Reactions of spirocyclopropane-containing 1- and 2-pyrazolines with electrophilic reagents

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Hydrochlorination of spiro(1-pyrazoline-3,1′-cyclopropanes) proceeds regioselectively at the azocyclopropane group to form 3-(2-haloethyl)pyrazoline derivatives. If the latter contain a halogen atom in the heterocycle, they are readily converted into (2-haloethyl)pyrazole hydrohalides. Bromination of 3-cyanospiro(2-pyrazoline-5,1′-cyclopropane) with *N*-bromosuccinimide at 20 °C proceeds with retention of the cyclopropane ring to form 3-bromo-3-cyanospiro(1-pyrazoline-5,1′-cyclopropane), which is converted into (2-bromoethyl)cyanopyrazole in ~60% yield at ~20 °C after 3—4 days.

Key words: spiro(1-pyrazoline-3,1′-cyclopropanes), spiro(2-pyrazoline-5,1′-cyclopropanes), 3-(2-haloethyl)pyrazolines and 3-(2-haloethyl)pyrazoles, hydrochlorination, acylation, bromination with *N*-bromosuccinimide.

Previously,[1—4] we have demonstrated that diazocyclopropanes generated *in situ* can undergo 1,3-dipolar cycloaddition to different unsaturated compounds to form spiro(1- and 2-pyrazoline-3(5),1′-cyclopropanes). In these cases, 1-pyrazolines containing the spiro-fused cyclopropane fragment adjacent to the azo group react with acyl chlorides[5—7] to form the corresponding 1-acyl-3-(2-chloroethyl)-2-pyrazolines, *viz.*, products of addition of acyl chlorides to the azocyclopropane system, in virtually quantitative yields. These reactions are accompanied by the opening of the cyclopropane ring. As part of continuing studies, in this work we investigated protonation, acylation, and bromination of a number of spiro(1-pyrazoline-3,1′-cyclopropanes) and spiro(2-pyrazoline-5,1′-cyclopropanes) with the aim of revealing the mutual effect of the small ring and the azo group.

When gaseous HCl was passed at 0 °C through a solution of 1-pyrazoline **1**, which was prepared by adding diazocyclopropane generated *in situ* to bicyclo[2.2.1]hept-2-ene,[1] the cyclopropane ring in compound **1** was cleaved to form the formal 1,5-addition product **2** containing the 2-chloroethyl substituent. According to the ^{1}H NMR spectral data, the degree of conversion of pyrazoline **1** depends on the amount of HCl added. When the reagents were taken in an approximately equimolar ratio, only half of pyrazoline **1** was converted into compound **2**. The complete conversion of the starting pyrazoline required no less than a twofold molar excess of HCl, which is indirect evidence that 2-pyrazoline **2** was formed as its hydrochloride. The structure of the resulting compound was established by ^{1}H and ^{13}C NMR spectroscopy (with the use of standard homo- and heteronuclear double resonance techniques). Thus the presence of only one set of signals in the ^{1}H and ^{13}C NMR spectra indicates that only one of the possible isomers was formed. The spin-spin coupling constant $J_{1,2}$ is equal to ~1 Hz and corresponds to the *exo* isomer. The lowest-field signal belongs to the H(2) proton because this atom is adjacent to the N(3) atom. No protons are bound to the C(5) atom because no additional splitting is observed in the spectrum of the chloroethyl substituent. The ^{13}C NMR spectrum completely confirms the proposed structure. The removal of the solvent from the reaction mixture afforded very hygroscopic colorless crystals (the yield was ~95%). However, we failed to isolate the free base by neutralizing a solution of compound **2** in CH_2Cl_2 with Et_3N or K_2CO_3 because substantial resinification occurred.

The reaction of pyrazoline **1** with benzyl bromide also proceeded as the formal 1,5-addition to the azocyclopropane system. However, this reaction proceeded substantially more slowly than the reaction with HCl. In particular, keeping of an equimolar mixture of compound **1** and $PhCH_2Br$ in $CDCl_3$ at 5 °C for 2 days afforded (according to the ^{1}H NMR spectral data) (2-bromoethyl)pyrazoline **3**. Compound **3** and the initial reagents were present in the resulting mixture in an approximately equal molar ratio. An increase in the reaction time or in the temperature led to a noticeable increase in the degree of side reactions. Pyrazoline **3** was isolated in the individual state in ~40% yield by preparative TLC and was characterized by ^{1}H and ^{13}C NMR spectroscopy (with the use of the {C,H}-correlation)

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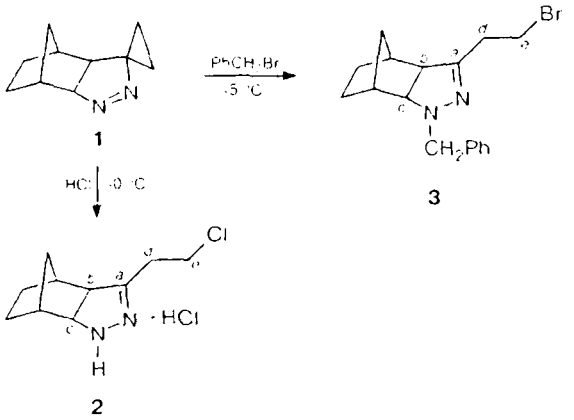
and mass spectrometry. Pyrazoline **3**, like compound **2**, existed as the *exo* isomer, and we failed to detect even traces of another isomer. It should be noted that the signals for the methylene protons of the NCH_2Ph group are observed in the ^1H NMR spectrum as well-resolved doublets with spin-spin coupling constants ^2J = 13.5 Hz. The nonequivalence of the protons at the C^d atom of the bromoethyl fragment is manifested in the ^1H NMR spectrum of this compound. This nonequivalence is most pronounced for the CH_2 groups in the $^{13}C-^1H$ COSY spectrum in which C(8), C(9), C(10), and NCH_2 give two cross-peaks each. Pyrazoline **3** can be isolated with a purity of up to 93% because the bromine atom readily enters into substitution reactions and further purification leads only to losses of the target compound. In spite of the fact that compounds **2** and **3** are structurally similar, they can be formed according to different reaction mechanisms. However, it can be suggested that the opening of the small ring occurs at the final stage to form the haloethyl fragment.

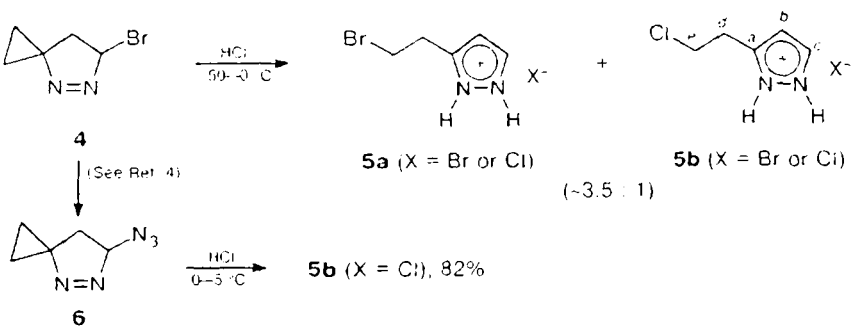


1 **3** **2**

Previously, it has been demonstrated[4] that the reactions of 5-bromospiro(1-pyrazoline-3,1′-cyclopropane) (**4**) with different nucleophilic reagents (PhO^-, PhS^-, N_3^-, or MeO^-) either proceed with retention of the spirane structure or are accompanied by conversions into 3-substituted pyrazoles. It was of interest to study the reactivity of pyrazoline **4** with respect to electrophilic reagents, first of all, with respect to HCl. For this purpose, a mixture of gaseous HCl with an inert gas was passed through a solution of compound **4** in $CDCl_3$ at 0 or −50 °C, and the course of the reaction was monitored by recording ^1H NMR spectra of the reaction mixture. The degree of conversion of the initial pyrazoline **4** appeared to be dependent on the amount of HCl passed. The complete conversion required an approximately equimolar amount of HCl. A double set of triplet signals (the ratio is ~3.5 : 1), which correspond to pyrazoles containing the 2-bromo- and 2-chloroethyl fragments (**5a,b**), respectively, is observed in the region of methylene protons of the resulting products. Moreover, the ^1H NMR spectra of the reaction mixture measured at −50 °C are characterized by the presence of two broadened singlets with equal intensities at δ 15–16. These singlets coalesce into one broad signal upon warming of the sample. Therefore, the conversion of the product into hydrohalide proceeded readily along with the formal 1,5-addition of HCl to the azocyclopropane system of pyrazoline **4**. It should be noted that (2-bromoethyl)pyrazole rather than its 2-chloroethyl analog was predominantly formed due, apparently, to a substantial contribution of intramolecular processes which accompanied this reaction.

2-Chloroethylpyrazole hydrochloride (**5b**, X = Cl) was also readily obtained when HCl was passed through a solution of azidopyrazoline **6** in dioxane under a stream of Ar at 0–5 °C. In this case, the target product was obtained in 82% yield as a colorless crystalline precipitate, which was characterized by elemental analysis and NMR spectroscopy (the ^1H NMR spectrum corresponds to that reported in the literature[8]). In the mass spectrum (EI) of the resulting compound, the maximum peaks at *m/z* 130 and 132 (the ratio is ~3 : 1) correspond, as expected, to free nonprotonated 2-chloroethylpyrazole rather to its hydrochloride.

According to the data of ^1H and ^{13}C NMR spectroscopy, the reaction of pyrazoline **4** with an equimolar amount of acetyl bromide in $CDCl_3$ resulted in the virtually complete disappearance of the initial pyrazoline **4** to form a mixture of two compounds in a ratio of ~1 : 1. One of the observed sets of signals corresponds to hydrobromide **5a** (X = Br), whereas the second set of signals is assigned to *N*-acetyl-3-(2-bromoethyl)pyrazole (**7**). After treatment of the reaction mixture with water, only one set of signals corresponding to pyrazole **7** is retained in the NMR spectra (a solution in $CDCl_3$).

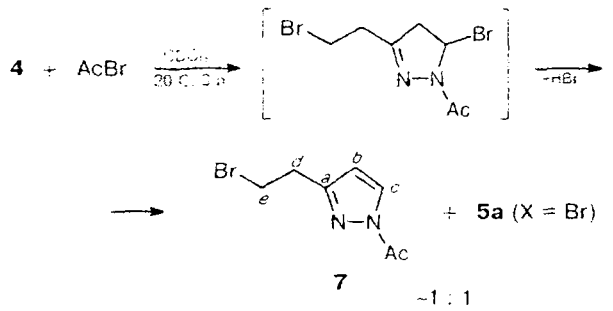


4 **5a** (X = Br or Cl) **5b** (X = Br or Cl)

(~3.5 : 1)

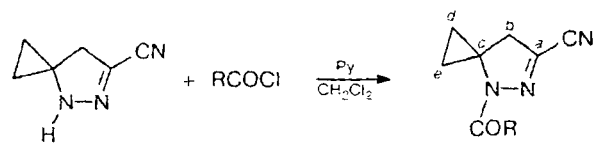
6

Therefore, not only the 1,5-addition of AcBr but also the elimination of HBr from an intermediate adduct occurs upon acylation of pyrazoline **4**. This elimination is responsible for the formation of hydrobromide **5a**.



It should be noted that the reaction with the use of AcCl instead of AcBr also afforded predominantly bromo derivative **7** rather than a compound containing the 2-chloroethyl substituent. This fact indicates that the bromoethyl fragment is formed primarily due to migration of the bromine atom from the heterocycle rather than from acyl halide, *i.e.*, this process is intramolecular.

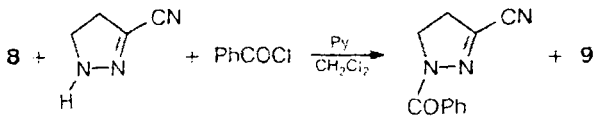
It is known[9] that 2-pyrazolines, which do not contain substituents at the nitrogen atom, can undergo alkylation and acylation to form the corresponding *N*-substituted 2-pyrazolines. However, our attempts to perform alkylation of 3-cyanospiro(2-pyrazoline-5,1′-cyclopropane) (**8**) under the action of MeI (20 °C, 3 h) resulted in a mixture of different compounds, which were difficult to identify. In turn, the reactions of compound **8** with benzoyl chloride or cyclopropanecarboxylic acid chloride in the presence of an equimolar amount of Py (20 °C, 0.5 h) proceeded more selectively. However, in these cases the complete conversion of the initial pyrazoline **8** also resulted in the formation of acylation products **9** and **10** in only 50—55% yields. Therefore, the presence of the free NH group in pyrazoline **8** changes the direction of the reaction. The retention of the small ring in the reaction products indicates that the mutual arrangement of the spirocyclopropane fragment and the double bond in the pyrazoline is of great importance.



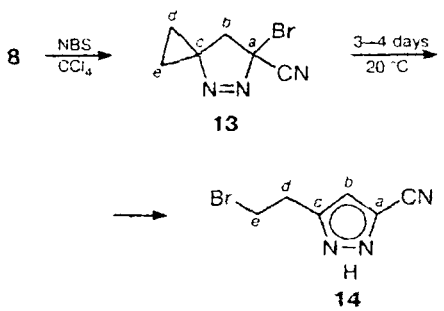
R = Ph (**9**), *cyclo*-C_3H_5 (**10**)

In the ^{1}H NMR spectrum of pyrazoline **9**, the singlet signal for the protons at the C^b atom is shifted downfield compared to that of the initial pyrazoline **8** ($\Delta\delta$ 0.23). In addition, two multiplet signals appear in the aromatic region and two symmetrical multiplets are observed at δ 0.85 and 2.35. The latter are typical of the protons of the cyclopropane ring, in which a pair of protons directed toward the nitrogen atoms is strongly deshielded by the benzoyl substituent.

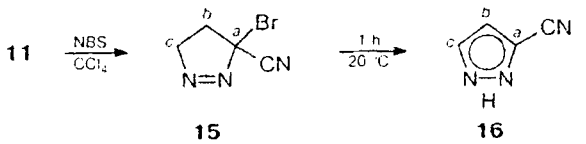
With the aim of comparing the reactivities of 2-pyrazolines, which differ by the presence or absence of the cyclopropane fragment, we studied benzoylation (20 °C) of a mixture of pyrazolines **11** and **8** with PhCOCl when the reagents were taken in an equimolar ratio. According to the data of ^{1}H and ^{13}C NMR spectroscopy of the reaction mixture, pyrazoline **11** was predominantly subjected to acylation to give compound **12** (2 h) in ~90% yield. This fact indicates[10] that pyrazoline **11** is substantially more reactive than spiro-fused analog **8**.



Then we studied bromination of cyanopyrazolines **8** and **11** under the action of *N*-bromosuccinimide (NBS). Both reactions were performed at 10—20 °C using an equimolar ratio of the reagents and CCl_4 as the solvent. The reaction of pyrazoline **8** with NBS readily proceeded in the absence of radical initiators and was completed in 3 h to form 3-bromo-3-cyanospiro (1-pyrazoline-5,1′-cyclopropane) (**13**), which was isolated as a yellow crystalline compound in ~80% yield and was characterized by ^{1}H and ^{13}C NMR spectroscopy. However, pyrazoline **13** underwent virtually complete isomerization into (2-bromoethyl)cyanopyrazole (**14**) after 3—4 days. Dissolution of the resulting mixture in a minimum amount of CH_2Cl_2 and subsequent treatment of the solution with CCl_4 afforded pyrazole **14** in ~60% yield. The formation of this compound is supported by the fact that the ^{1}H NMR spectrum has two triplets at δ 3.38 and 3.62 and a singlet at δ 6.64 corresponding to the proton of the pyrazole ring. The ^{13}C NMR spectrum has only one set of signals, which may correspond either to a rapid exchange process in the heteroaromatic structure in solution or, less probable, to the fixed position of the proton at the N(1) or N(2) atom. Our data do not give an unambiguous answer to the question as to the position of the proton in the molecule (additional studies are required). Compound **14** is rather stable only in a solution and it readily undergoes resinification in the solid state.



The reaction of NBS with cyanopyrazoline **11** proceeded analogously to form 3-bromo-3-cyano-1-pyrazoline (**15**) in ~50% yield. Pyrazoline **15** containing one ring is even less stable than pyrazoline **13** containing the spiro-fused cyclopropane fragment. Compound **15** completely decomposed within 1 h after the removal of the solvent, this process being sharply accelerated as HBr was eliminated. Cyanopyrazole (**16**) was isolated from the reaction products in ~65% yield by extraction with dichloromethane. The results obtained in this work allow one to state that the presence of the spiro-fused cyclopropane fragment slows down conversions of pyrazolines that contain readily leaving groups into more stable pyrazoles.



15 **16**

To summarize, our studies demonstrated that spirocyclopropane-containing dihydropyrazoles readily react with electrophilic reagents. These reactions can proceed either with the opening or with retention of the cyclopropane ring. Although the reaction mechanism was not studied in detail, it is apparent that the direction of the process is most substantially affected by the structures of the initial dihydropyrazoles; primarily, it depends on whether the spiro unit is located in the vicinity or at a large distance from the double bond in the heterocycle.

Experimental

The ^1H 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 $CDCl_3$ solutions 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 introduction of the sample). The ^{13}C NMR spectra are given in Table 1.

Ether, hexane, pyridine, benzene, and CH_2Cl_2 were purified according to standard procedures.

5-(2-Chloroethyl)-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene hydrochloride (2). A stream of Ar with the addition of dry gaseous HCl, which was prepared from NaCl (26 mg, 0.45 mmol) and H_2SO_4 (0.1 g, 1.0 mmol), was slowly (2 mL min^{-1}) passed through a solution of spiro(3,4-diazatricyclo-[5.3.1.0^{2,6}]dec-3-ene-5,1′-cyclopropane) **1** (see Ref. 1) (49 mg, 0.3 mmol) in $CDCl_3$. According to the data of ^1H NMR spectroscopy, the reaction mixture contained ~45% of the initial pyrazoline **1**. The NMR spectrum has a set of signals corresponding to a new compound in which the cyclopropane fragment was cleaved. Then the equal amount of dry HCl was passed at 0 °C and, as in the first case, the mixture was kept at 1 h and analyzed by ^1H and ^{13}C NMR spectroscopy. All signals observed in the spectra and their integral intensities correspond to compound **2**, whereas the signals of the initial pyrazoline are virtually absent. Evaporation of the solvent afforded colorless crystals, which readily deliquesce in air. The yield was 70 mg (95%). ^1H NMR ($CDCl_3$), δ: 10.3 (br.s, 2 H, NH and HCl); 3.95 (br.d, 1 H, H(2), $J_{2,6}$ = 7.5 Hz); 3.76 (br.t, 2 H, CH_2Cl, J = 6.6 Hz); 3.26 (br.d, 1 H, H(6), $J_{2,6}$ = 7.5 Hz); 2.88 (m, 3 H, H(1) and C^dH_2); 2.42 (m, 1 H, H(7)); 1.55 (m, 2 H, *exo*-H(8) and *exo*-H(9)); 1.10—1.35 (m, 4 H, *endo*-H(8), *endo*-H(9), and 2 H(10)).

3-Benzyl-5-(2-bromoethyl)-3,4-diazatricyclo[5.2.1.0^{2,6}]-dec-4-ene (3). A mixture of pyrazoline **1** (49 mg, 0.3 mmol) and $PhCH_2Br$ (51 mg, 0.3 mmol) in CH_2Cl_2 (0.4 mL) was kept at 5 °C for 2 days. According to the data of ^1H NMR spectroscopy, the reaction mixture contained approximately equal molar amounts of the unconsumed initial compounds and *N*-alkylation product **3** ($PhCH_2Br$: **1** : **3** ≈ 1 : 1 : 1). Then the reaction mixture was separated by preparative TLC (silica gel L; a 1 : 1 ether—hexane mixture as the eluent). Product **3** was obtained as a viscous yellowish liquid in a yield of 40 mg (~40%, the purity was 93%), R_f 0.62 (ether—hexane, 1 : 1). ^1H NMR ($CDCl_3$), δ: 7.25—7.40 (m, 5 H, Ph); 4.39 and 4.06 (both d, 1 H each, NCH_2, ^2J = 13.5 Hz); 3.60 (t, 2 H, CH_2Br, J = 7.0 Hz); 3.18 (dt, 1 H, H(2), $J_{2,6}$ = 9.1 Hz, J = 1.2 Hz); 2.80 (m, 3 H, H(6) and C^dH_2); 2.30 (m, 1 H, H(1)); 2.00 (m, 1 H, H(7)); 1.25—1.70 (m, 3 H, 1 H_b(10), *exo*-H(8) and *exo*-H(9)); 0.90—1.20 (m, 3 H, 1 H_b(10), *endo*-H(8) and *endo*-H(9)). The partial mass spectrum, m/z (I_{rel} (%)): 334 (1.5) and 332 (1.5) $[M]^+$, 253 (2), 185 (4), 91 (100).

3-(2-Bromoethyl)- (5a) and 3-(2-chloroethyl)pyrazole (5b) hydrohalides. Dry gaseous HCl under a slow stream of Ar was passed through a solution of bromopyrazoline **4** (see Ref. 4)

Table 1. ^{13}C NMR spectra (δ) of 4,5-diazaspiro[2.4]heptenes and pyrazoles

Compound	C^a	C^b	C^c	C^d	C^e	CN	Other C atoms
2	178.3	61.3	62.7	32.8	32.6		39.7 (C-1), 38.1 (C-7), 24.3 (C-8), 27.0 (C-9), 39.2 (C-10)
3	151.8	58.8	71.2	32.7	29.0		42.7 (C-1), 39.3 (C-7), 24.1 (C-8), 28.4 (C-9), 33.4 (C-10), 59.5 (NCH_2), 138.0, 128.2, 129.2, 127.1 (*i*-, *o*-, *m*-, and *p*-Ph)
5b	145.3	107.2	132.8	26.6	41.6		
7	154.8	109.6	129.0	30.2	32.1		21.8 (Me), 169.6 (C=O)
9	133.9	43.4	46.4	11.9	11.9	113.6	127.7, 127.8, 129.4, 131.4 (Ph); 167.6 (C=O)
10	126.6	43.6	45.9	9.1	9.1	113.5	12.1 (CH_2CH_2), 12.2 (CH), 172.8 (C=O)
13	96.2	41.7	69.7	15.6	13.3	117.1	
14	142.9	110.1	125.2	28.9	30.0	113.9	
15	110.7	53.1	61.2			114.3	
16	124.5	110.8	130.1			113.8	

(60 mg, 0.34 mmol) in $CDCl_3$ at 0 or −50 °C, and the course of the reaction was monitored by ^1H NMR spectroscopy (at −50 °C, two broadened signals for acidic protons were observed at δ 15—16). In both cases, the reaction mixture appeared to be a mixture of two pyrazole hydrohalides **5a** and **5b** in a ratio of ~3.5 : 1 as the initial bromopyrazoline **4** was consumed. ^1H NMR ($CDCl_3$), δ, **5a**: 8.00 (d, 1 H, H^c, J = 2.2 Hz); 6.63 (d, 1 H, H^b, J = 2.2 Hz); 3.75 (t, 2 H, CH_2Br, J = 6.6 Hz); 3.54 (t, 2 H, C^dH_2, J = 6.6 Hz); **5b**: 7.90 (d, 1 H, H^c, J = 2.1 Hz); 6.59 (d, 1 H, H^b, J = 2.1 Hz); 3.91 (t, 2 H, CH_2Cl, J = 6.5 Hz); 3.42 (t, 2 H, C^dH_2, J = 6.6 Hz).

3-(2-Chloroethyl)pyrazole hydrochloride (5b). Dry gaseous HCl under a slow stream of Ar was passed through a solution of azidopyrazoline **6** (see Ref. 4) (0.10 g, 0.75 mmol) in dry dioxane (2 mL) at 0—5 °C for 3 min. A colorless precipitate formed as the HCl was passed. Then this precipitate was filtered off and washed with cooled dioxane, and hydrochloride **5b** was obtained in a yield of 0.10 g (82%). The ^1H NMR spectrum is in complete agreement with the published data[8] as well as with the signals assigned to compound **5b** in the previous experiment. The partial mass spectrum, m/z (I_{rel} (%)): 130 (26) and 132 (9) [M − HCl]$^+$, 95 (78), 81 (100). Found (%): C, 36.28; H, 4.93; Cl, 42.91. $C_5H_7ClN_2 \cdot HCl$. Calculated (%): C, 35.95; H, 4.83; Cl, 42.45.

1-Acetyl-3-(2-bromoethyl)pyrazole (7). AcBr (16 mg, 0.13 mmol) was added to a solution of bromopyrazoline **4** (20 mg, 0.11 mmol) (see Ref. 4) in $CDCl_3$ (0.4 mL) at 20 °C. The reaction mixture was kept for 3 h and then the ^1H NMR spectrum was recorded. The signals in this spectrum demonstrated that compounds **7** and **5a** were present in approximately equal amounts. Then the reaction mixture was treated with H_2O, CH_2Cl_2 (1 mL) was added, the organic layer was dried with Na_2SO_4, the solvent was removed, and a yellow waxy substance was obtained in a yield of 16 mg (~50%), which, according to the ^1H NMR spectral data, contained ~94% of compound **7**. ^1H NMR ($CDCl_3$), δ: 8.19 (d, 1 H, H^c, J = 2.5 Hz); 6.38 (d, 1 H, H^b, J = 2.5 Hz); 3.67 (t, 2 H, CH_2Br, J = 7.0 Hz); 3.28 (t, 2 H, C^dH_2, J = 7.0 Hz); 2.70 (s, 3 H, Me). The partial mass spectrum, m/z (I_{rel} (%)): 216 (5) and 218 (4) [M]$^+$, 174 (17) and 176 (18), 137 (29), 95 (100), 81 (92).

4-Benzoyl-6-cyano-4,5-diazaspiro[2.4]hept-5-ene (9). PhCOCl (of chemically pure grade; 0.11 g, 0.83 mmol), which was freshly distilled *in vacuo*, was added to a solution of cyanopyrazoline **8** (see Ref. 3) (0.10 g, 0.83 mmol) and Py (0.06 g, 0.83 mmol) in CH_2Cl_2 (3 mL) at 20 °C over 10 min. The reaction mixture was kept for 2 h and then treated with water. The organic layer was separated and dried with Na_2SO_4. The solvents were removed and the residue was recrystallized from MeOH. Pyrazoline **9** was obtained as yellow-orange crystals in a yield of 0.10 g (55%), m.p. 155—157 °C. ^1H NMR ($CDCl_3$), δ: 7.64 and 7.42 (both m, 2 H and 3 H, Ph); 3.21 (s, 2 H, C^bH_2); 2.35 (m, 2 H, H^d and H^e, directed toward the N atom of the heterocycle); 0.85 (m, 2 H, H^d and H^e, directed away from the N atom of the heterocycle). The partial mass spectrum, m/z (I_{rel} (%)): 225 (3) [M]$^+$, 173 (13), 105 (100), 77 (62). Found (%): C, 69.63; H, 4.80; N, 18.47. $C_{13}H_{11}N_3O$. Calculated (%): C, 69.32; H, 4.92; N, 18.66.

6-Cyano-1-cyclopropylcarbonyl-4,5-diazaspiro[2.4]hept-5-ene (10). A mixture of cyanopyrazoline **8** (32 mg, 0.26 mmol) and cyclopropanecarboxylic acid chloride (see Ref. 11) (32 mg, 0.3 mmol) in benzene (0.5 mL) was kept at 10 °C for 10 h. Then the solvent was removed *in vacuo* and the residue was recrystallized from MeOH. Product **10** was obtained as colorless crystals in a yield of 32 mg (60%), m.p. 72—74 °C. ^1H NMR ($CDCl_3$), δ: 3.21 (s, 2 H, H^b); 2.52 (tt, 1 H, CH in *cyclo*-C_3H_5CO, J_{cis} = 7.9 Hz, J_{trans} = 4.6 Hz); 2.11 (m, 2 H, H^d and H^e, directed toward the N atom of the heterocycle); 0.72 (m, 2 H, H^d and H^e, directed away from the N atom of the heterocycle); 0.98 and 0.88 (both m, 2 H, each, CH_2 in *cyclo*-C_3H_5CO). The partial mass spectrum, m/z (I_{rel} (%)): 189 (7) [M]$^+$, 69 (100), 41 (58). Found (%): C, 63.39; H, 5.80; N, 22.17. $C_{12}H_{11}N_3O$. Calculated (%): C, 63.48; H, 5.86; N, 22.21.

6-Bromo-6-cyano-4,5-diazaspiro[2.4]hept-4-ene (13). NBS (0.356 g, 2.0 mmol) was added to a solution of cyanopyrazoline **8** (0.245 g, 2.0 mmol) in dry CCl_4 (2 mL). The reaction mixture was stirred at 5 °C for 1 h and then filtered. The solvent was removed *in vacuo* and the waxy residue was treated with ether (4 mL). After the removal of the ether, compound **13** was obtained as yellow crystals in a yield of 0.316 g (79%), m.p. 72—74 °C. ^1H NMR ($CDCl_3$), δ: 2.81 and 2.50 (both d, 1 H each, H^b, ^2J = 14.9 Hz); 2.04 and 1.89 (both m, 1 H each, H^d and H^e, directed toward the N=N group); 1.42 (m, 2 H, H^d and H^e, directed away from the N=N group). The partial mass spectrum, m/z (I_{rel} (%)): 201 (0.3) and 199 (0.3) [M]$^+$, 184 (10) and 186 (9), 120 (97), 106 (100). Found (%): C, 36.40; H, 3.19; Br, 39.71. $C_6H_6BrN_3$. Calculated (%): C, 36.03; H, 3.02; Br, 39.94.

3(5)-(2-Bromoethyl)-5(3)-cyanopyrazole (14). A sample of pyrazoline **13** (0.22 g) was kept at 20 °C for 3 days and then dissolved in CH_2Cl_2 (2 mL), and CCl_4 (4 mL) was added. The crystals that precipitated were filtered off and dried *in vacuo*. Pyrazole **14** was obtained in a yield of 0.14 g (64%), m.p. 83—84 °C (with decomp.). ^1H NMR ($CDCl_3$), δ: 8.80 (br.s, 1 H, NH); 6.64 (s, 1 H, H^b); 3.62 and 3.34 (both t, 2 H each, CH_2CH_2Br, J = 6.5). The partial mass spectrum, m/z (I_{rel} (%)): 201 (28) and 199 (32) [M]$^+$, 120 (100), 106 (98).

3-Bromo-3-cyano-4,5-dihydropyrazole (15). NBS (1.07 g, 6.0 mmol) was added with intense stirring to a solution of 3-cyano-2-pyrazoline (**11**) (see Ref. 12) (0.57 g, 6.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solution immediately turned red. The solvent was removed *in vacuo*, the residue was treated with ether, the precipitate was filtered off, and the ether was removed *in vacuo*. Pyrazoline **15** was obtained in a yield of 0.55 g (52%); the purity was ~93% (according to the ^1H NMR spectral data). ^1H NMR, δ: 5.08 and 4.71 (both m, 1 H each, C^cH_2); 2.61 and 2.28 (both m, 1 H each, C^bH_2). The partial mass spectrum, m/z (I_{rel} (%)): 175 (3) and 173 (2) [M]$^+$, 149 (4) and 147 (3), 94 (24), 40 (100).

The resulting pyrazoline **15** is rather stable in solutions at temperatures below 0 °C. However, compound **15** completely decomposed in the absence of solvents during 1 h. 3-Cyanopyrazole (**16**) was isolated in ~65% yield from the decomposition products upon their treatment with CH_2Cl_2. The ^1H NMR spectrum and the melting point of the resulting compound correspond to the published data.[13] The partial mass spectrum, m/z (I_{rel} (%)): 93 (82) [M]$^+$, 66 (25), 43 (100).

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