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Addition of diazocyclopropane generated *in situ* to acrylic acid derivatives and transformations of resulting functionally substituted spiro(pyrazolinecyclopropanes)

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The reaction of diazocyclopropane generated *in situ* with acrylonitrile or methyl acrylate to give 1 : 1, 1 : 2, and 2 : 1 cycloadducts was carried out. The products resulting from 1,3-dipolar cycloaddition and subsequent isomerization, *viz.*, 3-cyano- and 3-methoxycarbonylspiro(2-pyrazoline-5,1′-cyclopropanes), isolated in the first step in ~70% yield, react in an alkaline solution with the above acrylates or diazocyclopropane as C(3)-nucleophiles to give the corresponding 3-(2′-cyanoethyl)-, 3-(2′-methoxycarbonylethyl)-, or 3-(cyclopropylazo)-1-pyrazolines. The thermal deazotization of these pyrazolines to spiropentane derivatives was investigated.

Key words: spiro(2-pyrazoline-5,1′-cyclopropanes), spiropentanes, 1,3-dipolar cycloaddition, nucleophilic addition, thermolysis, NMR spectra.

The reactions of diazoalkanes with electron-deficient double bonds in olefins occur mostly as 1,3-dipolar cycloaddition to give 1-pyrazolines; when the latter contain α-H atom they normally readily isomerize to 2-pyrazolines.[1–3] In the case of alkenes with electron-withdrawing substituents at the double bond, cycloaddition of diazoalkanes is, as a rule, regiospecific and is accompanied by the formation of a new C—C bond at the less substituted olefinic carbon atom. The few known reactions in which diazocyclopropanes are generated *in situ* and then trapped also occur according to the above principles; in addition, as could be expected, the interaction of diazocyclopropane (DCP) with α-substituted α,β-unsaturated carbonyl compounds yields the corresponding 1-pyrazolines,[4–6] while the reaction of 2,2-diphenyldiazocyclopropane with diethyl maleate containing an α-H atom affords the corresponding 2-pyrazoline.[7]

In this work, we studied in detail the reaction of unsubstituted DCP with the acrylic acid derivatives acrylonitrile (AN) and methyl acrylate (MA), which contain no additional substituents in the α-position. The structures and the composition of the reaction products varied substantially depending on the reaction conditions and the ratio of the reactants. Since preliminary experiments have shown that under usual conditions of generation of DCP,[8,9] accomplished by adding *N*-nitroso-*N*-cyclopropylurea (NCU) to a mixture of an unsaturated compound and MeONa in a solvent, a side reaction involving the addition of methanol to the electron-deficient double bond of AN and MA occurs to a considerable extent, we changed the order in which the reactants were added, namely, a methanolic solution of MeONa was slowly added at −15 to −25 °C to a stirred mixture of an unsaturated compound and NCU in CH_2Cl_2. After that, the solvents were removed *in vacuo*, and the residue was analyzed by ^1H and ^{13}C NMR spectroscopy. In this case, the reaction mixture contained virtually no 3-methoxypropionitrile or methyl 3-methoxypropionate resulting from the addition of methanol to AN or MA. Thus, the major reaction products could be clearly identified against the background of minor admixtures; measurement of the integral intensities of all the signals in the NMR spectrum with allowance for the overall amount of the reaction products made it possible to estimate their yields.

For example, decomposition of NCU with sodium methoxide in the presence of AN or MA at 1 : 1.2 : 1 molar ratio of reactants gives compounds, formed as major products (yield ~70%), whose ^1H and ^{13}C NMR spectra exhibit similar sets of signals (Tables 1 and 2) that are in good agreement with the structure of the expected 3-substituted spiro(2-pyrazoline-5,1′-cyclopropanes) **1** and **2**. In particular, their ^1H NMR spectra contain two symmetrical multiplets in a high field (δ 0.8–0.95) corresponding to the protons of the cyclopropane ring, singlets at δ 3.0 (CH_2 of the pyrazoline ring), and broadened signals for the NH group at δ 6.1.

It should be noted that pyrazolines **1** and **2** are rather labile compounds, and an attempt to purify them by preparative TLC (silica gel, ether—benzene) results in a noticeable loss of the main substance and in the appearance of a great number of additional ^1H NMR signals not exhibited in the spectra of the crude reaction prod-

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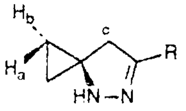
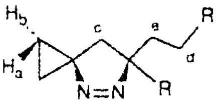
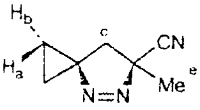
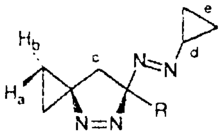
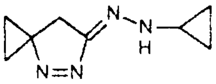
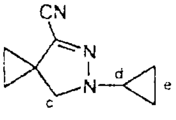
Table 1. ^1H NMR spectra of functionally substituted spiro(pyrazolinecyclopropanes) ($CDCl_3$, δ, *J*/Hz).

Compound		R	H_a	H_b	H_c	H_d	H_e	OMe	NH	^2J_c	$^3J_{de}$
	**1**	CN	0.93 m (2 H)	0.86 m (2 H)	2.98 s (2 H)				6.20 br.s (1 H)		
	2	COOMe	0.89 m (2 H)	0.80 m (2 H)	3.00 s (2 H)			3.85 s (3 H)	6.10 br.s (1 H)		
	**3**	CN	1.90 m (2 H)	1.31 m (2 H)	2.38 *, 1.98 d (1 H)	2.88 m (2 H)	2.36 m * (3 H)			13.0	
	4	COOMe	1.80 m (2 H)	1.16 m (2 H)	2.29 d (1 H), 1.69 d (1 H)	2.40 m *	2.40 m * (4 H)	3.81 s (3 H), 3.69 s (3 H)		13.0	
	**12** **		1.83 m * (3 H)	1.21 m (2 H)	2.32 d (1 H), 1.82 d *		1.75 s (3 H)			13.0	
	**5**	CN	1.96 m (2 H)	1.37 m * (4 H)	2.47 s (2 H)	3.63 tt (1 H)	1.61 m (2 H), 1.37 m *				6.7 (*cis*), 3.4 (*trans*)
	6	COOMe	1.82 m (2 H)	1.15 m (2 H)	2.39 d, (1 H), 2.13 d (1 H)	3.64 tt (1 H)	1.43 m (2 H), 1.23 m (2 H)	3.86 s (3 H)		13.4	6.8 (*cis*), 3.4 (*trans*)
	**10**		1.82 m (2 H)	1.25 m (2 H)	2.30 s (2 H)	2.93 q (1 H)	0.75 d (4 H)		5.30 br.s (1 H)		5.1
	**18**		0.72 m (4 H)		3.56 s (2 H)	2.51 tt (1 H)	1.13 m (2 H), 0.92 m (2 H)				6.6 (*cis*), 3.5 (*trans*)

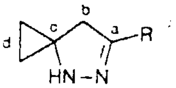
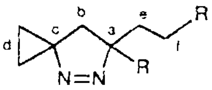
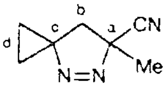
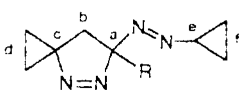
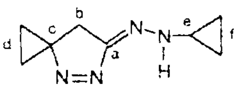
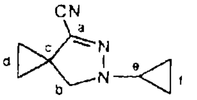
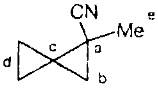
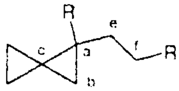
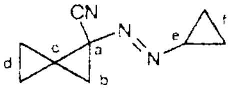
* Overlapping signals for nonequivalent protons; their overall integral intensity is given in parentheses.

** ^1H NMR spectrum in C_6D_6 (250 MHz): 1.56 d (1 H), 1.22–1.39 m (2 H), 1,12 s (3 H), 0.83 d (1 H), 0.30–0.47 m (2 H).

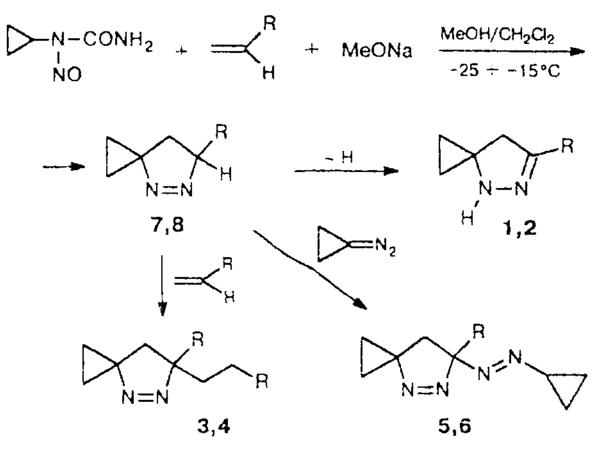
ucts. Ester **2** was found to be more labile than nitrile **1**, and therefore, in the subsequent transformations it was used without additional purification. Since compound **1** is more stable, treatment of the reaction mixture obtained from NCU and AN with a 1 : 2 benzene—hexane mixture made it possible to isolate pyrazoline **1** as fine slightly yellowish crystals with a purity of ~95% (^1H NMR data).

When the unsaturated substrates are taken in a 2—2.3-fold molar excess with respect to NCU, the reaction mostly yields the corresponding bis-adducts. For example, the reaction of DCP generated *in situ* with a twofold molar excess of AN at −15 °C gives 3-cyano-3-(2-cyanoethyl)spiro(1-pyrazoline-5,1′-cyclopropane) (**3**) as the major reaction product (yield ~60%), in addition to 2-pyrazoline **1** (yield ~15%). Compound **3** was isolated in a pure state by preparative TLC. According to the data of elemental analysis, this compound corresponds to the product of the interaction of DCP with two molecules of AN. The IR spectrum of this product contains medium-intensity bands at ν 2252 and 1535 cm^{-1}, characteristic of C≡N and N=N bonds. The ^1H NMR spectrum of dinitrile **3**, along with the signals corresponding to the pairs of the methylene protons in the *cyclo*-C_3H_4 fragment, contains two doublets with the spin-spin coupling constant ^2J = 13 Hz, characteristic of the separated methylene group in the asymmetrically substituted pyrazoline ring. The ^{13}C NMR spectrum clearly identifies the presence of secondary (methylene) and quaternary carbon atoms (see Tables 1 and 2). The chemical shifts of the C(3) and C(5) atoms, together with the fact that the geminal methylene protons in the pyrazoline ring are nonequivalent, indicate that the cyanoethyl fragment is bound to the C(3) atom rather than to the N(1) atom, which would be the case if the alternative compound, *N*-substituted 2-pyrazoline, was formed.

Table 2. ^{13}C NMR spectra of substituted spiro(pyrazolinecyclopropanes) and spiropentanes ($CDCl_3$, δ).

Compound		R	C_a	C_b	C_c	C_d	C_e	C_f	CN or CO	OMe
	**1**	CN	142.4	39.8	45.3	12.9			115.2	
	2	COOMe	162.4	37.7	45.5	12.8			163.2	51.9
	**3**	CN	83.6	35.1	71.2	15.1 and 14.9	32.8	13.4	117.9 and 117.1	
	4	COOMe	96.1	31.2	70.0	15.0 and 14.6	29.1	33.4	173.0 and 170.9	53.0 and 51.9
	**12**		81.2	37.2	70.3	14.6 and 14.0	24.1		117.6	
	**5**	CN	107.9	35.0	72.8	15.3 and 15.1	50.9	11.0	115.1	
	6	COOMe	106.7	31.3	70.2	14.7 and 14.5	50.8	9.9	167.8	53.1
	**10**		162.7	25.7	66.3	16.0	31.5	6.6		
	**18**		128.7	60.4	28.4	6.0	34.2	12.2	112.5	
	**13**		10.0	21.0	22.9	6.4 and 5.0	18.9		123.6	
	**14**	CN	14.8	20.2	22.9	6.3 and 5.6	29.7	15.5	121.1 and 118.3	
	15	COOMe	28.3	20.2	25.1	6.4 and 5.2	32.1 and 28.2		174.5 and 173.8	51.6 and 51.4
	**16**		50.4	23.0	25.6	6.1 и 5.3	50.1	9.3	117.2	

The reaction of DCP with excess MA occurs in a similar way. The addition of a solution of MeONa in MeOH to a mixture of NCU and MA at a 1.4 : 1 : 2.2 molar ratio of the reactants also affords bis-adduct **4** as the major product (yield 56—58%), the yield of monoadduct **2** being 14—16%. In this case, the major product, diester **4**, unlike monoadduct **2**, was successfully isolated from the reaction mixture with ~95% purity using preparative TLC. The ^1H and ^{13}C NMR spectra of this compound contain nearly the same set of signals as the spectra of 1-pyrazoline **3**, which has a similar structure (see Tables 1 and 2). The presence of two singlets of equal intensities for the nonequivalent methoxy groups confirms the fact that adduct **4** incorporates two methyl acrylate fragments. It should be noted that the signals for the cyclopropane-ring protons in the spectra of 1-pyrazolines **3** and **4** are shifted downfield with respect to the corresponding signals in the spectra of spiro(2-pyrazoline-5,1′-cyclopropanes) **1** and **2**; the largest shift (Δδ ~0.9) is observed for the protons directed at the nitrogen atoms (see Table 1, H_a atoms).



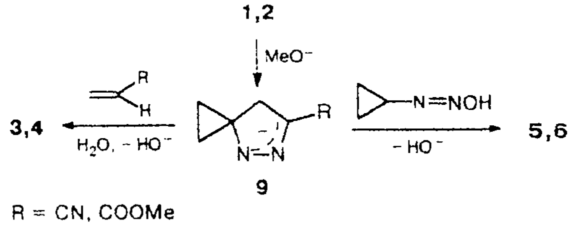
R = CN (**1**, **3**, **5**, **7**). COOMe (**2**, **4**, **6**, **8**)

The formation of pyrazolines **1**—**4** suggests that the process starts with normal 1,3-dipolar cycloaddition of diazocyclopropane to AN or MA giving 1-pyrazolines **7** or **8**, which subsequently isomerize to 2-pyrazolines **1** or **2** or, under alkaline reaction conditions, add to the next molecule of AN or MA, according to the pattern of nucleophilic addition to electron-deficient olefins, with the retention of the 1-pyrazoline structure in the final bis-adducts **3** or **4**.

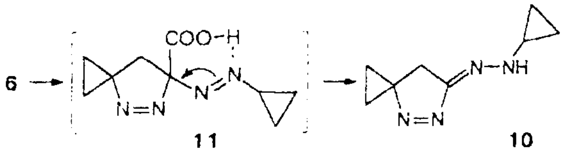
Another result that is unexpected from our viewpoint was obtained when AN or MA reacted with an excess of diazocyclopropane generated *in situ* (at an NCU : MeONa : olefin molar ratio of ~2 : 2.5 : 1). In this case, cyclopropylazopyrazolines **5** and **6** resulting from the reaction of two DCP molecules with one AN or MA molecule were obtained as the major products. In addition to the signals of 2-pyrazolines **1** and **2**, the ^{1}H NMR spectra of the reaction mixtures obtained after removal of the solvents *in vacuo* indicated the presence of new compounds responsible for a signal at δ ~3.6 with a fairly typical pattern resembling a septet in its appearance. Taking into account the overall amount of the products formed and the integral intensities of the ^{1}H NMR signals, the yields of azopyrazolines **5** and **6** are ~50—60%, and those of 2-pyrazolines **1** and **2** are 20—25%. In the case of acrylonitrile, the product of the double addition of DCP was isolated with ~94% purity using preparative TLC on neutral Al_2O_3. Unfortunately, attempts to isolate azopyrazoline **6** in a pure state were unsuccessful. High-vacuum distillation (~0.1 Torr) or preparative TLC on various sorbents led to further transformations of this compound and to the appearance of more complex NMR spectra. Nevertheless, analysis of the ^{1}H and ^{13}C NMR spectra of the reaction mixture containing azopyrazoline **6**, recorded after subtraction of the signals due to 2-pyrazoline **2** and signals with obviously low integral intensities corresponding to impurities, resulted in a set of signals, similar to those of azopyrazoline **5**. In fact, in both cases, selective decoupling experiments revealed that the septet at δ 3.6 is actually a triplet of triplets with proportional spin-spin coupling constants, J_1 ~3.4 and J_2 ~6.8 Hz, which is quite typical of a methine proton in a cyclopropane ring that is bound to a heteroatom. In the case of ester **6**, the signals for the methylene protons of the pyrazoline ring are manifested as two doublets with the spin-spin coupling constant ^2J = 13.4 Hz, while in the case of cyanopyrazoline **5**, these signals are degenerated into a singlet with doubled integral intensity (see Table 1). The number and the positions of signals in the ^{13}C NMR spectra (see Table 2) also indicate that the structures of pyrazolines **5** and **6** result formally from the insertion of a second DCP molecule into the C—H bond of pyrazolines **7** and **8** activated by electron-withdrawing substituents and that only one isomer with respect to the azo-group is formed in each case; apparently, this is the *trans*-isomer.[10]

Taking into account the facts that the above-discussed reactions occur under alkaline conditions and that none of the ^{1}H NMR spectra of the reaction mixtures exhibited signals that in any way could be attributed to 1-pyrazolines **7** and **8**, we suggested that the corresponding bis-adducts can also be formed *via* 2-pyrazolines **1** and **2**. To verify this hypothesis, we studied the reactions of 2-pyrazolines **1** and **2**, prepared beforehand, with an equimolar amount of AN or MA and with DCP generated *in situ*. These experiments were carried out under the same conditions, *viz.*, by adding a MeONa/MeOH solution at −15 to −20 °C to a solution of pyrazolines **1** and **2** and the corresponding acrylates or NCU in CH_2Cl_2. It was found that the corresponding bis-adducts, dinitrile **3** and diester **4** or, correspondingly, azopyrazolines **5** and **6**, are formed in all cases in 75—85% yields.

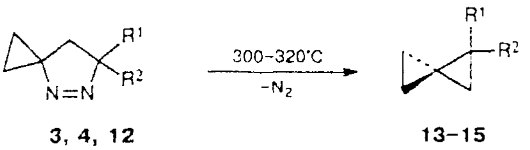
Thus, the formation of adducts from 2-pyrazolines **1** and **2** both with acrylates and with DCP indicates that anions like **9** are generated in the reaction mixture through the action of bases and that these anions subsequently react mostly as C(3)-nucleophiles rather than as N-nucleophiles. In addition, substantial accumulation of 2-pyrazoline **1** or **2** in the reaction mixture at equimolar amounts of an olefin and NCU (see above) implies that the rates of generation of DCP and of its 1,3-dipolar cycloaddition are much higher than the rates of the formation of bis-adducts **3** and **4**. Azopyrazolines **5** and **6** are produced in a reaction formally similar to azo coupling of aromatic diazonium salts with various substrates including 2-pyrazolines.[11] In terms of this analogy, we cannot rule out the possibility that the anion **9** reacts with cyclopropyldiazohydroxide preceding DCP or with the corresponding diazonium cation, both resulting from the alkaline decomposition of NCU rather than with DCP itself.[12]



It has already been noted that the attempts to purify azopyrazoline **6** were accompanied by its subsequent transformations. In fact, the separation of the reaction mixture containing azopyrazoline **6** by preparative TLC on neutral Al_2O_3 results in the isolation of ~65% (of the initial amount) of a colorless crystalline compound, whose elemental analysis, mass spectra, and ^{1}H and ^{13}C NMR spectra indicate that it contains no methoxycarbonyl fragment and are in good agreement with the structure of cyclopropylhydrazone **10** (yield ~89%). The signals of the spiro(1-pyrazoline-5,1′-cyclopropane) protons in the ^{1}H NMR spectrum of this compound are manifested approximately in the same region as those in the spectra of cyclopropylazopyrazolines **5** and **6**; however, unlike the latter case, the signals for the cyclopropane ring protons are shifted upfield (Δδ ~0.6), and the vicinal spin-spin coupling constants are unexpectedly equal (Table 1). Apparently, compound **10** is formed *via* hydrolysis of the ester group in azopyrazoline **6** followed by decarboxylation of pyrazoline-3-carboxylic acid **11**.

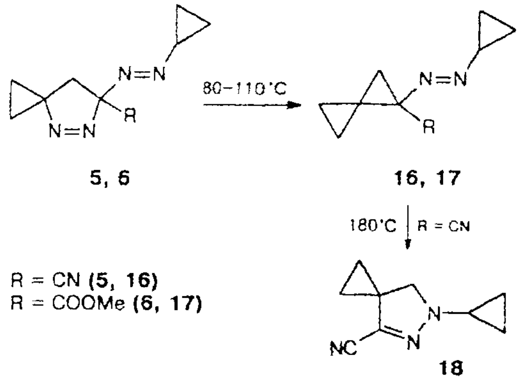


Previously it has been shown[6] that decomposition of NCU under the action of MeONa in the presence of methyl methacrylate gives the adduct of DCP at the double bond of methyl methacrylate, *viz.*, the corresponding 1-pyrazoline, in 70% yield; upon thermal deazotization this compound is smoothly converted into methyl 1-methylspiropentanecarboxylic acid. Similarly, unlike unsaturated AN and MA, methacrylonitrile also reacts with diazocyclopropane to give 3-cyano-3-methylspiro(1-pyrazoline-5,1′-cyclopropane) (**12**) in a yield of up to 80%. Thermolysis of pyrazoline **12** as well as of functionally substituted pyrazolines **3** and **4** having similar structures, which is carried out by passing these compounds through a quartz tube at 300–310 °C under inert atmosphere, leads to the elimination of nitrogen and affords the corresponding spiropentane derivatives **13–15**, retaining all of the functional groups in their molecules, in 80–90% yields, while the isomeric olefins are virtually absent. The compounds obtained were isolated by vacuum distillation and identified by the data of elemental analysis, mass spectra, and IR and NMR spectra (Tables 2 and 3).



R^1 = CN, R^2 = Me (**12, 13**), CH_2CH_2CN (**3, 14**);
R^1 = COOMe, R^2 = CH_2CH_2COOMe (**4, 15**)

It is noteworthy that the thermolysis of cyclopropylazopyrazoline **5** also occurs fairly selectively and is accompanied by elimination of the intracyclic nitrogen atoms. For example, refluxing a solution of azopyrazoline **5** in toluene for 3 h affords 1-cyano-1-(cyclopropylazo)spiropentane (**16**) in a yield of >85%. This compound was isolated in a pure state by vacuum distillation followed by recrystallization from hexane as a colorless finely crystalline material and characterized by elemental analysis and by mass, IR, and NMR spectra. The presence of the spiropentane fragment resulting from the exclusive elimination of the intracyclic nitrogen atoms is corroborated by the substantial upfield shifts of the corresponding signals in the ^{1}H and ^{13}C NMR spectra and by the retention of the specific multiplet pattern for the methine proton in the azacyclopropane fragment at δ 3.48 (Tables 2 and 3). Slow deazotization of azopyrazoline **5** occurs even at 20 °C; for example, according to the ^{1}H NMR data, keeping its solution in CH_2Cl_2 for 2 months affords a mixture of compounds **5** and **16** in a ratio of ~3 : 1.



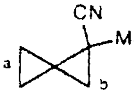
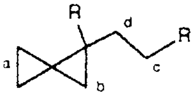
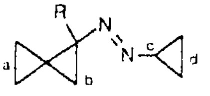
R = CN (**5, 16**)
R = COOMe (**6, 17**)

At higher temperatures (180 °C, sealed tube, 40 min), azospiropentane **16** undergoes further transformations and gives 3-cyano-1-cyclopropylspiro(2-pyrazoline-4,1′-cyclopropane) (**18**) in 88% yield; this compound results from azocyclopropane—pyrazoline rearrangement[13] (similar to vinylcyclopropane—cyclopentene rearrangement) that selectively involves only the substituted cyclopropane ring. Most of the signals in the ^{1}H NMR spectrum of the product are exhibited in the high-field region and indicate the presence of two cyclopropane fragments not connected to one another. The signals corresponding to the $H_2C(5)$ methylene fragment in the ^{1}H and ^{13}C NMR spectra (see Tables 1 and 2) are shifted downfield with respect to the corresponding signals of pyrazoline **1**, which indicates that it is bound to the N atom.

Thermolysis of pyrazoline ester **6** (a reaction mixture containing no less than 85% compound **6** was used) carried out by refluxing the compound in toluene or benzene occurs less selectively than that of azopyrazoline **5**; complete conversion of the initial pyrazoline **6** affords a complex mixture of products in which the proportion of spiropentane **17** does not exceed 20% (^{1}H NMR spectrum, Table 3).

These results indicate that the general pattern of an easy isomerization of 1-pyrazolines to 2-pyrazolines occurring in the presence of an active hydrogen atom at C(3) does not change when a spiro-coupled cyclopropane ring is attached to the pyrazoline ring. In addition, the spiro(2-pyrazoline-5,1′-cyclopropanes) synthesized exhibit high selectivity in the addition to multiple bonds, acting as efficient C(3)-nucleophiles.

Table 3. ^{1}H NMR spectra of functionally substituted spiropentanes ($CDCl_3$, δ, J/Hz).

Compound	R	H_a	H_b	H_c	H_d	OMe	^2J_b	^2J_d	$^3J_{de}$
 **13**		0.82–1.18 m (5 H) *	1.66 d (1 H), 1.13 *		1.37 s (3 H)		4.6		
 **14**	CN	0.95–1.21 m (4 H)	1.79 d (1 H), 1.39 d (1 H)	2.61 t (2 H)	2.02 br.dt (1 H), 1.85 dt (1 H)		4.8	14.3	7.1
15	COOMe	0.80–1.03 m (4 H)	1.70 br.d (1 H), 1.10 d (1 H)	2.50 m (2 H)	2.22 m (1 H), 1.63 ddd (1 H)	3.68 s (3 H)	3.7	14.0	9.5 and 6.2
 **16**	CN	1.05–1.25 m (6 H) *	2.27 d (1 H), 2.18 d (1 H)	3.48 tt (1 H)	1.36 m (2 H), 1.05–1.25 m *		4.8		6.6 (*cis*), 3.3 (*trans*)
17	COOMe	0.83 m (2 H), 1.12 m (2 H)	2.18 d (1 H), 2.08 d (1 H)	3.59 tt (1 H)	1.31 m (2 H), 1.02 m (2 H)	3.88 s (3 H)	3.7		6.8 (*cis*), 3.4 (*trans*)

* Overlapping signals for nonequivalent protons; their overall integral intensity is given in parentheses.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker AM-300 (300 and 75.47 MHz) spectrometers for solutions in $CDCl_3$ containing 0.1% tetramethylsilane as the internal standard. GC/MS analysis was carried out using a Finnigan MAT INCOS-50 instrument (EI, 70 eV, a 30 m long RSL-200 capillary column). IR spectra were obtained on a Bruker IFS-113v spectrometer in thin films.

3-Cyanospiro(2-pyrazoline-5,1′-cyclopropane) (1). At −25 to −20 °C, a solution of sodium methoxide (0.80 g, 15 mmol) in 3 mL of MeOH was added with vigorous stirring over a period of 2 min to a mixture of *N*-nitroso-*N*-cyclopropylurea (1.55 g, 12 mmol) and acrylonitrile (0.64 g, 12 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred for an additional 10 min at the same temperature, then the temperature was raised to 10 °C, and an additional ~0.5 mL of water was added. The organic layer was dried with anhydrous $MgSO_4$, the solvent was evaporated *in vacuo*, and the yellow waxy residue (1.22 g) was analyzed by ^{1}H NMR spectroscopy (the content of the main component was ~85%). Then the reaction mixture was treated with a benzene—hexane mixture (1 : 2) or purified by preparative TLC (silica gel L, ether—hexane, 1 : 1, R_f = 0.38), and pyrazoline **1** was isolated as a finely crystalline precipitate, yield ~70%, m.p. 46–48 °C. IR (ν/cm^{-1}): 2237 (C≡N). Partial mass spectrum, m/z (I(%)): 121 (38) M$^+$, 120 (36), 107 (48), 106 (100), 94 (17), 93 (29). Found (%): C, 59.11; H, 5.71; N, 34.81. $C_6H_7N_3$. Calculated (%): C, 59.49; H, 5.82; N, 34.69. The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

3-Methoxycarbonylspiro(2-pyrazoline-5,1′-cyclopropane) (2). This compound was prepared from *N*-nitroso-*N*-cyclopropylurea (1.55 g, 12 mmol), methyl acrylate (1.03 g, 12 mmol), and MeONa (0.80 g, 15 mmol) by a procedure similar to that described previously as a yellow waxy mixture (1.51 g) containing ~85% pyrazoline **2**, according to the ^{1}H NMR spectrum; calculated yield 69%. MS, m/z (I(%)): 154 (11) M$^+$, 139 (8), 122 (30), 113 (33), 59 (77), 55 (100). ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

3-Cyano-3-(2-cyanoethyl)spiro(1-pyrazoline-5,1′-cyclopropane) (3). *A.* At −15 °C, a solution of sodium methoxide (1.08 g, 20 mmol) in 5 mL of MeOH was added over a period of 15 min to an vigorously stirred mixture of *N*-nitroso-*N*-cyclopropylurea (1.95 g, 15 mmol) and acrylonitrile (1.64 g, 31 mmol) in 15 mL of CH_2Cl_2. The mixture was stirred for an additional 10 min; then the temperature was raised to 10 °C, and 5 mL of water was added. The organic layer was separated, and the aqueous layer was extracted with 5 mL of CH_2Cl_2 and dried with anhydrous $MgSO_4$. The solvents were evaporated *in vacuo*, and the residue (1.88 g) was analyzed by NMR spectroscopy. Judging from the integral intensities of the signals, the mixture contained ~73 mol.% pyrazoline **3** (yield ~60%) and ~18 mol.% pyrazoline **1**. The reaction mixture was separated using preparative TLC (silica gel L, ether—CH_2Cl_2, 3 : 1), and the target product was isolated as a viscous slightly yellowish liquid, R_f = 0.76. IR (ν/cm^{-1}): 2252 m (C≡N), 1535 m (N=N). Found (%): C, 61.75; H, 5.87; N, 32.43. $C_9H_{10}N_4$. Calculated (%): C, 62.05; H, 5.79; N, 32.16. The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

B. At −18 °C, a solution of sodium methoxide (0.65 g, 12 mmol) in 4 mL of MeOH was added over a period of 10 min to an vigorously stirred mixture of 3-cyanospiro(2-pyrazoline-5,1′-cyclopropane) (**1**) (1.22 g, 10 mmol) and acrylonitrile (0.53 g, 10 mmol) in 7 mL of CH_2Cl_2. Then the reaction mixture was worked up as described in method *A* to give 1.46 g (84%) of pyrazoline **3**, whose characteristics were identical to those of the sample prepared by method *A*.

3-Methoxycarbonyl-3-(2-methoxycarbonylethyl)spiro(1-pyrazoline-5,1′-cyclopropane) (4). *A.* A solution of sodium methoxide (0.92 g, 17 mmol) in 5 mL of MeOH was added at −20 °C over a period of 15 min to an vigorously stirred mixture of *N*-nitroso-*N*-cyclopropylurea (1.55 g, 12 mmol) and methyl acrylate (2.15 g, 25 mmol) in 15 mL of CH_2Cl_2. The mixture was stirred for 10 min, the temperature was raised to 10 °C, and 5 mL of water was added. The organic layer was separated, and the aqueous layer was extracted with 5 mL of CH_2Cl_2 and dried with anhydrous Na_2SO_4. The solvents were evaporated *in vacuo*, and the residue (2.11 g) was analyzed by NMR spectroscopy. Judging from the integral intensities of the signals, the mixture contained ~72 mol.% pyrazoline **4** and ~19 mol.% pyrazoline **2** (calculated yields ~58% and 15%, respectively). The reaction mixture was separated using preparative TLC (silica gel L, ether—CH_2Cl_2, 3 : 1), and the target product was isolated with a purity of ~95% as a viscous slightly yellowish liquid, R_f = 0.76. IR (v/cm^{-1}): 1739 s (COO), 1535 w (N=N). Found (%): C, 54.53; H, 6.56; N, 11.97. $C_{11}H_{16}N_2O_4$. Calculated (%): C, 54.99; H, 6.71; N, 11.66. ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

B. A solution of sodium methoxide (0.59 g, 11 mmol) in 4 mL of MeOH was added at −20 °C over a period of 10 min to a vigorously stirred mixture containing 2-pyrazoline **2** (1.44 g, ~8 mmol) and methyl acrylate (0.69 g, 8 mmol) in 7 mL of CH_2Cl_2. Then the reaction mixture was worked up as described in method *A* to give 1.53 g (80%) of pyrazoline **4**, whose characteristics were identical to those of the sample prepared by method *A*.

3-Cyano-3-(cyclopropylazo)spiro(1-pyrazoline-5,1′-cyclopropane) (5). At −15 to −20 °C, a solution of sodium methoxide (0.70 g, 13 mmol) in 5 mL of MeOH was added over a period of 10 min to a vigorously stirred mixture of 2-pyrazoline **1** (1.22 g, 10 mmol) and *N*-nitroso-*N*-cyclopropylurea (1.42 g, 11 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred for 10 min, the temperature was raised to 15 °C, 1 mL of water was added, and the organic layer was separated and dried with anhydrous Na_2SO_4. The solvents were evaporated *in vacuo*, and the residue (1.70 g) was first analyzed by ^{1}H NMR spectroscopy (the proportion of the main component was no less than 85%), yield ~77%, and then purified using preparative TLC (Al_2O_3, ether—benzene, 3 : 2) to give azopyrazoline **5** as a yellowish viscous liquid, R_f = 0.70, purity ~94%. IR (v/cm^{-1}): 2241 m (C≡N), 1574 w and 1535 m (N=N), 1030 m (cyclopropane). The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

3-(Cyclopropylazo)-3-methoxycarbonylspiro(1-pyrazoline-5,1′-cyclopropane) (6). This compound was obtained from 1.45 g of a reaction mixture containing ~8 mmol of 2-pyrazoline **2** (see above), *N*-nitroso-*N*-cyclopropylurea (1.10 g, 8.5 mmol), and MeONa (0.55 g, 10 mmol) by a procedure similar to that described above. After evaporation of the solvents, the residue was dissolved in C_6H_6 and quickly filtered through a relatively thin layer of Al_2O_3 (basic). Removal of the benzene gave 1.48 g of a reaction mixture that contained, according to the ^{1}H NMR spectrum, ≥90% azopyrazoline **6** (yield >75%). The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

Spiro(1-pyrazolin-3-one-5,1′-cyclopropane) cyclopropylhydrazone (10). Azopyrazoline **6** prepared in the previous experiment (0.055 g) was applied on a preparative TLC plate with Al_2O_3 (neutral) and eluted with an ethyl acetate—CH_2Cl_2 mixture (1 : 3). The zone with R_f 0.6—0.8 was washed out with ether. Removal of the solvent gave 0.036 g (~89%) of hydrazone **10** as a colorless crystalline material, m. p. 117—119 °C. IR (v/cm^{-1}): 3255 s (NH), 1612 m (C=N), 1504 w (N=N), 1019 (cyclopropane). Found (%): C, 58.73; H, 7.47. $C_8H_{12}N_4$. Calculated (%): C, 58.52; H, 7.37. The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

3-Cyano-3-methylspiro(1-pyrazoline-5,1′-cyclopropane) (12). This compound was obtained from methacrylonitrile (1.36 g, 21 mmol), *N*-nitroso-*N*-cyclopropylurea (2.71 g, 21 mmol), and MeONa (1.62 g, 30 mmol) at −20 °C by a procedure described previously.[8,9] The reaction gave 2.19 g (~78%) of pyrazoline **12** as a yellowish liquid, b.p. 65—68 °C (0.6 Torr). The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

1-Cyano-1-methylspiropentane (13). A solution of pyrazoline **12** (0.54 g, 4 mmol) in 1.5 mL of C_6H_6 was passed for 10—13 min at 300 °C through a 18-cm-long quartz tube with an inner diameter of 0.6 cm, filled 2/3 full with finely divided quartz. Then 0.6 mL of pure C_6H_6 was passed; vacuum microdistillation of the pyrolyzate gave 0.37 g (87%) of spiropentane **13** as a colorless liquid, b.p. 62—65 °C (18 Torr). MS, *m/z* (*I*(%)): 107 (3) M$^+$, 106 (37), 92 (22), 80 (28), 79 (38), 39 (100). The ^{1}H and ^{13}C NMR spectra are presented in Tables 2 and 3.

1-Cyano-1-(2-cyanoethyl)spiropentane (14). Pyrolysis of pyrazoline **3** (0.53 g, 3 mmol) carried out as described above gave 0.37 g (85%) of spiropentane **14** as a colorless liquid, b.p. 78—82 °C (1 Torr). IR (v/cm^{-1}): 2248 and 2234 m (C≡N), 1020 m (cyclopropane). MS, *m/z* (*I*(%)): 146 (1) M$^+$, 145 (5), 107 (15), 106 (32), 79 (100). Found (%): C, 73.33; H, 6.87; N, 19.89. $C_9H_{10}N_2$. Calculated (%): C, 73.94; H, 6.89; N, 19.17. The ^{1}H and ^{13}C NMR spectra are presented in Tables 2 and 3.

1-Methoxycarbonyl-1-(2-methoxycarbonylethyl)spiropentane (15). The reaction of pyrazoline **4** (0.43 g, 1.8 mmol) carried out in a similar way gave 0.29 g (76%) of spiropentane **15** as a yellowish liquid, b.p. 94—97 °C (0.2 Torr). IR (v/cm^{-1}): 1720 and 1733 s (COO), 1017 m (cyclopropane). MS, *m/z* (*I*(%)): 181 (8) (M−OMe)$^+$, 182 (5), 152 (13), 139 (14), 125 (30), 40 (100). Found (%): C, 61.83; H, 7.87. $C_{11}H_{16}O_4$. Calculated (%): C, 62.25; H, 7.60. The ^{1}H and ^{13}C NMR spectra are presented in Tables 2 and 3.

1-Cyano-1-(cyclopropylazo)spiropentane (16). A solution of azopyrazoline **5** (0.95 g, 5 mmol) in 3 mL of toluene was refluxed for 3 h until evolution of nitrogen ceased. Vacuum distillation gave 0.66 g (84%) of a yellowish substance that readily crystallized. Recrystallization of the product from hexane afforded spiropentane **16** as small colorless crystals, m.p. 73—75 °C. IR (v/cm^{-1}): 2237 s (C≡N), 1518 w (N=N), 1018 s (cyclopropane). MS, *m/z* (*I*(%)): 161 (22) M$^+$, 160 (19), 146 (17), 133 (19), 132 (55), 106 (82), 39 (100). Found (%): C, 66.88; H, 6.82; N, 26.19. $C_9H_{11}N_3$. Calculated (%): C, 67.06; H, 6.88; N, 26.06. The ^{1}H and ^{13}C NMR spectra are presented in Tables 2 and 3.

Thermolysis of 3-methoxycarbonyl-3-(cyclopropylazo)spiro(1-pyrazoline-5,1′-cyclopropane) (6). A solution of azopyrazoline **6** (0.66 g, 3 mmol) in 3 mL of toluene was heated at 95 °C for 2 h; evolution of nitrogen was observed. The ^{1}H NMR spectrum of the residue obtained after removal of the toluene showed that the initial azopyrazoline **6** was virtually absent. Removal of the solvent and vacuum microdistillation (at a bath temperature of 90—100 °C, 0.1 Torr) gave 0.15 g of a yellowish liquid that contained, judging from the ^{1}H NMR spectrum, ~75% azospiropentane **17**. MS, *m/z* (*I*(%)): 194 (1.3) M$^+$, 179 (1.5), 135 (48), 59 (42), 41 (100), 39 (83). The ^{1}H NMR spectrum is presented in Table 3.

3-Cyano-1-cyclopropylspiro(2-pyrazoline-4,1′-cyclopropane) (18). A mixture of azospiropentane **16** (0.32 g, 2 mmol) and 2 mL of *p*-xylene was heated in a sealed tube at 180 °C for 40 min. The solvent was evaporated *in vacuo* (15 Torr), and the colored residue was recondensed at 0.4 Torr (at a bath temperature of 85—90 °C) to give 0.28 g (88%) of pyrazoline **18** as a slightly colored liquid. Found (%): C, 66.81; H, 6.72. $C_9H_{11}N_3$. Calculated (%): C, 67.06; H, 6.88. The ^{1}H and ^{13}C NMR spectra are presented in Tables 1 and 2.

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