Synthesis, Photolysis, and Thermolysis of Azoalkanes Derived from Spirocyclopropane-Substituted Norbornenes: Competitive Nitrogen Loss and Diazoalkane Formation

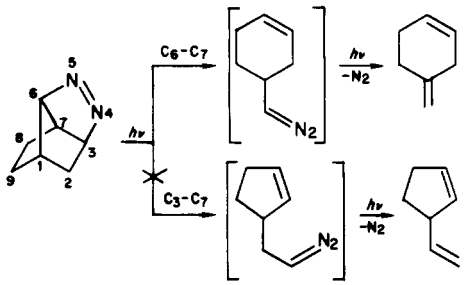
Waldemar Adam,*† Markus Dörr,†‡ Karlheinz Hill,† Eva-Maria Peters,§ Karl Peters,§ and Hans Georg von Schnering§

Institut für Organische Chemie, Universität Würzburg, D-8700 Würzburg, West Germany, and Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, West Germany

Received August 27, 1984

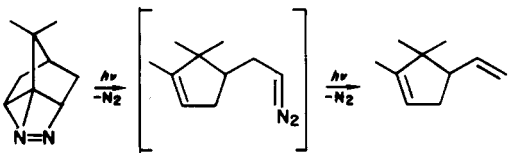
The azoalkanes 4′,5′-diazaspiro(cyclopropane-1,2′-tricyclo[4.3.0.0^{3,7}]non-4′-ene) (**3a**), 4′,5′-diazaspiro(cyclopropane-1,8′-tricyclo[4.3.0.0^{3,7}]non-4′-ene) (**3b**), and 4′,5′-diazadispiro(cyclopropane-1,2′-tricyclo[4.3.0.0^{3,7}]non-4′-ene-8′,1″-cyclopropane) (**3c**) were prepared from the corresponding spirocyclopropane-substituted norbornenes spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (**1a**), spiro(bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane) (**1b**), and dispiro(cyclopropane-1,2′-bicyclo[2.2.1]hept-5′-ene-7′,1″-cyclopropane) (**1c**) by cycloaddition with 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD), affording the respective urazoles **2a–c** and subsequent hydrolysis and oxidation. X-ray structures of the urazoles **2b,c** confirmed the preferred regioselectivity in the PTAD cycloaddition with the spirocyclopropane-substituted norbornenes **1b,c**. Benzophenone triplet-sensitized photolysis of the azoalkanes **3a–c** led quantitatively to the respective tricycloalkanes **4a–c** via nitrogen loss. While in the thermolysis of the azoalkanes **3a,c** the tricycloalkanes **4a,c** were formed essentially quantitatively, also traces of methylenecyclohexenes **5a,c** were detected as denitrogenation products. In the case of **3b** the major thermolysis product was the pyrazole **7b**, resulting from Diels–Alder retrocyclization. The direct photolysis (n,π^* excitation) gave the tricycloalkanes **4a–c** as major products, together with appreciable amounts of methylene cyclohexenes **5a–c**, the latter increasing with increasing temperature of the direct photolysis. On laser irradiation of the azoalkanes **3a–c** with the 333.6-nm line in all cases a yellow transient color was observed, which corresponded to the diazoalkanes **6a–c**. On prolonged photolysis, the diazoalkanes **6a–c** afforded the methylenecyclohexenes **5a–c**. Spirocyclopropane substitution affected the relative proporation of tricycloalkane and methylenecyclohexene products. A mechanism is postulated in which the diazenyl diradicals **8a–c** figure as common intermediates for the thermal and triplet-sensitized and direct photochemical denitrogenations of the azoalkanes **3a–c**. Differences in spin multiplicities (singlet vs. triplet) and electronic configurations ($D_{\sigma,\sigma}$ vs. $D_{\sigma,\pi}$) allow rationalization of the distinct behavior of the diazenyl diradicals **8**.

Recently we demonstrated[1] that the minor products in the direct photolysis of the azoalkane 4,5-diazatricyclo-[4.3.0.0^{3,7}]non-4-ene were derived from secondary photolytic denitrogenation of the transient diazoalkane (eq 1), presumably via the corresponding carbene intermediate.



(1)

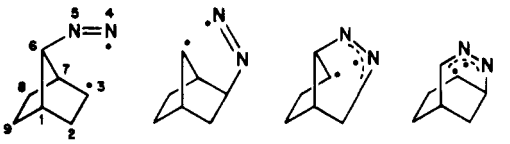
A number of retrocleavages of strained azoalkanes into diazoalkanes have been reported[2] over the years, especially lately.[3] However, it was surprising that only C_6–C_7 retrocleavage to the methylenecyclohexene, but no C_3–C_7 retrocleavage to the vinylcyclopentene (eq 1) had taken place, although cases of the latter have been documented.[4] For example, the azoalkane 7,7,8-trimethyl-2,3-diazatricyclo[4.2.1.0^{4,8}]non-2-ene gave on direct photolysis the corresponding cyclopentenyl-type diazoalkane (eq 2).



(2)

† Institut für Organische Chemie.
‡ Undergraduate research participant, spring 1982.
§ Max-Plank-Institut für Festkörperforschung.

However, in this particular case it must be kept in mind, that in view of the symmetrical nature of the azoalkane, no alternative such as in eq 1 obtains. Since concerted retrocleavage is photochemically forbidden on grounds of orbital symmetry arguments,[5] the answer to this photochemical regioselectivity must be sought in the four possible diradical intermediates below. These correspond to



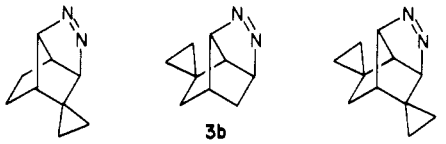
initial C_3–N_4 and C_6–N_5 cleavages leading to diazenyl-type diradicals or initial C_3–C_7 and C_6–C_7 cleavages leading to hydrazonyl-type diradicals, respectively. Subsequent fragmentation of the diradicals derived from initial C_3–N_4 and C_6–C_7 cleavages would give eventually the observed

(1) Adam, W.; Carballeira, N.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 5473.
(2) (a) Bianchi, G.; De Micheli, C.; Gandolfi, R. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 721. (b) Givens, R. S. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, pp 227–347.
(3) (a) Padwa, A.; Kumagai, T.; Tohidi, M. *J. Org. Chem.* **1983**, *48*, 1834. (b) Dolbier, W. R., Jr.; Al-Fekri, D. M. *Tetrahedron Lett.* **1983**, *24*, 4047. (c) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333. (d) Kumagai, T.; Ohba, Y.; Mukai, T. *Tetrahedron Lett.* **1982**, *23*, 439. (e) Padwa, A.; Caruso, T.; Nahm, S.; Rodriguez, A. *J. Am. Chem. Soc.* **1982**, *104*, 2865. (f) Padwa, A.; Rodriguez, A. *Tetrahedron Lett.* **1981**, *22*, 187. (g) Padwa, A.; Ku, H. *Tetrahedron Lett.* **1980**, *21*, 1009. (h) Nishizawa, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1980**, *102*, 1176.
(4) (a) Adam, W.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 1699. (b) Adam, W.; Gillaspey, W. D.; Peters, E.-M.; Peters, K.; Rosenthal, R. J.; von Schnering, H. G. *J. Org. Chem.*, preceding paper in this issue.
(5) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum-Rosetta, 1975.

0022-3263/85/1950-0587$01.50/0

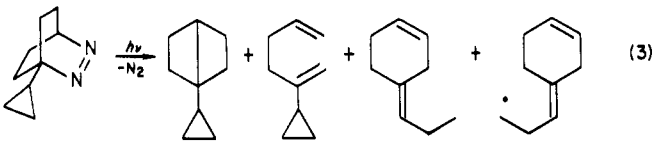
methylenecyclohexene, while for the diradicals derived from initial C_3–C_7 and C_6–N_5 cleavages the vinylcyclopentene would be formed.

To distinguish between these mechanistic options, we decided to prepare the spirocyclopropane-substituted azoalkanes below. We hoped that the cyclopropylcarbinyl



3a 3b 3c

probe[6] would allow us to test the influence of spirocyclopropane substitution on the four possible fragmentation modes of the pyrazoline ring in these azoalkanes. Our intentions were also encouraged by the recent report[7] that cyclopropylcarbinyl involvement does take place in the photolysis of the azoalkane 1-cyclopropyl-2,3-diazabicyclo[2.2.2]oct-2-ene (eq 3), as evidenced by the last two

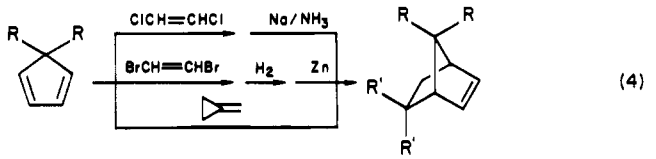


(3)

products. Besides permitting possibly a differentiation among the different fragmentation modes of the pyrazoline ring in the electronically excited azoalkane through cyclopropylcarbinyl stabilization,[6b,c] the cyclopropylcarbinyl "free radical clock"[6a] might provide us with some insights as to the lifetimes and chemical behavior of the potential 1,3-diradicals that are derived from the spirocyclopropane-substituted azoalkanes (**3a–c**).[8] Presently we report the details of this investigation.

Results

Starting Materials. Spironorbornenes 1a–c. The preparation of the spironorbornene **1a** by cycloaddition of 1,2-dibromoethene to spiro[2.4]hepta-4,6-diene and subsequent hydrogenation and debromination (eq 4) was previously described.[9] Alternatively, spironorbornene **1a**



(4)

1a, R + R = $-(CH_2)_2-$/R' = H
1b, R = H/R' + R' = $-(CH_2)_2-$
1c, R + R = R' + R' = $-(CH_2)_2-$

was prepared by the use of 1,2-dichloroethene as dienophile, followed by dechlorination with sodium in liquid ammonia (eq 4). Both, spironorbornenes **1b,c** were prepared by cycloaddition of methylenecyclopropane[10] to cyclopentadiene and spiro[2.4]hepta-4,6-diene, respectively (eq 4). In the meantime the preparation of **1b** by cyclopropanation of 5-methylenenorbornene was reported by Zefirov et al.[11]

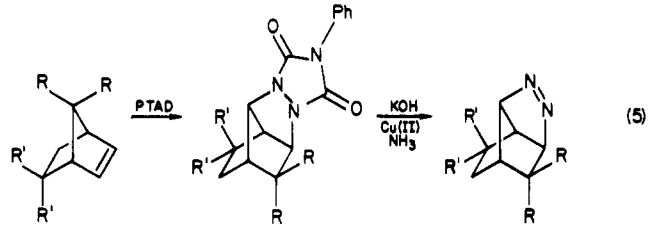
Table I. Selected Chemical Shifts of Norbornene[a] and Its Spiro Derivatives 1a–c

atom	chemical shifts, δ[b] norbornene[a]	1a	1b	1c
1-H	2.84	2.05	2.01	1.35
4-H	2.84	2.05	2.90	2.15
C-1	42.0	47.29	50.67	55.55
C-3	24.8[c]	25.23[c]	38.10	38.78
C-4	42.0	47.29	43.76	49.30

[a] Given for comparison (cf. ref 13). [b] In $CDCl_3$ and Me_4Si as internal standard; proton shifts at 400 or 90 MHz and carbon shifts at 100 MHz. [c] In contrast to the nomenclature rules, the methylene group is numbered as C-3 to have the same numbering for all norbornenes.

The 400-MHz ^1H NMR spectrum of spironorbornene **1b** supports its structure. Decoupling experiments allowed a definitive assignment of the signals (cf. Experimental Section). The ^1H NMR spectrum of dispironorbornene **1c** is less complex because of the spirocyclopropane substitution at the 7-position. The signals of the C-3 methylene protons appear as an AB system (J_{gem} = 10.2 Hz, δ_A = 1.25, δ_B = 1.90) of which the B part is split into a doublet of doublets by coupling with the neighboring bridgehead proton ($J_{3x,4}$ = 3.7 Hz). An appreciable anisotropic effect of the spirocyclopropane ring[12] can be observed, which shifts the neighboring bridgehead protons 0.7–0.9 ppm upfield. In contrast, in the ^{13}C NMR such cyclopropane substitution causes a downfield shift of the neighboring methylene and bridgehead carbons of ca. 13 and 5–8 ppm, respectively (Table I). Klessinger[14] reported a similar effect for the cyclopropane ring.

Urazoles 2a–c. Analogous to the cycloaddition of 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) with norbornene **1a**, which led to the urazole **2a**,[15] the substrates **1b,c** afforded the urazoles **2b,c**, respectively (eq 5).



(5)

1 2 3

Structure assignment of the urazoles **2b,c** rests on X-ray analysis (see the paragraph at the end of the paper about supplementary material). It is of import to note that the spirocyclopropane ring in the ethano bridge of the norbornenes **1b,c** directs the attack of the electrophilic PTAD to give mainly, if not exclusively, the urazoles **2b,c**. The relative low yields of urazole products are due to the formation of substantial amounts of high molecular weight materials, a characteristic feature of these sluggish PTAD cycloadditions. Therefore, the crude reaction mixture could not be searched for isomeric urazoles by means of ^1H NMR. However, after passing through a short silica

(6) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. (b) Bernlöhr, W.; Beckhaus, H.-D.; Peters, K.; von Schnering, H. G.; Rüchardt, C. *Chem. Ber.* **1984**, *117*, 1013. (c) Bernlöhr, W.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1984**, *117*, 1026.
(7) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860.
(8) (a) Adam, W.; De Lucchi, O. *Angew. Chem.* **1980**, *92*, 815. (b) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.
(9) Alder, K.; Ache, H.-J.; Flock, F. H. *Chem. Ber.* **1960**, *93*, 1888.
(10) Köster, R.; Arora, S.; Binger, P. *Synthesis* **1971**, 322.
(11) Kazimirchik, I. V.; Lukin, K. A.; Bebikh, G. F.; Zefirov, N. S. *Zh. Org. Khim.* **1983**, *19*, 105.
(12) Günther, H. "NMR-Spektroskopie"; Thieme Verlag: Stuttgart, 1973.
(13) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. "Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden"; Springer Verlag: Berlin, 1976.
(14) Asmus, P.; Klessinger, M. *Liebigs Ann. Chem.* **1975**, 2169.
(15) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.

Table II. Selected Proton Resonances and Coupling Constants of the Urazoles 2a–c[a] and Azoalkanes 3a–c[b]

	chemical shifts, δ, and coupling constants (J)[c]					
H	2a	2b	2c	3a	3b	3c
1	2.15	2.75	2.25	1.49	2.02	1.61
7	2.90	2.10	2.35	2.38	1.71	1.85
3	3.80 (d, 2.0)	4.45 (dd, 5.1, 2.1)	3.85 (d, 1.9)	4.10 (dd, 2.3, 1.0)	4.94 (ddd, 4.0, 2.5, 0.9)	4.17 (dd, 2.2, 1.0)
6	4.40 (t′, 2.1)	4.60 (t′, 2.2)	4.65 (t′, 2.2)	5.15 (t′, ~2.3)	5.27 (t′, ~2.0)	5.40 (t′, 2.2)

[a] At 90 MHz in $CDCl_3$ and Me_4Si as internal standard. [b] At 400 MHz in $CDCl_3$ and Me_4Si as internal standard. [c] Pattern and coupling constants in parenthesis.

gel column to remove the high molecular weight materials, no isomeric urazoles could be detected by 400-MHz ^1H NMR.

The IR spectra of the urazoles **2a–c** show the expected carbonyl frequencies at 1720 and 1760–1790 cm^{-1}. Selected proton chemical shifts and coupling constants are given in Table II. Again the shielding effect of the cyclopropane ring is clearly evident. The chemical shifts and coupling constants are characteristic for the bridgehead protons adjacent to the nitrogen atoms. For example, the signals of the 6-H protons appear as pseudotriplets (t′) at δ 4.4–4.7 due to similar coupling constants (ca. 2 Hz) with the 1-H and 7-H protons. The 3-H proton also couples with the 7-H proton (ca. 2 Hz) and in the case of urazole **2b** with the 2-*endo*-H (5.1 Hz). As expected for these unsymmetrical structures, the ^{13}C NMR spectra (cf. Experimental Section) show all the carbon atoms as distinct signals, but some were difficult to assign with certainty.

Azoalkanes 3a–c. The azoalkanes were prepared in 50–80% yield from the corresponding urazoles **2a–c** by basic hydrolysis with potassium hydroxide in isopropyl alcohol and subsequent oxidation with cupric chloride[15,16] (eq 5). They possess a characteristic, camphorlike odor.

The spectral data are in accord with the proposed structures. For example, the UV absorptions appear in the 340–360-nm region with log ε values between 2.2 and 2.5. Selected proton chemical shifts are summarized in Table II. The 6-H bridgehead protons give characteristic broad pseudotriplets (t′) at δ 5.1–5.4 due to similar coupling constants (ca. 2.2 Hz) with the 1-H and 7-H protons. The signals of the 3-H protons appear at δ 4.94 for azoalkane **3b** and at δ 4.1–4.2 for azoalkanes **3a,c** due to the shielding effect of the neighboring spirocyclopropane ring. While for azoalkanes **3a,c** the signal of the 3-H proton consists of a doublet of doublets by coupling with 6-H and 7-H, in the case of azoalkane **3b** it exhibits additional coupling with the 2-*endo*-H. Furthermore, a remarkable upfield anisotropic effect (Δδ ~1) by the azo group can be observed for the 2-*exo*-H. For the azoalkane **3b** this proton resonates at δ 0.77, while for the corresponding urazole **2b** it appears at δ 1.7. Dreiding models show clearly that the 2-*exo*-H is located above the azo group.

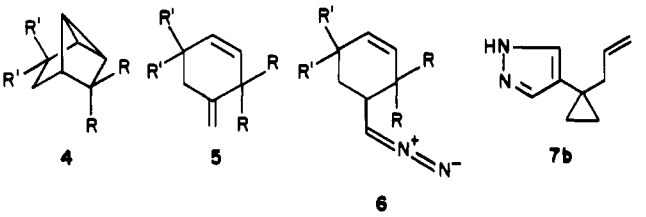
The ^{13}C NMR exhibit distinct resonances for each carbon atom. Due to the azo linkage and the spirocyclopropane ring, which cause significant downfield shifts, a definitive assignment of the carbon signals can be made. Selected characteristic carbon resonances are given in Table III.

Characterization of Products. Tricycloalkanes 4a–c. The tricycloalkanes **4a–c** were obtained in the direct and benzophenone-sensitized photolyses and vacuum flash thermolysis of the azoalkanes **3a–c** and isolated by preparative GC. The elemental composition and IR and MS data were consistent with the proposed structures, but identification rests mainly on the ^{13}C and ^1H NMR spectral assignments.

Table III. Selected Carbon Resonances of the Azoalkanes 3a–c

		chemical shifts, δ		
C	pattern	3a	3b	3c
1	d	41.56	34.24	43.31
3	d	86.96 or 87.66	80.90	87.10 or 88.00
6	d		85.85	
7	d	57.84	63.90	66.09
9	t	30.85	43.10	41.52

[a] At 100 MHz in $CDCl_3$ and Me_4Si as internal standard.



According to their highly unsymmetrical structure, each carbon atom appears as a distinct resonance and is located in the expected chemical shift range. In the off-resonance spectrum it was difficult to assign the individual carbon atoms with certainty. For this reason fully coupled spectra were run to determine the actual carbon–hydrogen coupling constants. For convenience, the results for the skeleton carbon atoms are collected in Table IV. The spirocyclopropane carbon atoms were not considered in this analysis; besides, it was difficult to differentiate the carbon atoms of a particular spirocyclopropane moiety.

As expected,[12,13] the cyclopropane carbons C-1 and C-7 stand out with the largest J_{C-H} values, ranging between 175–190 Hz. These carbons are contained both in the cyclopropane and cyclobutane rings of the bicyclo[2.1.0]-pentane fragment. Furthermore, the fact that C-7 in spirotricycloalkanes **4a,c** is shifted to lower field due to spirocyclopropane substitution at C-6, allows a definitive assignment. The C-2 carbon exhibits carbon–hydrogen J values ranging between 161–163 Hz, which is reasonable for a normal cyclopropane carbon.[12,13] The remaining doublet resonance must correspond to the bridgehead carbon C-5, showing carbon–hydrogen J values in the range of 144–150 Hz, which compares well with the 142-Hz value found in norbornene.[12] Finally, the triplet carbon resonance of C-4 could be easily distinguished from the spirocyclopropanemethylenes in view of its low carbon–hydrogen J values ranging between 127–131 Hz.

The ^1H NMR spectra of the tricycloalkanes **4a–c** were all rather complex even at 400 MHz. Extensive decoupling experiments and computer simulation with the LAOCOON III program[17] were essential in all cases. The optimized results of selected skeleton protons are given in Table V.

(16) (a) Heyman, M.; Bandurco, V. T.; Snyder, J. P. *J. Chem. Soc. D* **1971**, 297. (b) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5845.

(17) Bothner-By, A. A.; Castellano, S. in DeTar, D. F. "Computer Programs for Chemistry"; A. W. Benjamin: New York, 1968; Vol. 1.

Table IV. Selected Carbon Resonances and CH Coupling Constants of the Tricycloalkanes 4a–c[a]

		4a		4b		4c	
C	pattern	δ	J, Hz	δ	J, Hz	δ	J, Hz
1	d	24.46	189.1	27.87	184.0	26.56	183.5
2	d	25.30	161.0	30.32	161.9	32.39	163.0
3	t	24.16	126.8	b	b	b	b
4	t	32.92	126.8	46.20	130.7	43.67	130.0
5	d	45.35	149.9	39.34	147.8	46.22	144.5
6	t	b	b	27.95	135.7	b	b
7	d	22.66	175.0	15.61	175.0	23.17	178.5

[a] At 100 MHz in $CDCl_3$ and Me_4Si as internal standard. [b] The quaternary spirocarbons have not been considered here (cf. Experimental Section).

Table V. Selected Proton Resonances of Tricycloalkanes 4a–c[a]

	chemical shifts, δ[b]		
H	4a	4b	4c
1	2.41	2.37	2.61
2	1.55	0.96	1.10
4-*exo*	1.59	2.05	2.03
4-*endo*	1.46	1.13	1.12
5	2.17	2.50	2.23
7	1.26	1.41	1.30

[a] At 400 MHz in $CDCl_3$ and Me_4Si as internal standard. [b] Values optimized by computer simulation with the LAOCOON III program; for coupling constants cf. Experimental Section.

The spirocyclopropane protons were well separated from the remaining protons, falling into the δ 0.0–0.8 range, and were not specifically considered. Again, the up field shift caused by the adjacent spirocyclopropane ring manifests itself for the 2-H protons in the case of tricycloalkanes **4b,c** and for the 5-H protons in the case of **4a,c**. This anisotropic effect is also visible for the 7-H proton in the case of the tricycloalkanes **4a,c**, but of reduced magnitude. Furthermore, while in tricycloalkane **4a** the 4-exo and 4-endo protons are located nearly at the same chemical shifts, δ 1.59 and 1.46, respectively, a juxtapposed spirocyclopropane ring as in the tricycloalkanes **4b,c** causes a large down field shift of the 4-exo proton and a large up field shift of the 4-endo proton.

The relatively large coupling constant $J_{5,6x}$ = 8.0 Hz stands out. In view of the bicyclo[2.1.0]pentane moiety, these two protons are obliged to be essentially cis to one another. As a further consequence, the coupling between the 3-exo and 4-endo protons is rather small (~1 Hz), because the dihedral angle between these protons is nearly 90° (cf. Dreiding models).

Methylenecyclohexenes 5a–c. The methylenecyclohexenes **5a–c** were obtained in low yields (<10%) in the direct photolyses of the azoalkanes **3a–c**. They were isolated by means of preparative GC. Not enough material could be collected for elemental analyses, but the detection of the parent peak in the GC–MS[18] confirmed the correct compositions C_9H_{12} and $C_{11}H_{14}$ for **5a,b** and **5c**, respectively. By means of GC–FTIR analysis[19] on the photolysate, the *exo*-methylene group was detected at 1653 and 1655 cm^{-1} respectively for the methylenecyclohexenes **5a** and **5b**. In the case of **5c**, the concentration of the photolysate was too low to observe the characteristic *exo*-methylene band. Unequivocal structure elucidation of the methylenecyclohexenes **5a–c** rests on ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra. The olefinic protons were especially helpful in this assignment, although computer simulation[17] was essential. The endocyclic olefinic protons give AB patterns, further coupled to the adjacent allylic protons. The δ_A values are located at 5.70, 5.11, and 5.01 ppm and the δ_B values at 4.99, 5.63, and 5.13 ppm respectively for the methylenecyclohexenes **5a–c**, with typical cis coupling (J_{AB}) of 9.5–9.8 Hz.[12,13] The exocyclic olefinic protons come as distinct complex multiplets in the expected δ 4.4–4.8 range; however, the signals could not be assigned with certainty to the individual protons. The ^{13}C resonances appeared at the expected δ values and were assigned on the basis of their multiplicities and chemical shifts (cf. Experimental Section).

The suspicion[1,4,20] that the methylenecyclohexenes **5a–c** were secondary photoproducts of the intermediary diazoalkanes **6a–c** could be verified by conducting the direct photolysis with the 333-nm UV line of the 18-W argon ion laser at 50 °C. The resulting yellow photolysates exhibited weak visible absorption in the 460-nm region and sharp bands at 2060–2070 cm^{-1} in the IR spectrum, both characteristic of the diazo group.

Pyrazole 7b. As already stated, the vacuum flash thermolysis of the azoalkanes **3a–c** afforded the tricycloalkanes **4** as main products, except azoalkane **3b** for which the major product was the pyrazole **7b**. Elemental analysis confirmed the $C_9H_{12}N_2$ composition and the MS the appropriate parent peak. The NH group was clearly visible in the IR spectrum at 3150 cm^{-1} and in the ^1H NMR (400 MHz) at δ 9.70. The aromatic protons of the pyrazole ring appear as a singlet at δ 7.39 The allyl group protons are observed as complex multiplets, which could be assigned by computer simulation.[17] Typical values for δ and J were obtained (cf. Experimental Section). The protons of the cyclopropane ring appear as a singlet at δ 0.73. The ^{13}C NMR (100 MHz) is consistent with the pyrazole structure.

Quantitative Product Analysis. The product compositions of the direct and benzophenone-sensitized photolyses and the vacuum flash thermolyses were determined by GC. The quantitative results are summarized in Table VI. Mass balance was assessed by means of quantitative ^1H NMR analysis with electronic integration against an internal standard. As the results in Table VI show (last column), a substantial product deficit was registered; however, at least 98% (relative yield) of the volatile products were characterized. Presumably undefined high molecular weight products, undetected by GC and ^1H NMR, were formed. Indeed, control experiments showed that the tricycloalkanes **4a–c** were unstable toward the vacuum flash thermolysis conditions of the azoalkanes **3a–c** since only ca. 70% of **4a–c** could be recovered. The tricycloalkanes **4a–c** were stable toward the direct pho-

(18) We thank Prof. Schreier and Dr. Idstein, Institute of Pharmacy (University of Würzburg), for running the GC–mass spectra for us and Dr. Lange's staff (University of Würzburg) for measuring the mass spectra.

(19) We thank Prof. H. Rupprecht and his staff, Institute of Pharmacy (University of Regensburg), for measuring the IR spectra of the methylenecyclohexenes **5a,c** and Dr. H. A. Witek, Bio-Rad Laboratories GmbH, Section Digilab (München), for running the GC–FTIR spectrum on the methylenecyclohexene **5b** for us.

(20) Regitz, M. "Diazoalkane: Eigenschaften und Synthesen"; Georg Thieme Verlag: Stuttgart, 1977; Chapter 8.5 and references cited therein.

Table VI. Product Distribution of Denitrogenation of Azoalkanes 3a-c

azoalkane	conditn	convern, (%)	relative yields, %[a] tricycloalkanes 4a-c	relative yields, %[a] methylene-cyclohexenes 5a-c	absolute yield, %[b]
3a	VFT (ca. 400 °C (20 torr))	100	>99	trace	70–80
	$h\nu$, 4 °C[c,d]	100	97	3	82
	$h\nu$, 30 °C[c,e]	90	94	6	
	$h\nu$, Ph_2CO, 30 °C[d,f,g]	65	100		90
3b	VFT (ca. 380 °C (20 torr))	100	22[l]		80
	$h\nu$, 4 °C[c,d]	100	>99	trace	81
	$h\nu$, 30 °C[c,h]	95	99	1	
	$h\nu$, 110 °C[c,h]	100	94	6	
	$h\nu$, Ph_2CO, 30 °C[d,f,i]	15	100		92
3c	VFT (ca. 350 °C (20 torr))	100	>99	trace	65–75
	$h\nu$, 4 °C[c,d]	100	99	1	79
	$h\nu$, 30 °C[c,j]	75	97	3	
	$h\nu$, 70 °C[c,j]	60	93	7	
	$h\nu$, 110 °C[c,j]	65	91	9	
	$h\nu$, Ph_2CO, 30 °C[d,f,k]	65	100		95

[a] Determined by CGC on 50-m OV-101, 50-m Apiezon L, or 50-m Carbowax columns, operated at injector and detector temperatures of 200 °C, column temperatures of 110 °C for azoalkane **3a,b** and 130 °C for **3c**, and a nitrogen pressure of 1.0 kg/cm^2; product yields are within ca. 10% of the stated values for the minor products and within ca. 3% for the major products and are normalized to 100% conversion; in all cases (<2%) several unidentified volatile products were observed. [b] Absolute yields based on 100% conversion, determined by ^{1}H NMR analysis (cf. Experimental Section). [c] Degassed benzene solutions by bubbling through nitrogen (ca. 20 min) or by applying the freeze–pump–thaw technique; Rayonet irradiation at 350 nm. [d] Photolysis was carried out on preparative scale (cf. Experimental Section) by laser irradiation. [e] [**3a**] = 0.0103 M in benzene. [f] Same conditions as in footnote c but in the presence of benzophenone. [g] [**3a**] = 0.0052 M and [Ph_2CO] = 0.060 M in benzene. [h] [**3b**] = 0.0098 M in benzene. [i] [**3b**] = 0.0098 M and [Ph_2CO] = 0.100 M in benzene. [j] [**3c**] = 0.0150 M in benzene. [k] [**3c**] = 0.0065 M and [Ph_2CO] = 0.065 M in benzene. [l] Major product was pyrazole **7b** (78%).

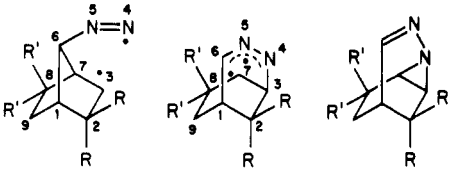
tolysis conditions in the Rayonet as well as laser irradiation. Since in the benzophenone-sensitized photolyses the tricycloalkanes **4a–c** were formed essentially quantitatively, control experiments on the photostability under these conditions were dispensed with.

Of interest is the fact that in the direct photolyses of the azoalkanes **3a–c**, either Rayonet or laser irradiation, the tricycloalkanes **4a–c** (major products) and the methylenecyclohexenes **5a–c** (minor products) were formed. However, only in the laser irradiations was it possible to detect the transient diazoalkanes **6a–c**, the precursors to the methylenecyclohexenes **5a–c**. Due to the narrow line width (<0.1 nm) and the high intensity in the laser irradiations compared to traditional light sources, sufficient diazoalkane accumulates for detection. In this context it is significant to note (Table VI) that the amount of the dienes **5a–c** increased with increasing temperature of the direct photolysis. On the other hand, the benzophenone-sensitized photolysis gave only the tricycloalkanes. While these were also the exclusive products in the vacuum flash thermolysis, in the case of the azoalkane **3b** the major product was the pyrazole **7b**, but no diene **5b** was formed.

Discussion

A number of interesting facts emerge from the quantitative product data of Table VI that require mechanistic rationalization. First of all, a good parallel exists between the behavior of the parent azoalkane derived from norbornene (eq 1) and the spirocyclopropane-substituted azoalkanes **3**: (a) Triplet-sensitized photolysis gives exclusively the respective tricycloalkanes **4**. (b) Also in the thermolysis (VFT) the tricycloalkanes **4** are formed essentially exclusively (traces of the methylenecyclohexenes cannot be excluded), except with azoalkane **3b** for which the pyrazole **7b** is the preferred product. (c) Direct photolysis leads primarily also to the respective tricycloalkanes **4** and additionally small (<10%) amounts of the corresponding methylenecyclohexenes **5** but no vinylcyclopentenes are formed. (d) The relative proportion of methylenecyclohexenes **5** increases with increasing temperature. (e) Although no spirocyclopropane ring-opened products could be detected, qualitatively speaking the proportion of methylenecyclohexenes **5** increases through spirocyclopropanation at the 2-position, i.e., **5a** > **5c** > **5b**. (f) Diazoalkanes **6** have been detected spectroscopically in the laser photolyses of all three azoalkanes **3** and shown to afford the methylenecyclohexenes **5** on prolonged photolyses.

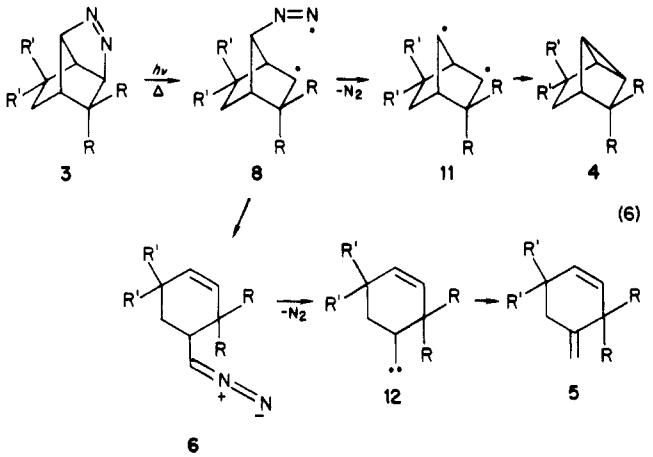
Of the four possible modes that were a priori considered of cleaving the pyrazole ring in the electronically excited azoalkanes **3**, the ones involving initial C_6–N_5 and C_3–C_7 breakage can be immediately discarded on the grounds that no vinylcyclopentene products were detected. This leaves us with the initial C_3–N_4 cleavage leading to the diazenyl-type diradical **8** or the initial C_6–C_7 cleavage affording the hydrazonyl-type diradical **9** as mechanistic alternatives. The advantage of the diazenyl diradical **8** derives from the fact that it can serve as a common intermediate for both the formation of tricycloalkanes **4** via loss of nitrogen by means of C_6–N_5 cleavage and generation of diazoalkanes **6** and eventually methylenecyclohexenes **5** by means of C_6–C_7 fragmentation. This would constitute a convenient product branching step, which is required by our experimental data. Since there exists no reasonable channel for the hydrazonyl-type diradicals **9** to generate the tricycloalkanes **4** (main products), its intervention as intermediate would require to postulate product branching directly in the excited azoalkanes **3**, with the hydrazonyl diradicals **9** leading to the diazoalkanes **6** and eventually methylenecyclohexenes **5** (minor products) and the diazenyl diradical **8** affording the tricycloalkanes **4** (major products). Either one single excited state of the azoalkane partitions between these two possible product channels or



8 9 10

two distinct excited states serve as precursors to the diradicals 8 and 9. Speaking against the latter alternative is the fact that laser irradiation (333.6 nm) and Rayonet irradiation (300–350 nm) did not alter the proportion of tricycloalkane 4 and methylenecyclohexene 5 products. It appears that two closely lying excited states of the azoalkanes 3 are not involved in these photolyses. Furthermore, the hydrazonyl diradicals 9 would be expected to afford azirane-type products 10,[3c,21] which were not observed. Last but not least, spirocyclopropanation at the 8-position in diradicals 9 would be expected to promote diazoalkane 6 formation through cyclopropylcarbinyl stabilization.[6b,c] However, quite the contrary is observed experimentally (item e), in that cyclopropanation at the 2-position appears to manifest itself, which is consistent with preferred diazenyl diradical 8 formation.

In analogy to the azoalkane in eq 2,[4b] we propose that the initial step in the photochemical and thermal denitrogenation of azoalkanes 3 involves C_3–N_4 cleavage to give the diazenyl diradicals 8 (eq 6). For this tritopic process[22]



the Salem diagram[23] (cf. Figure 1 in ref 4b) is informative. Therefore, in analogy to the model case, thermal activation leads to a $D_{\sigma,\sigma}$-type singlet diazenyl diradical 8 which prefers to denitrogenate into tricycloalkane 4 via the 1,3-diradical 11. Only for the azoalkane **3b** with spirocyclopropanation at the 8-position does Diels–Alder retrocyclization into the pyrazole **7b** predominate over diazenyl diradical 8 formation.

The triplet-sensitized photolysis of the azoalkanes 3 affords initially a $D_{\sigma,\pi}$-type triplet diazenyl diradical 8. Subsequent direct denitrogenation leads to the triplet 1,3-diradical 11, which via intersystem crossing[24] cyclizes into the tricycloalkane 4 (eq 6). Alternatively, during C_3–N_4 rupture in the triplet n,π*-state of the azoalkane 3 a jump onto the triplet n,σ*-surface leading to the $D_{\sigma,\sigma}$-type triplet diazenyl diradical 8 takes place.

Finally, in the direct photolysis the singlet n,π*-state of the azoalkane 3 affords the $D_{\sigma,\pi}$-type singlet diazenyl diradical 8, which on C_6–C_7 rupture produces the diazoalkane 6. The observed activation energy for this cleavage is reasonable on energy grounds. On subsequent denitrogenation the carbene intermediate 12 results, which serves as immediate precursor to the methylenecyclohexene 5. Alternatively, crossover between the singlet n,π*- and n,σ*-surfaces generates the $D_{\sigma,\sigma}$-type singlet diazenyl diradical 8 and on subsequent denitrogenation the tricycloalkane 4 is obtained via the intermediary 1,3-diradical 11.

The orbital pictures in Figure 1 (cf. ref 4b) for the diazenyl diradicals 8 attempt to account for the preferred nitrogen loss vs. preferred diazoalkane formation. Thus, for the $D_{\sigma,\sigma}$-diradical the C_6–N_5 bond is optimally aligned for loss of ground-state nitrogen leading to the 1,3-diradical 11, while for the $D_{\sigma,\pi}$-diradical such cleavage would generate electronically excited nitrogen. Instead, the C_6–C_7 bond can be positioned for preferential cleavage into the diazoalkane.

Postulating that on thermolysis and photolysis of the azoalkanes 3 the diazenyl diradical 8 figures as a common intermediate provides an inherently consistent mechanism for the decomposition of these azoalkanes. Such stepwise one-bond cleavages are becoming accepted as general fact in thermal denitrogenations of azoalkanes.[25] Whether this is the case in photochemical decompositions[23] requires further experimentation. For the azoalkanes 3 investigated here, however, the proposed stepwise one-bond cleavage constitutes a convenient mechanistic construct, provided that differences in the spin multiplicities (singlet vs. triplet) and in the electronic configurations ($D_{\sigma,\sigma}$ vs. $D_{\sigma,\pi}$) are considered for the intermediary diazenyl diradicals.

Competing with the proposed stepwise cleavage in the thermolysis of azoalkanes to the diazenyl diradicals are concerted cycloreversions such as nitrogen extrusions,[26a,b] pyrazole formation,[26c–f] and even cleavage into diazoalkane.[2,3] Apparently delicate energy differences control which course of action prevails. For example, in the present study the azolkane **3b** prefers Diels–Alder retrocleavage into pyrazole **7b**, while the azoalkanes **3a,c** traverse exclusively the stepwise route via the diazenyl diradicals. On one hand the spirocyclopropane at the C-2 position discourages the Diels–Alder retrocleavage because a methylenecyclopropane moiety would result; on the other hand, cyclopropylcarbinyl stabilization[6b,c] promotes diazenyl diradical formation. Consequently, spirocyclopropane substitution has served as a useful mechanistic probe in the denitrogenation of norbornene-derived azoalkanes.

Experimental Section

General Methods. IR spectra were obtained on the following instruments: Beckman Acculab 4, Perkin-Elmer Infrared-Photometer 580 with Interdata Calculator 6/16,[19] Bio-Rad Digilab FTS-IR coupled with capillary GC.[19] UV spectra were obtained on a Varian Cary 17. ^{1}H NMR data were obtained on the following instruments: Hitachi-Perkin-Elmer R-24 B (60 MHz), Varian EM-390 (90 MHz), Bruker WM-400 (400 MHz). ^{13}C NMR data were obtained by using a Bruker WM-400 (100 MHz).[27] Chemical shifts are given in δ relative to tetramethylsilane or chloroform for protons and deuteriochloroform for carbons. Coupling con-

(21) (a) Adam, W.; De Lucchi, O. *J. Am. Chem. Soc.* **1980**, *102*, 2109. (b) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 400. (c) Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4133.

(22) (a) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (b) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41. (c) Devaquet, A. *Pure Appl. Chem.* **1975**, *41*, 455.

(23) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639.

(24) (a) Doubleday, Jr., C.; McIver, Jr., J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. (b) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

(25) (a) Hiberty, P. C.; Jean, Y. *J. Am. Chem. Soc.* **1979**, *101*, 2538. (b) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529. (c) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7102. (d) Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 6849.

(26) (a) Sheridan, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5140. (b) Askani, R.; Hornykiewytsch, T.; Müller, K. M. *Tetrahedron Lett.* **1983**, *24*, 5513. (c) Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4133. (d) Adam, W.; Carballeira, N.; De Lucchi, O. *J. Am. Chem. Soc.* **1981**, *103*, 6406. (e) Hinshaw, J. C.; Allred, E. L. *Chem. Commun.* **1969**, 72. (f) Tsuruta, H.; Kurabayashi, K.; Mukai, T. *J. Am. Chem. Soc.* **1968**, *90*, 7167.

(27) We thank Dr. Scheutzow and his staff (University of Würzburg) for measuring the 400-MHz ^{1}H and 100-MHz ^{13}C spectra.

stants are given as absolute values. Mass spectra (MS) (70 eV) were obtained on the following instruments: Varian MAT CH 7, Finnigan MAT 44 coupled with capillary GC.[18] Melting points were taken on a Reichert Thermovar Kofler apparatus and are uncorrected. Combustion analyses for elemental composition were run in-house or by Professor G. Maier's staff at the Institute of Organic Chemistry, University of Giessen. Thin-layer chromatography (TLC) were obtained on Polygram SIL/G/UV (40 × 80 mm), Machery and Nagel. Column chromatography utilized silica gel 70–230 mesh ASTM (activity III). Analytical gas chromatography was performed on Carlo Erba Strumentazione Model 2900 Fractovap Series or Model 4100 instruments equipped with capillary columns and an FID. Preparative gas chromatography were performed on Varian Aerograph 920 or Carlo Erba Strumentazione Model 4200 instruments. The photolyses were run in a Rayonet Photochemical Reactor (75W, 250V), Southern New England Ultraviolet Company, equipped with 350-nm lamps or in a Coherent CR-18 Supergraphite Argon Ion Laser with the 334-, 351-, and 364-nm lines. Commercial reagents and solvents were purchased from standard chemical suppliers and used as such, if not mentioned otherwise. Known compounds were prepared according to literature procedures. Cycloadditions were done in a 80-mL steel autoclave, Carl Roth GmbH and Co., Karlsruhe, FRG. Volatile, liquid compounds were purified by preparative gas chromatography before combustion and MS analysis. Reaction mixtures after aqueous workup were dried over $MgSO_4$ or Na_2SO_4.

Spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (1a). A sample of 8.50 g (45.0 mmol) of 5,6-dichlorospiro(bicyclo[2.2.1]-hept-2-ene-7,1′-cyclopropane)[28] in 10 mL of *n*-pentane was added dropwise to a solution of 6.50 g (283 mmol) of sodium in 100 mL of liquid ammonia at −78 °C while stirring mechanically. After complete addition, the mixture was stirred for an additional 30 min, ca. 10 mL of water carefully added, followed by ca. 10 mL of *n*-pentane, and the solution was warmed to 20 °C. After evaporation of most of the ammonia, the layers were separated and the aqueous layer was extracted with *n*-pentane (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried, and concentrated by distillation over a 20-cm Vigreux column. Fractionation of the residue at 40 torr afforded 2.90 g (54%) of a colorless oil: bp 45–50 °C (40 torr) [lit.[9] bp 63 °C (60 torr)]; IR (CCl_4) 3140, 3060, 2970, 2900, 2870, 1425, 1335, 1005 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.1–0.6 (m, 4 H, 2′-H, 3′-H), 0.9–1.1 (m, 2 H), 1.4–1.9 (m, 2 H), 2.05 (mc, 2 H, 1-H, 4-H), 6.0 (pseudo t, J = 1.9 Hz, 2 H, 2-H, 3-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.03 (t), 7.70 (t), 25.23 (t, C-5, C-6), 43.89 (s, C-7), 47.29 (d, C-1, C-4), 135.46 (d, C-2, C-3).

Spiro(bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane) (1b). A mixture of 9.30 g (0.171 mol) of methylenecyclopropane,[10] 14.0 g (0.212 mol) of cyclopentadiene, and ca. 2 mg of hydroquinone was heated in an autoclave at 190 °C for 14 h. Distillation over a 15-cm Vigreux column yielded 8.00 g (39%) of a colorless oil: bp 34 °C (20 torr); IR (neat) 3150, 3070, 3000, 2980, 2950, 2910, 2870, 1570, 1340, 1050, 1020, 720, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.25–0.60 (m, 4 H, 2′-H, 3′-H), 1.11 (dd, $J_{3n,3x}$ = 10.8, $J_{3n,7a}$ = 2.5 Hz, 1 H, 3-*endo*-H), 1.50 (dm, $J_{7a,7s}$ = 7.2, $J_{7a,1}$ = 2.0, $J_{7a,4}$ = 2.0 Hz, 1 H, 7-*anti*-H), 1.68 (dm, 1 H, 7-*syn*-H), 1.70 (dd, $J_{3x,4}$ = 3.5 Hz, 1 H, 3-*exo*-H), 2.01 (m, 1 H, 1-H), 2.90 (m, 1 H, 4-H), 6.14 (dd, $J_{6,5}$ = 5.6, $J_{6,1}$ = 2.8 Hz, 1 H, 6-H), 6.18 (dd, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.64 (t), 11.82 (t), 23.44 (s, C-2), 38.10 (t, C-3), 43.76 (d, C-4), 49.68 (t, C-7), 50.67 (d, C-1), 135.42 (d), 136.57 (d); MS (70 eV), *m/e* 120 (11%, M^+), 105 (30), 91 (41), 66 (100). Anal. C_9H_{12} (120.2). Calcd: C, 89.94; H, 10.06. Found: C, 89.87; H, 10.01.

Dispiro(cyclopropane-1,2′-bicyclo[2.2.1]hept-5′-ene-7′,1″-cyclopropane) (1c). A sample of 8.00 g (87.0 mmol) of spiro-[2.4]hepta-4,6-diene,[9] 4.00 g (74.1 mol) of methylenecyclopropane, and ca. 2 mg of hydroquinone were heated in an autoclave at 190 °C for 17 h. The crude mixture was concentrated by rotoevaporation at 0 °C and 20 torr. Distillation of the residue afforded 3.10 g (29%) of a colorless oil (bp 64–65 °C (20 torr)), which contained ca. 5% dibromoethane as impurity: IR (neat) 3135, 3070, 3000, 2970, 2940, 2930, 2865, 1575, 1425, 1330, 1010, 925 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.15–0.70 (m, 8 H, 2-H, 3-H, 2″-H, 3″-H), 1.25 (d, $J_{3'n,3'x}$ = 10.2 Hz, 1 H, 3′-*endo*-H), 1.35 (m, 1 H, 1′-H), 1.90 (dd, $J_{3'x,4}$ = 3.7 Hz, 1 H, 3-*exo*-H), 2.15 (m, 1 H, 4′-H), 6.25 (m, 2 H, 5′-H, 6′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 5.66 (t), 7.90 (t), 8.65 (t), 11.27 (t), 24.44 (s, C-2′), 38.78 (t, C-3′), 45.31 (s, C-7′), 49.30 (d, C-4′), 55.55 (d, C-1′), 135.81 (d), 136.42 (d); MS (70 eV), *m/e* 146 (15%, M^+), 145 (27), 131 (67), 117 (83), 105 (52), 91 (100), 77 (55), 65 (50), 51 (52), 39 (58). Anal. $C_{11}H_{14}$ (148.2). Calcd: C, 90.35; H, 9.65. Found: C, 90.35; H, 9.62.

General Procedure for the Preparation of the Urazoles 2a–c. A sample (ca. 20 mmol) of the corresponding olefin and ca. 45 mmol of PTAD were dissolved in ca. 100 mL of methylene chloride and magnetically stirred at 20 °C for 2 days in a stoppered flask. The reaction progress was monitored by ^1H NMR and more PTAD was added until at least 80% of the olefin had reacted. The precipitate of the brown reaction mixture was removed by filtration and the filtrate concentrated by rotoevaporation (40 °C (20 torr)). The residue was chromatographed on silica gel (ca. 20:1 ratio of adsorbant to substrate) eluting with a 10:1 ratio of CH_2Cl_2/EtOAc. The urazoles were purified by repeated recrystallization from ethanol.

***N*-Phenyl-4′,5′-diazaspiro(cyclopropane-1,2′-tricyclo-[4.3.0.0^{3,7}]nonane)-4′,5′-dicarboximide (2a),** 2.44 g (34% lit.[15] 50%), colorless prisms, mp 154–156 °C (lit.[15] mp 184 °C), was obtained from 2.90 g (24.2 mmol) of olefin **1a** and 12.0 g (68.6 mmol) of PTAD: ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.64 (t), 8.11 (t), 19.14 (t), 26.84 (t), 27.60 (s), 47.01 (d), 50.16 (d), 67.02 (d), 69.95 (d), 125.63 (d), 128.21 (d), 129.16 (d), 132.02 (s), 155.75 (s), 156.27 (s).

***N*-Phenyl-4′,5′-diazaspiro(cyclopropane-1,8′-tricyclo-[4.3.0.0^{3,7}]nonane)-4′,5′-dicarboximide (2b),** 2.51 g (20%), colorless prisms, mp 120–121 °C, was obtained from 5.10 g (42.4 mmol) of olefin **1b** and 18.0 g (103 mmol) of PTAD: IR (KBr) 3060, 2990, 2975, 2950, 2920, 2860, 1785, 1715, 1505, 1410, 1275, 1135, 770, 745, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.3–0.8 (m, 4 H, 2-H, 3-H), 1.25 (dd, $J_{9'n,9'x}$ = 12.0, $J_{9'n,1'}$ = 0.9 Hz, 1 H, 9′-*endo*-H), 1.60–2.05 (m, 3 H, 2′-H, 9′-*exo*-H), 2.10 (m, 1 H, 7′-H), 2.75 (m, 1 H, 1′-H), 4.45 (dd, $J_{3',2'n}$ = 5.1, $J_{3',7'}$ = 2.1 Hz, 1 H, 3′-H), 4.60 (pseudo-t, $J_{6',1'} \simeq J_{6',7'} \simeq$ 2.2 Hz, 1 H, 6′-H), 7.3–7.5 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.85 (t), 12.02 (t), 16.35 (s), 32.97 (t), 40.61 (t), 41.13 (d), 55.14 (d), 61.81 (d), 67.52 (d), 125.43 (d), 128.18 (d), 129.11 (d), 131.94 (s), 156.18 (s), 156.75 (s); MS (70 eV), *m/e* 295 (27% M^+), 176 (14), 119 (35), 106 (14), 93 (100), 77 (32), 66 (12). Anal. $C_{17}H_{17}N_3O_2$ (295.3). Calcd: C, 69.14; H, 5.80; N, 14.23. Found: C, 69.23; H, 5.68; N, 14.04.

***N*-Phenyl-4′,5′-diazadispiro(cyclopropane-1,2′-tricyclo-[4.3.0.0^{3,7}]nonane-8′,1″-cyclopropane)-4′,5′-dicarboximide (2c),** 2.50 g (37%), colorless prisms, mp 187–190 °C, was obtained from 3.00 g (20.5 mmol) of olefin **1c** and 16.0 g (91.4 mmol) of PTAD: IR (KBr) 3080, 3040, 3000, 2970, 1770, 1720, 1505, 1495, 1410, 1130 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.4–1.3 (m, 8 H, 2-H, 3-H, 2″-H, 3″-H), 1.45 (dd, $J_{9'n,9'x}$ = 12.0, $J_{9'n,1'}$ = 1.2 Hz, 1 H, 9′-*endo*-H), 1.90 (dd, $J_{9'x,1'}$ = 2.6 Hz, 1 H, 9′-*exo*-H), 2.25 (m, 1 H, 1′-H), 2.35 (m, 1 H, 7′-H), 3.85 (d, $J_{3',2'n}$ = 1.9 Hz, 1 H, 3′-H), 4.65 (pseudo-t, $J_{6',1'} \simeq J_{6',7'} \simeq$ 2.2 Hz, 1 H, 6′-H), 7.25–7.6 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.19 (t), 9.04 (t), 11.03 (t), 12.49 (t), 16.62 (s; C-8′), 28.15 (s; C-2′), 38.19 (t; C-9′), 48.93 (d), 58.33 (d), 67.52 (d), 69.61 (d), 125.60 (d), 128.21 (d), 129.15 (d), 132.03 (s), 155.64 (s), 156.35 (s); MS (70 eV), *m/e* 321 (81%, M^+), 173 (14), 144 (68), 131 (33), 129 (36), 117 (78), 105 (34), 91 (100), 77 (41), 65 (23). Anal. $C_{19}H_{19}N_3O_2$ (321.3). Calcd: C, 71.01; H, 5.96; N, 13.08. Found: C, 70.83; H, 5.87; N, 13.20.

General Procedure for the Preparation of the Azoalkanes 3a–c. A sample (ca. 7 mmol) of the corresponding urazole was added to a solution of ca. 60 mmol or potassium hydroxide in ca. 50 mL of isopropyl alcohol and refluxed under nitrogen for 16 h. The reaction mixture was diluted with ca. 25 mL of ice water and concentrated HCl was added to adjust the pH to 1–2. After warming to 50 °C for ca. 4 min, the mixture was cooled to ca. 5 °C with an ice bath and neutralized with 6 M ammonia to pH 7–8, and 15 mL of an aqueous 3 M copper(II) chloride solution was added. The color of the reaction mixture turned dark red and after some time a red-brown solid precipitated. Precipitation was complete when the supernatent solution was green colored. The solid was collected on a Buchner funnel, washed with ca. 30 mL of water and then dissolved in 200 mL of aqueous 2 N am-

(28) Wilcox, C. F., Jr.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 4258.

monia. The blue solution was extracted with methylene chloride (4 × 60 mL), and the combined organic layers were washed with 2 N HCl (3 × 40 mL) and water (2 × 40 mL), dried, and concentrated by rotoevaporation at 10 °C (25 torr). The residue was purified by bulb-to-bulb distillation and/or sublimation.

4′,5′-Diazaspiro(cyclopropane-1,2′-tricyclo[4.3.0.0^{3,7}]non-4′-ene) (3a), 0.980 g (81%), waxy solid, mp 55–75 °C (sublimed at 120 °C (20 torr)), was obtained from 2.40 g (8.14 mmol) of urazole **2a**: IR (neat) 3080, 2990, 2965, 2915, 2880, 1495, 1255, 1020, 960, 940 cm^{-1}; UV (benzene) λ_{max} (log ϵ) 341 (2.21), 348 nm (2.29); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.2–0.8 (m, 4 H, 2-H, 3-H), 1.49 (mc, 1 H, 1′-H), 1.60–1.70 (m, 2 H), 1.78–1.93 (m, 2 H), 2.38 (m, 1 H, 7′-H), 4.10 (dd, $J_{3',7'}$ = 2.3, $J_{3',6'}$ = 1.0 Hz, 1 H, 3′-H), 5.15 (br t, $J_{6',1'} \cong J_{6',7'} \cong$ 2.3 Hz, 1 H, 6′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 4.00 (t), 7.34 (t), 18.99 (t, C-8′), 24.77 (s, C-2′), 30.85 (t, C-9′), 41.56 (d, C-1′), 57.84 (d, C-7′), 86.96 (d), 87.66 (d); MS (70 eV), *m/e* 120 (0.4%, $M^+ - N_2$), 105 (13), 91 (100), 79 (13), 65 (14), 51 (14), 39 (37). Anal. $C_9H_{12}N_2$ (148.2). Calcd: C, 72.93; H, 8.16; N, 18.90. Found: C, 72.81; H, 8.24; N, 18.32.

4′,5′-Diazaspiro(cyclopropane-1,8′-tricyclo[4.3.0.0^{3,7}]non-4′-ene) (3b), 1.17 g (90%), colorless oil (bulb-to-bulb distillation at ca. 100 °C (0.1 torr)), was obtained from 2.50 g (8.46 mmol) of the urazole **2b**: IR (neat) 3070, 2990, 2950, 2870, 1495, 1465, 1455, 1280, 1065, 1020, 965 cm^{-1}; UV (benzene) λ_{max} (log ϵ) 337 (2.37), 344 nm (2.51); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.26–0.54 (m, 4 H, 2-H, 3-H), 0.77 (dddd, $J_{2'x,2'n}$ = 12.1, $J_{2'x,1'}$ = 6.5, $J_{2'x,9'x}$ = 2.4, $J_{2'x,7'}$ = 1.2 Hz, 1 H, 2′-*exo*-H), 1.49 (dd, $J_{2'n,3'}$ = 4.0 Hz, 1 H, 2′-*endo*-H), 1.55 (dd, $J_{9'n,9'x}$ = 11.6, $J_{9'n,1'} \cong$ 0.6 Hz, 1 H, 9′-*endo*-H), 1.71 (m, 1 H, 7′-H), 2.02 (m, 1 H, 1′-H), 2.13 (d of m, $J_{9'x,1'}$ = 3.6 Hz, 1 H, 9′-*exo*-H), 4.94 (ddd, $J_{3',7'}$ = 2.3, $J_{3',6'}$ = 0.9 Hz, 1 H, 3′-H), 5.27 (br t, $J_{6',1'} \cong J_{6',7'}$ = 2.0 Hz, 1 H, 6′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.04 (t), 11.86 (t), 16.65 (s, C-8′), 28.69 (t, C-2′), 34.24 (d, C-1′), 43.10 (t, C-9′), 63.90 (d, C-7′), 80.90 (d, C-3′), 85.85 (d, C-6′); MS (70 eV), *m/e* 148 (0.5%, M^+), 105 (40), 91 (62), 79 (40), 66 (100), 39 (31). Anal. $C_9H_{12}N_2$ (148.2). Calcd: C, 72.93; H, 8.16; N, 18.90. Found: C, 72.66; H, 8.26; N, 19.10.

4′,5′-Diazadispiro(cyclopropane-1,2′-tricyclo[4.3.0.0^{3,7}]-non-4′-ene-8′,1″-cyclopropane) (3c), 1.00 g (80%), colorless, waxy solid (sublimed at 130° C (20 torr)), mp 50–53 °C, was obtained from 2.30 g (7.17 mmol) of the urazole **2c**: IR (neat) 3075, 3000, 2950, 2930, 2870, 1490, 1455, 1430, 1255, 1025 cm^{-1}; UV (benzene) λ_{max} (log ϵ) 341 (2.12), 349 nm (2.20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.2–1.0 (m, 8 H, 2-H, 3-H, 2″-H, 3″-H), 1.61 (br s, 1 H, 1′-H), 1.64 (dd, $J_{9'n,9'x}$ = 12.0, $J_{9'n,1'}$ = 0.6 Hz, 1 H, 9′-*endo*-H), 1.85 (m, 1 H, 7′-H), 2.10 (dd, $J_{9'x,1'}$ = 2.6 Hz, 1 H, 9′-*exo*-H), 4.17 (dd, $J_{3',7'}$ = 2.2, $J_{3',6'}$ = 1.0 Hz, 1 H, 3′-H), 5.40 (br t, $J_{6',1'} \cong J_{6',7'}$ = 2.2 Hz, 1 H, 6′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 4.85 (t), 8.40 (t), 10.47 (t), 12.34 (t), 16.75 (s, C-8′), 25.51 (s, C-2′), 41.52 (t, C-9′), 43.31 (d, C-1′), 66.09 (d, C-7′), 87.10 (d), 88.00 (d); MS (70 eV), *m/e* 145 (4%, $M^+ - N_2 - H$), 131 (29), 117 (50), 105 (18), 91 (100), 77 (23), 65 (19), 51 (21), 39 (48). Anal. $C_{11}H_{14}N_2$ (174.2). Calcd: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.84; H, 8.05; N, 16.31.

General Procedure for the Preparation of the Tricycloheptanes 4a–c. A solution of ca. 0.4 mmol of the corresponding azoalkane in ca. 1 mL of benzene was deaerated by bubbling a slow stream of nitrogen gas for ca. 30 min through the solution and was irradiated with an argon ion laser with the 334, 351-, and 364-nm lines at ca. 4 °C. The reaction progress was checked by means of capillary GC and ^{1}H NMR and usually all azoalkane was consumed within ca. 20 min. The relative product distribution is given in Table VI. The tricycloheptanes were isolated by preparative GC with a 1.5-m glass column, packed with 10% Carbowax M on Chromosorb, operated at injector, detector, and column temperatures of 200, 200, and 90 (products **4a,b**) or 120 °C (product **4c**), respectively, and a carrier gas pressure (N_2) of 0.4 kg/cm^2.

Spiro(cyclopropane-1,6′-tricyclo[3.2.0.0^{2,7}]heptane) (4a), 37.0 mg (65%), colorless oil, was obtained from 70.0 mg (0.472 mmol) of azoalkane **3a**: IR (neat) 3060, 3035, 2990, 2940, 2900, 2870, 2850, 1305, 1240, 1005, 900, 810, 770, 740, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.03–0.12 (m, 2 H, cyclopropane H), 0.40–0.49 (m, 2 H, cyclopropane H), 1.26 (d of pseudo-t, $J_{7',2'}$ = 5.3, $J_{7',1'}$ = 5.1, $J_{7',5'}$ = 2.2 Hz, 1 H, 7′-H), 1.46 (dd of pseudo-t, $J_{4'n,4'x}$ = 11.7, $J_{4'n,3'n}$ = 7.8, $J_{4'n,5'}$ = 1.1, $J_{4'n,3'x}$ = 1.0 Hz, 1 H, 4′-*endo*-H), 1.55 (pseudo-q, $J_{2',1'}$ = 4.9, $J_{2',3'x}$ = 4.8 Hz, 1 H, 2′-H), 1.59 (m, $J_{4'x,3'x}$ = 10.5, $J_{4'x,3'n}$ = 8.2, $J_{4'x,5'}$ = 3.0 Hz, 1 H, 4′-*exo*-H), 1.94 (m, $J_{3'x,3'n}$ = 12.3, $J_{3'x,5'}$ = 1.2 Hz, 1 H, 3′-*exo*-H), 2.01 (d of pseudo-t, 1 H, 3′-*endo*-H), 2.17 (mc, $J_{5',1'}$ = 3.0 Hz, 1 H, 5′-H), 2.41 (d of pseudo-t, 1 H, 1′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.13 (t), 8.70 (t), 22.66 (d, J = 175.0 Hz, C-7′), 24.16 (t, J = 126.8 Hz, C-3′), 24.46 (d, J = 189.1 Hz, C-1′), 24.78 (s, C-6′), 25.30 (d, J = 161.0 Hz, C-2′), 32.92 (t, J = 126.8 Hz, C-4′), 45.35 (d, J = 149.9 Hz, C-5′); MS (70 eV), *m/e* 119 (2%, $M^+ - 1$), 105 (16), 92 (98), 91 (100), 79 (26), 67 (28), 51 (11), 39 (25). Anal. C_9H_{12} (120.2). Calcd: C, 89.94; H, 10.06. Found: C, 90.34; H, 10.21.

Spiro(cyclopropane-1,3′-tricyclo[3.2.0.0^{2,7}]heptane) (4b), 30.2 mg (67%), colorless oil, was obtained from 45.0 mg (0.304 mmol) of azoalkane **3b**: IR (neat) 3070, 3040, 3000, 2980, 2960, 2930, 2870, 2860, 1450, 1430, 1285, 1245, 1015, 955, 810, 785, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.35–0.75 (m, 4 H, 2-H, 3-H), 0.96 (pseudo-t, $J_{2',7'}$ = 5.7, $J_{2',1'}$ = 5.2, $J_{2',6'x} \cong$ 0.5 Hz, 1 H, 2′-H), 1.13 (br d, $J_{4'n,4'x}$ = 11.5, $J_{4'n,5'} \cong$ 1.0 Hz, 1 H, 4′-*endo*-H), 1.38 (ddd, $J_{6'n,6'x}$ = 9.1, $J_{6'n,1'}$ = 2.7, $J_{6'n,5'}$ = 0.9 Hz, 1 H, 6′-*endo*-H), 1.41 (mc, $J_{7',1'}$ = 4.5, $J_{7',6'x}$ = 4.0, $J_{7',5'}$ = 2.4 Hz, 1 H, 7′-H), 2.05 (dd, $J_{4'x,5'}$ = 3.4, $J_{4'x,6'x} \cong$ 1.1 Hz, 1 H, 4′-*exo*-H), 2.30 (d of pseudo-t, $J_{6'x,5'}$ = 8.0, $J_{6'x,1'} \cong$ 0.6 Hz, 1 H, 6′-*exo*-H), 2.37 (mc, $J_{1',5'}$ = 2.9 Hz, 1 H, 1′-H), 2.50 (m, 1 H, 5′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.86 (t), 12.77 (t), 15.61 (d, J = 175.0 Hz, C-7′), 21.63 (s, C-3′), 27.87 (d, J = 184.0 Hz, C-1′), 27.95 (t, J = 135.7 Hz, C-6′), 30.32 (d, J = 161.9 Hz, C-2′), 39.34 (d, J = 147.8 Hz, C-5′), 46.20 (t, J = 130.7 Hz, C-4′); MS (70 eV), *m/e* 120 (5%, M^+), 105 (45), 91 (65), 79 (37), 66 (100), 51 (12), 39 (30). Anal. C_9H_{12} (120.2). Calcd: C, 89.94; H, 10.06. Found: C, 90.19; H, 10.15.

Dispiro(cyclopropane-1,3′-tricyclo[3.2.0.0^{2,7}]heptane-6′,1″-cyclopropane) (4c), 59.0 mg (69%), colorless oil, was obtained from 100 mg (0.574 mmol) of the azoalkane **3c**: IR (neat) 3060, 3020, 2990, 2960, 2920, 2900, 2840, 1445, 1420, 1225, 1015, 1000, 900, 890, 815, 805 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.05–0.80 (four sets of m, 8 H, 2-H, 3-H, 2″-H, 3″-H), 1.10 (pseudo-t, $J_{2',7'}$ = 5.2, $J_{2',1'}$ = 5.1 Hz, 1 H, 2′-H), 1.12 (br d, $J_{4'n,4'x}$ = 11.5, $J_{4'n,5'} \cong$ 0.9 Hz, 1 H, 4′-*endo*-H), 1.30 (d of pseudo-t, $J_{7',1'}$ = 4.9, $J_{7'5'}$ = 2.4 Hz, 1 H, 7′-H), 2.03 (dd, $J_{4'x,5'}$ = 3.6 Hz, 1 H, 4′-*exo*-H), 2.23 (mc, $J_{5',1'}$ = 3.2, 1 H, 5′-H), 2.61 (d pseudo-t, 1 H, 1′-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.03 (t), 10.13 (t), 11.25 (t), 13.04 (t), 22.17 (s, C-3′), 23.17 (d, J = 178.5 Hz, C-7′), 26.05 (s, C-6′), 26.56 (d, J = 183.5 Hz, C-1′), 32.39 (d, J = 163.0 Hz, C-2′), 43.67 (t, J = 130.0 Hz, C-4′), 46.22 (d, J = 144.5 Hz, C-5′); MS (70 eV), *m/e* 145 (7%, $M^+ - 1$), 131 (40), 117 (50), 105 (20), 91 (100), 77 (30), 65 (16), 51 (14), 39 (27). Anal. $C_{11}H_{14}$ (146.2). Calcd: C, 90.35; H, 9.65. Found: C, 90.47; H, 9.78.

4-(1-(2-Propenyl)cyclopropyl)-1*H*-pyrazole (7b). A sample of 100 mg (0.676 mmol) of the azoalkane **3b** was pyrolyzed by subliming it at ca. 120 °C (20 torr) through a hot tube consisting of Pyrex glass (35-cm long, diameter = 1.3 cm), which was externally heated at ca. 360 °C by means of resistance wire. The pyrolysate was condensed onto a cold finger kept at liquid nitrogen temperature. After flushing the apparatus with nitrogen and warmup to ca. 15 °C, the product mixture was recovered from the cold finger by dissolving it with ca. 1 mL of $CDCl_3$. Its composition was determined by ^{1}H NMR (90 MHz); the substance was a 4:1 mixture of the pyrazole **7b** and the tricycloheptane **4b**. The solution was concentrated by rotoevaporation at 30 °C (20 torr) and the residue recrystallized twice from *n*-hexane, affording 40 mg (40%) of the pyrazole **7b**: colorless needles; mp 62–64 °C; IR (KBr) 3140, 3120, 3080, 2950, 2840, 1650, 1430, 1390, 1380, 1140, 995, 960, 915, 835, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.73 (s, 4 H, cyclopropyl H), 2.31 (d of pseudo-t, $J_{7,8}$ = 6.8, $J_{7,9c}$ = 1.5, $J_{7,9t}$ = 1.1 Hz, 2 H, 7-H), 5.00 (d of m, $J_{9c,8}$ = 17.1, $J_{9c,9t}$ = 2.2 Hz, 1 H, 9-*cis*-H), 5.03 (d of m, $J_{9t,8}$ = 10.2 Hz, 1 H, 9-*trans*-H), 5.82 (m, 1 H, 8-H), 7.39 (s, 2 H, 3-H, 5-H), 9.70 (br s, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.14 (t, cyclopropyl), 15.73 (s, C-6), 43.05 (t, C-7), 116.47 (t, C-9), 126.77 (s, C-4), 132.06 (d, C-3, C-5), 136.22 (d, C-8); MS (70 eV), *m/e* 148 (52%, M^+), 147 (35), 133 (98), 120 (38), 119 (52), 107 (70), 106 (14), 93 (22), 80 (100), 53 (34), 39 (41). Anal. $C_9H_{12}N_2$ (148.2). Calcd: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.70; H, 8.16; N, 18.66.

Detection of Diazoalkanes 6a–c. A solution of ca. 0.27 mmol of the corresponding azoalkane in ca. 2.5 mL of benzene was transferred into a UV cuvette and deaerated by bubbling a slow stream of nitrogen gas through the solution for 20 min. The sample was irradiated with the 333-nm line of the argon ion laser

at 40–50 °C and the reaction progress monitored by UV. After 15–20 min all azoalkane was consumed and a broad UV absorption between 400 and 530 nm indicated the presence of the diazoalkane. The reaction mixture was concentrated by rotoevaporation (0 °C (20 torr)) and the residue exhibited the expected diazo stretching band at 2060–2070 cm^{-1}.

General Procedure for the Generation of the Methylenecyclohexenes 5a–c. A solution of ca. 0.6 mmol of the corresponding azoalkane in ca. 1 mL of benzene or toluene, respectively, was deaerated by bubbling a slow stream of nitrogen gas through the solution for ca. 30 min and irradiated as above but at elevated temperatures. The photolysis was monitored by capillary GC and shown to be finished after ca. 20 min. The relative product distributions are given in Table VI. The cyclohexenes and the corresponding tricycloheptanes were isolated by preparative GC with a 1.5-m glass column, packed with 10% Carbowax M on Chromosorb, operated at injector, detector, and column temperatures of 200, 200, and 90 (for the products of the azoalkanes **3a,b**) or 110 °C (for the products of azoalkane **3c**), respectively, and a carrier gas pressure (N_2) of 0.30–0.45 kg/cm^2.

8-Methylenespiro[2.5]oct-4-ene (5a) was obtained as colorless oil from 200 mg (1.35 mmol) of azoalkane **3a** by irradiation at ca. 60 °C in benzene: IR (CCl_4) 3081, 3025, 3004, 2941, 2918, 2902, 2842, 1653 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) AA'XX' (δ_A = 0.72, δ_X = 0.97, J_A = 9.4, J_X = 9.4, J = 4.1, J' = 6.6 Hz, 4 H, 1-H, 2-H), 2.21 (mc, $J_{6,7}$ = 6.4, $J_{6,5}$ = 3.9, $J_{6,4}$ = 2.0, 2 H, 6-H), 2.44 (br t, 2 H, 7-H), 4.46 (br s, 1 H, 9-H), 4.58 (m, 1 H, 9-H), 4.99 (dt, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.70 (dt, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.96 (t, C-1, C-2), 23.16 (s, C-3), 26.72 (t, C-6), 32.66 (t, C-7), 102.73 (t, C-9), 125.24 (d, C-5), 134.27 (d, C-4), 149.89 (s, C-8); MS (70 eV), *m/e* 120 (22%, M^+), 105 (47), 91 (100), 79 (40), 77 (34), 65 (18), 58 (5), 51 (18), determined by capillary GC–MS.

7-Methylenespiro[2.5]oct-4-ene (5b) was obtained as a colorless oil from 100 mg (0.676 mmol) of azoalkane **3b** by irradiation at 110 °C in toluene: IR 3078.4, 3028.2, 3008.9, 2935.6, 1654.9, 1427.3, 1014.6, 995.3, 922.0, 887.3 cm^{-1}, determined by capillary GC–FTIR; ^1H NMR ($CDCl_3$, 400 MHz) AA'BB' (δ_A = 0.55, δ_B = 0.57, J_A = 10.8, J_B = 10.8, J = 4.6, J' = 6.1 Hz, 4 H, 1-H, 2-H), 2.17 (br s, 2 H, 8-H), 2.83 (m, $J_{6,5}$ = 3.5, $J_{6,4}$ = 2.4 Hz, 2 H, 6-H), 4.73 (m, 1 H, 9-H), 4.79 (m, 1 H, 9-H), 5.11 (dt, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 5.63 (dt, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.51 (t, C-1, C-2), 33.68 (t, C-6), 42.17 (t, C-8), 108.23 (t, C-9), 124.67 (d, C-5), 134.92 (d, C-4), C-3 and C-7 not detected due to insufficient sample; MS (70 eV), *m/e* 120 (20%, M^+), 105 (61), 91 (100), 79 (36), 77 (28), 65 (19), 58 (6), 51 (17), determined by capillary GC–MS.

9-Methylenedispiro[2.2.2.2]dec-4-ene (5c) was obtained as a colorless oil from 210 mg (1.21 mmol) of azoalkane **3c** by irradiation at ca. 60 °C in benzene: IR (CCl_4) 3079, 3023, 3001, 2957, 2927, 2865, 2854, 2739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) AA'BB' (δ_A = 0.59, δ_B = 0.61, J_A = 10.1, J_B = 10.1, J = 4.4, J' = 6.1 Hz, 4 H, 1-H, 2-H), AA'XX' (δ_A = 0.77, δ_X = 1.01, J_A = 9.4, J_X = 9.4, J = 4.2, J' = 6.5 Hz, 4 H, 7-H, 8-H), 2.30 (br s, 2 H, 10-H), 4.52 (br s, 1 H, 11-H), 4.57 (m, 1 H, 11-H) AB (δ_A = 5.01, δ_B = 5.13, J = 9.5 Hz, 2 H, 4-H, 5-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.21 (t, C-1, C-2), 16.64 (t, C-7, C-8), 20.09 (s, C-3), 23.25 (s, C-6), 42.51 (t, C-10), 103.17 (t, C-11), 132.63 (d), 132.72 (d) (C-4, C-5), 148.25 (s, C-9); MS (70 eV), *m/e* 146 (9%, M^+), 131 (42), 117 (100), 115 (41), 103 (12), 91 (79), 77 (22), 65 (20), 51 (22), determined by capillary GC–MS.

Product Distribution in the Direct Irradiation of the Azoalkanes 3a–c. A 1-mL aliquot of a stock solution of ca. 0.1 mmol of the corresponding azoalkane in 10 mL of benzene was transferred into a Pyrex tube and degassed by means of three freeze–pump–thaw cycles. The reaction vessel was placed into the Rayonet photoreactor, equipped with 350-nm lamps, and irradiated at ca. 30 °C. The reaction progress was monitored via capillary GC. It was shown that the main products were the tricycloalkanes **4a–c** (90–95%) and the methylenecyclohexenes **5a–c** (1–7%). Minor products were detected but not identified. The results are given in Table VI. Control experiments showed that the tricycloalkanes **4a–c** were stable toward the photolysis conditions.

Benzophenone-Sensitized Photolysis of the Azoalkanes 3a–c. A 1-mL aliquot of a ca. 0.01 M azoalkane and 0.1 M benzophenone solution in benzene was transferred into a Pyrex tube and degassed by three freeze–pump–thaw cycles. The solution was irradiated at ca. 30 °C in a Rayonet photoreactor, equipped with 350-nm lamps. The reaction progress was monitored via capillary GC. The quantitative results are given in Table VI. Minor products were detected but could not be identified.

Determination of Mass Balance in the Photolysis of the Azoalkanes 3a–c. A solution of ca. 0.2 mmol of the corresponding azoalkane in 0.5 mL of C_6D_6 (in the case of the sensitized photolysis ca. 1.2 mmol benzophenone was added) was placed in a NMR tube, deaerated by bubbling a slow stream of nitrogen gas through the solution for ca. 20 min, and irradiated with the argon ion laser by using the 334-, 351-, and 354-nm lines at ca. 4 °C. ^1H NMR (60 MHz) monitoring revealed complete consumption of the azoalkane after ca. 20 min of irradiation. To the photolysate ca. 0.12 mmol of trioxane was added as an internal standard and the quantitative analysis of the products was carried out by means of 90 MHz ^1H NMR.[12] The absolute yields (%) were determined by integration of the δ 2.6 product protons vs. the δ 4.8 internal standard protons. The results are listed in Table VI.

Vacuum Flash Thermolysis of the Azoalkanes 3a–c. A sample of 0.11 mmol of the corresponding azoalkane was placed into a 5-mL round-bottomed flask and pyrolyzed by subliming it at 140 °C (20 torr) through a hot tube consisting of Pyrex glass (35 cm long, diameter = 1.3 cm), which was externally heated by means of resistance wire at ca. 360 °C. The products were collected in a cold trap, kept at liquid nitrogen temperature. After warming up to 20 °C, the products were dissolved in C_6D_6, the relative product distribution (%) was determined by capillary GC, and the absolute yields (%) were determined by 90 MHz ^1H NMR with trioxane as an internal standard. The results are given in Table VI.

X-ray Crystallography. The orientation matrix and the cell parameters were determined from all clear colorless crystals of given dimensions on a SYNTEX-P3 four circle diffractometer. Measurement of intensities: ω scan, 1° range, Mo Kα, 2θ maximum = 55°. The structures were solved by direct-phase determination. Positional and thermal parameters could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial backing.

Registry No. **1a**, 7125-50-0; **1b**, 6572-50-5; **1c**, 94348-06-8; **2a**, 73818-01-6; **2b**, 94348-07-9; **2c**, 94348-08-0; **3a**, 94348-09-1; **3b**, 94348-10-4; **3c**, 94348-11-5; **4a**, 24976-95-2; **4b**, 94348-12-6; **4c**, 94348-13-7; **5a**, 94348-14-8; **5b**, 94348-15-9; **5c**, 94369-83-2; **7b**, 94348-16-0; PTAD, 4233-33-4; 5,6-dichlorospiro(bicyclo[2.2.1]-hept-2-ene-7,1'-cyclopropane), 93117-29-4; methylenecyclopropane, 6142-73-0; cyclopentadiene, 542-92-7; spiro[2.4]hepta-4,6-diene, 765-46-8.

Supplementary Material Available: X-ray pictures (Figure 1) and structural data (Tables VII–XI) of urazoles **2b,c** (6 pages). Ordering information is given on any current masthead page.