Formation of polycyclic hydrocarbons containing a spiropentane or methylenecyclobutane moiety upon thermal decomposition of cyclopropane-containing 1-pyrazolines*

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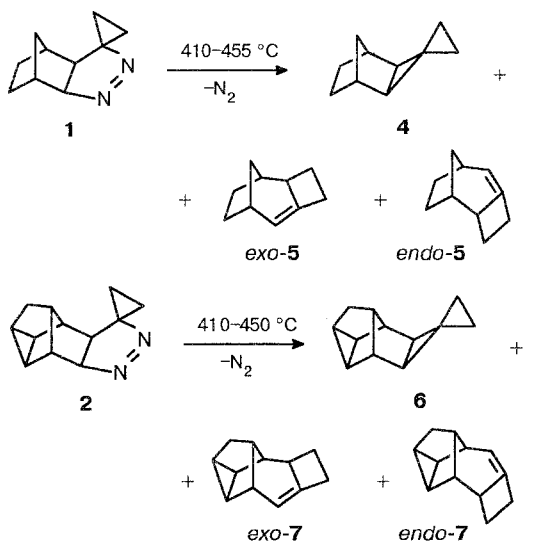
1-Pyrazolines **1** and **2** obtained by 1,3-dipolar cycloaddition of diazocyclopropane to norbornene or deltacyclene undergo dediazotization at 410—450°C to give a mixture of strained hydrocarbons, namely, spiro{cyclopropane-1,3′-tricyclo[3.2.1.$0^{2,4}$]octane} (**4**) or spiro{cyclopropane-1,4′-pentacyclo[4.4.0.$0^{2,8}$.$0^{3,5}$.$0^{7,9}$]decane} (**6**) and isomeric tricyclo[5.2.1.$0^{2,5}$]dec-5-enes (**5**) or pentacyclo[6.4.0.$0^{2,10}$.$0^{3,6}$.$0^{9,11}$]dec-6-enes (**7**) in a 30—70% overall yield. An increase in temperature favors the isomerization of spiro hydrocarbons **4** and **6** to the respective unsaturated hydrocarbons **5** and **7**. The latter undergo cyclopropanation with diazomethane in the presence of $Pd(acac)_2$ or $(PhO)_3P \cdot CuCl$ to afford polycyclanes **9a,b** or **10a,b** containing a spiro[2.3]hexane moiety condensed at the *cis*-1,4 position. Unsaturated 1-pyrazoline **3** obtained from diazocyclopropane and norbornadiene decomposes at 330—370°C with elimination of cyclopentadiene to give 3(5)-vinylpyrazole in a yield up to 75%.

Key words: polycyclic spiro{cyclopropane-1,3′-pyrazolines-1}, polycyclic 1,2-spiropentanes, 1,4-spirohexanes and methylenecyclobutanes (anti-Bredt olefines), pyrolysis, catalytic cyclopropanation with diazomethane.

We have shown previously[2] that diazocyclopropane generated by the decomposition of *N*-nitroso-*N*-cyclopropylurea with sodium methoxide efficiently adds *in situ* to norbornene double bonds to give the corresponding 1-pyrazolines containing a spiro-bonded cyclopropane moiety.

In the present work we studied the thermal decomposition of 1-pyrazolines **1—3** obtained by reactions of diazocyclopropane with norbornene, deltacyclene, and norbornadiene. Unlike the majority of other 1-pyrazolines, compounds **1** and **2** have high photochemical and thermal stability. In particular, they remain almost unchanged after direct and sensitized photolysis by a mercury lamp at 50°C and after prolonged heating of the condensed phase at 200—220°C. At higher temperatures, they decompose vigorously, which is accompanied by resinification of the reaction mixture. However, when vapors of compounds **1** and **2** are passed through a quartz tube at temperatures above 400°C, their partial dediazotization occurs to give $C_{10}H_{14}$ and $C_{12}H_{14}$ hydrocarbons, respectively,[1] in each case as mixtures of two structural isomers easily separable by preparative GLC (SE-30). According to ^1H and ^{13}C NMR spectral data, compounds with smaller retention times correspond to the expected saturated hydrocarbons having symmetric structures with an *exo*-oriented spiropentane moiety. The other pair of hydrocarbons turned out to be a mixture of two geometric isomers, *exo*- and *endo*-**5** and *exo*- and *endo*-**7**, which have unsymmetric structures and contain a trisubstituted double bond.



*Some of the results reported in this paper have been presented at the VIIIth European Symposium on organic chemistry (Barcelona, August—September 1993), *cf.* Ref. 1.

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Table 1. Pyrolysis of polycyclic pyrazolines **1** and **2** at various temperatures

Starting pyrazoline	Temperature/°C	Conversion (%)	Yield of hydrocarbons	
			4 or **6**	**5** or **7**
1	415	30	24	4
	435	48	22	23
	455	78	12	59
2	410	29	24	3
	450	80	11	60

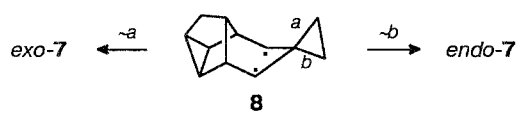
Note: pyrazoline : hexane ~1 : 3 v/v, addition rate ~5 mL h^{-1}, a quartz tube 1.0 cm in diameter.

The conversion of the starting pyrazolines, as well as the yields and ratio of compounds formed depend on the pyrolysis temperature (Table 1). The conversion of compounds **1** and **2** at 410—415 °C is only *ca.* 30 %, and spiropentanes **4** and **6**, respectively, are the main products in the hydrocarbon fraction. On the contrary, dediazotization at 450—455 °C occurs by 78—80 %, and unsaturated hydrocarbons **5** or **7** are the predominating reaction products. Most likely, they are formed due to thermal isomerization of the spiropentanes **4** or **6** formed initially. Indeed, as we have shown in separate experiments, hydrocarbons **4** and **6** isolated in an individual state readily undergo thermal transformations into unsaturated compounds **5** and **7**. The isomeric ratios of hydrocarbons formed both by the decomposition of pyrazolines (**1** and **2**) and by the isomerization of spiropentanes **4** and **6** are almost similar and equal to ~1.6 : 1 in the case of tricyclodecens **5** (the *endo*-isomer predominates) and ~1 : 1 in the case of pentacyclododecenes **7**.

This type of isomerization of spiropentanes into methylenecyclobutanes involving the cleavage of a peripheral bond is well known in the series of usual spiropentanes.[3,4] It is characteristic that this process also occurs rather selectively in the case of strained polycyclic structures and terminates at the stage of polycycloalkenes with a double bond at the angular carbon atom incorporated into the small cycle, *i.e.*, the process gives the so-called anti-Bredt structures.

The formation of a mixture of an approximately equal amount of *exo*- and *endo*-**5** or *exo*- and *endo*-**7** from the respective *exo*-isomers of **4** or **6** is likely to occur *via* a nearly plane biradical **8** in which the CH_2 groups, which are geometrically nonequivalent relative to the norbornene moiety, migrate to the radical center with equal probability (cleavage of bonds *a* and *b*).

Hydrocarbons **5** and **7** are stable in an inert atmosphere. However, they readily undergo oxidation and polymerization when stored in the air.

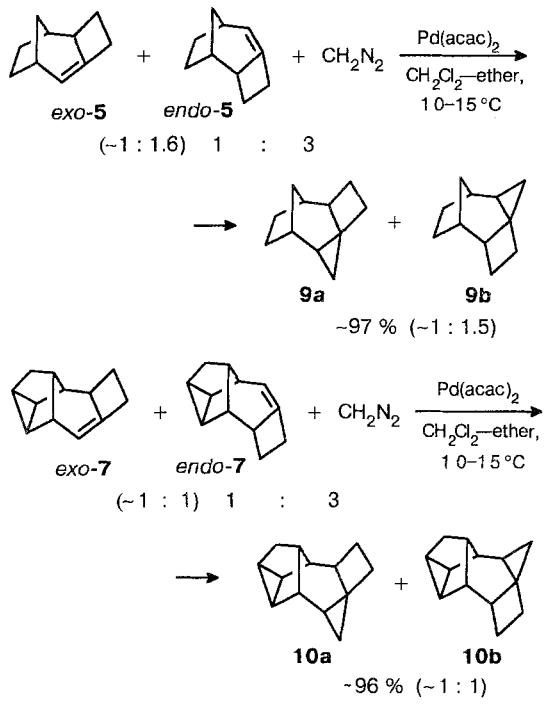


8

The structures of the compounds obtained were confirmed based on their ^{13}C and ^{1}H NMR spectra (Tables 2 and 3). The assignment of signals in the corresponding spiropentane-containing hydrocarbons **4** and **6** did not involve any difficulties. The *exo*-position of the annelated spiropentane moiety was established based on the small value of coupling constants of the vicinal protons H^a and H^c ($J < 1.5$ Hz). Since attempts of preparative separation of isomers of unsaturated hydrocarbons **5** and **7** failed and their usual homonuclear resonance spectra are very complex, the signals in the ^{13}C and ^{1}H NMR spectra were assigned using standard procedures COSY-90 for the $^{1}H—^{1}H$ correlation and LAOCN3-XHCORRD for the $^{1}H—^{13}C$ correlation. The assignment of isomers of compounds **5** and **7** to the *exo* and *endo* series was performed based on the coupling constants of the H^a and H^c protons, which, by analogy to the coupling constants of similar protons in derivatives of bicyclo[3.2.1]oct-2-ene,[5] should differ significantly depending on the *exo* or *endo* position of the H^c proton. If this proton has an *exo* orientation, the coupling constant is $^{3}J = 4.5—5.5$ Hz, while with *endo* orientation, $^{3}J = 1—2$ Hz. Quantum-chemical calculations of molecules of *exo*- and *endo*-**7** by the MNDO-PM3 method showed that the dihedral angle H^aCCH^c is ~88° in the *exo* isomer ($^{3}J = 1—2$ Hz) and 53—54° in the *endo* isomer ($^{3}J = 3.5—4$ Hz). Thus, the presence of an additional condensed cyclobutane ring in compounds **5** and **7** does not change the general correlations of changing the coupling constant of vicinal protons H^a and H^c in the corresponding *exo*- and *endo*-isomers. In accordance with these correlations, the structure of *endo*-isomers was assigned to isomers **5** and **7** characterized by markedly higher coupling constants for the H^a and H^c protons (^{3}J ~5.5 Hz) (Table 3). Furthermore, the downfield position of the *exo*-H^c signal of *endo*-**5** in comparison with its *exo*-isomer and the downfield shift of the *endo*-H^c signal of the *exo*-**5** isomer due to the anisotropy of the cyclopropane ring confirm the validity of this assignment of the isomers.

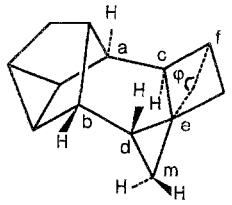
Further, we studied the catalytic cyclopropanation of unsaturated compounds with diazomethane. It turned out that, unlike in substituted alkenes,[6] the intracyclic double bond in hydrocarbons **5** and **7**, although it is trisubstituted, can undergo cyclopropanation with diazomethane in the presence of Pd compounds. Undoubtedly, this is related with a high strain of the molecule due to the removal of substituents at the double bond from coplanarity. According to the calculations, the length of the double bond is ~0.133 nm; the dihedral angles $C^bC^dC^eC^c$ and $H^dC^dC^eC^g$ in *exo*-**7** are 7.3 and 27°, while in *endo*-**7** they are 6.0 and 24.5°. It should be noted that the few known examples of the cyclopropanation of trisubstituted double bonds with diazomethane in the presence of Pd compounds are

Scheme 1



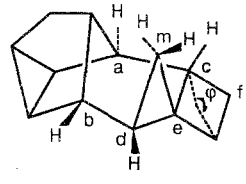
typical of strained cyclic structures. In particular, the cyclopropanation of the substituted norbornene[7,8] and intracyclic methylenecyclopropane[9] double bonds with diazomethane in the presence of $Pd(OAc)_2$ gave the corresponding cyclopropane adducts in moderate yields. We found that the addition of 0.5—1.0 mol.% $Pd(acac)_2$ and a threefold molar excess of diazomethane in ether—methylene dichloride to a solution of olefin **5** or **7** results in an almost complete cyclopropanation of the latter into tetracyclo[6.2.1.$0^{2,4}$.$0^{4,7}$]undecanes (**9**) or hexacyclo[7.4.0.0.$^{2,11}0^{3,5}$.$0^{5,8}$.$0^{10,12}$]tridecanes (**10**) in the yields >96% (Scheme 1).

Each of the cyclopropane adducts **9** and **10** is a mixture of two isomers in the same ratios as those of the original olefins **5** and **7**. Quantum-chemical calculations of the molecular structures of compound **10** showed that four geometric isomers can actually exist due to the small probability of conformational transformations (because of a non-plane structure of the cyclobutane ring; $\angle\varphi$ is the angle of the deviation of the fourth C atom from the plane formed by three remaining carbon atoms) in the spirohexane moiety involved in the polycyclic structure. The less strained structures **10a** and **10b**, in which the H^c and H^d atoms are in the *trans*-position, are more energetically favorable. In this case, the peripheral C^f atom of the cyclobutane moiety is located almost in the plane of the cyclopropane ring, whereas in compounds **10c,d** it is out of the plane (the angle between the *ef* diagonal and the plane of the cyclopropane ring is 17.1° for **10c** and 8.1° for **10d**).



10a

ΔH^f_0 = 270.0 kJmol^{-1},
r_{de} = 0.150 nm,
r_{ce} = 0.153 nm,
$\angle\varphi$ = 170°



10b

ΔH^f_0 = 269.2 kJmol^{-1},
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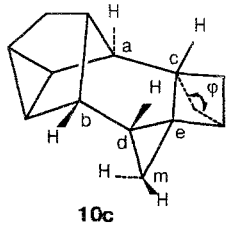
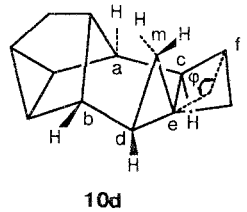
r_{ce} = 0.153 nm,
$\angle\varphi$ = 169°



10c

ΔH^f_0 = 394.7 kJmol^{-1},
r_{de} = 0.150 nm,
r_{ce} = 0.153 nm,
$\angle\varphi$ = 153°



10d

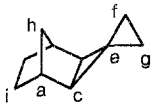
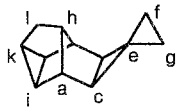
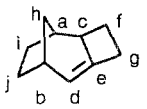
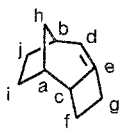
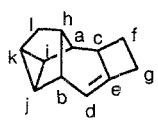
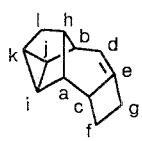
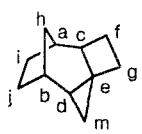
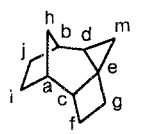
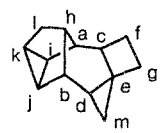
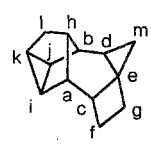
ΔH^f_0 = 468.4 kJmol^{-1},
r_{de} = 0.150 nm,
r_{ce} = 0.154 nm,
$\angle\varphi$ = 158°

It should be noted that the use of the less selective copper catalysts,[10] in particular, $(PhO)_3P \cdot CuCl$, in the cyclopropanation of olefins **5** likewise results in the two most stable isomers, **9a** and **9b**. Unlike the reaction in the presence of $Pd(acac)_2$, the yield of cyclopropane adducts is only 60—65% when the reaction is carried out with the same reagent ratio. Of the unreacted olefins, *endo*-**5** predominates markedly (the *endo*:*exo* ratio is ~7:1), which indicates its lower reactivity.

The structures of hydrocarbons **9** and **10** obtained were established based on their ^1H and ^{13}C NMR spectra (Tables 2 and 3). Since the preparative separation of the isomers is impossible and the pattern of the overlapping signals of isomers **9** is complex, the complete assignment of signals in the ^1H NMR spectrum was only performed for hydrocarbons **10**. By analogy with compounds **5** and **7**, the structures **10a** ($J_{ac} \leq 1.5$ Hz, $J_{bd} \sim 7$ Hz) and **10b** ($J_{ac} \sim 6.5$ Hz, $J_{bd} \sim 2$ Hz) with transoid positions of the H^c and H^d protons were assigned based on the observed and calculated coupling constants of the vicinal protons H^a, H^d, H^c, and H^d (the dihedral angles $H^aC^aC^cH^c$ and $H^bC^bC^dH^d$ are 80.5 and 27.3° for **10a** and 45.3 and 62.7° for **10b**, respectively).

Thus, the data obtained imply that the catalytic cyclopropanation of the intracyclic double bond of hydrocarbons **5** and **7** occurs strictly regioselectively and results in the addition of a methylene moiety at the less sterically hindered side due to the noncoplanarity of the ethylene moiety.

Table 2. Mass and ^{13}C NMR spectra of the polycyclic hydrocarbons synthesized

Compound		^{13}C NMR spectrum ($CDCl_3$), δ								MS,
		C^a,C^b	C^c	C^d	C^e	C^f,C^g	C^h	C^i,C^j,C^k C^l,C^m		*m/z* (I_{rel} (%))
	*exo*-**4**	36.25	22.98		11.55	5.75 3.97	30.08	29.37		133 $[M-H]^+$ (2) 119 $[M-CH_3]^+$ (15) 91 $[C_7H_7]^+$ (100)
	*exo*-**6**	43.24	24.58		14.60	5.89 5.56	32.79	18.02 16.29	31.16	157 $[M-H]^+$ (4) 143 $[M-CH_3]^+$ (32) 129 $[C_9H_{11}]^+$ (100)
	*exo*-**5**	34.97 33.29	55.81	125.07	139.88	24.39 32.26	34.88	33.42 32.89		134 $[M]^+$ (19) 119 $[M-CH_3]^+$ (20) 91 $[C_7H_7]^+$ (100)
	*endo*-**5**	36.31 35.78	50.10	118.90	138.57	21.10 31.78	37.00	34.95 22.40		134 $[M]^+$ (24) 119 $[M-CH_3]^+$ (19) 91 $[C_7H_7]^+$ (100)
	*exo*-**7**	36.28 40.01	50.70	114.38	137.55	24.45 32.44	35.27	20.30 17.63 15.01	34.37	158 $[M]^+$ (35) * 143 $[M-CH_3]^+$ (48) 129 $[C_9H_{11}]^+$ (100)
	*endo*-**7**	42.28 41.11	44.41	115.92	141.39	25.61 32.74	41.65	22.47 13.54 10.35	33.50	*
	**9a**	36.66 31.72	44.44	27.13	17.05	27.79 21.68	29.67	26.12 32.55	12.66	148 $[M]^+$ (5) 120 $[M-C_2H_4]^+$ (79) 79 $[C_6H_7]$ (100)
	**9b**	34.25 (2C)	44.38	24.74	19.27	28.14 21.90	30.86	20.11 33.29	15.65	*
	**10a**	38.75 43.73	38.17	18.72	17.60	27.09 22.37	32.91	14.11 12.59 13.63	33.71 14.23	172 $[M]^+$ (36) * 144 $[M-C_2H_4]^+$ (90) 129 $[C_9H_{11}]^+$ (100)
	**10b**	40.46 41.29	38.49	22.10	18.49	28.25 22.72	31.33	17.47 10.91 13.02	34.02 15.58	*

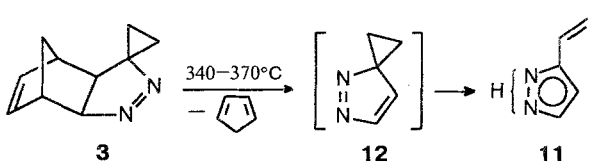
* The mass spectrum was obtained for a mixture of isomers.

The thermal decomposition of spiro{3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3-ene-5,1′-cyclopropane} (**3**) (ratio of *exo* and *endo* isomers ~4 : 1) obtained by the addition of diazacyclopropane to norbornadiene,[2] unlike that of pyrazolines **1** and **2**, occurs in another way and is almost not accompanied by the liberation of nitrogen. In this case, the major and the most favorable process involves the elimination of cyclopentadiene and the formation of

Table 3. ^{1}H NMR spectra of polycyclic hydrocarbons

Compound	H^a,H^b	H^c	H^d	H^f,H^g	H^h	H^i,H^j,H^k	H^l	H^m
exo-**4**	2.24 q J ~ 1.7	1.01 br.c		0.72 m 0.53 m AA'BB'	1.42 m 0.64 d.q J_{gem}= 9.8	1.45 m 1.26 m		
exo-**6**	2.08 br.d J_{ah} ~ 2.7	1.47 br.c		0.72 m 0.61 m AA'BB'	1.67 m	1.10 br.d J_{ik} ~5.5 1.17 m	1.43 m	
exo-**5**	2.00 m 2.36 m	2.76 br.t J ~ 8–9 J_{ac}< 2	5.78 d.t J_{bd}= 7.5 J ~ 2.4	1.89 and 1.48 m 2.58 and 2.36 m	1.30 t J ~ 3.0	1.35–1.85 m		
endo-**5**	2.20 m 2.39 m	3.20 m J_{ac}~ 5.5	5.23 m	1.62–1.78 m 2.64 and 2.41 m	1.77 m 1.62 m	1.5–1.74 m		
exo-**7**	1.45 m 1.98 d.t J_{bd}= 7.0 J ~ 1.5	3.11 m (br.t, J ~ 8–9, J_{ac} < 2)	5.38 d.t J_{bd}= 7.0 J ~ 2.3	1.93 and 1.48 m 2.60 and 2.36 m	~1.7 m	1.20 t.t 0.93 t.t 1.13 t.q J_{ij} = J_{ik} = 5.5 J ~ 1.5	1.44 m 1.40 d.t J_{gem}= 9.8 J ~ 1.7	
endo-**7**	1.84 d.t J_{ac}= 5.3 J ~ 1.6 2.01 m	3.07 m	5.40 m	1.96 and 1.71 m 2.63 and 2.41 m	~1.7 m	1.33 t.t 0.90 t.t 1.05 t.q J_{ij} = J_{ik} = 5.5 J ~ 1.5	1.42 m	
10a	1.48 br.q J ~ 1.6 2.07 br.d J_{bd} ~ 6.8	2.62 br.t J ~ 7.5 (J_{ac}< 2)	0.83 br.d.d.d J_{bd} ~ 6.8 J_{cis} ~ 8.3 J_{trans} ~ 4.8	1.82–1.95 m 2.21 and 1.50 m	1.78 m	0.62 t.t 0.59 t.t 1.01 t.q J_{ij} ~J_{ik} ~5.5 J ~ 1.5	1.38 d.q 1.31 d.t J_{gem}= 9.8 J ~ 1.5	0.38 d.d J_{cis}= 8.3 J_{gem}= 4.9 0.42 t J_{trans}= 4.8
10b	1.54 d.t J_{ac} ~ 6.5 J ~ 1.5 1.90 m	2.68 br.q J ~ 7–8 (J_{ac} ~6.5)	0.95 d.d.d J_{cis}= 8.3 J_{trans}= 4.9 J_{bd}~2.0	2.0–2.18 m 2.22 and 1.72 m	1.15 m	1.20 t.t 1.00 t.t 1.09 t.q J_{ij} ~ J_{ik} ~ 5.5 J ~ 1.4	1.28 t J ~ 1.5	0.40 d.d J_{cis}= 8.3 J_{gem}= 4.9 0.17 t J_{trans}= 4.9

3(5)-vinylpyrazole (**11**).[11] The almost complete conversion of pyrazoline **3** already occurs at 370 °C, and the yield of **11** is ~75 %. The primary product of the retrodienic reaction, 4,5-diazaspiro[2,4]heptadiene (**12**), was not found in the reaction products, which indicates its easy isomerization into the thermally stable pyrazole **11**. The *endo* isomer is likely to decompose somewhat more easily than the *exo* isomer. For example, if the reaction temperature is 340 °C, when the conversion of pyrazoline **3** is ~55 %, the content of the *exo* isomer in the unreacted pyrazoline **3** increases twofold (the ratio of the *exo* and *endo* isomers of **3** changes from 4 : 1 to (7—8) : 1).



3 **12** **11**

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Experimental

The compounds obtained and their mixtures were analyzed by GLC (200×0.3 cm columns with 5 % SE-30 on Inerton N-Super and 100×0.3 cm with 10 % Carbowax 20M on Chromaton N-AW-HMDS) and by chromato-mass-spectroscopy on a Finnigan MAT INCOS-50 instrument (70 eV) with an RSL-200 column 30 m in length. Preparative separation was made on a 120×1.3 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 MHz), Bruker AMX-400 (400 MHz), and Bruker AC-200 (200 MHz) spectrometers for solutions in $CDCl_3$ containing 0.1 % TMS as the internal standard. Quantum-chemical calculations were performed by the MNDO-PM3 method using the AMPAC program package.[12] Standard heats of formation were obtained with full geometry optimization.

Polycyclic spirocyclopropane-containing pyrazolines **1—3** were synthesized according to Ref. 2.

Thermal decomposition of pyrazolines was performed by slowly passing (~5 mL h^{-1}) a solution of the respective pyrazoline in hexane (~1 : 3, v/v) through a quartz tube (d = 1 cm) filled with finely milled quartz for 15 cm and purged with a stream of argon (4—5 mL min^{-1}). When the reaction was completed, a further 2 mL of hexane was passed through the tube, and the pyrolysate was analyzed by GLC. The solvent

was then evaporated, the residue was distilled *in vacuo*, and the hydrocarbons **4**—**7** were isolated by preparative GLC.

Pyrolysis of spiro{3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene-5,1′-cyclopropane} (1). The pyrolysis of pyrazoline **1** was performed at 430 °C. Vacuum distillation of the pyrolysate gave 1.24 g (45 %) of a hydrocarbon fraction with b.p. 66—69 °C (11 Torr) containing 49 % of spiro{cyclopropane-1,3′-tricyclo[3.2.1.$0^{2,4}$]octane} (**4**) and 51 % of isomeric tricyclo[5.2.1.$0^{2,5}$]dec-5-enes (**5**) (*endo* : *exo* ~1 : 1.7 according to GLC and ^{1}H NMR spectral data). The pyrolysis of pyrazoline **1** at 415 °C and 455 °C was performed similarly (see Table 1). Hydrocarbons **4** and **5** were separated by preparative GLC (140 °C). The ^{1}H and ^{13}C NMR spectra of compounds **4**, *exo*-, and *endo*-**5** are given in Tables 2 and 3.

Pyrolysis of spiro{3,4-diazapentacyclo[6.4.0.$0^{2,6}$.$0^{7,11}$.$0^{10,12}$]dodec-3-ene-5,1′-cyclopropane} (2). The pyrolysis of pyrazoline **2** was performed at 450 °C. Vacuum distillation of the pyrolysate gave 1.8 g (71 %) of a hydrocarbon fraction with b.p. 82—89 °C (6 Torr) containing ~16 % of spiro{cyclopropane-1,4′-pentacyclo[4.4.0.$0^{2,8}$.$0^{3,5}$.$0^{7,9}$]decane (**6**) and 84 % of isomeric pentacyclo[6.4.0.$0^{2,10}$.$0^{3,6}$.$0^{9,11}$]dodec-6-enes (**7**) (*endo* : *exo* ~1 : 1 according to ^{1}H NMR). The pyrolysis of pyrazoline **2** at 410 °C was performed similarly (see Table 1). Hydrocarbons **6** and **7** were separated by preparative GLC (158 °C); compound **6** has b.p. 82—82.5 °C (6 Torr), n_D^{20} 1.5256. The ^{1}H and ^{13}C NMR spectra of compounds **6**, *exo*-, and *endo*-**7** are given in Tables 2 and 3.

Thermolysis of spiro{cyclopropane-1,3′-tricyclo[3.2.1.$0^{2,4}$]-decane} (4). Similarly to the pyrolysis of pyrazolines, hydrocarbon **4** (0.27 g) in hexane (1.5 mL) was passed through a quartz tube at 455 °C. According to GLC and ^{1}H NMR spectral data, the residue obtained after the removal of the solvent contained ~22 % of the original compound **4** and ~78 % of isomeric hydrocarbons, *exo*- and *endo*-**5** in the ratio ~1 : 1.6.

Thermolysis of spiro{cyclopropane-1,4′-pentacyclo-[4.4.0.$0^{2,8}$. $0^{3,5}$.$0^{7,9}$]decane} (6). Similarly to the previous experiment, hydrocarbon **6** (0.4 g) in hexane (1.5 mL) was passed through a quartz tube at 445 °C. The solvent was removed, and the residue was distilled *in vacuo* to give 0.3 g of a colorless liquid containing (according to GLC and ^{1}H NMR spectral data) ~25 % of the original compound **6** and ~75 % of isomeric hydrocarbons, *exo*- and *endo*-**7** in the ratio ~1 : 1.

Pyrolysis of spiro{3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene-5,1′-cyclopropane} (3). A solution of pyrazoline **3** (2.4 g, 0.015 mol) (a ~4 : 1 mixture of *exo*- and *endo*-isomers) in hexane (6 mL) was passed through a quartz tube at 340 °C. Distillation of the pyrolysate *in vacuo* gave 0.55 g (~40 %) of 3(5)-vinylpyrazole, b.p. 83—84 °C (1 Torr) and 1.4 g (~44 %) of unreacted pyrazoline **3** containing the *exo*- and *endo*-isomers in the ratio ~8 : 1 (^{1}H NMR data).

Similar procedure starting from compound **3** (2 g) at 370 °C followed by distillation of the pyrolysate *in vacuo* gave 0.87 g (~75 %) of 3(5)-vinylpyrazole (**11**), while the original pyrazole was practically absent. ^{1}H NMR, δ (*J*/Hz): 7.53 and 6.41 (d, H-4 and H-5, $J_{4,5}$ = 2.3); 6.72 (dd, =CH, J_{trans} = 17.4, J_{cis} = 11.0); 5.73 (dd, 1 H in =CH_2, J_{trans} = 17.4, J_{gem} = 1.0), 5.33 (dd, 1 H in =CH_2, J_{cis} = 11.0, J_{gem} = 1.0).

Tetracyclo[6.2.1.$0^{2,4}$.$0^{4,7}$]undecane (9). *a*) Pd acetylacetonate (3 mg) in CH_2Cl_2 (1 mL) was added at 10 °C to a solution of unsaturated hydrocarbons **5** (*exo* : *endo* ~1 : 1.6) (0.15 g, 1 mmol) in CH_2Cl_2 (1.5 mL) and a distilled 0.6 *M* ethereal solution of diazomethane (5 mL, ~3 mmol). When gas evolution was ceased and the solution discolored, the solvents were removed *in vacuo* and the residue was analyzed by NMR and chromato-mass-spectrometry. The content of the original olefins **5** did not exceed 3 %, and the ratio **9a** : **9b** was ~1 : 1.5. ^{1}H NMR (250 MHz), δ (*J*/Hz): 2.64 (br.dt, H-7 in isomer **9b**, $J_{7,8}$ ~6.5, *J* ~7.5); 1.05 (br.dt, H-2 in **9a**, $J_{1,2}$ ~J_{cis} ~7.9, J_{trans} ~4.8), 0.92 (br.d, H-11, J_{gem} ~12.0), 0.57 (ddd, H-2 in **9b**, J_{cis} ~8.5, J_{trans} ~5.0, $J_{1,2}$ ~1.5); The remaining signals overlap and appear at 2.12—2.40, 0.83—2.02, and 0.30—0.49 ppm.

b) A distilled 0.6 *M* ethereal solution of diazomethane (5 mL, ~3 mmol) was added dropwise at 5 °C to a mixture of unsaturated hydrocarbons **5** (*exo* : *endo* ~1 : 1.6) (0.15 g, 1 mmol) in CH_2Cl_2 (2 mL) and $(PhO)_3P \cdot CuCl$ (5 mg). When the reaction was completed, the solvent was removed *in vacuo* and the residue was analyzed by NMR and chromato-mass-spectrometry. The resulting mixture contained ~35 % of unreacted olefins **5** (*exo* : *endo* ~1 : 7) and ~65 % of cyclopropane adducts **9a** and **9b** in the ratio ~1.1 : 1.

Hexacyclo[7.4.0.$0^{2,11}$.$0^{3,5}$.$0^{5,8}$.$0^{10,12}$]tridecane (10). $Pd(acac)_2$ (5 mg) in CH_2Cl_2 (1 mL) was added at 10 °C to a solution of unsaturated hydrocarbons **7** (*exo* : *endo* ~1 : 1) (0.32 g, 2 mmol) in CH_2Cl_2 (3 mL) and a distilled 0.6 *M* ethereal solution of diazomethane (10 mL, ~6 mmol). When gas evolution was ceased and the solution discolored, the solvents were removed *in vacuo* and hexane (4 mL) was added to the residue. According to chromato-mass-spectroscopy data, the solution contained cyclopropane adducts **10** (as a poorly resolved peak) and less than 4 % of the original hydrocarbons **7**. The reaction mixture obtained was filtered through a thin layer of silica gel. The solvent was evaporated, and the residue was distilled *in vacuo* to give 0.25 g of a colorless liquid, b.p. 83—85 °C (4 Torr). The ^{1}H and ^{13}C NMR spectra are presented in Tables 2 and 3. According to the integral intensities, the ratio of **10a** to **10b** is ~1 : 1.

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