Tetrahedron Vol 40, No 2, pp 391 to 403, 1984
Printed in Great Britain

0040-4020/84 $3.00 + .00
Pergamon Press Ltd

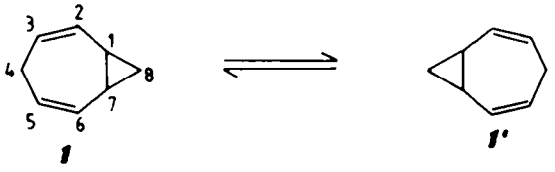
4,8-SUBSTITUTED HOMOTROPILIDENES FROM CYCLOHEPTATRIENES

JÜRGEN K. KETTENRING and GERHARD MAAS*
Fachbereich Chemie der Universität Kaiserslautern, Postfach 3049, D-6750 Kaiserslautern, West Germany

(*Received in Germany* 21 *February* 1983)

Abstract A versatile synthesis for 4,8-mono-, di-, tri- and tetrasubstituted homotropilidenes (bicyclo[5.1.0]octa - 2,5 - dienes) is described. The C_8 unit of the homotropilidene framework is built up from cycloheptatriene (C_7) and diazoalkane (C_1) subunits. Diazoalkane addition to Diels–Alder adducts of cycloheptatrienes and 1,2,4 - triazoline - 3,5 - diones, photochemical ring contraction of the Δ^1-pyrazolines formed, and degradation of the urazole unit gives the azo compounds **8**. The latter yield homotropilidenes in a smooth $[_6\!2_s + {}_6\!2_s + {}_6\!2_s]$-cycloreversion. The ability of the homotropilidenes to undergo a Cope rearrangement depends on the pattern of substitution.

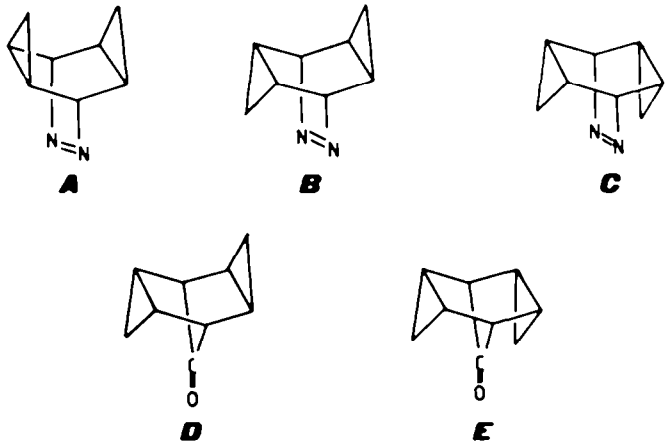
A variety of synthetic methodologies has been developed over the past twenty years for the construction of the homotropilidene (bicyclo[5.1.0]octa - 2,5 - diene, **1**⇌**1'**) framework. Among them,[1] the most straightforward way, namely direct cyclopropanation of the inner double bond of cycloheptatrienes by carbenes or carbenoids, is of only minor importance. So far, only the parent compound[2] and some spiro[homotropilidene - 8,5' - cyclopentadienes][3] were obtained by this route.



1 **1'**

In view of the ability of compounds with azo or carbonyl bridges to undergo chelotropic fragmentation,[4,5] it is not surprising that the tetracyclic compounds **A**–**E** have been aimed for as immediate homotropilidene precursors.

It is well established that an *anti*-relation between the leaving group and a cyclopropane ring, like in **A**, **B** and **D**, dramatically lowers the activation energy for N_2 or CO extrusion, as compared to the *syn*-configurated isomers;[5-7] only in the former case are favorable steric conditions for a concerted $[_6\!2_s + {}_6\!2_s + {}_6\!2_s]$ cycloreversion given,[8,9] which under cyclopropane ring opening leads to homotropilidene. Indeed, *exo,endo* - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]decenes of type **B** suffer nitrogen loss at 0–60°,[10] whereas azo compounds of the *exo,exo* type **C** are usually stable up to 120–150°.[11] Similarly, **D**[7] and some methyl-substituted derivatives[1,14,15] decarbonylate in the range of 100–170°, but **E** remains unchanged even at 280°.[7] However, both CO loss from **E**[7] and nitrogen extrusion from substituted compounds of type **C**[12,13] can be induced by UV irradiation; in this case, biradical intermediates are produced. As **A** bears two cyclopropane rings in *anti*-position to the azo bridge, a particularly smooth thermal N_2-elimination to yield a homotropilidene would be expected. However, compounds of this kind are not yet known. Structurally related diazasnoutenes (both cyclopropane carbon atoms connected by a bond) have been used by Paquette and coworkers as a convenient entry into the semibullvalene system.[16]



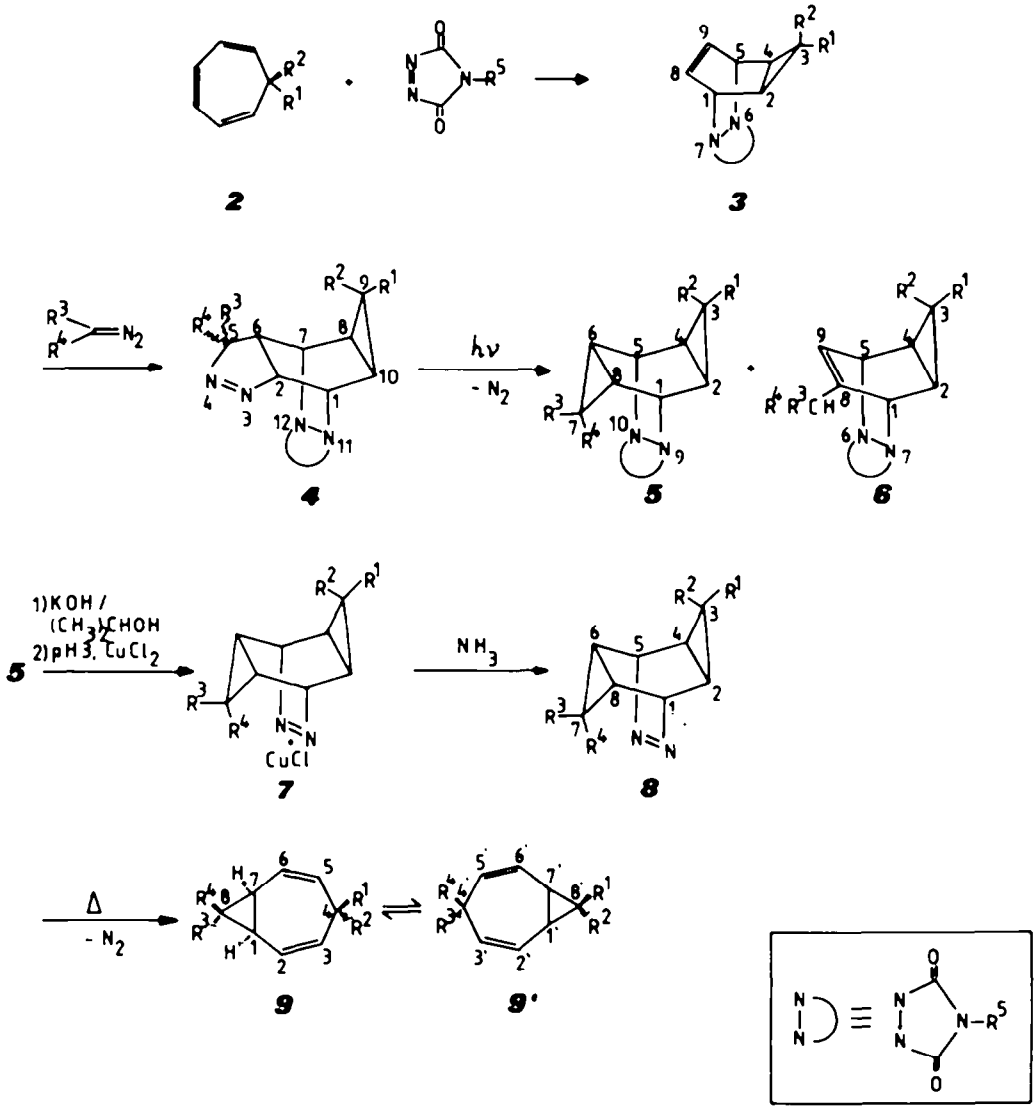
A **B** **C** **D** **E**

Recently, we have described a synthetic access to azo compounds of type **B** which starts from the Diels–Alder adducts of 4 - phenyl - 1,2,4 - triazoline - 2,5 - dione to cycloheptatrienes and which allowed us to prepare some 4-alkyl- or phenyl-substituted homotropilidenes **1** or their valence tautomers **1'**.[10] In order to gain insight into the influence of substituents on the valence tautomerism, we have now used this approach for the synthesis of a variety of 4(8)-mono-, di-, tri- and tetrasubstituted homotropilidenes.

Synthesis of the homotropilidenes

The synthetic sequence as outlined in Scheme 1 has already been described by us for homotropilidenes **9⇌9'a,b,c,g**,[10] but as we report here, it is neither restricted to alkyl- or phenyl-substituted nor to 4(8)-monosubstituted homotropilidenes. Most of the Diels–Alder adducts **3** from 7-substituted cycloheptatrienes and 4-phenyl- (or methyl-) - 1,2,4 - triazolinedione are known, and so is their stereochemistry at C-3: In case of monosubstitution, the substituent will occupy the *exo*-position at C-3 except for the cyano group in which case a smaller amount of the *endo*-isomer is also formed. For **3i**, the *endo*-orientation of the cyano group is derived from the chemical shift (δ 6.4) of the olefinic protons H-8,9 in the ^{1}H-NMR spectrum; this shift compares well with δ 6.33 for the olefinic protons in **3h**. The configurational assignment of the C-3 epimers **3h** and **3g** follows unambiguously from the ^{3}J cyclopropane coupling constants, as $^3J_{cis}$ is larger than $^3J_{trans}$. Moreover, the low-field shift of the olefinic protons in **3i** compared to **3g** (δ 6.12) corresponds to the magnetic anisotropy of the cyano group which is comparable to that of a carbon–carbon triple bond.[17]

The Diels–Alder adducts **3** undergo a [3 + 2] cycloaddition with diazomethane, diazoethane or 2-diazopropane to form the Δ^1-pyrazolines **4**. For the diazopropane adducts **4p–v**, the *exo*- orientation of the pyrazoline ring is clearly derived from the ^{1}H-NMR spectra, in which no long-range coupling between H-2,6 and the cyclopropane protons H-8,10 is observed; this excludes an M-type configurational relationship between both pairs of nuclei. In all other



Scheme 1.

2,3	a	b	c	d	e	f	g	h	i	j
R^1	H	Me	$CHMe_2$	Ph	$POPh_2$	CN	CN	H	Me	OMe
R^2	H	H	H	H	H	H	H	CN	CN	H
(R^5)	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me	Me	Ph

4-9	a	b	c	d	e	f	g	h	i	j	k	l	m*)
R^1	Me	$CHMe_2$	Ph	$POPh_2$	CN	Me	H	Me	$CHMe_2$	Ph	$POPh_2$	CN	H
R^2	H	H	H	H	H	CN	H	H	H	H	H	H	CN
R^3	H	H	H	H	H	H	Me	Me	Me	Me	Me	Me	Me
R^4	H	H	H	H	H	H	H	H	H	H	H	H	H
(R^5)	Ph	Ph	Ph	Ph	Ph	Me	Ph	Ph	Ph	Ph	Ph	Me	Me

4-9	n	o	p	q	r	s	t	u	v
R^1	Me	OMe	H	Me	$CHMe_2$	Ph	$POPh_2$	CN	Me
R^2	CN	H	H	H	H	H	H	H	CN
R^3	Me	Me	Me	Me	Me	Me	Me	Me	Me
R^4	H	H	Me	Me	Me	Me	Me	Me	Me
(R^5)	Me	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me

*) only **4**

cases, evidence for the *exo*-attack of the diazoalkane comes from the well-established *exo*-configuration of the newly formed cyclopropane ring in **5** (see below).

Although the photochemical Δ^1-pyrazoline→cyclopropane ring contraction is a standard procedure, difficulties are encountered for the transformation of some Δ^1-pyrazolines **4** to diazatetracyclodecanes **5**. Like **4a,b,c,g**,[10] the diazomethane adducts **4d–f** and the diazoethane adducts **4h–o** remain unaltered upon UV irradiation (λ = 254 and 280 nm) in benzene solution at room temperature; only in acetonitrile, very slow nitrogen extrusion takes place. Similar to other photochemically reluctant azoalkanes,[5] the quantum yield of N_2 elimination can be drastically enhanced by raising the temperature or by radical-stabilizing substituents on the carbon atoms adjacent to the azo group. Thus, the transformation **4**→**5** can be carried out conveniently by photolysis in boiling benzene or acetonitrile. The diazopropane adducts **4p–v**, on the other hand, react smoothly at room temperature. The olefins **6e,f,n** were isolated as by-products in these reactions.

Upon irradiation of the pyrazoline **4m** (R^1 = H, R^2 = CN), not only ring contraction but also complete epimerization at C-9 takes place, and the same tetracyclodecane **5l** (R^1 = CN, R^2 = H) is obtained as from photolysis of the pyrazoline **4l**, even with virtually the same yield.

For all diazoethane adducts **4g–o** the photochemical ring contraction leads exclusively to the C-7 epimer of **5g–o** in which the methyl group points away from the urazole ring (R^3=Me). This structure is indicated by relatively small ^3J(H-6,8, H-7) coupling constants (*ca* 3–4 Hz, see Table 2), as is usual for a cyclopropane *trans*-coupling. The *exo*-configuration of the C6-C7-C8-cyclopropane ring can be derived from ^{1}H-NMR spectra as well, keeping in mind the magnetic anisotropy of a cyclopropane ring.[18,19] In the *endo*, *exo*-configuration of **5**, H-6 and H-8 get in the shielding region of the *endo*-cyclopropane ring; indeed, they are observed at higher field (δ 0.5–1.1 ppm) than the cyclopropane protons H-2,3 (δ 1–2 ppm) for which no such influence exists.

Several methods have been developed for the degradation of an urazole ring to an azo compound.[16,20,21] For compounds **5**, ring cleavage with potassium hydroxide in boiling isopropyl alcohol and oxidation with $CuCl_2$ of the resulting semicarbazide,[22,23] which was not isolated, emerged as the method of choice which furnished the stable cuprous chloride complexes **7**. As we mentioned earlier,[10] the forcing conditions for saponification of the urazole ring may hamper the synthesis of homotropilidenes with hydrolyzable substituents. But under carefully controlled reaction conditions (see Experimental), which include reaction termination before complete conversion, even cyano- or phosphoryl-substituted homotropilidenes can be prepared along this route.

The free azo compunds **8** are easily obtained from their CuCl complexes by action of ammonia. As expected from the presence of a cyclopropane ring *anti* to the azo bridge, they exhibit rather low thermal stability. Most of them slowly split off nitrogen on storing at room temperature, some of them (**8i,j,o**)

Table 1. ^{1}H-NMR (90 MHz, in $CDCl_3$, δ in ppm, TMS as standard, coupling constants in Hz) and IR data of pyrazolines **4**

	H-1	H-7	H-5	H-2	H-6	H-8,10	H-9	Others	IR (in KBr, cm^{-1})
4e[a]	5.53 m	← 4.54-4.98 →			← 2.03-2.5 →			7.43 (N-Ph)	2240 (CN), 1760,1705 (C
4f	5.63 t'[b]	4.60-4.88 →	5.4 dm ^3J=10.5		~2.95	1.63-1.87	—	1.42 (s,C9-Me) 3.05 (N-Me)	2230 (CN), 1780, 1715 (CO)
4h	5.48 t'	4.60 t'	4.68-5.33		1.65 m	← ~1.4[c] →		1.03 (s,C9-Me) 1.38 (d, ^3J = 7.5, C5-Me) 7.23-7.55 (N-Ph)	1770, 1710 (CO)
4i	4.47 t'	4.62 t'	4.68-5.10		1.63 m	1.43[c]	~0.83[d]	0.97 (7H-isopropyl) 1.50 (d, ^3J = 7.5, C5-Me) 7.27-7.58 (N-Ph)	1765, 1710 (CO)
4j	5.63 t'	4.78 t'	4.88-5.17		←1.68-2.10 →		~2.20[c] ^3J=3	1.53 (d, ^3J = 7.5, C5-Me) 6.98-7.55 (N-Ph and C-Ph)	1760, 1705 (CO)
4k	5.53 t'	4.68 t'	4.78-5.05		2.25 m	~2.0	1.81 dt ^3J = 4.5, $\|^2J_{P,H}\|$ = 8	1.45 (d, ^3J = 7.5, C5-Me) 7.33-8.03 (15 H-arom.)	1770, 1705 (CO), 1435 (P-Phenyl), 1165 (P=O)
4l	5.54 t'	~1.4[c]	5.03 dq	~1.4[c]	1.68 m	← 2.06-2.38 →		1.45 (d, ^3J = 7.5, C5-Me) 3.07 (N-Me)	2240 (CN) 1768, 1710 (CO)
4m	5.55 t'	← 4.61-5.05 →			1.80 m	← 1.90-2.33 →		1.43 (d, ^3J = 7.5, C5-Me) 3.05 (s, N-Me)	2240 (CN), 1763, 1702 (CO)
4n	e)	4.71 m	5.06 m	e)	2.42 dt[f]	~1.5-1.9[c]	—	1.42 (s, C9-Me) 1.45 (d, ^3J = 7.5, C5-Me) 3.03 (N-Me)	2226 (CN) 1765, 1712 (CO)
4o	5.50 t'	4.60 t'	4.68-5.12		←1.65-1,93 →		~3.32[g]	1.46 (d, ^3J = 7.5, C5-Me) 3.28 (s, OMe) 7.30-7.53 (N-Ph)	1765, 1708 (CO)
4p[h]	5.60 [4.2, 4.2, 9.0, 3.0, 7]	4.59	—	4.73	←1.47-1.86 →		0.70 t (2H)	1.18, 1.78 (C5-Me)	1768, 1700 (CO)
4q[h,i]	5.58 [4.9, 4.9, 9.0, 2.5, 4.8]	4.35	—	4.70	~1.73[c]	← 1.05-1.50 →		1.03 (C9-Me) 1.18, 1.73 (C5-Me) 7.23-7.76 (N-Ph)	1765, 1700 (CO)
4r[h]	5.62 [3.6, 3.6, 9.0, 2.1, 5.1]	4.56	—	4.71	1.72[c]	1.27-1.58	d)	0.98 (7H-isopropyl) 1.22, 1.78 (C5-Me) 7.25-7.60 (N-Ph)	1763, 1708 (CO)
4s[h]	5.72 [4.2, 4.2, 9.0, 3.0, 5.4]	4.70	—	4.90	1.97 m	1.89 m	2.23 t ^3J=3	1.27, 1.80, (C5-Me) 6.96-7.58 (C-Ph and N-Ph)	1760, 1705 (CO)
4t	5.73[j]	k)	—	k)	←2.20-2.48 →		1.58 dt ^3J = 3.2 $\|^2J_{P,H}\|$ = 7.5	1.25, 1.78 (C5-Me) 7.35-7.90 (15 H-arom.)	1770, 1705 (CO) 1435 (P-Phenyl) 1180 (P=O)
4u[a,h]	5.53 [3.9, 3.9, 9.0, 2.3, 5.1]	4.68	—	4.84	1.87	2.12 m	~2.4[l]	1.10, 1.53 (C5-Me) 3.29 (N-Me)	2238 (CN) 1760, 1700 (CO)
4v[h]	5.75 [4.5, 4.5, 9.0, 2.8, 5.5]	4.68	—	5.30	2.60	~1.65[c]	—	1.26, 1.75 (C5-Me) 1.43 (C9-Me) 3.06 (N-Me)	2228 (CN) 1765, 1705 (CO)

[a] In [D_6]DMSO. - [b] t' = Pseudotriplet. - [c] Partly superposed by a methyl signal. - [d] Superposed by isopropyl signal. - [e] H- and H-7 appear at δ 5.43-5.77 as partly overlapping multiplets. - [f] ^3J(H-6,H-2) = 9, ^3J(H-6,H-7) = 3.6. - [g] Partly superposed by methoxy signal. - [h] Given in brackets are the following coupling constants: ^3J(H-1,H-2), ^3J(H-1,H-10), ^3J(H-2,H-6), ^3J(H H-7), ^3J(H-7,H-8). - [i] 200 MHz spectrum. - [j] ^3J(H-1,H-2) = ^3J(H-1,H-10) = 4.5. - [k] H-7 and H-2 show up at δ 4.63-4.90 as part overlapping multiplets. - [l] Almost hidden by solvent peak.

Table 2. ^{1}H-NMR data of 9,10 - diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]decanes 5 (90-MHz, in $CDCl_3$, TMS as standard, δ in ppm, coupling constants J in Hz)

	H-1,5	H-2,4	H-3	H-6,8	H-7anti	H-7syn	Others
5e	4.93m	← 2.08-2.30 →		1.13m	← 0.53-~1.0 →		7.49 (N-Ph)
5f	5.05m	a)	-	a)	0.88[b]	1.10[b]	1.47 (s, C3-Me)
					[7, 7.5, 4.5]		3.05 (s, N-Me)
5h	4.87m	1.20m	1.73m	0.92m	—	1.06	1.06 (C3-Me and C7-Me)
5i[c]	4.88m	1.27m[d]	1.48dt[d]	0.87m	—	~1.22m	1.01 (broad s, $CHMe_2$ and $CHMe_2$)
				$^3J_{6(8),7}$ = 3.3			1.06 (C7-Me)[e]
							7.30-7.58 (N-Ph)
5j	5.00m	1.78m	2.86t	1.66m	—	1.27m	1.10 (C7-Me)[e]
			^3J = 3.4				6.66-7.63 (N-Ph)
5k[c]	5.00m	← 2.2 - 2.3 →		0.93m	—	1.38[f]	1.10 (C7-Me)[e]
5l	4.88m	2.07m	2.27t	0.86m	—	1.27m	1.05 (C7-Me)[e]
			^3J = 3.0				3.10 (N-Me)
5n	5.00m	1.58m	—	g)	—	g)	1.10 (C7-Me)[e]
							1.47 (C3-Me)
							3.05 (N-Me)
5o	4.84m	1.63m	3.83t	0.84m	—	1.21m	1.00 (C7-Me)[e]
			^3J = 1.5				3.30 (O-Me)
							7.20-7.60 (N-Ph)
5p	4.90m	~1.45m	h)	0.67[i]	—	—	1.00 (C7-anti-Me)
							1.40 (C7-syn-Me)
							7.14-7.60 (N-Ph)
5q	4.94m	1.20m	1.53m	0.73[i]	—	—	0.97 (d, ^3J = 6.5, C3-Me)
							1.03 (C7-anti-Me)
							1.43 (C7-syn-Me)
							7.22-7.63 (N-Ph)
5r	4.87m	1.28m	j)	0.78[i]	—	—	0.98 (7H-isopropyl)
							1.05 (C7-anti-Me)
							1.45 (C7-syn-Me)
							7.30-7.68 (N-Ph)
5s	5.10m	1.83m	2.61t	0.90[i]	—	—	1.12 (C7-anti-Me)
			^3J = 2.4				1.50 (C7-syn-Me)
							6.98-7.67 (H-arom.)
5t	5.07m	1.98-2.17		0.78[i]	—	—	1.07 (C7-anti-Me)
							1.47 (C7-syn-Me)
							7.30-7.88 (15 H-arom.)
5u	4.98m	1.98-2.14		0.73[i]	—	—	1.05 (C7-anti-Me)
							1.40 (C7-syn-Me)
							3.08 (N-Me)
5v	5.12m	1.60m	—	1.38[k]	—	—	1.10 (C7-anti-Me)
							1.40, 1.45 (C7-syn-Me and C3-Me)
							3.07 (N-Me)

a) H-2,4 and H-6,8 both appear at δ 1.55-1.80. - b) H-7anti, H-7syn, H-6 and H-8 form an AB_2 system; given in brackets are: $|^2J$(H-7anti,H-7syn)|, ^3J(H-7anti,H-6(8)), ^3J(H-7syn,H-6(8)). - c) 200 MHz spectrum. - d) ^3J(H-2(4),H-3endo) = 3.3. - e) ^3J(H-7anti,CH_3) ≈ 6. - f) ^3J(H-7syn,H-6(8)) = 3.5. - g) Ca. δ 1.2-1.4; superposed by methyl signal at δ 1.47. - h) H-3exo: δ 0.52, $|^2J|$ = 6.6, ^3J = 7.5; H-3endo: δ 1.12dt, ^3J = 3.0. - i) Pseudotriplet. - j) Superposed by other aliphatic signals. - k) Partly superposed by methyl signal.

suffer complete N_2 loss even during preparation (20–0°), and the corresponding homotropilidenes are isolated. The methyl-substituted homotropilidenes **9a**⇌**9'a**, **9g**⇌**9'g** and **9h**⇌**9'h** were recently also prepared by decarbonylation of a type **D** precursor.[14] However, the high temperatures for this reaction cause partial isomerization of the systems with an *endo*-methyl group at C-8.

The ^{1}H-NMR spectra of the azo compounds **8** (Table 3) confirm the *exo,endo*-configuration of both cyclopropane rings in the molecular framework, as discussed before for the urazoles **5**.

As the N=N double bond exhibits a similar magnetic anisotropy as the C=C bond, nuclei above the plane containing the double bond system are expected to be shielded. Indeed, the *syn*-protons at C-7 in **8d,e,f,h–o** and the *syn*-methyl groups at C-7 in **8p–v** show up at higher field than in the corresponding compounds **5**; the difference amounts to *ca* 1.3–1.5 ppm in the former case and to *ca* 0.5 ppm in the latter.

Constitution and configuration of homotropilidenes **9**

Homotropilidenes, like other *cis*-divinylcyclopropane systems, are able to undergo a Cope rearrangement which yields valence-isomeric homotropilidenes.[2,24] As discussed in the introduction, the cyclopropane ring *anti* to the azo bridge in **8** will be opened up during the chelotropic [$_\sigma$2$_s$ + $_\sigma$2$_s$ + $_\sigma$2$_s$] nitrogen ejection, thus producing homotropilidene **9**. Depending on the pattern of substitution, which may influence both the activation barrier for valence tautomerism and the ground-state energy difference between the two isomers, either **9** or **9'** may exist alone or a rapid interconversion **9**⇌**9'** may be observed in solution at a given temperature. All three cases are met in the 4(8)-substituted homotropilidenes described in this paper: According to room temperature ^{1}H-NMR spectra (200 MHz), **9k**, **p–v** and **9'e,f,l,n** exist as individual isomers whereas **9h**⇌**9'h**, **9i**⇌**9'i**, **9j**⇌**9'j** exhibit valence tautomerism with **9h**, **9i**, **9j** as energetically favored isomers. The presence of **9'd** in the spectrum of **9d** is not certain,

Table 3. ^{1}H-NMR data of 9,10 - diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - enes **8** (90 MHz, δ values, TMS as standard, coupling constants J in Hz)

	H-1,5	H-2,4	H-3	H-6,8	H-7anti	H-7syn	Others
8d [a]	5.64 m	1.73 dm $^3J_{P,H}$ = 12	2.35 dt $\lvert^2J_{P,H}\rvert$=7.5 ^3J = 3.6	0.98 m	0.13 [b] [6, 7.5, 3]	-0.43 [b]	6.86-7.48 (H-arom.)
8e [c]	5.68 m	1.73 m	2.22 t ^3J=3	0.80 m	0.13 [b] [6.6, 7.6, 3.5]	-0.45 [b]	—
8f [c]	5.80 m	1.29 m	—	~1.40	0.27 [b] [6, 7.5, 3]	-0.43 [b]	1.35 (s, Me)
8l [c]	5.78 m	1.74 m	2.33 t ^3J = 3.5	0.75 m	—	-0.23 m	0.85 (d, ^3J = 6.5, Me)
8n [c]	5.82 m	d)	—	d)	—	-0.20 m	0.90 (d, ^3J = 6, C7-Me) 1.98 (s, C3-Me)
8p [c]	5.63 m	1.55	0.60 [e]	1.08	—	—	0.80; 0.88 (C7-Me)
8q [c]	5.57 m	~0.80	1.88 qt [6.5,3.2]	~0.80	—	—	0.75; 0.80 (C7-Me) 0.95 (d, ^3J = 6.5, C3-Me)
8r [a]	5.73 m	~0.90	1.84 m	~0.90	—	—	0.88; 0.98 (C7-Me) ~0.98 ($CH\underline{Me}_2$ and $C\underline{H}Me_2$)
8s [a]	5.82 m	1.40 m	3.00 t ^3J = 3	f)	—	—	0.90; 0.99 (C7-Me) 6.88-7.33 (H-arom.)
8t [a]	5.82 m	1.67 dm $^3J_{P,H}$=12	2.42 dt $\lvert^2J_{P,H}\rvert$=8, ^3J = 3.4	~0.90	—	—	0.87; 0.95 (C7-Me) 7.40-7.9 (H-arom.)
8u [c]	5.86 m	1.76 m	2.30 t ^3J = 3	~0.80	—	—	0.83; 0.93 (C7-Me)
8y [c]	5.97	1.45	—	1.27	—	—	0.87; 0.93 (C7-Me) 1.38 (s, C3-Me)

[a] In $CDCl_3$. - [b] H-7anti, H-7syn, H-6 and H-8 form an ABM_2 system; given in brackets are $\lvert^2J$(H-7anti, H-7syn)$\rvert$; ^3J(H-7anti H-6(8)); ^3J(H-7syn, H-6(8)). - [c] In Cl_2DC-$CDCl_2$. - [d] H-2,4 and H-6,8 both appear at δ 1.13-1.32. - [e] Both H-3exo and H-3endo. - [f] Superposed by methyl signals.

as **9d** could not be obtained in a pure form, so that signals of impurities eventually obscure the signals from **9'd**.

While the influence of substituents on the valence isomerization will be discussed in a separate paper,[25] only the arguments for the spectral assignment of homotropilidenes **9** and **9'** are presented here. For the interpretation of ^{1}H-NMR spectra (Table 4), we profit by a detailed analysis of the parent compound's spectrum,[26] which at the same time established a chair-like ground-state conformation for homotropilidene itself. Recently, this conformation was found also in the solid state of 2,6-diphenylhomotropilidene.[27] The close similarity of the ^{1}H-NMR spectra of our 4(8)-monosubstituted homotropilidenes **9**, **9'** to that of the parent system leads us to assume a chair-like conformation **9C**, **9'C** for them, too.

The assignment of *exo*/*endo*-substitution at C-8 and quasiequatorial/quasiaxial-substitution at C-4 for homotropilidenes which are singly substituted at C-8 and/or C-4, rests upon the recognition of the position of the respective geminal hydrogen. *Exo*- and *endo*-hydrogens at C-8 can be distinguished by the vicinal coupling constants with cyclopropane protons H-1,7, for which $^3J_{cis}$ is always larger than $^3J_{trans}$ (*ca* 9 Hz vs 4.5–5.6 Hz). Furthermore, H-8*endo* points into the region of diamagnetic anisotropy of the double bonds C2–C3 and C5–C6, and is therefore registered at appreciably higher field than H-8*exo*. Similarly, the quasiaxial hydrogen H-4a is deshielded by *ca* 0.3–0.6 ppm compared to the quasiequatorial H-4e, as it is reached by the magnetic anisotropy of the cyclopropane ring; besides, H-4a is characterized by a complex splitting pattern which is caused by coupling with H-3,5, H-2,6 and H-1,7, whereas for H-4e, only a triplet is observed because of coupling with H-3,5.[26] An additional ^{2}J(H-4a, H-4e) coupling constant of 20–21 Hz is found in **9'e**, **9'f** and **9p**.

In the cyano, methyl-substituted homotropilidenes **9'f** and **9'n**, the *exo*-position of the cyano group may be derived by comparison with the 8 - *endo* - cyanohomotropilidenes **9'e** and **9'l**. By switching the cyano group from the *endo* to the *exo*-position at C-8 cyclopropane protons H-1,7 should move downfield, and the olefinic protons H-2,6 and H-3,5 upfield because of the magnetic anisotropy of the cyano function. Indeed, small shifts (0.15–0.17 ppm) in the expected direction are observed. Finally, the constitution of the tetrasubstituted homotropilidene **9v** is established by the chemical shift of the protons H-1,7. This signal is close to the range observed for the other 8,8-dimethylsubstituted homotropilidenes **9p** u, whereas it is shifted by *ca* 0.6–0.8 ppm downfield in the 8 - cyano - substituted systems **9'e**, **l**, **f** and **n**.

The configuration at C-4 and C-8 which is established by the preceding arguments, confirms the predicted stereochemical course of the ring-opening fragmentation of **8**. On the other hand, the valence tautomerism **9** ⇌ **9'** is accompanied by an exchange pattern which brings an *endo*-substituent at C-8 in the quasiequatorial position at C-4, and an *exo*-substituent at C-8 in the quasiaxial position at C-4, and *vice versa*. This is readily explained by assuming a conformational change from chair to boat to precede the Cope rearrangement of homotropilidenes.[2,26,28]

EXPERIMENTAL

Melting and decomposition points were taken in a heat block and are uncorrected. For Kugelrohr distillations, oven temperatures are given. Preparative column chromatography was done on silica gel (0.05–0.2 mm) from Macharey and Nagel. Photolyses were carried out in Pyrex glass vessels with a high-pressure mercury lamp (Philips HPK 125W); the set-up was flushed with dry nitrogen prior to irradiation.

^{1}H-NMR spectra: Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz). If not stated otherwise, spectra were taken for $CDCl_3$ solutions; chemical shifts refer to TMS and are on the δ scale. IR spectra: Beckman IR 20A and Beckman Accu-Lab 3. Elemental analyses: Perkin-Elmer Microanalyser Model 240.

Starting materials

The following materials were prepared by published procedures: Cycloheptatrienes **2f** (≡ **2g,h**),[29] **2i**;[30] Diels Alder adducts **3a**,[31] **3b–e**[10] and **3d,j**;[32] urazole **5d**;[10] 4 - methyl - 1,2,4 - triazoline - 3,5 - dione (NMTD).[33]

Diels–Alder adducts **3**[34]

A solution of 2.26 g (20 mmol) NMTD in 30 mL acetone was added dropwise to 20 mmol **2f** (≡ **2g,h**) in 20 mL ether, cooled to 0°. After stirring for another 30 min, the ppt was filtered off giving 55% anti - 3 - cyano - 6,7 - diaza - exo - tricyclo[3.2.2.0^{2,4}] non - 9 - ene - 6,7 - dicarboxylic acid methylimide (**3g**), m.p. 206–208° dec. ^{1}H-NMR: δ 1.23 (t, $^3J_{trans}$ = 3 Hz, 3-H), 2.30 (m, 2,4-H), 3.03 (s, N-Me), 5.20 (m, 1,5-H), 6.12 (pseudotriplet, 8,9-H). IR (KBr): 3070–2940 (CH), 2240 (CN); 1778, 1700 (CO); 1450 cm^{-1}. Found: C, 57.1; H, 4.43; N, 24.4. Calc for $C_{11}H_{10}N_4O_2$: C, 57.38; H, 4.38; N, 24.34%.

The filtrates are evaporated and the residue was recrystallized from acetone to give 8% syn - 3 - cyano - 6,7 - diaza - exo - tricyclo[3.2.2.0^{2,4}] non - 8 - ene - 6,7 - dicarboxylic acid methylimide (**3h**), m.p. 165–166° dec. ^{1}H-NMR: δ 1.27 ($^3J_{cis}$ = 9 Hz, 3-H), 2.25 (m, 2,4-H), 3.03 (s, N-Me), 5.30 (m, 1,5-H), 6.33 (pseudo-triplet, 8,9-H). IR (KBr): 3090, 3008 (CH), 2238 (CN); 1763, 1700 (CO), 1460 cm^{-1}. Found: C, 57.1; H, 4.39; N, 24.5. Calc for $C_{11}H_{10}N_4O_2$: C, 57.38; H, 4.38; N, 24.34%.

Syn - 3 - cyano - anti - 3 - methyl - 6,7 - diaza - exo - tricyclo[3.2.2.0^{2,4}]*non - 8 - ene - 6,7 - dicarboxylic acid*

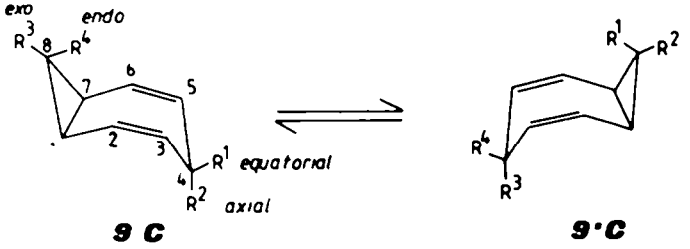


Table 4. ^{1}H-NMR data of homotropilidenes **9**, **9'** (200 MHz, δ values, TMS as standard, coupling constants J in Hz)

	Solvent [a] / Temp. [K]	H-1,7	H-2,6 [b]	H-3,5 [b]	H-4a	H-4e	H-8exo	H-8endo	Others
9d [c]	C 293	1.56 m	6.12 dm $^3J_{2,3}$ = 10.5	5.50 m	4.32 dm $\lvert^2J_{P,H}\rvert$ = 21	—	1.08 m	c)	7.38-7.78, 7.78-8.20 (H-arom.)
9'e	B 293	2.17 [d] [9.3]	5.73 [10.5, 3.5, 2.8]	5.94	3.08 dm $\lvert^2J\rvert$ = 20.7	2.77 dt $^3J_{3,4e}$ = 7.0	1.98 [d] [9.3]	—	—
9'f	B 293	2.33 [e]	5.57 [11.1, 3.0, 2.9]	5.76	3.06 dm $\lvert^2J\rvert$ = 20	2.70 dt $^3J_{3,4e}$ = 6.7	—	—	1.16 (s, Me)
9b	C 293	1.24 m	5.72 [11.2, 3.2, 2.8]	5.29	3.14 m	—	—	0.38 tq [5.25, 6.5]	1.09 (d, J = 6.5, C8-Me) 0.98 (d, J = 7.7, C4-Me)
9'b	C 293	1.57 m	5.46 $^3J_{2,3}$ = 11.2	5.64 $^3J_{3,4e}$ = 6.3	—	2.78 tq	f)	—	0.84 (d, J = 6.7, C8-Me) 1.17 (d, J = 7.0, C4-Me)
9i	C 303	1.28 m	5.84 [10.4, 3.4, 2.5]	5.41	3.00 m	—	—	0.43 tq [5.6, 6.0]	0.84 (d, J = 6.4, CH-$\underline{Me}_2$) 1.10 (d, J = 6.0, C8-Me) ca. 1.5 (C$\underline{H}$ Me_2)
9'i	C 303	1.53 dm	⟵ 5.61 ⟶		—	2.84 m	g)	—	0.90 (d, J = 6.8, CH-$\underline{Me}_2$) 1.18 (d, J = 7.2, C4-Me)
9j	A 293	1.36 m	5.88 [11.5, 3.7, 1.8]	5.52	4.36 m	—	—	0.64 [5, 6.9]	1.16 (d, 6.9, Me) 7.12-7.48 (H-arom.)
9k	A 263	1.19 m	6.09 $^3J_{2,3}$ = 10.5 $^4J_{2,H}$ = 3.5	5.37 $^3J_{3,4a}$ = 4.0	4.12 dm $\lvert^2J_{P,H}\rvert$ = 24.5	—	—	0.80 tq [4.5, 6.3]	1.07 (d, ^3J = 6.3, Me) 7.39-7.61 and 7.76-7.91 (H-arom.)
9'l	B 298	2.18 [d] 9.3	5.62 $^3J_{2,3}$ = 10.5 $^3J_{3,4e}$ = 7.2	5.98	—	2.96 tq [7.2, 7.2]	1.97 [d] [9.3]	—	1.23 (d, ^3J = 7.2, Me)
9'n	B 298	2.33 m	5.46 $^3J_{2,3}$ = 11.3 $^3J_{3,4e}$ = 6.9	5.83	—	2.84 tq [6.9, 7.2]	—	—	1.16 (s, Me) 1.21 (d, ^3J = 7.2, C4-Me)
9o [h]	A 233	1.33 m	5.73 [10.9, 5.5, 1.8]	5.95	4.69 m	—	—	0.66 "q" [4.5, 6.0]	1.14 (d, ^3J = 6.0, C8-Me) 3.34 (s, O-Me)
9p	C 298	1.41 [i]	5.71 [12, 3.6, 3.2]	5.54	3.18 dm ^2J = 20.8	2.70 dt $^3J_{3,4e}$ = 6.3	—	—	0.86 (C8-endo-Me) 1.21 (C8-exo-Me)
9q	C 298	1.36 [i]	5.55 [11.8, 3.2, 2]	5.36	3.30 m	—	—	—	0.88 (C8-endo-Me) 1.08 (d, ^3J = 7.6, C4-Me) 1.15 (C8-exo-Me)
9r	C 298	0.95 [i]	5.32 [11.2, 3.5, 2.5]	5.10	2.68 m	—	—	—	0.43 (d, ^3J = 7, CH$\underline{Me}_2$), 0.48 (C8-endo-Me), 0.69 (C8-exo-Me), 1.23 (C$\underline{H}Me_2$)
9s	C 298	1.47 [i]	5.64 [11.5, 3.2, 2.3]	5.33	4.48 m	—	—	—	1.02 (C8-endo-Me) 1.18 (C8-exo-Me) 7.13-7.35 (H-arom.)
9t	C	1.53 [i]	5.85 [11,3, 2.3]	5.98	4.63 dm $\lvert^2J_{P,H}\rvert$ = 17.5	—	—	—	0.89 (C8-endo-Me) 1.15 (C8-exo-Me) 7.53-7.66 and 8.00-8.71 (H-arom.)

Table 4. *Contd*

	Solvent [a] Temp. [K]	H-1,7	H-2,6[b]	H-3,5[b]	H-4a	H-4e	H-8exo	H-8endo	Others
9u	C	1.43[i]	← 5.68-5.89 →		4.67m	—	—	—	0.92 (C8-endo-Me)
	298								1.18 (C8-exo-Me)
9v	C	1.61[i]	5.79	5.48	—	—	—	—	0.92 (C8-endo-Me)
	298		$^3J_{2,3}$ = 10						1.19 (C8-exo-Me)
									1.52 (C4-Me)

[a] A = $CDCl_3$; B = Cl_2DC-$CDCl_2$; C = $[D]_5$nitrobenzene. - [b] H-2,6 and H-3,5 form a AB-type system with additional splitting; given in brackets are: ^3J(H-2,H-3), ^3J(H-3,H-4a) and $|^4J$(H-2,H-4a)|. - [c] Contains impurities; H-8endo cannot be assigned with certainty. - [d] H-1,7 and H-8 form an AB_2 system; given in brackets is ^3J. - [e] AA'XX' system with H-2,6. - [f] Superposed by methyl signals. - [g] Superposed by isopropyl doublet. - [h] Most signals are broadened at 273 K. - [i] Broadened singulet or very narrow quartet.

methylimide (**3i**). A solution of 2.26 g (20 mmol) NMTD in 30 mL acetone was added dropwise to 20 mmol **2i** in 20 mL ether, cooled to 0°. After stirring for another 30 min, the solvent was evaporated and the residue was recrystallized from ether to give 94% **3i**, m.p. 159–161° dec. ^{1}H-NMR: δ 1.45 (s, C-Me), 1.90 (pseudo-t, 2,4-H), 3.05 (s, N-Me), 5.25 (m, 1,5-H), 6.4 (pseudo-t, 8,9-H). IR (KBr): 3080–2920 (CH), 2230 (CN); 1765, 1705 (CO); 1610, 1460 cm^{-1}. Found: C, 58.2; H, 5.03; N, 23.3. Calc for $C_{12}H_{12}N_4O_2$: C, 59.00; H, 4.95; N, 22.94%.

Δ_1-Pyrazolines **4**[34]

General procedure for diazomethane or diazoethane addition. Excess diazomethane (from 10 g ≙ 98 mmol N - methyl - N - nitrosourea[35]) in 70 mL ether or excess diazoethane (from 11.7 g = 100 mmol N - ethyl - N - nitrosourea[36]) in 80 mL ether was added to 10 mmol of the respective Diels–Alder adduct **3** in 100 mL DMF. The mixture was set aside in the dark for 8–12 d (2–4 d for diazoethane addition). The ppt was filtered off and washed well with ether. The filtrate was diluted with 600 mL ether and cooled to −20° for 2 h, whereupon more crystals were obtained. If no ppt was obtained, the solvent was evaporated at 80°/20 mmHg and the residue was treated with a little cold ethanol. The following Δ^1-pyrazolines were obtained (NMR and IR data in Table 1):

anti - 9 - *Cyano* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4e**). From **3f** and diazomethane. Yield 70%; m.p. 265–272° dec. Found: C, 60.0; H, 4.30; N, 24.5. Calc for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14%.

syn - 9 - *Cyano* - *anti* - 9 - *methyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4f**). From **3i** and diazomethane. Yield 65%, m.p. 228–230° dec. Found: C, 54.6; H, 5.02; N, 29.2. Calc for $C_{13}H_{14}N_6O_2$: C, 54.53; H, 4.93; N, 29.36%.

5 - *anti* - 9 - *Dimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4h**). From **3b** and diazoethane. Yield 78%, m.p. 188–190° dec. Found: C, 63.8; H, 5.66; N, 20.9. Calc for $C_{18}H_{19}N_5O_2$: C, 64.07; H, 5.68; N, 20.76%.

anti - 9 - *Isopropyl* - 5 - *methyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4i**). From **3c** and diazoethane. Yield 70%, m.p. 225–226° dec. Found: C, 65.5; H, 6.41; N, 19.4. Calc for $C_{20}H_{23}N_5O_2$: C, 65.73; H, 6.34; N, 19.70%.

5 - *Methyl* - *anti* - 9 - *phenyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4j**). From **3d** and diazoethane. Yield 82%, m.p. 220–223° dec. Found: C, 68.9; H, 5.23; N, 17.2. Calc for $C_{23}H_{21}N_5O_2$: C, 69.16; H, 5.30; N, 17.53%.

anti - 9 - *Diphenylphosphoryl* - 5 - *methyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4k**). From **3e** and diazoethane. Yield 85%, m.p. 235–238° dec. The compound crystallized with 0.5 mol-equiv. DMF. Found: C, 64.9; H, 5.35; N, 13.8. Calc for $C_{29}H_{26}N_5O_3P$·0.5DMF: C, 65.41; H, 5.31; N, 13.75%.

anti - 9 - *Cyano* - 5 - *methyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4l**). From **3g** and diazoethane. Yield 73%; slow dec. above 250°. Found: C, 54.1; H, 5.04; N, 29.1. Calc for $C_{13}H_{14}N_6O_2$: C, 54.54; H, 4.93; N, 29.36.

syn - 9 - *Cyano* - 5 - *methyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4m**). From **3h** and diazoethane. Yield 82%, m.p. 228–231° dec. Found: C, 54.4; H, 4.88; N, 29.2. Calc for $C_{13}H_{14}N_6O_2$: C, 54.54; H, 4.93; N, 29.36%.

syn - 9 - *Cyano* - 5, *anti* - 9 - *dimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4n**). From **3i** and diazoethane. Yield 64%, m.p. 219–221° dec. Found: C, 55.9; H, 5.39; N, 28.5. Calc for $C_{14}H_{16}N_6O_2$: C, 55.99; H, 5.37; N, 27.99%.

anti - 9 - *Methoxy* - 5 - *methyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4o**). From **3j** and diazoethane. Yield 66%, m.p. 158–160° dec. Found: C, 60.6; H, 5.45; N, 19.8. Calc for $C_{18}H_{19}N_5O_3$: C, 61.19; H, 5.42; N, 19.82%.

General procedure for 2-diazopropane addition. To 5 mmol of the respective Diels–Alder adduct **3** in 40 mL DMF, cooled to −15°, 60 mL of a *ca* 1.5 M solution of 2-diazopropane in ether[37] were added, and the mixture was kept at −15° in the dark for 10 h. Diazopropane addition is repeated twice. The precipitated pyrazoline was then filtered and washed well with ether. The following diazopropane adducts were obtained.

5,5 - *Dimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4p**). From **3a**. Column chromatography over 60 g silica gel yields: (a) with 150 mL $CHCl_3$–ether (3:1) 62% unchanged **3a**; (b) with 200 mL $CHCl_3$–ethyl acetate (1:1) 21% **4p**, m.p. 202°. Found: C, 63.1; H, 5.61; N, 20.8. Calc for $C_{18}H_{19}N_5O_2$: C, 64.08; H, 5.68; N, 20.76%.

5,5,*anti* - 9 - *Trimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4q**). From **3b**. Yield 42%, m.p. 216–220° dec. Found: C, 64.8; H, 6.01; N, 20.2. Calc for $C_{19}H_{21}N_5O_2$: C, 64.96; H, 6.02; N, 19.43%.

5,5 - *Dimethyl* - *anti* - 9 - *isopropyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4r**), from **3c**. Yield 48%, m.p. 210–212° dec. Found: C, 66.1; H, 6.57; N, 18.3. Calc for $C_{21}H_{23}N_3O_2$: C, 66.47; H, 6.64; N, 18.46%.

5,5 - *Dimethyl* - *anti* - 9 - *phenyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4s**). From **3d**. Yield 50%, m.p. > 160° dec. Found: C, 68.9; H, 6.31; N, 15.8. Calc for $C_{24}H_{23}N_3O_2$: C, 69.71; H, 5.61; N, 16.94.

anti - 9 - *Diphenylphosphoryl* - 5,5 - *dimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid phenylimide* (**4t**), from **3e**. Yield 68%, m.p. 255° dec. The compound crystallizes with 0.5 mol-equiv. DMF. Found: C, 64.9; H, 5.75; N, 13.8. Calc for $C_{30}H_{28}N_3O_3P \cdot 0.5DMF$: C, 65.90; H, 5.53; N, 13.42%.

anti - 9 - *Cyano* - 5,5 - *dimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4u**), from **3g**. Yield 54%, m.p. 233–235° dec. Found: C, 55.7; H, 5.41; N, 27.9. Calc for $C_{14}H_{16}N_4O_2$: C, 55.99; H, 5.37; N, 27.99.

syn - 9 - *Cyano* - 5,5, *anti* - 9 - *trimethyl* - 3,4,11,12 - *tetraza* - *exo,endo* - *tetracyclo*[5.3.2.$0^{2,6}$.$0^{8,10}$]*dodec* - 3 - *ene* - 11,12 - *dicarboxylic acid methylimide* (**4v**), from **3i**. Yield 55%, m.p. 231° dec. Found: C, 56.9; H, 5.87; N, 27.0. Calc for $C_{14}H_{18}N_4O_2$: C, 57.31; H, 5.77; N, 26.74%.

Photolyses of Δ^1*-pyrazolines*

^{1}H-NMR and IR data of the resulting tetracyclodecanes **5** are collected in Table 2.

Photolysis of **4e**. A suspension of 1.00 g (3 mmol) **4e** in 40 mL boiling benzene was irradiated for 20 h. The solvent was removed and the residue was chromatographed over 40 g silica gel with 400 mL chloroform–ethyl acetate (1:1): (a) 0.12 g (16%) anti - 3 - cyano - 8 - methyl - 6,7 - diaza - exo - tricyclo[3.2.2.$0^{2,4}$]non - 8 - ene - 6,7 - dicarboxylic acid phenylimide (**6e**), m.p. 203–205° (from $CHCl_3$–ether). ^{1}H-NMR: 1.17 (t, ^3J = 3 Hz, 3-H), 1.90 (d, J = 1.8 Hz, Me), 2.3 (m, 2,4-H), 4.97–5.3 (m, 1,5-H), 5.73 (m, 9-H), 7.37 (m, N-Ph). IR (KBr): 3080–2850, 2240 (CN); 1763, 1710 (CO); 1490 cm^{-1}. Found: C, 66.3; H, 4.75; N, 17.8. Calc for $C_{17}H_{14}N_4O_2$: C, 66.65; H, 4.61; N, 18.29%. (b) 0.13 g (18%) of a mixture of **5e** and its C3-epimer. (c) 0.30 g (41%) anti - 3 - cyano - 9,10 - diaza - endo,exo - tetracyclo[3.2.2.$0^{2,4}$.$0^{6,8}$]decane - 9,10 - dicarboxylic acid phenylimide (**5e**); from acetone–ether pale-yellow needles with m.p. 188–192° dec. Found: C, 66.1; H, 4.64; N, 18.4. Calc for $C_{17}H_{14}N_4O_2$: C, 66.65; H, 4.61; N, 18.29%. (d) 0.20 g (20%) unchanged **4e**.

Photolysis of **4f**. A suspension of 1.20 g (4.19 mmol) **4f** in 100 mL boiling acetonitrile was irradiated for 40 h. After evaporation of the solvent, the residue was chromatographed on 160 g silica gel with 200 mL $CHCl_3$–ethyl acetate (3:2): (a) 0.15 g of a 45:45:10 mixture of **5f**, syn - 3 - cyano - anti - 3,8 - dimethyl - 6,7 - diaza - exo - tricyclo[3.2.2.$0^{2,4}$]non - 8 - ene -6,7 - dicarboxylic acid methylimide (**6f**), and an unknown compound (^{1}H-NMR: δ 6.20, all other superposed by signals of **5f** and **6f**). ^{1}H-NMR of **6f**: δ 1.43 (s, C-Me), 1.73 (m, 2,4-H), 1.93 (d, $|^4J|$ = 2 Hz, C C-Me), 3.00 (s, N-Me), 5.05 (m, 5-H), 5.23 (m, 1-H), 5.85 (dm, 9-H). (b) 0.10 g (12%, rel. to reacted **4f**) syn - 3 - cyano - anti - 3 - methyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]decane - 9,10 - dicarboxylic acid methylimide (**5f**); from ethanol colorless needles, m.p. 200–202° dec. Found: C, 59.5; H, 5.53; N, 21.4. Calc for $C_{11}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.64%. (c) 0.31 g (25%) unreacted **4f**.

General procedure for photolysis of diazoethane adducts **4h–o**

The solution or suspension of 4 mmol **4h–o** in boiling acetonitrile or boiling benzene was irradiated. The solvent was removed *in vacuo* and the residue was purified by column chromatography over 60 g silica gel with 200 mL $CHCl_3$–ethyl acetate (1:1). The following tetracyclodecanes were prepared (given are: the irradiated pyrazoline, solvent, irradiation time, isolated yield, melting point and solvent for recrystallization).

anti - 3,7 - *Dimethyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5h**). From **4h**, benzene, 18 h, 44%, m.p. 190–193° dec. (ethanol). Found: C, 69.4; H, 6.16; N, 13.6. Calc for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58%.

anti - 3 - *Isopropyl* - *anti* - 7 - *methyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5i**). From **4i**, acetonitrile, 12 h, 46%, m.p. 168° dec. (acetone–ether). Found: C, 70.8; H, 6.95; N, 12.6. Calc for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45%.

anti - 7 - *Methyl* - *anti* - 3 - *phenyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5j**). From **4j**, benzene, 24 h, 64%, m.p. 125–127° dec. (acetone). Found: C, 73.3; H, 5.71; N, 11.7. Calcd for $C_{23}H_{21}N_3O_2$: C, 74.37; H, 5.69; N, 11.30%.

anti - 3 - *Diphenylphosphoryl* - *anti* - 7 - *methyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5k**). From **4k**, acetonitrile, 7 h, 67%, m.p. 255° dec. (ethanol). Found: C, 69.3; H, 5.40; N, 9.6. Calc for $C_{29}H_{26}N_3O_3P$: C, 70.29; H, 5.28; N, 8.48%.

anti - 3 - *Cyano* - *anti* - 7 - *methyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid methylimide* (**5l**). From **4l** (or **4aa**), acetonitrile, 24 h, 68% (67%),m.p. 173–175° dec. (acetone–ether). Found: C, 59.8; H, 5.52; N, 21.8. Calc for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.69%.

anti - 3 - *Methoxy* - *anti* - 7 - *methyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5o**). From **4o**, benzene, 24 h, 23%, m.p. 151–152° dec. (ethanol). Found: C, 66.2; H, 5.95; N, 13.0. Calc for $C_{18}H_{19}N_3O_3$: C, 66.45; H, 5.89; N, 12.91%.

Photolysis of **4u**. The suspension of 1.12 g (3.73 mmol) **4u** in 100 mL boiling acetonitrile was irradiated for 24 h. The solvent was removed *in vacuo* and the residue was chromatographed over 160 g silica gel with 400 mL $CHCl_3$ ethyl acetate (3:1): (a) 0.09 g of a mixture of **5u** and syn - 3 - cyano - 8 - ethyl - anti - 3 - methyl - 6,7 - diaza - endo,exo - tricyclo[3.3.2.$0^{2,4}$]non - 8 - ene - 6,7 - dicarboxylic acid methylimide (**6u**). ^{1}H-NMR of **6u**: δ 1.13 (t, CH–CH_3), 1.40 (s, C3-Me), 1.85 (m, 2,4-H), 3.03 (s, N-Me), 3.45–4.03 (m, CH_2–CH_3), 4.93–5.33 (m, 1-H, 5-H), 5.83 (dm, 9-H). (b) 0.28 g (29%). syn - 3 - Cyano - anti - 3,anti - 7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]decane - 9,10 - dicarboxylic acid methylimide (**5u**), m.p. 184–186° dec. (ethanol). Found: C, 62.3; H, 6.23; N, 20.1. Calc for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58%.

General procedure for photolysis of diazopropane adducts **4p–v**

The suspension of 3 mmol of **4p–v** in 50 mL acetonitrile or benzene was irradiated at room temperature for 3–4 h. The solvent was removed and the residue was recrystallized. The following tetracyclodecanes were obtained (given are: the irradiated pyrazoline, solvent of photolysis, yield, m.p., solvent for recrystallization):

7,7 - Dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]decane - 9,10 - dicarboxylic acid phenylimide (**5p**). From **4p**, benzene, 70%, m.p. 145–150° dec. (ether). Found: C, 69.7; H, 6.26; N, 13.6. Calc for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58%.

anti - 3,7,7 - *Trimethyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5q**). From **4q**, acetonitrile, 95%, m.p. 195–198° dec. (ethanol). Found: C, 70.6; H, 5.52; N, 13.0. Calc for $C_{19}H_{21}N_3O_2$: C, 70.57; H, 6.55; N, 12.99%.

anti - 3 - *Isopropyl* - 7,7 - *dimethyl* - 9,10 - *diaza* - *endo,exo* - *tetracyclo*[3.3.2.$0^{2,4}$.$0^{6,8}$]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5r**). From **4r**, acetonitrile, 82%, m.p. 180–182° dec. (acetone–ether). Found: C, 70.2; H, 6.95; N, 11.7. Calc for $C_{21}H_{25}N_3O_2$: C, 71.77; H, 7.17; N, 11.96%.

7,7 - Dimethyl - anti - 3 - phenyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5a**). From **4a**, benzene, 88%, m.p. 199–202° dec. (ethanol). Found: C, 74.4; H, 6.09; N, 11.0. Calc for $C_{24}H_{23}N_3O_2$: C, 74.78; H, 6.01; N, 10.90%.

anti - 3 - Diphenylphosphoryl - 7,7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.2.2.0^{2,4}.0^{6,8}]*decane* - 9,10 - *dicarboxylic acid phenylimide* (**5t**). From **4t**, acetonitrile, 68%, m.p. 280° dec. (acetone). Found: C, 70.7; H, 5.63; N, 8.4. Calc for $C_{30}H_{28}N_3O_3P$: C, 70.72; H, 5.54; N, 8.15%.

anti - 3 - Cyano - 7,7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]*decane* - 9,10 - *dicarboxylic acid methylimide* (**5u**). From **4u**, acetonitrile, 74%, m.p. 220° dec. (ethanol). Found: C, 61.2; H, 5.83; N, 20.8. Calc for $C_{14}H_{16}N_4O_2$: C, 61.72; H, 5.92; N, 20.58%.

anti - 3 - Cyano - syn - 3,7,7 - trimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]*decane* - 9,10 - *dicarboxylic acid methylimide* (**5v**). From **4v**, acetonitrile, 76%, m.p. 230° dec. (ethanol). Found: C, 62.3; H, 6.33; N, 20.1. Calc for $C_{15}H_{18}N_4O_2$: C, 62.92; H, 6.34; N, 19.57.

Cuprous chloride complexes

General procedure for urazole ring degradation of alkyl, phenyl, methoxy and cyano substituted tetracyclodecanes **5**. Values in brackets refer to the cyano-substituted systems. A mixture of 5.1 [1] mmol of the respective tetracyclodecane **5** and 2.86 g (51 mmol) [0.28 g (5.0 mmol)] potassium hydroxide in 90 [10] mL 2-propanol was refluxed under nitrogen with magnetic stirring for 90 min [15–30 min, reaction control by TLC]. The solution was cooled to −20° [−10°], diluted with 20 mL water and acidified to pH ~ 3 with 1 N HCl. 2.75 g (16.1 mmol) [1.0 g (5.87 mmol)] cupric chloride dihydrate in 20 mL [10 mL] H_2O were added, whereupon deposition of the brick-red cuprous chloride complex began. The mixture was stirred for 2 h at room temperature and filtered with suction. The solid was washed successively with small amounts of water, methanol and ether. The following cuprous chloride complexes were thus obtained: **7e** (58%, m.p. 113–115° dec.); **7f** (91%); **7h** (33%, m.p. 98–104° dec.); **7i** (45%); **7j** (21%); **7l** (59%, m.p. 112–114° dec.); **7n** (93%, 113–115° dec.); **7o** (23%); **7p** (98%, m.p. 110–111°); **7q** (95%) m.p. 105° dec.); **7r** (78%, m.p. 120–122° dec.); **7s** (52%, m.p. 225–227° dec.); **7u** (56%, m.p. 118–120° dec.); **7v** (91%, m.p. 130° dec.).

General procedure for urazole ring degradation of phosphoryl-substituted tetracyclodecanes **5d**, **k**, **t**. The mixture of 0.5 mmol of **5d**, **k** or **t**, 0.02 g (3.6 mmol) potassium hydroxide and 15 mL 2-propanol was refluxed under nitrogen for 70 min. The solution was then cooled to 0°, diluted with 50 mL water and acidified with 1 N HCl to pH ~ 3. Upon addition of 1.5 g (8.8 mmol) cupric chloride dihydrate in 30 mL water, slow separation of the brown cuprous chloride complex began. After stirring at room temp. for 1 h, the complex was filtered off and washed successively with small volumes of water, methanol and ether. The following cuprous chloride complexes were obtained: **7d** (86%, m.p. 110° dec.); **7k** (96%, m.p. 110° dec.); **7t** (84%, m.p. 105° dec.).

Homotropilidenes[14]

General procedure for the liberation of the free azo compounds **8** *from their cuprous chloride complexes* **7**.[10] The cuprous chloride complex **7** was suspended in 30 mL ether, and aqueous ammonia (10%) was added dropwise until the brick-red color of **7** was discharged. The ether layer was separated and the aqueous phase was extracted with ether (3 × 20 mL). The combined organic layers were washed with 20 mL water and dried ($CaCl_2$). After removing the ether at 0°C/80 mmHg, the azo compound **8** was obtained.

cis - 4 - Diphenylphosphorylhomotropilidene (**9d**). 0.18 g (0.43 mmol) **7d** were treated as described above, except that ether was replaced by methylene chloride. The residue which remained after evaporation of the solvent at 0°/15 mmHg was triturated with ether: 0.04 g (28%) *anti - 3 - diphenylphosphoryl - 9,10 - diaza - endo,exo - tetracyclo*[3.3.2.0^{2,4}.0^{6,8}]*dec - 9 - ene* (**8d**), dec.p. 76°.

After heating 0.03 g in 0.5 mL [D_5]-nitrobenzene in a NMR tube for 1 h at 60°, **9d** was identified by its ^{1}H-NMR spectrum. **9d** was not pure, however, and the amount of impurities increased at higher temperatures (> 60°).

endo - 8 - Cyanohomotropilidene (**9'e**): From 0.15 g (0.58 mmol) **7e**, 68 mg (74%) anti - 3 - cyano - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - ene (**8e**) were obtained, dec.p. 59–61°. Slow nitrogen loss was observed even at room temperature. 0.06 g (0.36 mmol) **8e** was dissolved in 1 mL n-hexane and heated under nitrogen for 30 min to 60°. After cooling and evaporation of the solvent, 0.049 g (98%) **9'e** were obtained. **9'e** decomposed on attempted Kugelrohr distillation.

exo - 8 - Cyano - endo - 8 - methylhomotropilidene (**9'f**): 0.09 g (0.30 mmol) **7f** were treated as described in the general procedure, except that ether was replaced by methylene chloride: 0.043 g (82%) colorless anti - 3 - cyano - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - ene (**8f**); dec.p. 67°. Slow nitrogen loss took place already at room temperature. 0.04 g (0.23 mmol) solid **8f** were heated under nitrogen to 70°. The liquid was then purified by Kugelrohr distillation (100°/0.8 mmHg) to yield 0.018 g (54%) **9'f**. IR (film): 3018, 2968, 2940, 2866, 2223 (CN), 1653, 1646, 1448, 1372 cm^{-1}. Found: C, 80.0; H, 7.39; N, 9.3. Calc for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.64%.

exo - 8 - Methyl - cis - 4 - methylhomotropilidene ⇌ *endo - 8 - Methyl - trans - 4 - methylhomotropilidene* (**9h** ⇌ **9'h**). When **7h** (0.15 g, 0.57 mmol) was treated as given in the general procedure, the azo compound **8h** decomposed rapidly on evaporation of the ether at 0°C/80 mmHg. After Kugelrohr distillation (90°/40 mmHg) of the residue, one obtained 0.072 g (95%) pale-yellow homotropilidene **9h** ⇌ **9'h**. IR (film): 3002, 2945, 2940, 2893, 1662, 1452, 1440, 1375 cm^{-1}.

exo - 8 - Methyl - cis - 4 - isopropylhomotropilidene ⇌ *trans - 4 - Methyl - endo - 8 - isopropylhomotropilidene* (**9i** ⇌ **9'i**). When **7i** (0.21 g, 0.73 mmol) was treated as described in the general procedure, the azo compound **8i** decomposed under vigorous N_2 loss, when the solvent was evaporated at 0°. After Kugelrohr distillation (80°/15 mmHg) of the residue, one obtained 0.093 g (83%) **9i** ⇌ **9'i**. IR (film): 3003, 2958, 2926, 2869, 1662, 1460, 1385, 1368, 1361 cm^{-1}. Found: C, 87.8; H, 10.69. Calc for $C_{12}H_{18}$: C, 88.82; H, 11.18%.

exo - 8 - Methyl - cis - 4 - phenylhomotropilidene ⇌ *trans - 4 - Methyl - endo - 8 - phenylhomotropilidene* (**9j** ⇌ **9'j**). When **7j** (0.12 g, 0.37 mmol) was treated as described in the general procedure, the azo compound **8j** decomposed rapidly during removal of the solvent at 0°C. The residue was Kugelrohr distilled (120°/0.01 mmHg) and yielded 0.063 g (87%) **9j** ⇌ **9'j** as a pale-yellow viscous oil. IR (film): 3003, 2948, 2922, 2860, 1662, 1598, 1490, 1450, 1378 cm^{-1}. Found: C, 90.0; H, 8.06. Calc for $C_{13}H_{16}$: C, 91.78; H, 8.22%.

cis - 4 - Diphenylphosphoryl - exo - 8 - methylhomotropilidene (**9k**). 0.29 g (0.67 mmol) **7k** were treated as described in the general procedure, but methylene chloride was used instead of ether: 0.10 g (43%) anti - 3 - diphenylphosphoryl - anti - 7 - methyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - ene (**8k**). This compound loses nitrogen slowly at *ca* 50°, and vigorously at 164°. The solution of 0.09 g (0.26 mmol) **8k** in 1 mL chloroform was heated to 60° for 1 h. After cooling and removing the solvent *in vacuo*, the residue was triturated with a small volume of ethanol: 0.067 g (80%) pale-yellow crystals of **9k**, m.p. 167°. IR (KBr): 3075, 3020, 2944, 2863, 2850, 1656, 1482, 1440 (P-phenyl), 1196 (PO) cm^{-1}. Found: C, 78.5; H, 6.49. Calc for $C_{21}H_{11}PO$: C, 78.83; H, 6.61%.

endo - 8 - Cyano - trans - 4 - methylhomotropilidene (**9'l**). From 0.16 g (0.54 mmol) **7l**, 0.064 g (69%) anti - 3 - cyano - anti - 7 - methyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - ene (**8l**) were obtained, dec.p. 54–56°. On storing **8l** at room temperature, slow transformation to **9'l** took place.

A solution of 0.06 g (0.34 mmol) **8l** in mL n-hexane was heated under nitrogen to 60° for 1 h. After removing the solvent, one obtained 0.047 g (96%) yellow **9l**, most of which decomposed on attempted Kugelrohr distillation at 80°/0.02 mmHg. IR: 2235 cm^{-1} (CN). Found: C, 80.8; H, 7.39; N, 9.4. Calc for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65%.

exo - 8 - *Cyano* - *endo* - 8,*trans* - 4 - *dimethylhomotropilidene* (**9a**). **7a** (0.32 g, 0.99 mmol) was treated as described in the general procedure, but ether was replaced by methylene chloride: 0.146 g (79%) anti - 3 - cyano - syn - 3,anti - 7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8a**), dec.p. 48°. Slow decomposition was observed at room temperature.

Solid **8a** (0.14 g, 0.75 mmol) was heated under nitrogen to 60°. When the gas evolution had ceased, the oil was Kugelrohr distilled (100°/0.3 mmHg). One obtained 0.042 g (35%) liquid **9a**, which after some time crystallized; white needles, m.p. 35°. IR (film): 3010, 2962, 2925, 2865, 2225, (CN), 1664, 1540 cm^{-1}. Found: C, 82.8; H, 8.18; N, 8.70. Calc for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80%.

cis - 4 - *Methoxy* - *exo* - 8 - *methylhomotropilidene* ⇌ *endo* - 8 - *methoxy* - *trans* - 4 - *methylhomotropilidene* (**9o** ⇌ **9'o**). **7o** (0.12 g, 0.43 mmol) was treated as described in the general procedure. Under the reaction conditions, the azo compound decomposed completely, and after evaporation of the ether at 0°/80 mmHg, **9o** (0.023 g, 36%) remained as a yellow oil, which decomposed noticeably at room temperature.

8,8 - *Dimethylhomotropilidene* (**9p**). From **7p** (0.45 g, 1.72 mmol), one obtained after recrystallization (ether pentane) 0.27 g (97%) 7,7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8p**), dec.p. 55°. Slow decomposition was observed at room temperature.

Neat **8p** (0.25 g, 1.54 mmol) was heated under nitrogen to 60°, until N_2 evolution ceased. After Kugelrohr distillation one obtained 0.18 g (87%) **9p**. IR (film): 3002, 2988, 2938, 2880, 2860, 1666, 1473, 1451, 1375 cm^{-1}. ^{13}C-NMR: δ 15.9 (endo-$\underline{C}H_3$), 27.3 (C-8), 28.1 (exo-$\underline{C}H_3$), 30.3 (C-4), 31.1 (C-1,7), 127.4 and 128.1 (C-3,5, C-2,6). Found: C, 88.3; H, 10.30. Calc for $C_{10}H_{14}$: C, 89.49; H, 10.51%.

cis - 4,8,8 - *Trimethylhomotropilidene* (**9q**). From 0.82 g (2.89 mmol) **7q**, one obtained 0.42 g (80%) anti - 3,7,7 - trimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8q**), dec.p. 57°. Slow decomposition took place at room temperature. 0.30 g (1.80 mmol) **8q** were heated under nitrogen until N_2 evolution ceased. Kugelrohr distillation (100°/30 mmHg) of the residue yielded 0.24 g (91%) **9q**. IR (film): 3002, 2958, 2938, 2873, 2863, 1660, 1640, 1452, 1372 cm^{-1}. Found: C, 87.7; H, 10.55. Calc for $C_{11}H_{16}$: C, 89.12; H, 10.88%.

8,8 - *Dimethyl* - *cis* - 4 - *isopropylhomotropilidene* (**9r**). 0.45 g (1.45 mmol) **7r** yielded 0.21 g (74%) 7,7 - dimethyl - anti - 3 - isopropyl - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8r**); pale-yellow crystals with dec.p. 62° (ether). 0.18 g (0.93 mmol) **9r** were heated under nitrogen to 65° until nitrogen evolution was over. The residue was Kugelrohr distilled at 90°/0.15 mmHg; one obtained 0.138 g (84%) colorless **9r**. IR (film): 3002, 2950, 2869, 1645, 1459, 1452, 1382, 1369 cm^{-1}.

8,8 - *Dimethyl* - *cis* - 4 - *phenylhomotropilidene* (**9s**). **7s** was treated as described in the general procedure. Crystallization of the oily residue which remained after removing the solvent was induced by trituration with ether at −78°: 0.29 g (92%) 7,7 - dimethyl - anti - 3 - phenyl - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8s**), dec.p. 90–92°. Found: C, 80.3; H, 7.71; N, 11.9. Calc for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75%. A solution of 0.25 g (1.05 mmol) **8s** in 5 mL n-hexane was heated to 55° for 70 min. After evaporation of the solvent, the residue was purified by Kugelrohr distillation at 135°/0.01 mmHg and yielded 0.63 g (60%) **9s** as a liquid which solidified after some hours. IR (film): 3002, 2950, 2922, 2862, 1659, 1560, 1490, 1448, 1380 cm^{-1}. Found: C, 90.5; H, 8.58. Calc for $C_{16}H_{16}$: C, 91.34; H, 8.63%.

cis - 4 - *Diphenylphosphoryl* - 8,8 - *dimethylhomotropilidene* (**9t**). **7t** (0.14 g, 0.31 mmol) was treated as described in the general procedure. After evaporation of the solvent (methylene chloride) at 0°/15 mmHg, a solid residue was obtained, which after washing with ether furnished 0.07 g (61%) anti - 3 - diphenylphosphoryl - 7,7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8t**), m.p. 52°.

0.08 g (0.22 mmol) **8t** in 1 mL chloroform were heated under nitrogen to 60° for 1 h. After evaporation of the solvent, ethanol was added to the residue whereupon 0.063 g (85%) pale-yellow crystalline **9t** was obtained, m.p. 152°. IR (film): 3045, 3000, 2952, 2910, 2855, 1436 (P-phenyl); 1184 (P-O), 1119 cm^{-1}. Found: C, 78.3; H, 6.95. Calc for $C_{22}H_{21}OP$: C, 79.02; H, 6.93%.

cis - 4 - *Cyano* - 8,8 - *dimethylhomotropilidene* (**9u**). From 0.21 g (0.67 mmol) **7u**, one obtained 0.095 g (75%) anti - 3 - cyano - 7,7 - dimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8u**), dec.p. 61–62°. Slow decomposition was observed at room temperature.

A solution of 0.09 g (0.48 mmol) **8u** in 1 mL n-hexane was heated to 60° under nitrogen. After removing the solvent *in vacuo*, 0.073 g (96%) yellow **9u** was left, which decomposed on attempted Kugelrohr distillation. IR (film): 2250 cm^{-1} (CN).

trans - 4 - *Cyano* - *cis* - 4,8,8 - *trimethylhomotropilidene* (**9v**). **7v** (0.19 g, 0.59 mmol) furnished, after recrystallization from ether-pentane (−78°), 0.086 g (76%) anti - 3 - cyano - syn - 3,7,7 - trimethyl - 9,10 - diaza - endo,exo - tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec - 9 - ene (**8v**), dec.p. 68°. Slow decomposition at room temperature took place. **8v** (0.084 g, 0.44 mol) was heated under nitrogen to 70° for 15 min. Kugelrohr distillation at 100°/0.2 mmHg furnished 0.025 g (33%) liquid colorless **9v**. IR (film): 3018, 2965, 2930, 2223 (CN), 1662, 1450, 1378 cm^{-1}. Found: C, 82.5; H, 8.65; N, 8.7. Calc for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08%.

Acknowledgements- Generous support of this work by Prof. M. Regitz is gratefully acknowledged. J.K.K. thanks the Fonds der Chemischen Industrie for a scholarship. Moreover, our thanks go to Mrs Alester for the elemental analyses.

REFERENCES

[1]For a survey, see: R. Bicker, H. Kessler, A. Steigel and W.-D. Stohrer, *Chem. Ber.* **108**, 2708 (1975).
[2]W. v. E. Doering and W. R. Roth, *Tetrahedron* **19**, 715 (1963).
[3]H. Dürr, R Sergio and G. Scheppers, *Liebigs Ann. Chem.* **740**, 63 (1970).
[4]N. Trong Anh, *Die Woodward-Hoffmann-Regeln und ihre Anwendung*, pp. 165 ff. Verlag Chemie, Weinheim (1972).
[5]P. S. Engel, *Chem. Rev.* **80**, 99 (1980).
[6a]E. L. Allred, J. C. Hinshaw and A. L. Johnson, *J. Am. Chem. Soc.* **91**, 3382 (1969); [b]E. L. Allred and K. J. Voorhees, *J. Am. Chem. Soc.* **95**, 620 (1973); [c]L. A. Paquette and M. J. Epstein, *Ibid.* **93**, 5936 (1971); *Ibid.* **95**, 6717 (1973).
[7]S. C. Clarke and B. L. Johnson, *Tetrahedron* **27**, 3555 (1971).
[8]J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.* **91**, 777 (1969).
[9]W. L. Jorgensen, *Ibid.* **97**, 3082 (1975).
[10]G. Maas and J. K. Kettenring, *Chem. Ber.* **115**, 627 (1982).
[11]Ph.D. Thesis of A. Steigel 1971, T. Troll 1971, H. D. Fühlhuber 1977 and C. Gousetis 1978, all University of Regensburg, West Germany.
[12]H. D. Fühlhuber, B. Gousetis, T. Troll and J. Sauer, *Tetrahedron Letters* 3903 (1978).
[13]C. Gousetis and J. Sauer, *Ibid.* 1295 (1979).
[14]R. Bicker, Ph.D. Thesis, 1977; G. P. Zöphel, Ph.D. Thesis, 1979, University of Frankfurt, West Germany.
[15]In Ref. 14, decarbonylation was done under GC conditions, column temperature 250°.

[16]D. R. James, G. H. Birnberg and L. A. Paquette, *J. Am. Chem. Soc.* **96**, 7465 (1974).
[17]A. A. Cross and J. T. Harrison, *J. Am. Chem. Soc.* **85**, 3223 (1963).
[18]H. Günther, *NMR-Spektroskopie*, p. 91. Thieme, Stuttgart 1973.
[19]K. Torri and K. Kitahonuki, *J. Am. Chem. Soc.* **87**, 386 (1965).
[20]D. Kaufmann and A. de Meijere, *Tetrahedron Letters* 779 (1979).
[21]W. Adam, L. Arias and O. de Lucchi, *Synthesis* 543 (1981).
[22]M. Heymann, T. Bandureo and J. P. Snyder, *J. Chem. Soc.* Chem. Commun. 297 (1971).
[23]R. Jösel, Ph.D. Thesis, University of Karlsruhe, West Germany, 1978.
[24]G. Maier, *Valenzisomerisierungen*, p. 57 ff. Verlag Chemie, Weinheim (1972).
[25]G. Maas and J. K. Kettenring, *Chem. Ber.*, in press.
[26]H. Günther and J. Ulmen, *Chem. Ber.* **108**, 3132 (1975).
[27]H. Kessler, W. Ott, H. J. Lindner, H. G. von Schnering, E.-M. Peters and K. Peters, *Chem. Ber.* **113**, 90 (1980).
[28]H. Günther, J.-B. Pawliczek, J. Ulmen and W. Grimme, *Chem. Ber.* **108**, 3141 (1975).
[29]W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.* **79**, 352 (1957).
[30]F. G. Klärner, S. Yaslat and M. Kette, *Chem. Ber.* **110**, 107 (1977).
[31]R. C. Cookson, S. Gilani and I. D. R. Stevens, *J. Chem. Soc. C* 1906 (1967).
[32]W. Adam, M. Balci and B. Pietrzak, *J. Am. Chem. Soc.* **101**, 6285 (1979).
[33]H. Wamhoff and K. Wald, *Org. Prep. Proc. Int.* **7**, 251 (1975).
[34]For the use of *exo/endo* in the nomenclature of polycyclic systems and of *cis/trans* to characterize the stereochemical relation between cyclopropane ring and C-4 substituents in the homotropilidenes **9**, **9'**, see Ref. 10.
[35]F. Arndt, *Org. Synth. Coll. Vol.* **2**, 165 (1943).
[36]Houben-Weyl, *Methoden der Organischen Chemie*, Vol. X/4, p. 539. Thieme, Stuttgart (1968).
[37]S. D. Andrews, A. C. Day, P. Raimond and M. C. Whiting, *Org. Synth.* **50**, 27 (1970).