Thermal decomposition of strained spiro(1-pyrazoline-3,1′-cyclopropanes)

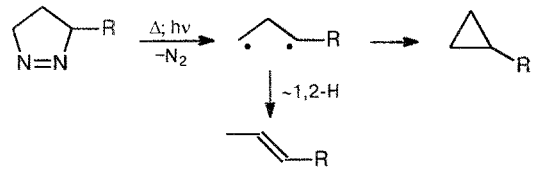
Yu. V. Tomilov, E. V. Shulishov, S. A. Yarygin, and O. M. Nefedov**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

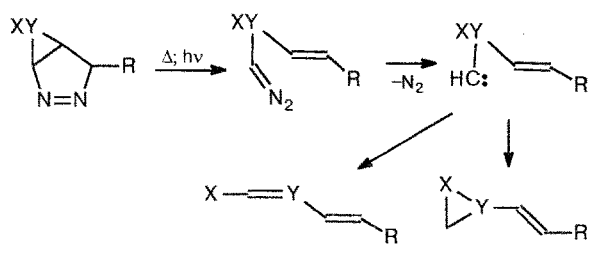
Pyrolysis (320–370 °C) of polycyclic 1-pyrazolines **1** and **2**, obtained by 1,3-dipolar cycloaddition of diazocyclopropane to 3,3-dimethylcyclopropene and spiro[2,3]hex-1-ene, yields complex mixtures of isomeric hydrocarbons, substituted methylenecyclopropanes being the main components. Pyrolysis of 6-ethenyl- (**4**) and 6-methoxy-6-methylcarbonyl-4,5-diazaspiro[2,4]hept-4-enes (**6**) at 310–320 °C proceeds more unambiguously to give vinyl- (**18**) and 1-methoxy-1-methylcarbonylspiropentanes (**20**) in ~85 and 95 % yields with respect to the transformed pyrazolines. Dediazotization of pyrazoline **3** obtained from diazocyclopropane and benzvalene requires more drastic conditions (~440 °C) and produces indane.

Key words: spiro(1-pyrazoline-3,1′-cyclopropanes), methylenecyclopropanes and spiropentanes, pyrolysis, isomerization, NMR spectra.

As a rule, 1-pyrazolines readily undergo thermal or photochemical decomposition to give cyclopropanes and/or olefins isomeric to the latter. To a considerable extent, the ease and direction of these transformations are determined by the nature of substituents at the pyrazoline ring, and the anticipated mechanism usually involves the formation of 1,3-biradical intermediates.[1–4]



However, in some cases, particularly when strained cyclic systems are involved, decomposition of pyrazolines gives complex mixtures of compounds, which are presumably formed through initial isomerization of a pyrazoline into a diazo compound followed by its decomposition to give a carbene, with subsequent transformations of the latter into stable reaction products.[4–6]



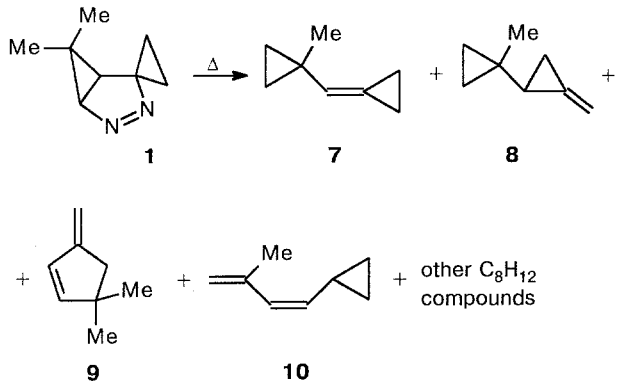
It should be noted that decomposition of pyrazolines that contain a spiro-bonded cyclopropane moiety most probably occurs by a biradical mechanism to give spiropentane derivatives.[3,7] On the other hand, decomposition of polycyclic pyrazolines incorporating condensed cyclopropane or cyclobutane moieties occurs less selectively,[5,8] while the fact that the reaction products contain dienes and other unsaturated compounds, along with diazo compounds found in certain cases,[8,9] suggests that carbenes participate in these transformations.

In the present work we studied the thermal decomposition of spiro(1-pyrazoline-3,1′-cyclopropanes) **1**–**6** whose molecules additionally contain an annelated cyclopropane moiety or an exocyclic double bond. These compounds were synthesized previously by 1,3-dipolar cycloaddition of diazacyclopropane generated *in situ* to 3,3-dimethylcyclopropene,[10] spiro[2,3]hex-1-ene,[11] benzvalene,[11] butadiene,[11] isoprene,[11] and methyl methacrylate,[12] respectively. The pyrolysis of pyrazolines was carried out by passing vapor of compounds **1**–**6** mixed with argon or hexane through a quartz tube with quartz packing at ambient pressure above 300 °C. A remarkable feature of 1-pyrazolines **1**–**6** is their rather high thermal stability. For example, pyrazolines **1**–**3** almost did not undergo transformations and remained unreacted below 300 °C or under irradiation by a mercury lamp (pentane, 20 °C, 8 h). It is noteworthy that 6,6-dimethyl-4-vinyl-2,3-diazabicyclo[3.1.0]hex-2-ene, which is isomeric to pyrazoline **1** and does not contain a spirocyclopropane moiety at the pyrazoline ring, decomposes under milder conditions (*n*-octane, 70 °C or *hν*, 0 °C) and can even be isomerized to the corresponding unsaturated diazo compound, $N_2CHCMe_2CH{=}CHCH{=}CH_2$ (see Ref. 8).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2203–2207, November, 1995.

1066-5285/95/4411-2109$12.50

From the viewpoint of synthesis of highly strained cyclic structures, pyrazolines **1—3** were of some interest. However, the possibility of synthesizing the corresponding spiro(bicyclobutanecyclopropanes) was doubtful due to the high dediazotization temperatures of compounds **1—3**. In fact, even when the conversion of **1** was low (~20% at 325 °C), spiro(4,4-dimethylbicyclobutane-2,1′-cyclopropane) was not found in the pyrolysis products. 1-(Cyclopropylidenemethyl)-1-methylcyclopropane (**7**) was identified as the main product of the hydrocarbon fraction.

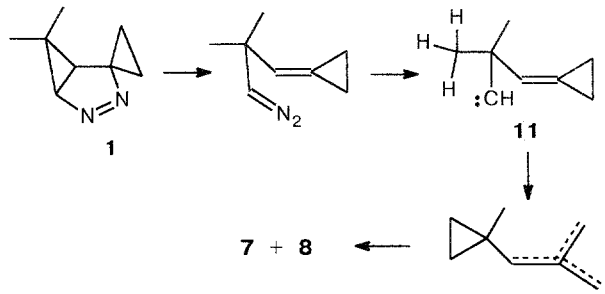


An increase in pyrolysis temperature to 355 and 370 °C results in a considerable increase in conversion of pyrazoline **1** (up to 84 % at 370 °C) and in formation of a mixture of hydrocarbons containing about ten C_8H_{12} isomers (GLC-MS data; see Table 1). The relative content of isomer **7** in the hydrocarbon fraction decreases from 75 to 39 %, which suggests that the selectivity of the process decreases, most likely due to secondary transformations of methylene- or vinylcyclopropanes formed.

The hydrocarbon fraction obtained was then separated (or enriched with certain components) by preparative GLC and the components were identified by ^1H and ^{13}C NMR spectra. As a result, four hitherto unknown hydrocarbons **7—10** containing one or two double bonds were characterized. As already noted above, compound **7**, which has the longest retention time among the C_8H_{12} isomers identified, is the main product of pyrolysis of pyrazoline **1**. The protons of two nonequivalent cyclopropane moieties manifest themselves in the ^1H NMR spectrum as pairs of symmetric signals. The low-field group of signals at δ 0.91 and 1.21 displays a distinct coupling constant with the olefinic proton (^4J = 1.9 Hz), which makes it possible to attribute these signals to protons in the methylenecyclopropane moiety.

The component of the reaction mixture next in quantity and having a similar structure is 1-methylene-2-(1-methylcyclopropyl)cyclopropane (**8**). According to data from ^1H NMR difference double resonance spectroscopy, this compound is characterized by the presence of five interacting protons, two of which are olefinic. Four protons in the strong field form a separate four-spin system and correspond to protons of the geminally substituted cyclopropane moiety. ^{13}C NMR data also confirm the proposed structure of substituted methylenecyclopropane **8**.

The formation of hydrocarbons **7** and **8** each containing one methyl group can easily be explained by nonsynchronous elimination of a nitrogen molecule and intermediate generation of carbene **11**, which transforms into the final products **7** and **8** by its insertion into a C—H bond of one of methyl groups. This transformation is rather typical of intramolecular reactions of alkylcarbenes.[13] In turn, the transformation of a substituted methylene group in the methylenecyclopropane moiety into a terminal group is a variant of trimethylenemethane rearrangement[14] and is also rather a usual process.



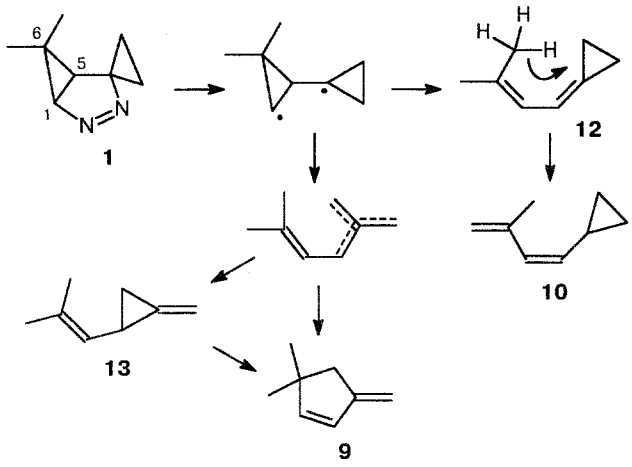
The next group of identified products of the pyrolysis of **1** includes dienes **9** and **10**, whose overall yield at 370 °C is ~22 %. Diene **9** has the shortest retention time (GLC) of the hydrocarbons obtained, while the retention time of diene **10** is almost the same as that of olefin **7**. The ^1H NMR spectra of both compounds contain signals typical of the $C{=}CH_2$ moiety (δ 4.7—5.0) and signals of two vicinal olefin protons, whose coupling constants make it possible to consider them as cyclopentene protons in the case of diene **9** (J = 5.1 Hz) and as *cis*-alkene protons in the case of compound **10**.

The formation of dienes **9** and **10**, unlike that of methylenecyclopropanes **7** and **8**, presumes retention of the C(1)—C(5) bond and cleavage of the C(5)—C(6) bond in the starting pyrazoline **1** and probably occurs by a biradical mechanism. Furthermore, the presence of *cis*-isomer **10** in the reaction mixture can result from isomerization of the intermediate 3-methylbut-2-enylidenecyclopropane **12** under the reaction conditions due to 1,5-hydride shift, while the formation of diene **9**

Table 1. Composition of products of the pyrolysis of pyrazoline **1**

Temperature (°C)	Degree of conversion (%)	Yield (%)	Composition of the hydrocarbon fraction (%)				
			7	**8**	**9**	**10**	other C_8H_{12}
325	20	18	75	6	7	7	5
355	63	58	56	13	10	12	9
370	84	77	39	18	13	15	15

requires trimethylenemethane and vinylcyclopropane—cyclopentene rearrangements. Under our experimental conditions, both of these processes probably occur synchronously due to low thermal stability of methylenevinylcyclopropane **13**, as the ^{1}H NMR spectrum of the reaction mixture does not contain signals corresponding to this compound.[15]

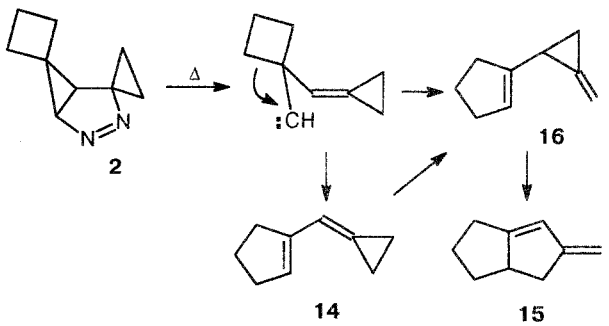


The scheme proposed for the formation of methylenecyclopentene **9** is confirmed by the previously reported thermal transformation of 1,1-dimethyl-2-methylene-3-vinylcyclopropane, whose structure is similar to that of diene **13**, into 1,1-dimethyl-2-methylenecyclopent-3-ene.[16]

Pyrolysis of pyrazoline **2** at 330 °C occurs with ~25 % degree of conversion and predominantly gives two isomeric C_9H_{12} hydrocarbons, 1-(cyclopropylidenemethyl)cyclopentene (**14**) and 3-methylenebicyclo-[3.3.0]oct-1-ene (**15**), in approximately equal quantities (overall yield 21 %). An increase in pyrolysis temperature to 370 °C increases the yield of diene **15** to ~44 %, while the yield of diene **14** remains almost unchanged, and several C_9H_{12} hydrocarbons appear in the reaction mixture, the conversion of **2** being as high as ~68 % under these conditions.

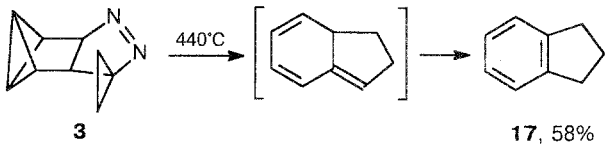
The main direction of thermal transformation of pyrazoline **2** probably also involves non-synchronous elimination of nitrogen and intermediate formation of carbene **16**. However, unlike the situation with pyrazoline **1** containing C—H bonds of methyl groups readily accessible to the carbene center, in this case stabilization of carbene occurs by 1,2-alkyl shift with transformation of the strained cyclobutane moiety into a cyclopentene moiety. The resulting methylenecyclopropanes **14** and particularly **16** are capable of undergoing subsequent thermal transformations; as a final result, diene **15** is predominantly formed.

The structures of hydrocarbons **14** and **15** in mixtures containing various amounts of isomers obtained at different temperatures were established by difference NMR spectroscopy. The presence of low intensity

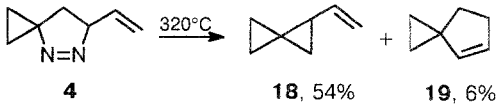


signals in the region typical of olefinic protons suggests the presence of several minor unsaturated hydrocarbons, which prevent unambiguous identification of signals corresponding to isomer **16**.

An unusually high thermal stability is displayed by 1-pyrazoline **3**, which contains both a spiro-bonded cyclopropane and bicyclobutane moieties. Pyrazoline **3** is decomposed to a considerable extent above 390 °C to give indane **17** as practically the only hydrocarbon obtained; the yield of **17** at 440 °C is ~58 %. Under drastic reaction conditions, both isomerization of the bicyclobutane moiety into a diene moiety and elimination of a nitrogen molecule by a biradical mechanism involving consecutive 1,2- and 1,3-hydride shifts are likely to occur; as a result, aromatic structure **17** is formed.



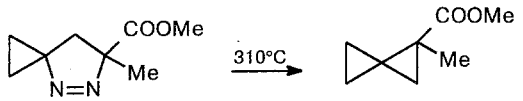
Pyrolysis of spiro(1-pyrazoline-3,1′-cyclopropanes) containing an exocyclic double bond (vinyl or methylene group) also results in different products. For example, the main dediazotization product of vinylpyrazoline **4** is vinylspiropentane (**18**) containing an admixture of isomeric spiro[2,4]hept-4-ene **19** (ratio ~9 : 1). The degree of conversion of **4** at 320 °C is ~66 %. Both compounds were identified by comparing their ^{1}H NMR spectra with those reported in the literature.[17,18]



6-(1-Methylethylidene)-4,5-diazaspiro[2,4]hept-4-ene (**5**) synthesized from diazacyclopropane and isoprene[11] has the highest thermal stability as it decomposes only above 400 °C. However, we were unable to identify any products because of strong resinification of the pyrolysate (the degree of conversion of **5** was ~65 %).

Of all the cases of pyrolysis studied, the transformation of functionally substituted pyrazoline **6** occurs the most

smoothly and selectively. The degree of conversion of **6** at 300—310 °C is ~95 %, the yield of 1-methoxy-1-methylcarbonylspiropentane (**20**) being ~90 %. The structure of the compound obtained was confirmed by elemental analysis and ^{1}H and ^{13}C NMR spectral data. The ^{1}H NMR spectrum (300 MHz) contains a distinct AX-system of two isolated protons of a substituted cyclopropane ring with a coupling constant of J_{gem} = 3.6 Hz and a series of multiplets in the upfield region (δ 0.65—0.95) corresponding to protons of the second cyclopropane ring. Because of strong deshielding effect of the ester group, signals of protons directed towards the former are shifted downfield (see Experimental).



6 **20**, ~90%

Thus, when a cyclopropane moiety is spiro-bonded to a pyrazoline ring, the thermal stability of 1-pyrazolines increases markedly; in most cases, this results in chemical transformations of all energetically strained moieties in the molecule when dediazotization is carried out under more drastic conditions.

Experimental

The compounds obtained and their mixtures were analyzed by GLC on a Perkin-Elmer chromatograph with automatic integration of peaks (capillary column) and by GLC-MS on a Finnigan MAT INCOS-50 instrument (70 eV) with a RSL-200 capillary column (30 m length). Preparative separation was performed on a 200 × 1.5 cm column with 5 % SE-30 on Chromaton N-AW-HMDS. ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 and 62.90 MHz) and Bruker AM-300 (300 and 75.47 MHz) instruments in $CDCl_3$ solutions containing 0.1 % $SiMe_4$ as the internal standard. Previously synthesized spiro(1-pyrazoline-3,1′-cyclopropanes) **1—6** (see Refs. 10—12) were used in this work.

Thermal decomposition of pyrazolines was carried out by passing (~10 mL h^{-1}) a solution of the corresponding pyrazoline in hexane (~1 : 3, v/v) through a quartz tube (1 cm internal diameter) packed with 12 cm of finely dispersed quartz and purged with a stream of argon (4—5 mL min^{-1}). After the reaction ceased, the tube was cooled, and hexane (2 mL) was simultaneously passed through it. The pyrolysate was then analyzed by GLC and GLC-MS. The solvents were removed, and the dediazotization products and unreacted pyrazolines were separated by distillation *in vacuo* and identified by NMR spectroscopy.

Pyrolysis of spiro{6,6-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene-4,1′-cyclopropane} (1). The reaction starting from pyrazoline **1** (1.36 g, 0.01 mol) at 325 °C followed by distillation of the pyrolysate *in vacuo* gave 0.20 g (~18 %) of a hydrocarbon fraction with b.p. 65—71 °C (50 Torr) containing nine components of C_8H_{12} composition, including ~75 % of methylenecyclopropane **7** and 1.08 g of the starting pyrazoline, whose ^{1}H NMR spectrum totally agreed with structure **1**. Pyrolysis of pyrazoline **1** at 355 and 370 °C was carried out similarly (see Table 1). The resulting hydrocarbon fractions were separated or enriched with the main components by preparative GLC (90 °C).

1-(Cyclopropylidenemethyl)-1-methylcyclopropane (7). ^{1}H NMR, δ: 5.41 (quint, 1 H, J = 1.9 Hz), 1.29 (s, 3 H, CH_3), 1.21 and 0.91 (two ddd, 2×2 H, J_{cis} = 8.5 Hz, J_{trans} = 4.5 Hz, ^4J = 1.9 Hz, 2 CH_2 cyclopropylidene), 0.63 and 0.54 (two m, 2×2 H, CH_2CH_2). ^{13}C NMR, δ: 125.4 (HC=), 117.5 (=C), 22.4 (CH_3), 18.1 (C), 15.0 (2 CH_2 cyclopropylidene), 3.3 (CH_2), 0.3 (CH_2). MS, *m/z* (*I*(%)): 108 M$^+$ (5), 107 (8), 93 (100), 91 (72), 79 (49), 77 (86).

1-Methyl-2′-methylenebicyclopropyl (8). ^{1}H NMR, δ: 5.31 (m, 2 H, $=CH_2$), 1.68, 1.11 and 0.78 (three m, 3×1 H, $CHCH_2$), 1.18 (s, 3 H, CH_3), 0.28 and 0.02 (two m, 3+1 H, CH_2CH_2). ^{13}C NMR, δ: 134.7 (=C), 102.9 ($=CH_2$), 23.9 (CH), 21.7 (CH_3), 16.0 (C), 12.0 (CH_2), 9.0 and 7.8 (CH_2CH_2). MS, *m/z* (*I*(%)): 107 (4), 93 (100), 91 (52), 79 (52), 77 (67).

5,5-Dimethyl-3-methylenecyclopent-1-ene (9). ^{1}H NMR, δ: 6.01 (br.d, 1 H, $J_{1,2}$ = 5.1 Hz, H-1), 5.91 (br.dd, 1 H, $J_{1,2}$ = 5.1 Hz, ^4J = 1.2 Hz, H-2), 4.83 and 4.74 (two m, 2×1 H, $=CH_2$), 2.36 (t, 2 H, J = 2.0 Hz, CH_2), 1.10 (s, 6 H, 2 CH_3). ^{13}C NMR, δ: 149.6 (C-2), 131.1 (C-1), 129.3 (C-3), 102.9 ($=CH_2$), 45.2 (C-4), 41.0 (C-5), 28.8 (2 CH_3). MS, *m/z* (*I*(%)): 108 M$^+$ (27), 93 (100), 91 (42), 77 (42).

***cis*-1-Cyclopropyl-3-methyl-1,3-butadiene (10).** ^{1}H NMR, δ: 5.80 (br.d, 1 H, J_{cis} = 11.5 Hz, H^a), 4.98 (m, 2 H, $=CH_2$), 4.77 (br.d, 1 H, J_{cis} = 11.5 Hz, J = 9.5 Hz, H^b), 1.97 (dd, 3 H, ^4J = 0.8 Hz, ^4J = 1.2 Hz, CH_3), 1.92 (m, 1 H, H^c), 0.79 (ddd, 2 H, J_{cis} = 7.8 Hz, J_{trans} = 4.0 Hz, J_{gem} = 5.8 Hz, CH^{d}CH^d), 0.38 (dt, 2 H, J_{trans} = 4.0 Hz, J_{gem} = 5.8 Hz, CH^{e}CH^e).

Pyrolysis of dispiro{2,3-diazabicyclo[3.1.0]-2-hexene-4,1′-cyclopropane-6,1″-cyclobutane} (2). The reaction starting from pyrazoline **2** (1.19 g, 0.008 mol) at 330 °C followed by distillation of the pyrolysate *in vacuo* gave 0.20 g (~21 %) of a hydrocarbon fraction with b.p. 62—66 °C (30 Torr) and 0.88 g of the starting pyrazoline, whose ^{1}H NMR spectrum totally agreed with structure **2**. Pyrolysis of pyrazoline **2** at 370 °C was carried out similarly. The main reaction products were identified by difference NMR spectroscopy of the hydrocarbon fractions obtained from both experiments.

1-(Cyclopropylidenemethyl)cyclopentene (14). ^{1}H NMR, δ: 6.59 (m, 1 H, H(2)), 5.66 (m, 1 H, HC=), 2.59 and 2.40 (two m, 2 H(3) and 2 H(5)), 1.94 (m, 2 H(4)), 1.22 and 1.08 (two m, 2 CH_2 cyclopropylidene). ^{13}C NMR, δ: 143.1 (C-1), 127.9 (C-2), 123.8 (C=), 115.8 (HC=), 32.6 and 32.4 (C-3 and C-5), 23.4 (C-4), 3.8 and 1.5 (CH_2CH_2). MS, *m/z* (*I*(%)): 120 M$^+$ (3), 105 (3), 92 (8), 91 (19), 39 (78), 27 (100).

3-Methylenebicyclo[3.3.0]oct-1-ene (15). ^{1}H NMR, δ: 5.78 (pseudo q, 1 H, J ~2.2 Hz, H(2)), 4.67 (m, 1 H), 4.60 (tt, 1 H, J = 2.3 Hz and 1.2 Hz, $=CH_2$), 2.93 (m, 1 H, H(5)), 2.70 (ddt, 1 H, J_{gem} = 15.2 Hz, $J_{4,5}$ = 7.0 Hz, J = 1.2 Hz, H(4)), 2.19 (d quint, J_{gem} = 15.2 Hz, J ~2.4 Hz, H(4)), 2.28 (m, 2 H) and 1.84—2.05 (m, 4 H, H(6), H(7) and H(8)). ^{13}C NMR, δ: 164.4 (C-1), 159.8 (C-3), 123.1 (C-2), 99.7 ($=CH_2$), 51.3 (C-5), 36.9, 31.7, 27.4 and 24.0 (4 CH_2). MS, *m/z* (*I*(%)): 120 M$^+$ (6), 105 (4), 92 (18), 91 (26), 39 (75), 27 (100).

Pyrolysis of spiro{7,8-diazatetracyclo[4.3.0.0^{2,4}.0^{3,5}]non-7-ene-9,1′-cyclopropane} (3). The reaction of pyrazoline **3** (1.31 g, 0.009 mol) at 440 °C followed by distillation of the pyrolysate *in vacuo* gave 0.66 g (62 %) of a colorless liquid with b.p. 74—75 °C (15 Torr), whose ^{1}H and ^{13}C NMR spectra corresponded to indane structure.

Pyrolysis of 6-vinyl-4,5-diazaspiro[2,4]hept-4-ene (4). The reaction of pyrazoline **4** (0.73 g, 0.006 mol) in pentane (2 mL) and ether (0.5 mL) at 320 °C followed by fractionation gave 0.34 g (~0.62 %) of a hydrocarbon fraction of C_7H_{10} composition with b.p. 79—83 °C (520 Torr) containing 86 % of vinylspiropentane (**18**)[17] and 9—10 % of spiro[2,4]hept-4-ene (**19**)[18] (GLC data).

Pyrolysis of 6-(1-methylethenyl)-4,5-diazaspiro[2,4]hept-4-ene (5). The reaction of pyrazoline **5** (0.82 g, 0.006 mol) in pentane (2 mL) and ether (0.5 mL) at 440 °C followed by cautious removal of the solvents from the pyrolysate (bath temperature did not exceed 50 °C) gave 0.28 g (35 %) of a residue, whose ^{1}H NMR spectrum corresponded to the starting pyrazoline **5**. Strong resinification was observed in the heating zone of the reaction tube. When the pyrolysis temperature was decreased, the degree of pyrazoline conversion decreased, but volatile products were not formed in considerable amounts.

6-Methoxy-6-methylcarbonyl-4,5-diazaspiro[2,4]hept-4-ene (6) was obtained from *N*-nitroso-*N*-cyclopropylurea (2.6 g, 0.02 mol) and methyl methacrylate (3.0 g, 0.03 mol) in the presence of MeONa by a procedure reported previously.[10,12] A weakly colored yellow-green liquid, yield 70 %, b.p. 80—82 °C (0.7 Torr). ^{1}H NMR, δ: 3.79 (s, 3 H, OMe), 2.30 (d, 1 H, J_{gem} = 12.2 Hz, H(7)), 1.74 (m, 2 H, H(1) and H(2)), 1.62 (d, 1 H, J_{gem} = 12.2 Hz, H(7)), 1.60 (s, 3 H, Me), 1.11 (m, 2 H, H(1) and H(2)). ^{13}C NMR, δ: 171.2 (CO), 92.6 (C-6), 69.1 (C-3), 52.4 (OMe), 35.1 (C-7), 22.0 (Me), 14.1, 13.3 (CH_2CH_2). MS, *m/z* (*I*(%)): 169 $[M+1]^+$ (0.4), 139 (2), 125 (28), 112 (9), 97 (20), 79 (51), 39 (100).

1-Methoxy-1-methylcarbonylspiropentane (20). The pyrolisis of pyrazoline **6** (2.02 g, 0.012 mol) at 310 °C followed by distillation of the pyrolysate *in vacuo* gave 1.5 g (~90 %) of a colorless liquid with b.p. 63—65 °C (10 Torr). ^{1}H NMR, δ: 3.59 (s, 3 H, OMe), 1.62 (d, 1 H, J_{gem} = 3.6 Hz, *cis*-H(2), 1.22 (s, 3 H, Me), 0.96 (d, 1 H, J_{gem} = 3.6 Hz, *trans*-H(2), 0.91 (m, 1 H, *syn*-H(4)), 0.65—0.85 (m, 3 H, *anti*-H(4) and 2 H(5)). ^{13}C NMR, δ: 175.8 (CO), 51.5 (OMe), 24.9 and 23.8 (C-1 and C-3), 22.1 (C-2), 17.6 (Me), 6.6 and 4,9 (C-4 and C-5). Found (%): C, 68.42; H, 8.68. $C_8H_{12}O_2$. Calculated (%): C, 68.55; H, 8.63.

This study was financially supported by the Russian Foundation for Basic Research (Grant No. 94-03-08902).

References

1. C. H. Jarboe, in *The Chemistry of Heterocyclic Compounds*, Ed. A. Weissberger, Wiley, 1967, **22**, 209.
2. W. Adam and O. De Lucchi, *Angew. Chem.*, 1980, **92**, 815.
3. Yu. V. Tomilov, E. V. Shulishov, A. B. Kostitsyn, and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 662 [*Russ. Chem. Bull.*, 1994, **43**, 612 (Engl. Transl.)].
4. P. S. Engel, *Chem. Rev.*, 1980, **80**, 99 (1-Pyrazolines: see p. 118).
5. D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, 1972, **94**, 1348.
6. D. F. Eaton, R. G. Bergman, and G. S. Hammond, *J. Am. Chem. Soc.*, 1972, **94**, 1351.
7. K. Shen and R. Bergman, *J. Am. Chem. Soc.*, 1977, **99**, 1655.
8. M. Schneider and B. Csacsko, *Angew. Chem.*, 1977, **89**, 905.
9. M. S. Baird and H. H. Hussain, *Tetrahedron*, 1987, **43**, 215.
10. Yu. V. Tomilov, E. V. Shulishov, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1057 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 939 (Engl. Transl.)].
11. Yu. V. Tomilov, E. V. Shulishov, G. P. Okonnishnikova, and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2199 [*Russ. Chem. Bull.*, 1995, **44**, 2105 (Engl. Transl.)].
12. Yu. V. Tomilov, G. P. Okonnishnikova, E. V. Shulishov, and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1993 [*Russ. Chem. Bull.*, 1994, **43**, 1880 (Engl. Transl.)].
13 A. R. Kraska, L. I. Cherney, and H. Shechter, *Tetrahedron Lett.*, 1982, **23**, 2163.
14. A. Greenberg and J. F. Liebman, *Organic Chemistry*, Ed. H. H. Wasserman, Academic Press, 1978, **38**, 105.
15. A. M. Brouwer and H. J. C. Jacobs, *Recl. Trav. Chim. Pays-Bas*, 1987, **106**, 48.
16. A. S. Kende and E. E. Riecke, *J. Am. Chem. Soc.*, 1972, **94**, 1397.
17. N. S. Zefirov, S. I. Kozhushkov, T. S. Kuznetsova, K. A. Lukin, and I. V. Kazimirchik, *Zh. Org. Khim.*, 1988, **24**, 673 [*J. Org. Chem. USSR*, **24** (Engl. Transl.)].
18. P. Bruckmann and M. Klessinger, *Chem. Ber.*, 1974, **107**, 1108.

Received July 14, 1995