities in the competing reactions with appropriate substrates, by analogy with unsubstituted parent compounds **2a** and **3a**.[3]

Diazocyclopropanes **2b,c** were trapped by methyl methacrylate, which is a fairly reactive dipolarophile and normally gives stable 1-pyrazoline derivatives in reactions with various aliphatic diazo compounds, including diazocyclopropane (**2a**) generated under various conditions.[6] The reactions were carried out at +5 °C in CH_2Cl_2 using K_2CO_3 as a base. In both cases, after the yellow color inherent in starting nitrosoureas **1b,c** disappeared, the reaction mixture was filtered through SiO_2 and the filtrate was concentrated to give pure 1-pyrazolines **4b,c** in 74 and 32% yields, respectively (Scheme 2). Each product was a mixture of *anti*- and *syn*-isomers; in the case of **4b**, the *anti*-isomer predominated, while for **4c**, the *syn*-isomer was the major product. In the ^1H NMR spectrum, each of the H(2) and H(7) protons of isomeric pyrazolines **4b** forms two isolated AB-systems with spin-spin coupling constants of 8.3 and 13.8 Hz, corresponding to the geminal protons of three- and five-membered rings. It is characteristic that the $H_a(7)$ proton in the *syn*-isomer appeared in a lower field (δ 2.61), due to the simultaneous deshielding influence of the Cl atoms of the ester group, whereas the $H_b(7)$ signal is in higher field (δ 1.62). In the *anti*-isomer, the discordant action of these groups results in a smaller distance between the signals of $H_a(7)$ and $H_b(7)$, which occur at δ 2.26 and 2.03, respectively. The deshielding effect of the diaza group leads to a downfield shift of the signals of the $H_a(2)$ protons opposite to this group by 0.83 ppm compared to the $H_b(2)$ signal.

Scheme 2



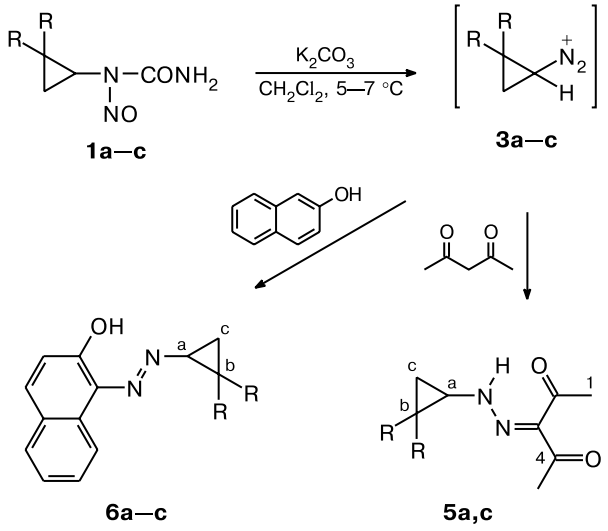
R = Cl (**b**), Me (**c**)

The ^1H NMR spectrum of a mixture of pyrazoline **4c** isomers is more complex. Besides eight doublets due to the H(2) and H(7) protons of *syn*- and *anti*-isomers, the high-field region contains six separate signals for the Me groups. The use of NOESY and {C,H}-correlation 2D techniques provided full assignment of the ^1H and ^{13}C NMR signals of *anti*- and *syn*-isomers of pyrazolines **4b,c**.

The cyclopropyldiazonium ions **3b,c** were trapped using 2-naphthol and acetylacetone as azo components (Scheme 3). It was found that decomposition of nitrosourea **1b** on treatment with moist K_2CO_3 in the presence of 2-naphthol results in cyclopropylazoarene **6b** in 27% yield, whereas with acetylacetone, no azo coupling product (**5b**) was detected even by direct NMR monitoring of the reaction mixture. According to the ^1H NMR spectrum, the only identifiable product formed in decomposition of compound **1b** was 1,1-dichloroallene, responsible for a singlet at δ 5.39.[7] It should be noted that under identical conditions in the presence of K_2CO_3, substituted nitrosoureas **1b,c** decompose much more slowly than the un-

substituted analog **1a**, their complete decomposition requiring at least 12 h instead of 2—3 h.

Scheme 3



R = H (**a**), Cl (**b**), Me (**c**)

Azoarene **6b** was isolated using preparative TLC and characterized by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum contains a three-spin system of protons of the cyclopropane ring as a doublet of doublets for each signal at δ 2.34, 2.42, and 4.27 and a low-field broadened doublet at δ 8.68, typical of the H(8) proton of the naphthalene ring (the analogous signal for unsubstituted 1-(cyclopropylazo)-2-naphthol[2] occurs at δ 8.72).

For estimating the reactivity of 2-naphthol and acetylacetone toward azo coupling with the cyclopropyldiazonium ions, we carried out their competing reaction with ion **3a**. This was done using nitrosourea **1a**, K_2CO_3, 2-naphthol, and acetylacetone in 1 : 2 : 4 : 4 molar ratio. According to ^{1}H NMR data, the reaction mixture contained compounds **6a** and **5a** in 6.3 : 1 ratio, respectively. Thus, 2-naphthol is actually more reactive in this reaction than acetylacetone. This difference seems to be even more pronounced in trapping of ion **3b**.

Unlike the (dichlorocyclopropyl)diazonium ion **3b**, the dimethyl analog **3c** forms azo coupling products both with 2-naphthol and with acetylacetone. The yields of adducts **6c** and **5c** amount to 55 and 29%, respectively. The generation of ion **3c** in the competitive reaction between 2-naphthol and acetylacetone results in adducts **6c** and **5c** in ~1.4 : 1 ratio. In the ^{1}H NMR spectrum, the Ac groups of cyclopropylhydrazone **5c** are responsible for two separate singlets with δ 2.33 and 2.51, due to their different positions with respect to the C=N bond. The signal with δ 2.95 for the methine proton of the cyclopropane fragment resembles a quintet; however, with selective NH-proton decoupling, this signal degenerates into a doublet of doublets with spin-spin coupling constants of 7.5 and 4.4 Hz, which is consistent with the expected structure of the trisubstituted cyclopropane fragment. In the ^{1}H NMR spectrum of azoarene **6c**, the low-field doublet at δ 8.76 is due to the H(8) proton, as in azoarenes **6a,b**. It is noteworthy that on going from **6b** to **6c**, the signal of the methine proton of the cyclopropane ring markedly shifts upfield (Δδ 0.67).

These results show that intermediate **3b** is the least stable* among the cyclopropyldiazonium ions studied and is fairly sensitive to the nature of the trapping reagent. It adds only to highly reactive azo components, for example, to 2-naphthol to give products in moderate yields. Conversely, the diazonium cation **3c**, having two Me substituents in the cyclopropane ring, is less sensitive to the nature of the azo component and can react with a larger number of such compounds. The lower yields of adducts **5c** and **6c** compared to the yields of unsubstituted compounds **5a** and **6a** are probably due to steric factors, *i.e.*, to the presence of Me substituents.

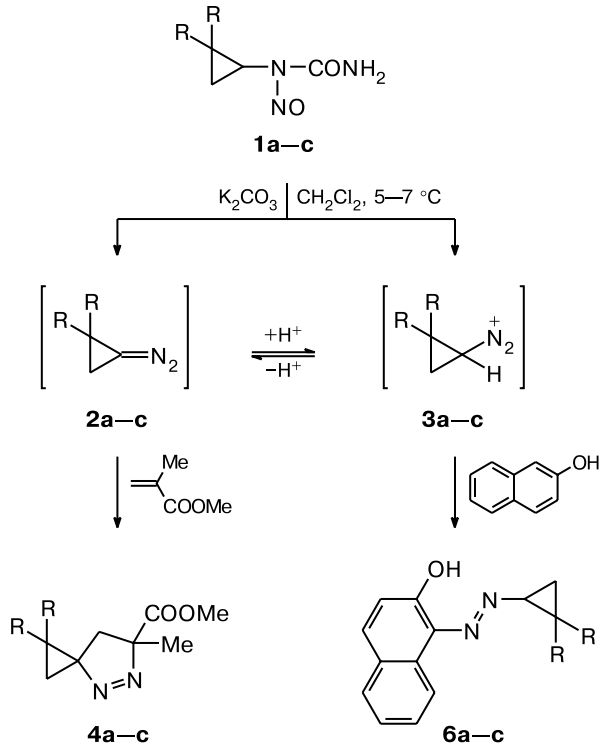
The data of the ^{1}H NMR spectra of pyrazolines **4b,c** and azoarenes **6b,c** were further used to determine the ratio of the products of competitive reactions between substituted diazocyclopropanes and cyclopropyldiazonium ions in 1,3-dipolar cycloaddition and azo coupling, respectively. The reactions (Scheme 4) were carried out by a standard procedure using cyclopropylnitrosoureas **1a—c**, K_2CO_3, methyl methacrylate, and 2-naphthol in 1 : 2 : 4 : 4 molar ratio. The yields and the ratios of the resulting adducts are summarized in Table 1.

Since an equimolar ratio of methyl methacrylate and 2-naphthol gave a fairly low yield of pyrazoline **4a** (≤4%), to determine the relative reactivities of the substrates more accurately, we repeated the experiment taking 4 moles of 2-naphthol and 12 moles of methyl methacrylate per mole of nitrosourea **1a**. The yields of adducts **4a** and **6a** were ~11 and 78%; thus, 2-naphthol has actually proved to be a ~20 times more active trapping agent than methyl methacrylate.

It can be seen from Table 1 that the introduction of two Cl atoms into the cyclopropane ring inverts the ratio of the trapping products of (dichlorocyclopropyl)diazonium **3b** and diazodichlorocyclopropane **2b**. In this case, the presence of even medium-strength electron-withdrawing substituents (such as Cl atoms) seems to induce a substantial shift of equilibrium in the system of intermediates **3b—2b** toward diazocyclopropane due to the easier proton abstraction from the diazonium ion. The magnitude of such shift was fairly difficult to predict.

* The high selectivity of the diazonium cation **3b** and the low yield of azo coupling products could be due to low current concentration of ion **3b** caused by a substantial shift of the equilibrium toward diazocyclopropane **2b**.

Scheme 4



In the case of dimethyl derivatives **2c** and **3c**, the azo coupling product prevails once again over the 1,3-dipolar cycloaddition product, although to a lesser extent than in the case of unsubstituted cyclopropyldiazonium. This is accompanied by a decrease in the overall yield of the trapping products of both diazo compound **2c** and diazonium ion **3c**, related apparently to the decrease in the reactivity due to steric factors and to a higher contribution of side processes, in particular, dediazotization.

The efficiency of 2-naphthol in the azo coupling with cyclopropyldiazonium ions **3a—c** is apparently provided, among other factors, by an optimal combination of the basic and nucleophilic properties of the naphtholate anions formed in the naphthol—K_2CO_3 system (for 2-naphthol, pK_a equals ~9.5)[8]. The naphtholate anions can act themselves as counter-ions for intermediates **3a—c**, which makes the azo coupling preferable. We showed that decomposition of nitrosourea **1a** easily proceeds at 5 °C on treatment with dry potassium naphtholate in CH_2Cl_2 (reactant molar ratio 1 : 3). The mixture immediately acquires a bright yellow color and, after vigorous stirring for ~15 min, it does not contain the starting nitrosourea any longer. Pure azo adduct **6a** was isolated from the reaction mixture in 66% yield by preparative TLC. Apparently, potassium naphtholate not only decomposes nitrosourea **1a** at least 8 times as fast as K_2CO_3 does, but is simultaneously azo coupled with the cyclopropyldiazonium cation **3a** generated *in situ*.

Table 1. Yields and ratios of pyrazolines **4a—c** and azonaphtholes **6a—c** under conditions of competitive reactions (molar ratio **1a—c** : methyl methacrylate : 2-naphthol = 1 : 4 : 4)

Nitrosourea	Yield (%)		Ratio **4** : **6**
	pyrazoline **4**	azoarene **6**	
1a	≤4	86	~1 : 22
1b	78	12	6.5 : 1
1c	16	48	1 : 3

Thus, we demonstrated the possibility of simultaneous generation and trapping of substituted diazocyclopropanes and the corresponding cyclopropyldiazonium ions by decomposition of *N*-cyclopropyl-*N*-nitrosoureas by moist K_2CO_3 in the presence of appropriate trapping agents. The type of substituents has a great influence on the equilibrium between the diazo compound and the diazonium ion. The generation of unsubstituted (**2a**) or *gem*-dimethyl-sibstituted diazocyclopropanes (**2c**) and cyclopropyldiazonium ions **3a,c** in the presence of methyl methacrylate and 2-naphthol results in the azo coupling products prevailing over the 1,3-dipolar addition products. The introduction of two Cl atoms into the cyclopropane ring results in an opposite ratio of the reaction products. In addition, in the case of generation of dimethyl derivatives **2c** and **3c**, the overall yield of trapping products of both diazocyclopropane **2c** and the cyclopropyldiazonium **3c** considerably decreases. Apparently, this is due to the lower reactivity of these intermediates caused by the steric effects of substituents in the cyclopropane ring.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.5 MHz) for solutions in $CDCl_3$ containing 0.05% Me_4Si as the internal standard; 2D NOESY experiments were performed on a Bruker DRX-500 spectrometer (500 MHz). Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct injection). UV spectrum was measured on a Specord M-40 spectrophotometer. *N*-(2,2-Dimethylcyclopropyl)-*N*-nitrosourea (**1c**) was synthesized by a previously reported procedure.[4] Chemically pure grade K_2CO_3 containing ~20% H_2O was used. TLC was done using Merck silica gel 60 (0.040—0.063 mm). Potassium 2-naphtholate was obtained by the reaction of potassium with 2-naphthol in toluene.

***N*-(2,2-Dichlorocyclopropyl)-*N*-nitrosourea (1b).** A ~20-fold excess of N_2O_3 (prepared from KNO_2 and 80% H_2SO_4) was passed through a suspension of *N*-(2,2-dichlorocyclopropyl)urea (340 mg, 2 mmol) and AcONa (246 mg, 3 mmol) in 12 mL of dry CH_2Cl_2 at −10 °C for 30 min. After a persistent green-blue color has appeared, the reaction mixture was cooled to −30 °C, 20 mL of light petroleum was added, and excess N_2O_3 was removed by passing a stream of argon through the suspension formed. The reaction mixture was filtered off at a temperature

not higher than −10 °C and the precipitate was washed with 30 mL of a light petroleum—CH_2Cl_2 mixture (2 : 1). The filtrate containing 2,2-dichlorocyclopropyl isocyanate was stored in a refrigerator and the precipitate collected on the filter was extracted with $CHCl_3$ at −10 °C (10×5 mL). The extract was quickly washed with a 1% solution of $NaHCO_3$ (2×10 mL) and H_2O (10 mL) and dried with Na_2SO_4 for 3 h at 5 °C. The removal of the solvents gave 118 mg (30%) of nitrosourea **1b** as small pale yellow crystals that slowly decompose starting from 110 °C and melt at 120—124 °C. The ^1H and ^{13}C NMR spectra correspond to those described previously.[4]

An excess of dry NH_3 was passed into the resulting solution of 2,2-dichlorocyclopropyl isocyanate in a mixture of light petroleum and CH_2Cl_2 (see above), the precipitate was filtered off, dried *in vacuo* at 0.1 Torr, and recrystallized from $CHCl_3$ to give 85 mg (25%) of *N*-(2,2-dichlorocyclopropyl)urea analogous to an authentic sample.

In another similar experiment, excess MeOH was added to the obtained solution of 2,2-dichlorocyclopropyl isocyanate, the solution was kept for 0.5 h and concentrated, and the residue was dried *in vacuo* (0.1 Torr) and recrystallized from an ether—pentane mixture (2 : 1) to give 74 mg (20%) of methyl *N*-(2,2-dichlorocyclopropyl)carbamate as colorless crystals, m.p. 69—70 °C. ^1H NMR (DMSO-d_6), δ: 1.57 (br.dd, 1 H, J_{gem} = 8.3 Hz, J_{trans} = 6.6 Hz); 1.93 (dd, 1 H, J_{cis} = 9.9 Hz, J_{gem} = 8.3 Hz); 3.22 (br.ddd, 1 H, J_{cis} = 9.9 Hz, J_{trans} = 6.6 Hz, J_{CH-NH} = 4.3 Hz); 3.59 (br.s, 3 H, OMe); 7.92 (br.d, 1 H, NH, J = 4.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.9 (CH_2); 38.4 (CH); 52.8 (OMe); 58.9 (CCl_2); 157.1 (CO). MS, *m/z* (I_{rel} (%)): 182 $[M(2\,^{35}Cl) - H]^+$ (1); 172 (1), 170 (8), 168 (12) $[M - Me]^+$; 150 (37), 148 (100) $[M - Cl]^+$.

Pyrazolines 4b,c (general procedure). Potassium carbonate (69 mg, 0.4 mmol) was added at 5—7 °C to a solution of methyl methacrylate (30 mg, 0.3 mmol) and nitrosourea **1b** (0.2 mmol, 39.6 mg) or **1c** (0.2 mmol, 31.4 mg) in 1 mL of CH_2Cl_2. The mixture was vigorously stirred for 12 h. The resulting suspension was centrifuged, the solution was concentrated, the precipitate was washed with $CHCl_3$ (2×0.3 mL), and the combined organic extracts were passed through a short SiO_2 layer. Evaporation gave pyrazolines **4b,c** as light-yellow oils.

1,1-Dichloro-6-methoxycarbonyl-6-methyl-4,5-diazaspiro[2.4]hept-4-ene (4b). Yield 35 mg (74%), a mixture of *anti*- and *syn*-isomers (1.6 : 1). Found (%): C, 40.27; H, 4.37; N, 11.98. $C_8H_{10}Cl_2N_2O_2$. Calculated (%): C, 40.53; H, 4.25; N, 11.82. MS, *m/z* (I_{rel} (%)): 236 $[M(2\,^{35}Cl)]^+$ (1); 181 (1), 179 (6), 177 (13) $[M - COOMe]^+$; 115 (12), 113 (37) $[M - COOMe - HCl - N_2]^+$; 41 (100). Pyrazoline ***anti*-4b**. ^1H NMR ($CDCl_3$), δ: 1.66 (s, 3 H, Me); 1.90 (d, 1 H, H_b(2), J_{gem} = 8.4 Hz); 2.03 (d, 1 H, H_b(7), J_{gem} = 13.8 Hz); 2.26 (d, 1 H, H_a(7), J_{gem} = 13.8 Hz); 2.71 (d, 1 H, H_a(2), J_{gem} = 8.4 Hz); 3.74 (s, 3 H, OMe). ^{13}C NMR (CD_3OD), δ: 22.2 (Me); 33.1 (C(2)); 35.1 (C(7)); 53.5 (OMe); 62.1 (C(1)); 79.1 (C(3)); 95.8 (C(6)); 171.4 (C=O). Pyrazoline ***syn*-4b**. ^1H NMR ($CDCl_3$), δ: 1.62 (d, 1 H, H_b(7), J_{gem} = 13.8 Hz); 1.65 (s, 3 H, Me); 1.88 (d, 1 H, H_b(2), J_{gem} = 8.3 Hz); 2.61 (d, 1 H, H_a(7), J_{gem} = 13.8 Hz); 2.72 (d, 1 H, H_a(2), J_{gem} = 8.3 Hz); 3.75 (s, 3 H, OMe). ^{13}C NMR (CD_3OD), δ: 21.9 (Me); 33.2 (C(2)); 35.2 (C(7)); 53.5 (OMe); 62.2 (C(1)); 79.0 (C(3)); 95.8 (C(6)); 171.6 (C=O).

6-Methoxycarbonyl-1,1,6-trimethyl-4,5-diazaspiro[2.4]hept-4-ene (4c). Yield 12.6 mg (32%) as a mixture of *anti*- and *syn*-isomers (1 : 1.2). Found (%): C, 61.06; H, 8.54; N, 14.43. $C_{10}H_{16}N_2O_2$. Calculated (%): C, 61.20; H, 8.22; N, 14.27. MS, *m/z* (I_{rel} (%)): 196 $[M]^+$ (1), 168 $[M - N_2]^+$ (2), 153 $[M - Pr]^+$ (28), 137 $[M - COOMe]^+$ (61), 125 $[M - N_2 - Pr]^+$ (13), 109 $[M - COOMe - N_2]^+$ (73), 67 (100). Pyrazoline ***anti*-4c**. ^1H NMR ($CDCl_3$), δ: 0.94 (d, 1 H, H_b(2), J_{gem} = 5.3 Hz); 1.13 (s, 3 H, Me_b); 1.49 (s, 3 H, Me_a); 1.57 (s, 3 H, Me); 1.65 (d, 1 H, H_b(7), J_{gem} = 12.9 Hz); 1.81 (d, 1 H, H_a(2), J_{gem} = 5.3 Hz); 2.12 (d, 1 H, H_a(7), J_{gem} = 12.9 Hz); 3.78 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$) δ: 21.6 (Me_a); 22.6 (Me); 23.5 (Me_b); 26.4 (C(1)); 28.6 (C(2)); 33.2 (C(7)); 52.8 (OMe); 78.05 (C(3)); 91.9 (C(6)); 171.9 (C=O). Pyrazoline ***syn*-4c**. ^1H NMR ($CDCl_3$), δ: 0.92 (d, 1 H, H_b(2), J_{gem} = 5.1 Hz); 1.14 (s, 3 H, Me_b); 1.45 (d, 1 H, H_b(7), J_{gem} = 12.8 Hz); 1.51 (s, 3 H, Me_a); 1.58 (s, 3 H, Me); 1.76 (d, 1 H, H_a(2), J_{gem} = 5.1 Hz); 2.31 (d, 1 H, H_a(7), J_{gem} = 12.8); 3.79 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 21.6 (Me_a); 22.3 (Me); 23.2 (Me_b); 25.9 (C(1)); 28.8 (C(2)); 33.5 (C(7)); 52.8 (OMe); 78.01 (C(3)); 92.0 (C(6)); 171.9 (C=O).

Azoarenes 6b,c (general procedure). 2-Naphthol (28.8 mg, 0.2 mmol) and K_2CO_3 (69 mg, 0.4 mmol) were added successively to a solution of nitrosourea **1b** (0.2 mmol, 39.6 mg) or **1c** (31.4 mg) in 1 mL of CH_2Cl_2 cooled to 5—7 °C and the mixture was vigorously stirred for 12 h. The resulting suspension was filtered, the precipitate was washed with $CHCl_3$ (3×0.3 mL), and the combined organic extracts were concentrated. The residue, which consisted of 2-naphthol and azo adducts **6b** or **6c** (^1H NMR data), was separated by preparative TLC (SiO_2, light petroleum—AcOEt as the eluent, 8 : 1), collecting a bright-yellow zone with R_f 0.5. The product was additionally purified by crystallization from hexane at −18 °C.

1-(2,2-Dichlorocyclopropylazo)-2-naphthol (6b). Yield 15.1 mg (27%), yellow needle crystals, m.p. 90—91 °C. Found (%): C, 55.31; H, 3.57; N, 9.70. $C_{13}H_{10}Cl_2N_2O$. Calculated (%): C, 55.54; H, 3.59; N, 9.96. ^1H NMR ($CDCl_3$), δ: 2.34 (dd, 1 H, H_c, J_{cis} = 9.1 Hz, J_{gem} = 8.1 Hz); 2.42 (dd, 1 H, H_c, J_{trans} = 6.1 Hz, J_{gem} = 8.1 Hz); 4.27 (dd, 1 H, H_a, J_{cis} = 9.1 Hz, J_{trans} = 6.1 Hz); 7.11 (d, 1 H, H(3), J = 9.1 Hz); 7.43 (ddd, 1 H, H(6), J = 8.0 Hz, J = 6.9 Hz, J = 1.2 Hz); 7.60 (ddd, 1 H, H(7), J = 8.5 Hz, J = 6.9 Hz, J = 1.4 Hz); 7.75 (br.d, 1 H, H(5), J = 8.0 Hz); 7.83 (br.d, 1 H, H(4), J = 9.1 Hz); 8.68 (br.d, 1 H, H(8), J = 8.5 Hz); 13.41 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 29.9 (C_c); 59.0 (C_a); 59.7 (C_b); 120.4 (C(3)); 121.5 (C(8)); 124.8 (C(6)); 128.2 (C(7)); 128.3 (C(5)); 128.3, 129.5, 132.8 (C(1), C(9), C(10)); 136.1 (C(4)); 154.6 (C(2)). MS, *m/z* (I_{rel} (%)): 246 (14), 244 (44) $[M - HCl]^+$; 217 (27), 215 (81) $[M - HCl - HCO]^+$; 209 $[M - HCl - Cl]^+$ (100). UV (hexane), λ_{max}/nm (ε): 227 (34900) (+ 206 sh (17100)), 254 (10400), 262 (9700) (+ 280 sh (3100)), 344 (5800), 386 (5900) (+ 418 sh (4600)).

1-(2,2-Dimethylcyclopropylazo)-2-naphthol (6c). Yield 26.3 mg (55%), yellow needle crystals, m.p. 38—40 °C. Found (%): C, 74.69; H, 6.64; N, 11.39. $C_{15}H_{16}N_2O$. Calculated (%): C, 74.97; H, 6.71; N, 11.66. ^1H NMR ($CDCl_3$), δ: 1.28 (s, 3 H, Me); 1.38 (dd, 1 H, H_c, J_{cis} = 7.6 Hz, J_{gem} = 5.3 Hz); 1.43 (s, 3 H, Me); 1.49 (dd, 1 H, H_c, J_{trans} = 3.9 Hz, J_{gem} = 5.3 Hz); 3.60 (dd, 1 H, H_a, J_{cis} = 7.6 Hz, J_{trans} = 3.9 Hz); 7.11 (d, 1 H, H(3), J = 9.0 Hz); 7.40 (ddd, 1 H, H(6), J = 8.1 Hz, J = 6.9 Hz, J = 1.2 Hz); 7.57 (ddd, 1 H, H(7), J = 8.5 Hz, J = 6.9 Hz, J = 1.4 Hz); 7.75 (br.d, 1 H, H(5), J = 8.1 Hz); 7.76 (br.d, 1 H, H(4), J = 9.0 Hz); 8.76 (br.d, 1 H, H(8), J = 8.5 Hz); 13.80 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ:

20.8 (Me); 24.6 (C_b); 25.3 (Me); 25.9 (C_c); 60.3 (C_a); 120.1 (C(3)); 121.6 (C(8)); 124.2 (C(6)); 127.7 (C(7)); 128.0 (C(5)); 128.1, 128.6, 132.5 (C(1), C(9), C(10)); 133.7 (C(4)); 152.9 (C(2)). MS, m/z (I_{rel} (%)): 240 $[M]^+$ (23), 225 $[M - Me]^+$ (18), 184 $[M - N_2 - CO]^+$ (17), 158 (54), 144 (33), 129 (78), 115 (68), 41 (100).

3-(2,2-Dimethylcyclopropyl)hydrazonopentane-2,4-dione (5c). Potassium carbonate (104 mg, 0.6 mmol) was added with stirring to a solution of nitrosourea **1c** (31.4 mg, 0.2 mmol) and acetylacetone (23.3 mg, 0.24 mmol) in 1.2 mL of CH_2Cl_2 cooled to 5—7 °C, and the mixture was vigorously stirred for 12 h. The resulting suspension was filtered, the precipitate was washed with CH_2Cl_2 (2×0.5 mL), the combined organic extracts were concentrated, and the residue was dried *in vacuo* (1 Torr). Hexane (1 mL) was added to the residue and the resulting suspension was centrifuged. Decanting and concentrating of the solution gave 11.3 mg (29%) of hydrazone **5c** as a light-yellow oil. Found (%): C, 61.34; H, 7.72; N, 14.48. $C_{10}H_{15}N_2O_2$. Calculated (%): C, 61.52; H, 7.74; N, 14.35. ^{1}H NMR ($CDCl_3$), δ: 0.90 (dd, 1 H, H_c, J_{cis} = 7.5 Hz, J_{gem} = 5.8 Hz); 0.93 (dd, 1 H, H_c, J_{trans} = 4.4 Hz, J_{gem} = 5.8 Hz); 1.10, 1.16 (both s, each 3 H, Me); 2.33, 2.51 (both s, each 3 H, COMe); 2.95 (m, 1 H, H_a, J_{cis} = 7.5 Hz, J_{trans} = 4.4 Hz, J_{CH-NH} = 3.75 Hz); 13.68 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 19.0 (C_c); 19.3 (Me); 20.0 (C_b); 24.9 (Me); 26.5, 31.3 (C(1), C(5)); 45.3 (C_a); 133.4 (C(3)); 196.8, 197.0 (C(2), C(4)). MS, m/z (I_{rel} (%)): 196 $[M]^+$ (2), 153 $[M - COMe]^+$ (11), 43 $[COMe]^+$ (100).

Competitive reactions (general procedure). 2-Naphthol (28.8 mg, 0.2 mmol) and K_2CO_3 (17.3 mg, 0.1 mmol) were successively added with stirring at 5—7 °C to a solution of nitrosourea **1a—c** (0.05 mmol) and acetylacetone (19.4 mg, 0.2 mmol) or methyl methacrylate (20 mg, 0.2 mmol) in 1 mL of CH_2Cl_2. The vigorous stirring was continued for 5 h at 5—7 °C and the reaction mixture was kept for ~12 h at the same temperature. The resulting suspension was filtered, the precipitate was washed with CH_2Cl_2 until the filtrate discolored (3×1 mL), and the combined organic extracts were concentrated and dried *in vacuo* (1 Torr). The yellow crystalline precipitate was completely dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy.

Reaction of *N*-cyclopropyl-*N*-nitrosourea (1a) with potassium 2-naphtholate. Potassium 2-naphtholate (27.3 mg, 0.15 mmol) was added with stirring at 4 °C to a solution of nitrosourea **1a** (6.5 mg, 0.05 mmol) in 1 mL of CH_2Cl_2. An intense yellow color appeared immediately. The vigorous stirring was continued for an additional 15 min at 4—5 °C, the reaction mixture was quickly filtered at a temperature not higher than 5 °C, and the precipitate was washed with 1 mL of CH_2Cl_2. The bright-yellow filtrate was concentrated and the residue was separated by preparative TLC (SiO_2, elution with light petroleum—AcOEt (8 : 1)), collecting the bright-yellow zone of the azo compound with R_f 0.5. The yield of azo compound **6a** was 7 mg (66%). The ^{1}H and ^{13}C NMR spectra correspond to those described previously.[2]

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