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THERMAL DECOMPOSITION OF SOME NEW SPIRO-1-PYRAZOLINES

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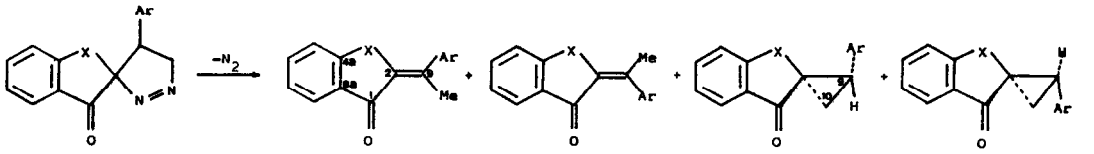
Abstract: The thermal decomposition of spiro-1-pyrazolines 2 obtained by the cycloaddition of exocyclic α,β-unsaturated ketones with diazomethane gives spirocyclopropanes 4 with high selectivity and the new β-methyl-3-benzylidene derivatives 3. The configuration and conformation of the thermolysis products 3 and 4 were elucidated by different n.m.r. methods.

In our previous paper we described the synthesis and stereochemistry of different spiro-1-pyrazolines obtained by the 1,3-dipolar cycloaddition of 2-arylidene-1-tetralones, 3-arylidene-chromanones, -1-thiochromanones, and -flavanones with diazomethane.[1] It was shown that this ring-closure reaction is regioselective, yielding stereohomogeneous spiro-1-pyrazolines in one step. The reaction of *E*-arylidenes (1a-1i) affords *trans*-pyrazolines (2a-2i regarding the carbonyl and aryl groups) while that of the *Z*-arylidenes 1d and 1g gives the corresponding *cis*-isomers 2d and 2g (Scheme 1). In chloroform solution a spontaneous tautomerization of the *trans* 1-pyrazolines to 2-pyrazolines was not observed. The cycloaddition reaction of the chalcones with diazomethane yields 3-benzoyl-4-phenyl-1-pyrazolines which rearrange into the conjugated 2-pyrazolines.[2] Thermal decomposition of these compounds led to β-methylchalcones as main product.[3]

In our present paper the thermal deazotation of *trans*- and *cis*-spiro-1-pyrazolines 2 and the structure elucidation and stereochemistry of the products obtained (3 and 4) will be reported.

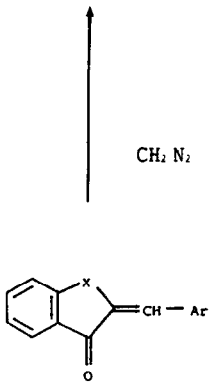
The *cis* and *trans*-spiro-1-pyrazolines 2 were thermally decomposed by heating them slightly above their melting points and the resulting mixture was investigated in chloroform-d solution by ^1H and ^{13}C n.m.r. methods.

Scheme 1



(*trans*) 2a-2i (*E*) 3a-3i (*Z*) 3a-3i (*trans*) 4a-4i (*cis*) 4a-4i

(*cis*) 2d, 2g



	X	Ar
E-1a	CH_2	phenyl
E-1b	$(CH_2)_2$	phenyl
E-1c	$(CH_2)_3$	phenyl
E-1d	SCH_2	phenyl
E-1e	OCH_2	phenyl
E-1f	OCHPh	phenyl
E-1g	$(CH_2)_2$	p-Cl-phenyl
E-1h	SCH_2	p-O_2N-phenyl
E-1i	OCH_2	p-Br-phenyl
Z-1d	SCH_2	phenyl
Z-1g	$(CH_2)_2$	p-Cl-phenyl

(*E*) 1a-1i

(*Z*) 1d, 1g

Thermal decomposition of spiropyrazolines 2 should give rise to β-methylbenzylidenes (*E*-3 and *Z*-3) and spirocyclopropanes (*cis*-4 and *trans*-4). The n.m.r. spectra of the crude products indicate always the appearance of one main product (yield over 74%) and two minor products, or in the case of the decomposition of *trans*-2d, *trans*-2h, *cis*-2d, and *cis*-2g of even all four isomers In most cases the ^1H and ^{13}C n.m.r. spectra showed three (or four) sets of signals with different intensity, allowing an easy identification of the signals originating from the appropriate isomers. The characteristic ^1H and ^{13}C n.m.r. chemical shifts are compiled in Tables 1,4, and 6. The numbering of the hydrogen and carbon atoms applied in Scheme 1 and the Tables is not in accordance with the IUPAC nomenclature. This modification facilitates, however, the comparison of the spectroscopically analogous atoms in compounds 3 and 4. Although the compounds investigated are racemates only one enantiomer is shown in each case, *viz.* that with (2*R*, 9*R*) configuration (4a-4c, 4e-4g, 4i and 4g). For compounds 4d and 4h the analogous steric arrangement cor-

responds to a (2*S*, 9*R*) configuration.

To achieve an unambiguous signal assignment and structure elucidation 1D proton-proton n.O.e. difference measurements, 1D and 2D semiselective INEPT and 2D heterocorrelation spectra were performed. The results of the n.O.e. and INEPT measurements are summarized in Tables 2, 3, and 5, the composition of the product mixtures in Table 7.

Table 1. Characteristic ^{1}H chemical shifts of compounds *E*-3a to *E*-3i

	3a	3b	3c	3d	3e	3f	3g	3h	3i
CH_3	2.72	2.45	2.37	2.37	2.54	2.62	2.40	2.32	2.49
	(2.25)	(2.18)	(2.13)	(2.25)	(2.20)	(2.25)	(2.15)	(2.24)	(2.17)
H_2-3	3.52	2.63	2.13	3.68	4.81	6.10[a]	2.61	3.57	4.77
	(3.78)			(3.97)	(5.13)	(6.62[a])	(2.93)	(3.96)	(5.11)
H_2-3a			1.52						
H_2-4		2.83	2.87				2.83		
							(3.07)		
H-8	7.82	8.16	7.93	8.25	8.01	7.87	8.13	8.23	7.98

[a] H-3 (1H)

data in parentheses correspond to the *Z*-3 isomers

A common characteristic of the ^{1}H n.m.r. spectra of the products obtained from the *trans*-spiropyrazolines 2a-2i is the appearance of a strong =C-CH_3 signal (0.8 molar ratio for *E*-3a to *E*-3i) at approx. 2.5 p.p.m. with a small triplet splitting ($^5J_{H,H}$ = 1.5 Hz; in the case of 3f this signal is a doublet). There is another minor methyl signal shifted upfield by 0.08-0.47 p.p.m. from the main signal showing the presence of the *Z*-isomers 3a-3i (0.04-0.1 molar ratio). The homoallylic $^5J_{H,H}$ coupling is smaller, *viz.* only *ca.* 1 Hz. The deshielding of the methyl protons in the main product is in accord with the *E*-geometry and is due to the peri-positioned C=O group.[4,5]

An unambiguous assignment of the *E*- and *Z*-configuration of the isomers 3 was achieved by the 1D n.O.e. measurements (Table 2). Irradiations of the CH_3 signal of the minor β-methyl-3-benzylidene derivatives result in n.O.e. intensity enhancements at H-3 protons proving their steric proximity in the *Z*-isomers while on saturating the methyl protons of the *E*-isomers an intensity increase was observed only for the H-2',6' signals.

In the *E*-3-isomers the H-3 protons are above the plane of the aryl group attached to C-9 and show an upfield shift of about 0.3 p.p.m. if compared to the corresponding protons in the *Z*-isomers. Another common feature of the proton spectra are the substantial paramagnetic shifts of the H-8 signals which is, first of all, a consequence of the anisotropic effect of the peri-carbonyl group.[4] While the alteration of the meta positionated X group can only slightly affect δH-8, the characteristic differences observed

Table 2. Results of n.O.e. measurements for compounds 3 and 4 in $CDCl_3$[a]

compound	proton irradiated	n.O.e. observed (%)
E-3a	CH_3	H-2',6'(7.1)
Z-3a	CH_3	H_2-3(8.3)
E-3e	H_2-3	H-2',6'(4.8)
	CH_3	H-2',6'(4.2)
Z-3e	CH_3	H_2-3(7.2)
E-3f	CH_3	H-2',6'(5.5)
Z-3f	CH_3	H-3(15.0)
cis-4d	H_{ax}-3	H_{eq}-3(19.0), H_t 10(10)
	H_{eq}-3	H_{ax}-3(22.5), H-9(5.2), H_t-10(3.2)
	H-9	H_{eq}-3(4.0), H_t-10(2.6), H-2',6'(3.4)
	H_t-10	H_{ax}-3(1.0), H_{eq}-3(2.6), H-9(3.4), H_c-10(16.5)
trans-4e	H_{ax}-3	H_{eq}-3(25.7), H_t-10(1.5)
	H_{eq}-3	H_{ax}-3(26.1), H_t-10(2.0)
	H-9	H_c-10(3.2), H-2',6'(1.9)
	H_t-10	H_{eq}-3(1.8), H_{ax}-3(1.2), H_c-10(18.3), H-2',6'(7.3)
	H_c-10	H-9(3.9), H_t-10(18.1)
trans-4f	H-9	H_c-10(4.7), H-2',6'(3.9)
	H_t-10	H-3(3.9), H_c-10(18.1), H-2',6'(10.0)
	H_c-10	H-9(8.0), H_t-10(19.4)
trans-4g	H_{ax}-3	H_{eq}-3(21.8), H_2-4(4.3), H_t-10(1.0)
	H_{eq}-3/H_c-10	H_{ax}-3(15.5), H_2-4(3.4), H-9(1.9), H_t-10(5.2)
cis-4g	H_{eq}-3	H_{ax}-3/H-9(25.9), H_{eq}-4(1.1), H_{ax}-4(1.9)
	H_{ax}-4	H_{eq}-3(2.1), H_{eq}-4(9.0)
	H_t-10	H_{eq}-3(1.9), H_{ax}-3/H-9(4.2), H_c-10(16.5)
	H-2,6	H-9(2.2), H_c-10(4.5)
cis-4g[b]	H_{eq}-3	H_{ax}-3(16.0), H_{eq}-4(1.1), H_{ax}-4(1.8), H-9(6.9), H_t-10(1)
trans-4h	H_{ax}-3	H_{eq}-3(32.7), H_t-10(1.6)
	H_{eq}-3	H_{ax}-3(33.5), H_t-10(2.0)
	H_t-10	H_{ax}-3(1.8), H_{eq}(2.6), H_c-10(28.5), H-2',6'(11.8)

[a] The symbols H_{ax}- and H_{eq}- refer to the position of the protons in the predominating conformer. In the case of the *trans*-compound 4g the ratio of the two half-chair conformers is nearly 1:1, here the signal at 1.62 p.p.m. is denoted as H_{ax}-3 while the signal at 1.82 as H_{eq}-3.

[b] Solvent: benzene-d_6

should reflect the deviation from the coplanarity of the condensed phenyl ring and the carbonyl group. The largest dihedral angle is expected with 3c where the condensed ring is seven-membered. Similar behaviour was observed for the dibromide adducts of the analogous 3-benzylidene derivatives.[6] Substitution of a phenyl group at C-3 (*E*-3i) caused an 0.14 p.p.m. upfield shift of the H-8 signal indicating a ring deformation *i.e.* a change of the conformation of the condensed saturated ring. The extreme δH-8 value for 3a is in accord with the increased C=O/ H-8 distance in this compound. For compounds 3b and 3d-3i the fused 6-membered saturated ring can exist in the form of two sofa conformations where C-3 is out of the plane formed by the other atoms of this ring, while for compound 3a two envelope conformations are expected. The multiplicity of the H_2-C(3) proton signals shows that at room temperature this pair of conformers rapidly interconverts and averaged coupling constants and chemical shifts are observed.

Scheme 2.

C D

In the case of 3f the two sofa conformers (C and D in Scheme 2) are energetically different. In C the phenyl is axial but in D equatorial. Considering the relatively small allylic coupling constant measured for the analogous *E*-3-benzylideneflavanone ($^4J_{H-2,H-8}$ = 0.95 Hz) Keane et al. concluded that the C-2 phenyl group is axial.[7] Because of the C-9 methyl (β) substitution there is only a homoallylic coupling for 3f ($^5J_{H-2,CH_3}$) which cannot be utilized for the conformational analysis. For the elucidation of the preferred conformation of 3f the coupling constant $^1J_{H-2\,C-2}$ (153 Hz) can be exploited. It is known that in an O-CH moiety the value of the $^1J_{CH}$ coupling is strongly affected by the relative spatial position of the free electron pair of the oxygen and the C-H bond.[8] In flavanone the phenyl adopts nearly exclusively the equatorial position[9] and we observed a value of $^1J_{OC\,H\,ax}$ = 146 Hz. In the *E*-3-benzylideneflavanone this $^1J_{OC\,H\,eq}$ is 152 Hz, while the time averaged $^1J_{OC\,H}$ value of the methylene protons in *E*-3e is 149 Hz. In the dibromide addition product of the *E*-3-benzylidenechromanone $^1J_{OC\,H\,ax}$ = 145 Hz, and $^1J_{OC\,H\,eq}$ = 156 Hz were measured, while in the analogous E-3-benzylideneflavanone dibromide derivate $^1J_{OC\,H\,eq}$ = 153 Hz.[6] This last value is in accordance with that measured for 3f indicating the preferred axial orientation of the C-2 phenyl group also in this case. Another approach to the elucidation of the stereochemistry around C-3 is available by applying the Karplus type dependence of $^3J_{CH}$ couplings on the dihedral angle. The potential value of $^3J_{CH}$ coupling constants in the conformational analysis of carbohy-

drates is well recognized and a number of empirical correlations between the magnitude of these coupling constants and the (C-)O-C(-H) torsional angle have recently been established.[11-14] Several 2D n.m.r. techniques have recently been reported to be capable of the precise measurement of long-range ^{13}C-^{1}H couplings in a reasonable time.[15-18] The modified version of 2D semiselective INEPT has been used for the measurement of $J_{H-3,C}$ couplings.[19] The data measured for compounds *E*-3f, *E*-3i and flavanone 5 are compiled in Table 3.

Table 3. Results of the 2D semiselective INEPT measurements of compounds *E*-3f, *E*-3i and flavanone 5

	$J_{H-3\ C-1}$	$J_{H-3,C-2}$	$J_{H-3\ C-4a}$	$J_{H-3\ C-9}$	$J_{H-3\ C-1'}$
E-3f	5.6	4.2	7.7	4.0	4.9
E-3i	4.3	3.8	4.8	4.8	
5	2.9	>1	1.0		

The accuracy of the $J_{H-3\ C}$ values is better than 0.1 Hz. Inspection of the molecular model of benzylidenechromanone 3e shows that the torsional angles for the (C-)O-C(-H_{eq}) and (C-)O-C(-H_{ax}) moieties are 180° and 80°, respectively. Applying the Karplus curve proposed for carbohydrates the expected $J_{H_{eq}-3\ C-4a}$ and $J_{H_{ax}-3\ C-4a}$ couplings are 7.5 Hz and 1 Hz, respectively.[12,14] The above mentioned Karplus curves fits the case where both carbon atoms are sp^3 hybridized, and so is our case, where C-4a is an sp^2 carbon; some deviation from this $^{3}J_{C\ H}$-values is allowed but it should be small. In *E*-3i the time averaged $J_{H-3\ C-4a}$ is 4.8 Hz, while in 3f this is 7.7 Hz. Aydin and Günther have recently shown that phenyl substitution on such a CH unit does not alter $^{3}J_{C\ H}$ couplings significantly.[20] Taking into account that the coupling constant $^{3}J_{H_{ax}-3\ C-4a}$ is 1.0 Hz in flavanone this reference value and the averaged coupling constant of 4.8 Hz for 3i leads to the conclusion that in 3f the C/D conformational equilibrium is almost entirely shifted to C, *i.e.* the C-3 phenyl strongly prefers the axial position.

The ^{13}C chemical shifts of compounds *E*-3a to *E*-3i (Table 4) gave further evidence for the β-methyl-3-benzylidene type structure of the main decomposition product of the *trans*-spiropyrazolines (2a-2i). For signal assignment besides the known substituent effects and additivity rules the assignment of the analogous 3-benzylidene derivatives[5], 2D carbon-proton correlation measurements were applied, too. In the proton coupled ^{13}C n.m.r spectra the aromatic para C-4' carbon signals show a doublet-of-triplet multiplicity allowing a distinction from the other aromatic carbons (C-5 - C-9) which give rise to a doublet-of-doublets. The semiselective INEPT measurements optimized for $J_{C\ H}$ = 7 Hz long-range couplings proved to be very useful not only for achieving an unambiguous assignment of the quaternary C-1, C-2, C-4a, C-8a, C-9, C-1' and C-1" atoms but also in cases where the complexity of the proton spectrum does not allow a simple 2D carbon-proton correla

Table 4. ^{13}C Chemical shifts (p.p.m.) of compounds *E*-3a to *E*-3i

	3a	3b	3c	3d	3e	3f[a]	3g	3h	3i
C-1	194.8	190.5	198.4	187.9	185.1	185.2	190.2	187.2	185.0
C-2	131.7	131.9	135.2	128.3	129.1	128.8	132.4	129.7	126.9
C-3	-	30.2	26.3	31.6	69.7	79.3	30.2	31.4	69.6
C-3a	-	-	26.6	-	-	-	-	-	-
C-4	33.2	30.2	31.7	-	-	-	30.1	-	-
C-4a	148.8	143.3	140.8	141.7	160.9	158.5	143.1	141.3	160.9
C-5	125.8	128.2	129.3	127.4	117.4	118.1	128.2	127.4	117.4
C-6	133.9	132.7	132.4	132.7	135.2	135.6	132.6	133.0	135.4
C-7	127.1	126.5	126.7	125.0	121.2	121.2	126.6	125.2	121.4
C-8	123.9	127.7	129.3	130.0	127.7	127.3	127.7	130.0	127.7
C-8a	139.9	134.4	138.3	132.6	123.0	123.2	134.3	132.2	122.9
C-9	150.6	148.0	148.0	149.1	152.4	152.7	146.4	148.8	150.9
CH_3	20.5	23.4	23.4	23.6	23.3	23.6	23.1	22.9	23.2
C-1'	143.6	143.6	143.4	142.4	141.4	141.7	141.9	145.6	140.2
C-2',6'	126.9	127.1	126.6	127.1	127.1	128.3	128.6	128.3	128.9
C-3',5'	128.4	128.3	128.2	128.6	128.4	128.4	128.5	124.0	131.7
C-4'	127.8	127.1	126.9	127.7	128.1	128.1	132.4	147.1	122.3

[a] C-1" 138.3, C-2",6" 127.1, C-3",5" 128.6, C-4" 128.0

tion (Table 5), *e.g.* in *E*-3c the semiselective polarization transfer from H-8 gives exclusively signals for C-1, C-4a and C-6, while the same experiment for H_2-4 allows not only the assignment of the carbons C-3, C-3a, C-4a and C-8a but also for C-5 as well, whose attached H-5 proton shows a signal overlapped by other aromatic proton signals.

^1H and ^{13}C n.m.r. spectra of *cis*-**4d** and *cis*-**4g**, the major products of the decomposition of pyrazolines *Z*-**2d** and *Z*-**2g**, are entirely different from those measured for the decomposition products of the *E*-2 isomers (Table 6). ^1H signals (1.22 and 2.29; 1.37 and 2.57, respectively) referring to a highly shielded methylene group, the small absolute value ($|^2J| = 4.9$ Hz) of the geminal coupling constant, ^{13}C signals appearing at 19.5 and 18.2 ppm, and the coupling constant $^1J_{C,H} = 163$ Hz unequivocally prove[21] the presence of a cyclopropane ring. A series of signals belonging to *cis*-**4g** have only 1% intensity but can unambiguously be detected among the decomposition products of *E*-**2g** as well.

Another series of signals of 8% (*trans*-**4d**) and 2% (*trans*-**4g**) intensity can also be detected in the n.m.r. spectra of the decomposition products of *cis*-**2d** and *cis*-**2g**, which are cyclopropane derivatives. These isomers were observed in the mixture obtained from *trans*-**2d** and *trans*-**2g** as well. A further characteristic of the thermal decomposition of the spiropyrazolines *cis*-**2** is that the occurrence of the formerly identified β-methyl-3-

Table 5. ^{1}H-^{13}C Long-range correlations for compounds *E*-3a to *E*-3i , *cis*-4d and *cis*-4g observed by semiselective 1D INEPT measurements (J_{CH} = 7Hz)

E-3a	CH_3	C-2, C-9, C-1'
	H_2-4	C-1, C-2, C-4a, C-5, C-8a, C-9
	H-8	C-1, C-4a, C-6
E-3b	H_2-3	C-1, C-2, C-4a, C-9
	H_2-4	C-2, C-4a, C-5, C-8a
	H-8	C-1, C-4a, C-6
E-3c	H_2-3	C-1, C-2, C-3a, C-4, C-9
	H_2-4	C-3, C-3a, C-4a, C-5, C-8a
	H-8	C-1, C-4a, C-6
E-3d	H_2-3	C-1, C-2, C-4a, C-9
	H-8	C-1, C-4a, C-6
E-3e	H-5	C-4a, C-7, C-8a
	H-2',6'	C-9
E-3f	H-3	C-1, C-4a, C-9, C-1", C-2",6"
E-3g	H-4	C-2, C-4a, C-5, C-8a
E-3h	CH_3	C-1, C-2, C-9, C-1'
	H-5	C-7, C-8a
E-3i	CH_3	C-2, C-9, C-1'
cis-4d	H-8	C-4a, C-6
cis-4g	H_{ax}-3/H-9	C-2, C-3, C-4, C-4a, C-9, C-2',6'
	H-5	C-4, C-7, C-8a
	H-7	C-5, C-8a
	H-8	C-1, C-4a, C-6
	H-2',6'	C-9, C-4'

benzylidene derivatives *E*-3 and *Z*-3 is less than 10%. The high selectivity observed for the isomer *E*-3 does not exist in this case.

Depending on their substitution pattern the spirocyclopropanes 4 can be *trans*- or *cis*-isomers. In a *trans*-isomer the carbonyl and the aryl groups are on opposite sides of the cyclopropane ring. H_2-10 methylene protons were differentiated according to their relative position to the carbonyl group as well.

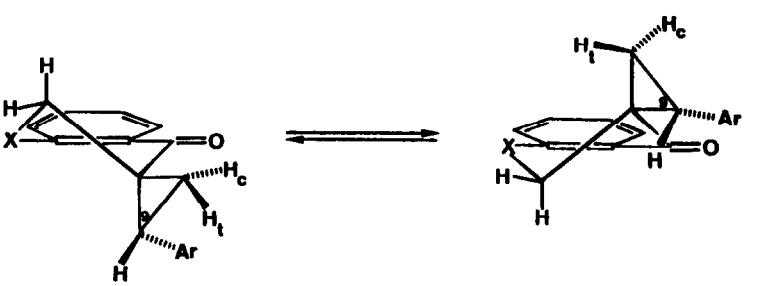
It is known that for cyclopropane derivatives $^{3}J_{cis} > {}^{3}J_{trans}$ and from this the relative position of the vicinal protons can be determined.[21] In our case a coupling constant of 9 Hz was measured for the H-9 and H-10 *cis*-protons, and 7.5 Hz for the *trans*-coupling. However, these data are not sufficient for the differentiation of the *cis*- and *trans*-arrangements of the aryl and carbonyl groups. Another difficulty is that the partially saturated ring can adopt two halfchair conformations (Scheme 3), easy interconversion of

Table 6. Characteristic ^1H and ^{13}C chemical shifts and proton-proton coupling constants (Hz) of compounds 4a-4i

	H_t-10	H_c-10	H-9	H-3	H-4	^3J_a	^3J_b	^2J_c	C-1	C-2	C-9	C-10
trans-4a	1.69	1.98	2.92			7.4	9.1	4.4		37.8	31.8	21.1
trans-4b	1.36	1.90	2.93			7.5	9.0	4.5	198.0	34.1	34.4	20.3
trans-4c	1.46	1.87	3.17			7.5	9.0	4.5		36.7	35.5	21.7
trans-4d	1.53	1.93	3.24	2.73		7.2	8.8	4.4		31.1	31.1	21.6
				2.98								
trans-4e	1.39	2.00	3.03	3.92		7.1	9.0	4.9	192.3	32.6	33.7	16.9
				4.28								
trans-4f	2.00	1.58	3.70	5.01		7.3	9.0	4.9	192.7	35.8	33.5	21.6
trans-4g	1.30	1.88	2.96	1.62	2.70	7.1	9.0	4.3	197.5	33.9	33.2	20.3
				1.82	2.70							
trans-4h	1.57	2.00	3.18	2.65		7.3	8.9	4.9	193.6	30.8	30.7	21.2
				3.03								
trans-4i	1.32	2.00	2.91	3.86		7.1	8.9	4.9	192.0	32.5	33.1	16.6
				4.30								
cis-4d	1.37	2.57	2.94	2.46		8.8	7.8	4.9	190.6	36.0	35.6	19.5
				4.00								
cis-4g	1.22	2.29	2.59	1.65	2.99	8.5	7.3	4.9	194.1	36.7	35.3	18.1
				2.59	3.29							

^3J_a : ^{3}H-9,H_t-10; ^3J_b : ^{3}H-9,H_c-10; ^2J_c : ^2H_t-10,H_c-10

Scheme 3.



A B

which is accompanied by the exchange of the axial/equatorial orientation of the bond (C-2)-(C-9). N.O.e. measurements provided useful informations not only on the configurations but also for the conformations.

The methylene protons H_2-3 and H_2-4 of *cis*-**4g** gave a first-order spectrum in which δH_{ax}-3 > δH_{eq}-3 and the coupling constant $J(H_{ax}$-3,H_{ax}-4) is 12.9 Hz. This latter value proves that the A/B equilibrium is shifted in favour of one conformer. Since in the course of the n.O.e. difference measurement intensity enhancement can be observed for the H_{ax}-3 and H_{eq}-3 signals on the irradiation of H-9 the dominance of conformer A is confirmed. Furthermore, spatial proximity of H_{ax}-3 and H_t-10 is possible only in this case.

In *trans*-**4g** the difference between the chemical shifts of the axial and equatorial methylene protons is considerably decreased, indicating that the amount of conformers A and B is almost the same in the equilibrium.

In the thiochromanone derivative *cis*-**4d** conformer A is the dominant. N.O.e. measurements prove that the H_t-10 proton is in spatial proximity to both the H_{eq}-3 and H_{ax}-3, while the H-9 is close only to the H_{eq}-3. In the *trans*-chromanone and -thiochromanone isomers the conformer A is favoured as well.

A common characteristic of the ^{1}H n.m.r. spectra of the spirocyclopropane derivatives **4** is the downfield shift of the H_c-10 signal as compared to H_t-10, which is mainly a consequence of the deshielding effect of the carbonyl in *cis*-position. In the isomers *cis*-**4** where the C-9 aryl group and the H_c-10 protons are on the same side of the cyclopropane ring, the chemical shift of H_c-10 is further enlarged while in the compounds *trans*-**4** the paramagnetic effect of the aryl ring influences the H_t-10 proton.

Reaction mechanism

The most comprehensively investigated property of the 1-pyrazolines is their ability to eliminate nitrogen, and thus to function as a source of substituted cyclopropanes.[22] Among the thermolysis products olefines are also found to minor extent. Cyclopropanes formed from 1-pyrazolines were thought to retain the configuration of the parent 1-pyrazolines.[23] Some cases are known, however, where they did not retain their configuration, and when 3,5-disubstituted pyrazolines were investigated, this was even inverted.[24] In the latter case this observation provided an experimental evidence for a trimethylene biradical intermediate and for its predicted preference for conrotatory ring closure.[25] The investigation of the thermal deazotation of optically active 3,5-substituted-1-pyrazolines indicated, however that another concurrent pathway should be considered as well.[26] It was shown that the trimethylene intermediate lies on the reaction profile for the conversion of cyclopropanes to olefines. Van Auken and Rinehardt proved that in the case of 3,4-disubstituted pyrazolines for a trimethylene biradical ("π-cyclopropane") two conrotatory routes to cyclopropane products are possible, each giving rise to a different stereoisomer.[24]

Decomposition of spiropyrazolines *cis*-**2** leads to cyclopropanes *cis*-**4** with high selectivity and yield, *i.e.* the original geometry of the pyrazoline is retained (Table 7). This can be explained by a route where at first the homolytic cleavage of the (C-3)-(N-2)

Table 7. Yield (%) of products 3 and 4 from the thermal decomposition of spiropyrazolines 2

pyrazoline 2	*E*-3	*Z*-3	*trans*-4	*cis*-4
trans-2a	84	10	6	0
trans-2b	88	6	6	0
trans-2c	80	5	15	0
trans-2d	86	4	10	0
trans-2e	83	4	13	0
trans-2f	89	4	7	0
trans-2g	77	7	15	1
trans-2h	74	7	18	1
trans-2i	80	5	15	0
cis-2d	8	3	8	81
cis-2g	7	7	2	84

bond occurs allowing a stabilization of the carbon radical by the effect of 3 attached carbons. In this intermediate, as a result of the different bulkiness of substituents, a slow rotation around (C-3)-C-9) and a fast one around (C-9)-(CH_2N_2) is expected. The same is likely in the trimethylene biradical formed after splitting off N_2. The lifetime of this intermediate should be short resulting in retention of configuration of the parent pyrazolines.

We can conclude that the stereochemistry of the deazotation of pyrazolines, even after extensive investigations is still not completely understood and substituents and their steric arrangement should have a profound influence upon the reaction path. The thermal decomposition of *cis*-spiro-1-pyrazolines can be utilized to generate the corresponding *cis*-spirocyclopropanes while that of the *trans*-spiro-1-pyrazolines produces the new β-methyl-3-benzylidene derivatives 3.

EXPERIMENTAL

Starting materials (2a-2i) were prepared as reported previously by us.[1] TLC was performed on KIESELGEL 60 F_{254} (Merck) layer using hexane:acetone (7:3 v/v).

General procedure for the thermal decomposition.

5.0 mmol of spiro-1-pyrazolines (2a-2i) were heated slightly above their melting points for 30 min and the disappearance of the starting material was monitored by TLC. The crude products were investigated by n.m.r. spectroscopy before purification. The purification was performed by column chromatograhpy on silica gel (Merck) column using

hexane:acetone (7:3 v/v) as eluant to afford the following major products.

***E*-2-(α-Methylbenzylidene)-1-indanone (*E*-3a).** Yield 64.2%, m.p. 78-79°C, Anal. Calcd. for $C_{17}H_{14}O$ (234.28) C, 87.14; H, 6.02; Found C, 87.28; H, 6.08.

***E*-2-(α-Methylbenzylidene)-1-tetralone (*E*-3b).** Yield 68.1%, oil, Anal. Calcd. for $C_{18}H_{16}O$ (248.31) C, 87.06; H, 6.49; Found C, 87.26; H, 6.53.

***E*-2-(α-Methylbenzylidene)-1-benzosuberone (*E*-3c).** Yield 68.9 %, oil, Anal. Calcd. for $C_{19}H_{18}O$ (262.33) C, 86.98; H, 6.91; Found C, 86.83; H, 6.87.

***E*-3-(α-Methylbenzylidene)-1-thiochromanone (*E*-3d).** Yield 67.2%, oil, Anal. Calcd. for $C_{17}H_{14}OS$ (266.28) C, 76.67; H, 5.29; Found C, 76.48; H, 5.23.

***E*-3-(α-Methylbenylidene)-chromanone (*E*-3e).** Yield 61.8%, oil, Anal. Calcd. for $C_{17}H_{14}O_2$ (250.28) C, 81.57; H, 5.63; Found C, 81.39; H, 5.59.

***E*-3-(α-Methylbenzylidene)-flavanone (*E*-3f).** Yield 76.0%, m.p. 174-175°C, Anal. Calcd. for $C_{23}H_{18}O_2$ (326.37) C, 84.63; H, 5.56; Found C, 84.73; H, 5.63.

***E*-2-(α-Methyl-4-chlorobenzylidene)-1-tetralone (*E*-3g).** Yield 71.1%, m.p. 75-76°C, Anal. Calcd. for $C_{18}H_{15}ClO$ (282.75) C, 76.45; H, 5.34; Found C, 76.32; H, 5.29.

***E*-3-(α-Methyl-4-notronezylidene)-1-thiochromanone (*E*-3h).** Yield 64.0%, m.p. 149-150°C, Anal. Calcd. for $C_{17}H_{13}NO_3S$ (311.27) C, 65.59; H, 4.20; Found C, 65.42; H, 4.17.

***E*-3-(α-Methyl-4-bromobenzylidene)-chromanone (*E*-3i).** Yield 66.7%, m.p. 104-105°C, Anal. Calcd. for $C_{17}H_{13}BrO_2$ (329.18) C, 62.02; H, 3.98; Found C, 62.16; H 3.92.

***cis*-3-(Phenylcyclopropyl)-1-thiochromanone (*cis*-4d).** Yield 64.3%, oil, Anal. Calcd. for $C_{17}H_{14}OS$ (266.28) C, 76.67; H, 5.29; Found C, 76.52; H, 5.21.

***cis*-2-(4-Chlorophenyl-cycloprophyl)-1-tetralone (*cis*-4g).** Yield 64.0%, oil, Anal. Calcd. for $C_{18}H_{15}ClO$ (282.75) C, 76.45; H, 5.34; Found C, 76.19; H, 5.28.

The n.m.r. spectra were obtained on Bruker AM-400 and AC-250 spectrometers at room temperature in $CDCl_3$. Chemical shifts are given on the δ scale. In the 1D measurements 64K data points were used for FID. For homonuclear n.O.e. experiments a delay time of 7s was applied. N.O.e. difference and 2D carbon-proton correlated experiments were run using

the Bruker software package. In the 2D experiments 1K x 1K data matrices were transformed. In the case of the 2D semiselective INEPT measurements the data matrices were 1K x 64 data points, and the spectral width in the F1 (proton) dimension was 16 Hz. Selected traces were zero-filled to give a final digital resolution of 0.06 Hz. Shifted sine-bell multiplication in the F2 (carbon) and Gaussian multiplication in F1 dimension was applied, before doing the Fourier transformations.

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