Photochemistry of the Azoalkanes 2,3-Diazabicyclo[2.2.1]hept-2-ene and Spiro[cyclopropane-1,7′-[2,3]diazabicyclo[2.2.1]hept-2-ene]: On the Questions of One-Bond vs. Two-Bond Cleavage during the Denitrogenation, Cyclization vs. Rearrangement of the 1,3-Diradicals, and Double Inversion

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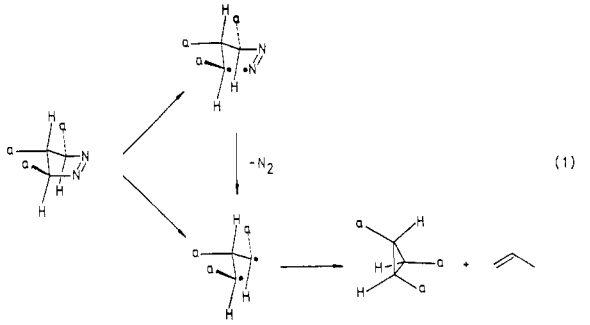
The thermolysis and 350-nm and 185-nm photolyses of the azoalkanes 2,3-diazabicyclo[2.2.1]hept-2-ene (**1a**) and spiro[cyclopropane-1,7′-[2,3]diazabicyclo[2.2.1]hept-2-ene] (**1b**) have been investigated. The exo/endo stereochemistry in the bicyclo[2.1.0]pentanes **2a,b** and in the rearranged olefin **3b** was determined by deuteration experiments using 5,6-*exo*-dideuterioazoalkanes **1a,b**-d_2. Whereas thermal and direct photochemical (350 nm; n, π^*) denitrogenation of azoalkane **1a**-d_2 led exclusively (>99%) to bicyclo[2.1.0]pentane **2a**-d_2 with preferential (1.54, 2.94) double inversion, the triplet-sensitized photolysis afforded nearly complete stereoequilibration. In 185-nm denitrogenation an unexpectedly high exo/endo ratio (3.1) for bicyclo[2.1.0]pentane **2a**-d_2 was found, besides isomerization to cyclopentene **2a**-d_2. Similar results were obtained in the denitrogenation of spiroazoalkane **1b**-d_2, which exhibited exo stereochemical preferences in both photoproducts spiro[bicyclo[2.1.0]pentane-5,1′-cyclopropane] **2b**-d_2 and bicyclo[3.2.0]hept-1-ene **3b**-d_2. The 350-nm photolysis of azoalkane **1b**-d_2 gave preferential formation of *exo*-spirobicyclo[2.1.0]pentane **2b**-d_2 and exo-olefin **3b**-d_2, whereas triplet-sensitized decomposition yielded almost complete loss of stereochemical preference in the olefin **3b**-d_2. The 185-nm photolysis of azoalkane **1b**-d_2 showed similar behavior compared with the azoalkane **1a**, e.g., at high exo/endo ratio in spirobicyclo-[2.1.0]pentane **2b**-d_2. Also olefin **3b** was formed with complete stereoequilibration. These diverse experimental results are discussed in terms of one-bond vs. two-bond cleavage processes leading to the diazenyl diradicals $D'_{\sigma,\sigma}$ and $D'_{\sigma,\pi}$ in the case of the low-energy activation (350-nm photolysis and thermolysis) and 1,3-cyclopentadiyls $D_{\sigma,\sigma}$ and $D_{\pi,\pi}$ on high-energy activation (185-nm activation). The relatively high degree of double inversion in the corresponding bicyclopentanes and the formation of rearranged cycloalkenes in the 185-nm photodenitrogenation is presumably a direct consequence of concerted two-bond cleavage via the formation of $^1D_{\sigma,\sigma}$ and zwitterionic states of the 1,3-diradical. A Salem diagram for one-bond and two-bond denitrogenation was most helpful in rationalizing these results mechanistically.

Especially in recent years azoalkanes have played an important role in mechanistic[1] and synthetic[2] problems. This paper deals with the mechanistic questions of one-bond cleavage of azoalkanes leading first to a diazenyl diradical (eq 1) vs. two-bond cleavage resulting directly in



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the 1,3-diradical and the cyclization of the latter into cyclopropanes with double inversion vs. rearrangement into propenes via 1,2-shift.

The question of one-bond vs. two-bond cleavage has been one of the notorious controversial mechanistic issues ever since the denitrogenation of azoalkanes has been investigated.[1] However, in the last few years consensus of opinion has been emerging both on the theoretical and experimental fronts. For example, in thermal denitrogenations quantum chemical calculations[3] agree that the most probable course of action is one-bond breakage leading first to a diazenyl diradical. Recent experimental evidence[4] is at least in principle consistent with this decomposition pathway even for symmetrically substituted bicyclic azoalkanes, provided that diazenyl diradical formation is reversible.

Although for photochemical denitrogenation (n,π^* excitation) two-bond cleavage leading directly to 1,3-diradicals is presumed as the favored denitrogenation route,[1] quantum chemical calculations[5] provide cogent arguments in support of one-bond cleavage via a diazenyl diradical, at least for the denitrogenation of cis diimide. Also some experimental evidence is available on this problem.[6] Furthermore, the fact that photoreluctant azoalkanes such as 2,3-diazabicyclo[2.2.2]octanes[7] reflect some of the features of their thermal denitrogenation, similar substituent dependence in the thermal and photochemical activation energies, would be consistent with one-bond cleavage leading first to diazenyl diradicals. Recent results from our laboratory concerning competitive diazoalkane vs.

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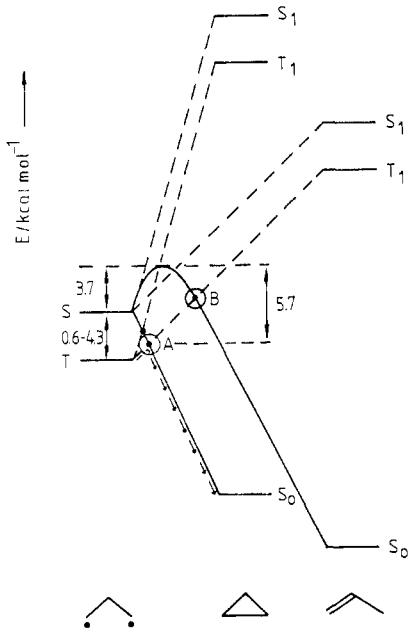


Figure 1. Energy diagram for cyclization and rearrangement of trimethylene diradicals.

cyclopropane formation in the direct photolysis of tricyclic azoalkanes[7] are more satisfactorily explained in terms of intervening diazenyl diradicals.[8]

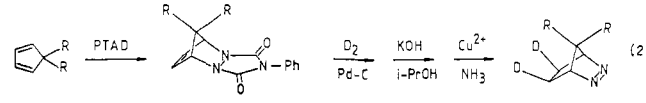
Once the 1,3-diradical has been generated, its chemical fate with respect to cyclization into cyclopropane vs. rearrangement to "propene" (eq 1) has been of considerable mechanistic interest.[9] The long-standing puzzle has been the fact that the triplet-sensitized denitrogenation of azoalkanes gave predominantly, if not exclusively, cyclization while the direct photolysis led at least to some rearrangement.[10] A convincing rationalization of this unusual behavior of triplet diradicals has been forwarded recently[11] on theoretical grounds. In view of the appreciable activation barrier (ca. 5 kcal/mol) for the rearrangement of the singlet 1,3-diradical via 1,2-shift into propene but none for its cyclization into cyclopropane, the triplet 1,3-diradical intersects earlier with the energy surface connecting the singlet 1,3-diradical and cyclopropane than with that connecting the singlet 1,3-diradical and propene (Figure 1). Efficient intersystem crossing[12] transforms the triplet 1,3-diradical essentially exclusively into cyclopropane product.

However, a still more perplexing feature of 1,3-diradicals derived from azoalkane denitrogenation has been the predominant formation of cyclopropanes with double inversion.[9] Two azoalkanes that have been extensively investigated in this respect have been 2,3-diazabicyclo[2.2.1]hept-2-ene (**1a**)[13] and spiro[cyclopropane-1,7′-[2,3-diazabicyclo[2.2.1]hept-2-ene] (**1b**),[14] leading to bicyclopentanes **2** via cyclization and cyclopentenes **3** via rearrangement of the intervening 1,3-diradicals. Some ingenious suggestions have been made to account for the preferential formation of *exo*-2,3-dideuterobicyclo[2.1.0]pentane from *exo*-2,3-diaza-5,6-dideuteriobicyclo[2.2.1]hept-2-ene (double inversion), ranging from concerted two-bond extrusion of nitrogen via simultaneous back-lobe overlap,[13e] initial diazenyl diradical formation with backside displacement of nitrogen by the carbon radical site,[14a] and the "recoil" effect[15] accompanying nitrogen departure leading to an inverted 1,3-cyclopentadiyl. Prior to planarization the latter cyclizes. The validity of these mechanisms has been argued extensively.[16]

We have shown[17] that upper excited states of azoalkanes, generated on 185-nm excitation, serve as effective means to denitrogenate even reluctant systems. In view of the aforementioned but still pending questions on one-bond vs. two-bond cleavages in the denitrogenation of azoalkanes and cyclization with double inversion vs. rearrangement of the resulting 1,3-diradicals, it seemed timely and instructive to us to investigate the 185-nm photolysis of the azoalkanes **1**. Indeed, preliminary results on azoalkane **1a** revealed that the amount of cyclopentene (rearrangement product) was substantially increased.[18] Presently we report the full details of this investigation on the exo-5,6-dideuterio derivatives of the azoalkanes **1**.

Results

Preparation of Deuterated Azoalkanes 1a,b-d_2. The spirocyclopropane-substituted azoalkane **1b**-d_2 was prepared analogously to the procedure published[13g] for the azoalkane **1a**-d_2 (eq 2) but with 4-phenyl-1,2,4-triazole-



3,5-dione (PTAD) as the dienophile. Catalytic deuteration of the urazoles and saponification with subsequent oxidation afforded the desired deuterated azoalkanes in high yield with over 95% exo dideuteration.

Product Studies. The denitrogenation products of the photolyses above 300 nm of the azoalkanes **1a,b** were the bicyclo[2.1.0]pentanes **2a,b** and the cyclopentenes **3a,b** (eq 3). with the former the predominating if not exclusive products (Table I). The absolute and relative yields (mol %) were established by capillary GC, using calibration

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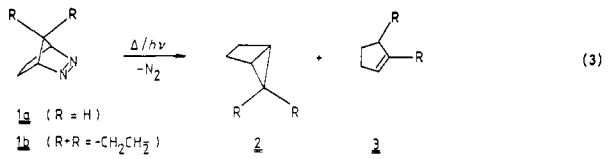
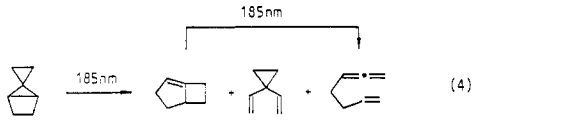


(3)

charts prepared with the authentic products relative to an internal standard (cf. Experimental Section). For those cases that were conducted under the reported[14a-c,e] conditions, the present quantitative results matched within the experimental error (<10% of the stated values). A control experiment confirmed that bicyclo[2.1.0]pentane (**2a**) was stable toward photolysis above 300 nm (Table I, entry 2).

More complex were the 185-nm photolyses of the azoalkanes **1a,b**. Prolonged irradiation afforded poor product balance (e.g., after 10 min 185-nm irradiation 80%) due to formation of undefined high molecular weight material, as evidenced by cloudy solutions and precipitation. It was, therefore, essential to conduct the 185-nm photolyses to low conversion (<20%).

Still more problematic was the fact that the photolysis products **2a,b** and **3a,b** were themselves photoactive at 185 nm. Concentration–time profiles clearly established that the primary products of the 185-nm photolyses of the azoalkanes **1a,b** were the bicyclo[2.1.0]pentanes **2a,b** and the cyclopentenes **3a,b**. Thus, the product yields of the 185-nm photolyses in Table I were corrected for secondary photolyses by extrapolation to zero time (t_0). The secondary photolysis products for azoalkane **1a** were 1,4-pentadiene and methylenecyclobutane, those of the spiroazoalkane **1b** are shown in eq 4. Since these secondary



(4)

products are of no relevance for the present study, the full details of the 185-nm photochemistry of the bicyclo[2.1.0]pentanes **2a,b** and cyclopentenes **3a,b** will be reported separately.

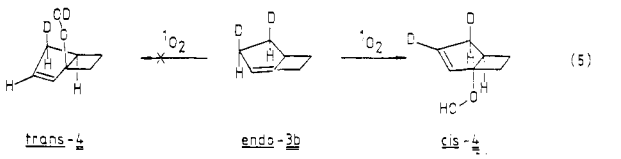
Since the major output of the 185-nm light source is 254-nm radiation (ca. 80%), a control experiment was run for bicyclopentane **2a** (Table I, entry 5). As expected, since **2a** showed essentially no absorption above 200 nm, no photoisomerization to cyclopentene occurred. The thermolysis of azoalkane **1a** gave also essentially exclusively the bicyclopentane **2a** when the temperature was below 200 °C and the decomposition was run under vacuum flash thermolysis condition (Table I, entry 6). When the thermolysis was run in a sealed tube at ca. 250 °C for 96 h (Table I, entry 7) cyclopentene was by far the major product. A control experiment on bicyclopentane **2a** under these conditions (Table I, entry 8) confirmed that it had rearranged into cyclopentene to the same extent as observed in the thermolysis of the azoalkane **1a**. The thermolysis[14c] of azoalkane **1b**-d_2 led almost exclusively to spirocyclopropane **2b**-d_2 (Table I, entry 13).

The quantum yields (ϕ_S) of substrate consumption, i.e., the azoalkanes **1a,b**, were determined with Aktinochrom R (248/334) as actinometer.[19] For the 185-nm photolyses *cis*-cyclooctene was used as actinometer.[20] The results are summarized in Table I. While the azoalkane **1a** denitrogenates with essentially 100% efficiency both on 350-nm and 185-nm irradiation (Table I, entries 1 and 4), it is surprising that for the spiroazoalkane **1b** the 350-nm photolysis is considerably more efficient than that of 185 nm (Table I, entries 9 and 11). Thus, not necessarily does more energy mean greater photoreactivity.

Stereochemistry. As in the reported studies,[14a,c] the exo-5,6-dideuterio substituents in the azoalkanes **1a,b** served as a tracer for the stereochemical course of the thermal and photochemical denitrogenations. ^{2}H NMR was utilized to diagnose the stereochemical fate of these deuterium atoms in the bicyclopentanes **2a,b** and the bicyclo[3.2.0]hept-1-ene (**3b**). The stereochemistry of the deuterium atoms in cyclopentene (**3a**) cannot be assessed since no exo/endo differentiation is possible.

The exo and endo 2,3-hydrogens and -deuteriums in bicyclo[2.1.0]pentane (**2a**) are located at 2.11 and 1.35 ppm, respectively, so that at 400 MHz in the case of ^{1}H NMR and 61.4 MHz in the ^{2}H NMR direct electronic integration sufficed to determine the exo/endo ratios. Similarly, direct electronic integration of the exo and endo 2,3-hydrogens and/or -deuteriums at 2.14 and 1.49 ppm in the spirobicyclopentane **2b** enabled the acquisition of the stereochemical course of this cyclization product in terms of the exo/endo ratio. The results are summarized in Table I.

More laborious was the determination of the stereochemistry of 2,3-dideuterio substituents in the bicyclo[3.2.0]hept-1-ene **3b**. The signals were too strongly coupled to permit a definitive assignment of the exo and endo positions. It was, therefore, essential to engage a chemical criterion. For this purpose the previously reported[14d] singlet oxygenation of bicycloheptene **3b** (eq 5) was uti-



(5)

lized. As illustrated for the *endo*-**3b**-d_2 isomer, the stereoselective ene reaction[21] with the exo hydrogen at C-3 will give the cis hydroperoxide **4**, while with the endo deuterium at C-3 it will lead to the improbable trans hydroperoxide **4**. The fact that *cis*-1-hydroperoxybicyclo[3.2.0]hept-2-ene (**4**) is formed exclusively[14d] in the singlet oxygenation of bicyclo[3.2.0]hept-1-ene (**3b**) allows a definitive differentiation of the exo and endo substituents in **3b**-d_2. Integration of the olefinic hydrogen and/or deuterium at the C-3 position in the hydroperoxide *cis*-**4** by ^{1}H and/or ^{2}H NMR vs. those at the C-4 and C-2 position provides a measure of the exo/endo ratio in the bicyclo[3.2.0]hept-1-ene **3b**-d_2. The results are given in Table I. The exo/endo ratios for the direct photolysis at 350 nm (Table I, entry 1) and gas-phase thermolysis at 180 °C (Table I, entry 6) of azoalkane **1a** match within experimental error those previously reported.[14e] Thus, double inversion is appreciable (1.54) in the direct photodenitrogenation (350 nm) of azoalkane **1a** (Table I, entry 1) and extraordinarily high (2.94) in the thermal gas-phase denitrogenation at 180 °C (Table I, entry 6). However, thermolysis in the sealed tube at 250 °C for extended time gave essentially no double inversion product (Table I, entry 7). A control experiment with bicyclopentane **2a**-d_2 under the same conditions revealed essentially complete loss of stereochemistry (Table I, entry 8). Isomerization was the consequence of subsequent stereomutation. On the other hand, direct irradiation at 350 nm of the bicyclopentane **2a**-d_2 with an initial exo/endo ratio of 2.94 ± 0.02 suffered no isomerization (Table I, entry 2) as expected since bi-

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Table I. Quantum Yields of Substrate Consumption (ϕ_S), Relative Yields (%) of Denitrogenation Products for Azoalkanes 1a,b, and Exo/Endo Ratios in the Bicyclopentanes 2a,b and the Olefin 3a

entry	substrate	conditions[a]	ϕ_S	product yields, (%) 2	3	exo/endo ratio 2	3
1	**1a**-d_2	350 nm, C_6H_6	1.0 ± 0.1[b]	>99	trace	1.54 ± 0.04	
2	**2a**-d_2	350 nm, n-C_6F_{14}, 2 h[c]		100		2.91 ± 0.04	
3	**1a**-d_2	350 nm, C_6D_6, $Ph_2C{=}O$ (3 M)	0.97[d]	>99	trace	1.15 ± 0.02	
4	**1a**-d_2	185 nm, n-C_7H_{16}	0.95 ± 0.04	49[e]	43[e]	3.1 ± 0.03[f]	
5	**2a**-d_2	254 nm, n-C_6F_{14}, 1 h[g]		100		2.73 ± 0.04	
6	**1a**-d_2	180 °C, VFT, 120–140 torr		99	1	2.94 ± 0.02	
7	**1a**-d_2	250 °C, sealed tube, 96 h		17	83	1.01 ± 0.04	
8	**2a**-d_2	250 °C, sealed tube, 96 h		20	80	1.09 ± 0.10	
9	**1b**-d_2	341 nm, n-C_5H_{12}	0.89 ± 0.04	92	8	2.32 ± 0.12	1.55 ± 0.08
10	**1b**-d_2	350 nm, n-C_5H_{12}, $Ph_2C{=}O$ (5 M)		9	91		1.20 ± 0.06
11	**1b**-d_2	185 nm, n-C_5H_{12}	0.53 ± 0.06	33	67	2.69 ± 0.13[h]	1.06 ± 0.05
12	**2b**-d_2	185 nm, n-C_5H_{12}[i]	0.49 ± 0.01		73[j]	2.03 ± 0.10[k]	
13	**1b**-d_2	140 °C, xylene[l]		99	1	*m*	

[a] All photolyses were performed at 25 °C. [b] Cf. ref 13b. [c] The exo/endo ratio of substrate was 2.94 ± 0.02. [d] Cf. ref 13h. [e] In addition to bicyclo[2.1.0] pentane (**2a**) and cyclopentene (**3a**) there were formed as secondary photoproducts 6% 1,4-pentadiene and 2% methylenecyclobutane; values calculated from the slope of concentration vs. time plots. [f] Value obtained from extrapolation vs. $t = 0$ (zero conversion). [g] The exo/endo ratio of substrate was 2.80 ± 0.01. [h] During the first 30 min of 185-nm irradiation no change in the exo/endo ratio was observed. [i] The exo/endo ratio of substrate was 1.97 ± 0.10. [j] In addition to bicyclo[3.2.0]hept-1-ene (**3b**) there were formed as secondary photoproducts 21% of 1,1-diethenylcyclopropane and 6% of 1,2,6-heptatriene; values calculated from the slope of concentration vs. time plots. [k] Within the experimental error (±5–10%) the exo/endo ratio in **2b**-d_2 was time independent even after 60 min of 185-nm irradiation. [l] Cf. ref 14c. [m] Unfortunately the bicyclo[2.1.0] pentane **2b**-d_2 undergoes facile exo/endo isomerization already at ca. 70 °C (ref 14c), which is well below the temperature required for denitrogenation of the azoalkane **1b**-d_2, so that the stereochemistry of the thermal denitrogenation of **1b**-d_2 could not be tested.

cyclopentane **2a**-d_2 is transparent at $\lambda > 250$ nm.

Benzophenone-sensitized denitrogenation of azoalkane **1a**-d_2 at 350 nm gave only little double inversion (1.15) on denitrogenation (Table I, entry 3). While this result was not unusual, it was most surprising that the 185-nm photolysis (Table I, entry 4) gave again a higher degree of double inversion (3.1) than in the 350-nm photolysis (1.54), an exo/endo ratio remarkably close to the gas-phase thermolysis value (Table I, entry 6). As expected, a control experiment at 254 nm (the major output of the 185-nm light source), starting with bicyclopentane **2a**-d_2 with an exo/endo ratio of 2.80 ± 0.01, showed no loss of stereochemistry (Table I, entry 5). Furthermore, it must be stressed that the stereochemical exo/endo ratios of the 185-nm photolysis of azoalkane **1a**-d_2 were corrected for secondary isomerization of the photoactive bicyclopentane **2a**-d_2 by extrapolation to zero-time (t_0) photolysis (Table I, entry 4).

Essentially similar, but not as dramatic, stereochemical results were obtained for the spiroazoalkane **1b**-d_2. In this case already the direct photolysis at $\lambda > 300$ nm (Table I, entry 9) gave an exceedingly high (2.32) exo/endo ratio for the spirobicyclopentane **2b**-d_2. Furthermore, appreciable double inversion (1.55) is also observed for the rearrangement product bicyclo[3.2.0]hept-1-ene **3b**-d_2 (Table I, entry 9).

Unfortunately, the exo/endo ratio of the spirobicyclopentane **2b**-d_2 in the benzophenone-sensitized photolysis at 350 nm (Table I, entry 10) could not be determined due to insufficient material. However, the bicyclo[3.2.0]-hept-1-ene product **3b**-d_2 showed a small degree of double inversion (1.20) in the benzophenone-sensitized photolysis (Table I, entry 10).

Finally, again the 185-nm photolysis of the spiroazoalkane **1b**-d_2 gave the highest degree of double inversion (2.69) in the spirobicyclopentane product **2b**-d_2 (Table I, entry 11). Yet, for the rearrangement product **3b**-d_2 the degree of double inversion was negligible (Table I, entry 11). A control experiment showed that the exo/endo ratios of both the cyclization product **2b**-d_2 and the rearrangement product **3b**-d_2 were independent of the time of 185-nm photolysis of spiroazoalkane **1b**-d_2. Also authentic spirobicyclopentane **2b**-d_2 with an initial exo/endo ratio of 1.97 ± 0.10 did not photoisomerize on prolonged irradiation at 185 nm (Table I, entry 12).

Discussion

To rationalize the experimental results of Table I, it is essential to recollect the significant features concerning product distribution (cyclization vs. rearrangement, i.e., bicyclopentane **2a,b** and cyclopentene **3a,b** products, respectively) and stereochemistry (exo vs. endo product, i.e., the degree of double inversion): (a) For both azoalkanes **1a,b** the cyclization products **2a,b** are formed predominantly (indeed, only traces of rearrangement product **3a** are observed for **1a**) in the direct photolyses at $\lambda > 300$ nm (Table I, entries 1 and 9) in high quantum yields. (b) The degree of double inversion in the direct photolysis ($\lambda > 300$ nm) is appreciable for the azoalkane **1a** (Table I, entry 1). (c) For the spiroazoalkane **1b** the degree of double inversion is relatively high for the cyclization product **2b** and appreciable retention for the rearrangement product **3b** in the direct photolysis at $\lambda > 300$ nm is noted (Table I, entry 9). (d) The triplet-sensitized (benzophenone) denitrogenation of azoalkane **1a** affords exclusively cyclization product **2a** with essentially complete loss of stereochemistry (Table I, entry 3). (e) For the spiroazoalkane **1b** the triplet-sensitized (benzophenone) process leads predominantly to rearrangement product **3b** with essentially complete loss of stereochemistry (Table I, entry 10). (f) The 185-nm photolysis of both azoalkanes **1a,b** generate rearrangement products **3a,b** in large amounts (Table I, entries 4 and 11). (g) The degree of double inversion is highest in the cyclization products **2a** for the 185-nm denitrogenation (Table I, entries 4). (h) The rearrangement product **3b** derived from the 185-nm photolysis is essentially completely isomerized (Table I, entry 11). (i) The thermal denitrogenations of the azoalkanes **1a,b** give predominantly cyclization products **2a,b** with a relatively high degree of double inversion for **2a**, but small amounts of the rearrangement products **3a,b** are formed as well (Table I, entries 6 and 13).

The most surprising result of the 185-nm photodenitrogenation of azoalkane **1a** is the higher degree of

double inversion (fact g) for the cyclization product **2a** compared to denitrogenation at above 300 nm (fact b) and at the same time the larger amount of rearrangement product **3a** (fact f). Thus, the more energetic denitrogenation (185-nm photolysis) generates the more reactive intermediate (rearrangement is competitive with cyclization), but the latter cyclizes more selectively (higher double inversion). None of the previous mechanistic suggestions[16] can alone account satisfactorily for these most unusual and hardly expected features about the denitrogenation of azoalkanes **1a,b**!

For example, a nitrogen-containing species such as a diazenyl diradical will explain the double inversion through a backside S_H2-type denitrogenation,[13e] but why should then more double inversion (facts b and g) be observed in the 185-nm vs. 350-nm photolysis of azoalkane **1a**? Still more puzzling, how can one rationalize the substantially increased (fact f) amount of the rearrangement product **3**? On the other hand, a vibrationally excited ("hot") nitrogen-free species such as a 1,3-cyclopentadiyl will substantially rearrange into cyclopentene, and this would be considerably more probable in the 185-nm vs. the 350-nm photodenitrogenation. However, how will such a hot fragment preferentially cyclize with double inversion into the bicyclopentane **2** with a greater stereoselectivity for the 185-nm process (facts b and g)? A planar nitrogen-free 1,3-cyclopentadiyl ($D_{\pi,\pi}$ singlet or triplet) is completely out of the question because it cannot lead to excess double inversion (facts b and g) nor can it rearrange (fact f). The recoil effect,[15] although much disputed,[16] would be expected to be more efficient for the 185-nm photoextrusion of nitrogen and thus afford a higher degree of double inversion (facts b and g). Yet, to rationalize the substantially increased amount of rearrangement (fact f) into cyclopentene, a vibrationally excited doubly inverted bicyclopentane would have to be invoked, which besides exo/endo isomerization extensively rearranges into cyclopentene. However, again the question must be posed why should any doubly inverted bicyclopentane be formed at all in the 350-nm photolysis (fact b), which only leads to traces of cyclopentene (fact a). Clearly, the mechanistic dilemma that is being confronted here derives from the fact that the 350-nm photodenitrogenation appears to operate predominantly via a diazenyl diradical, i.e., initial photochemical one-bond cleavage of the azoalkane, while the 185-nm photodenitrogenation presumably takes place mainly via a nonpolar nitrogen-free 1,3-cyclopentadiyl, i.e., direct photochemical two-bond cleavage of the azoalkane. Furthermore, the divergent chemical behavior of these two modes of excitation should be sought principally in the ca. twofold greater amount of energy that is being made available and the distinct nature of the excited states produced in the 185-nm vs. 350-nm photolyses. The heat of formation (ΔH_f) diagram in Figure 2 focuses on this point.

In this figure are given the estimated energies[22] of the azoalkane **1a**, bicyclopentane **2a** and cyclopentene (**3a**),

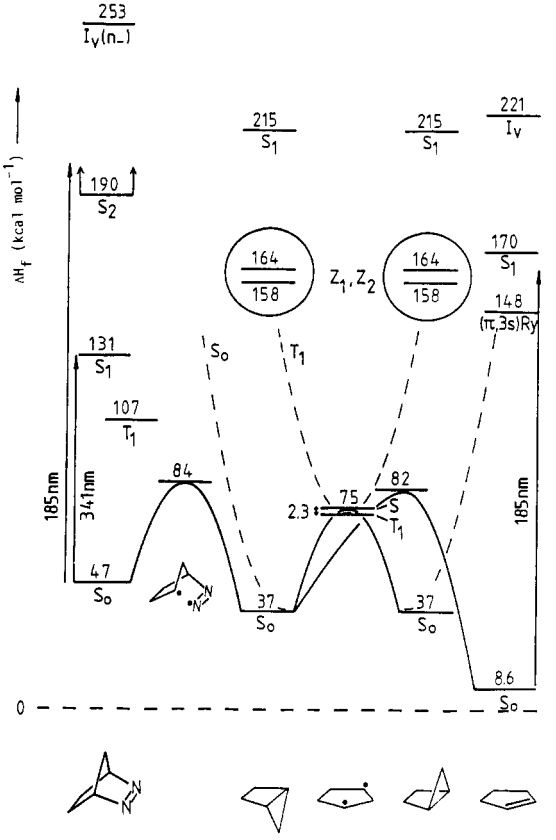


Figure 2. Heat of formation (ΔH_f) diagram for azoalkanes **1**, bicyclopentanes **2**, cyclopentenes **3**, diazenyl diradicals, and 1,3-cyclopentadiyl species and their excited states.

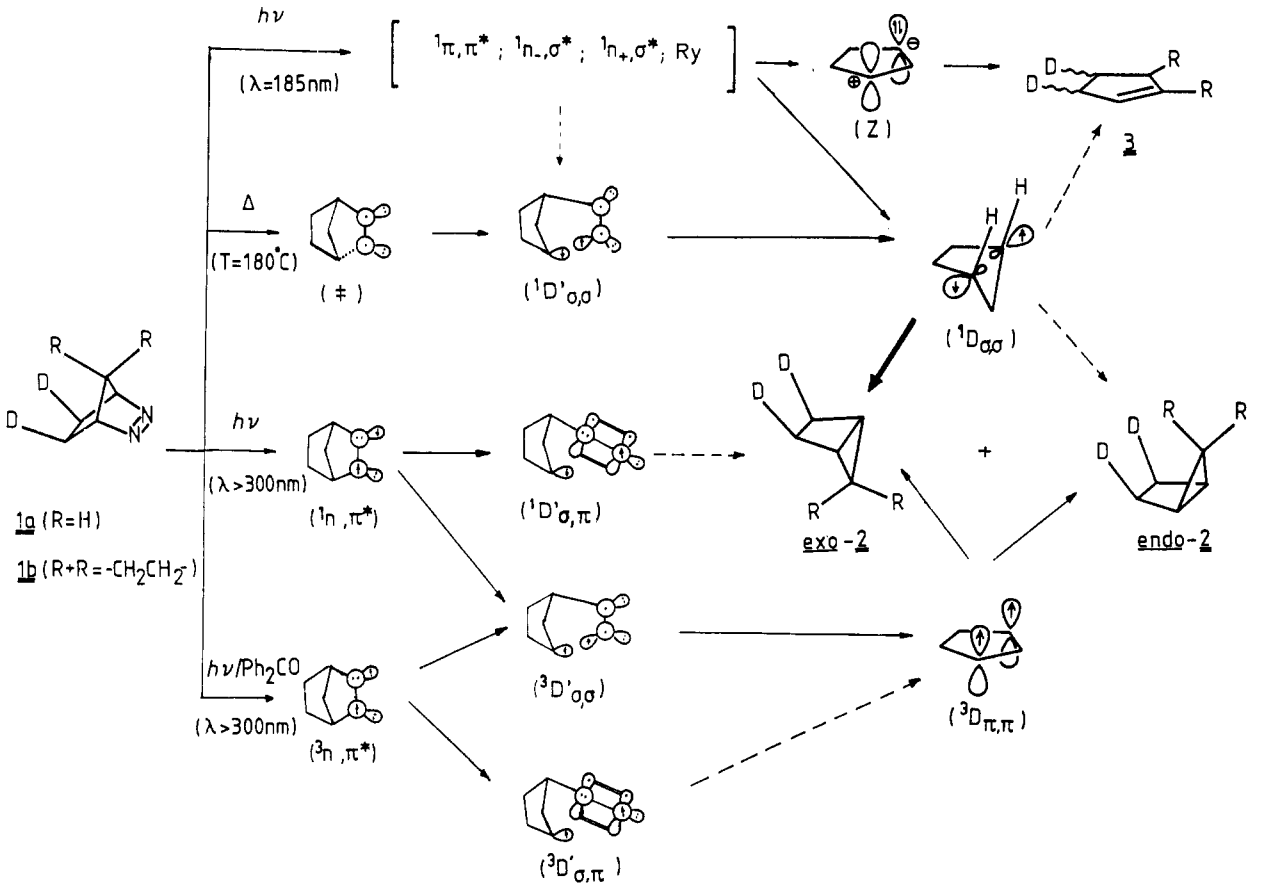
their various excited states and ionization potentials, and the various possible diradical species, including the diazenyl diradical and the diverse 1,3-cyclopentadiyls. The activation energies for the various thermal reactions (denitrogenation of azoalkane **1a**, stereoisomerization of the bicyclopentane **2a** and its rearrangement into cyclopentane) can be assessed from the energy differences of the respective states, which are connected for emphasis by the solid curves.

A number of important features become immediately apparent on inspection of Figure 2. Both modes of excitation (185- and 350-nm photolyses) provide sufficient energy to afford the singlet and triplet 1,3-cyclopentadiyls via two-bond cleavage. However, theoretical work[5] suggests (at least for cis diimide) that on $^{1,3}n,\pi^*$ excitation (direct and triplet-sensitized 350-nm photolyses) the concerted two-bond cleavage via 1,3-cyclopentadiyl requires double the activation energy as for the stepwise one-bond cleavage process via a diazenyl diradical. Thus, the stepwise mechanism should apply. On the other hand, the 185-nm photolysis provides sufficient energy to extrude nitrogen also via concerted two-bond cleavage. In fact, besides the singlet and triplet 1,3-cyclopentadiyls (S, T), even their excited zwitterionic forms (Z_1, Z_2) are accessible. Consequently, on the basis of energy considerations (Figure 2), the 350-nm photolysis of the azoalkane **1a** entails most probably stepwise (one bond) cleavage via diazenyl diradicals, while the 185-nm photolysis can engage the concerted (two bond) cleavage via 1,3-cyclopentadiyls. Although the notion of diazenyl species in the photochemistry of azoalkanes is not popular,[1] some experimental claims have been documented.[6-8]

A Salem diagram (Figure 3) provides further insight into the photomechanistic details of one-bond vs. two-bond cleavages of azoalkanes and the electronic nature of the

(22) (a) Wentrup, C. "Reaktive Zwischenstufen"; Georg Thieme Verlag: Stuttgart, 1979; Vol. 1, p 124. (b) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1975; Vol. II, p 26. (c) Robin, M. B. In "The Chemistry of the Hydrazo, Azo and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; Vol. I, p 1. (d) Conrad, M. P.; Pitzer, R. M.; Schaeffer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245. (e) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. (f) Davis, J. H.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1977**, *99*, 7111. (g) Casewit, C. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 4057. (h) Salem, L. *Science (Washington, D.C.)* **1976**, *191*, 822. (i) Cohen, S. G.; Zand, R,; Steel, C. *J. Am. Chem. Soc.* **1961**, *83*, 2895. (j) Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.* **1981**, *46*, 2116. (k) Steel, C.; Zand, R.; Hurwitz, P.; Cohen, S. G. *J. Am. Chem. Soc.* **1964**, *86*, 679.

Scheme I



diradical species that are formed. This diagram was originally developed for the photochemical decomposition of *cis*-diazene,[5] and is accordingly adapted for our present case of the azoalkanes 1. In the two-bond cleavage mode (left-hand side of Figure 3) the $^{1,3}n_-,\pi^*$ excitation does not correlate directly with the two possible 1,3-cyclopentadiyl fragments $^1D_{\sigma,\sigma}$ and $^3D_{\pi,\pi}$ because of different space symmetries. These $^{1,3}n_-,\pi^*$ excited states of the azoalkane 1 must correlate with higher excited states of the 1,3-cyclopentadiyl and through the appropriate surface jump lead to the $^1D_{\sigma,\sigma}$ and $^3D_{\pi,\pi}$ ground states. However, such a concerted process requires additional activation; in fact, the theoretical work[5] claims about double that of the one-bond cleavage. Consequently, the $^{1,3}n_-,\pi^*$ excited states should preferentially suffer stepwise decomposition (one-bond cleavage), leading either directly to diazenyl diradicals of the $^{1,3}D'_{\sigma,\pi}$ type or via surface jump to the $^{1,3}D'_{\sigma,\sigma}$ type (right-hand side of Figure 3). The latter alternative requires again additional activation in view of the different space symmetries. Typical values of activation energies for the decomposition of n,π^* excited azoalkanes are ca. 10 to 15 kcal/mol.[1]

In the 185-nm photolysis, on the other hand, upper excited states of the azoalkane 1 are reached (Figure 2),[17] possibly of the π,π^* and n,σ^* type besides the various Rydberg states.[18] As the Salem diagram reveals (left-hand side of Figure 3), the $^1n_-,\sigma_+^*$ excited state of the azoalkane 1 correlates with the $^1D_{\sigma,\sigma}$ ground state of the 1,3-cyclopentadiyl. Furthermore, the $^1\pi,\pi^*$ excited state correlates with the excited zwitterionic state Z of the 1,3-cyclopentadiyl. For both photochemical pathways direct conversion without activation is expected. Consequently, at least in principle the concerted denitrogenation (two-bond cleavage) of azoalkanes 1 to give 1,3-cyclopentadiyl species on 185-nm excitation is possible

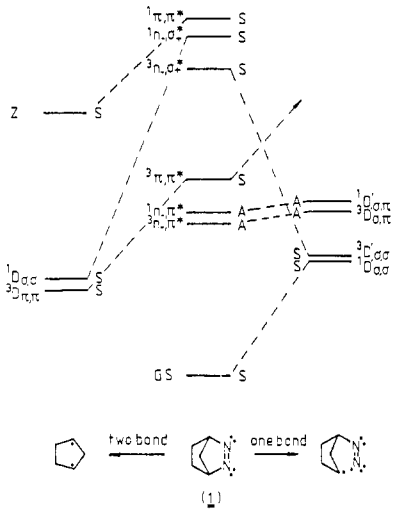


Figure 3. Salem diagram for stepwise (one-bond cleavage) and concerted (two-bond cleavage) denitrogenation of azoalkanes 1.

from the point of view of energy sufficiency (Figure 2) and state correlation (Figure 3). This should not be construed to mean that in the 185-nm photolysis only two-bond cleavage directly into 1,3-cyclopentadiyls takes place. For example, a number of Rydberg states such as (π,3s)Ry, (n,3s)Ry, and (σ,3s)Ry are possible, which could undergo one-bond cleavage leading to diazenyl diradicals. These are not considered in the Salem diagram (Figure 3) since neither theoretical nor spectroscopic data are presently available to correlate the respective states.

On the basis of the Salem diagram (Figure 3), we *postulate* that the 185-nm photolysis of azoalkanes 1 engages mainly concerted two-bond fragmentation leading directly

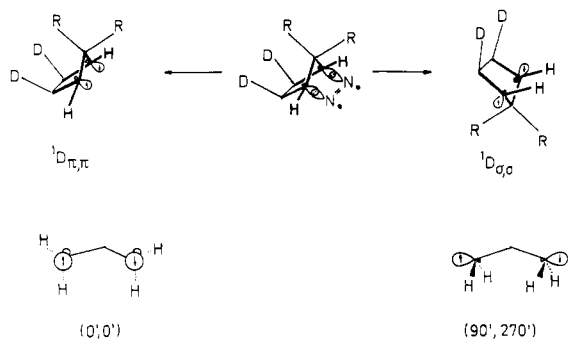


Figure 4. Formation of the pyramidalized $^1D_{\pi,\pi}$ and $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyls in the 185-nm denitrogenation of azoalkanes **1**. For convenience the corresponding pyramidalized (0',0') and (90',270') trimethylenes are shown.[11a]

to the 1,3-cyclopentadiyl intermediates $^1D_{\sigma,\sigma}$ and Z as precursors to the observed photoproducts (Scheme I). Of these the zwitterionic form Z is the logical source for the significant amounts (fact f) of the rearrangement product cyclopentene **3**. Either direct 1,2-shift of the substituent at the 2-position or cyclization first into bicyclopentane **2**, which would be expected to be vibrationally excited (hot) in view of the high exothermicity, and subsequent rearrangement are plausible alternatives to obtain cyclopentenes **3** in the 185-nm photolysis of azoalkanes **1**.

This leaves us with the $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl as the precursor for the stereoselective cyclization into the doubly inverted bicyclopentanes **2** (fact g). This unusual geometry of the 1,3-cyclopentadiyl is analogous to the so-called "inward-pyramidalized" conformation of $^1D_{\sigma\sigma}$-type trimethylene, for which theory[11a] predicts it to be the preferred singlet ground state by a few kilocalories. In Figure 4 the mode of formation of this inward-pyramidalized $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl is shown and for comparison also its pyramidalized $^1D_{\pi,\pi}$ conformation from the azoalkane **1**. For convenience the notation of the original paper,[11a] namely (0',0') and (90',270'), corresponding respectively to the pyramidalized $^1D_{\pi,\pi}$ and $^1D_{\sigma,\sigma}$ trimethylenes, are also given. For emphasis the pyramidalized trimethylene fragments are marked in boldface. The drawings in Figure 4 try to convey (cf. molecular models) that as the nitrogen leaves (concerted two-bond cleavage in the 185-nm photolysis) the lower energy conformation $^1D_{\sigma,\sigma}$ is obtained if the methylene bridge moves in the direction of the departing nitrogen molecule while the higher energy conformation $^1D_{\pi,\pi}$ results if the methylene bridge remains stationary. We postulate that this energy bias guides the nitrogen extrusion preferentially toward the inward-pyramidalized $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl. This remarkable species is favorably disposed toward cyclization via back-lobe overlap into the bicyclopentane *exo*-**2**. Of course, through thermal activation some of it can be induced to become a planar conformation and generate exo- and endo-isomerized bicyclopentanes **2** as minor pathway. Rearrangement into cyclopentenes **3** is, however, unlikely because the orbitals at the radical sites and those of the migrating substituent at the 2-position are essentially orthogonal. For a facile 1,2-shift planarization would be essential. This applies also to the spirocyclopropane-substituted 1,3-cyclopentadiyl derived from the azoalkane **1b**, which leads to completely isomerized cyclopentene **3b** (fact h) and requires a planar $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl intermediate.

Before entering into the mechanistic discussion of the 350-nm photolysis (n,π^* excitation) of the azoalkanes **1**, let us briefly consider their thermal denitrogenation. As already stated in the introduction, a diazenyl diradical is likely to intervene also in such symmetrical bicyclic azoalkanes.[3,4] The Salem diagram (Figure 3) reveals that the $^1D'_{\sigma,\sigma}$-type diazenyl diradical should be initially formed on one-bond cleavage. From spatial symmetry considerations (these are not shown in Figure 3), such a $^1D'_{\sigma,\sigma}$ diazenyl diradical correlates directly with ground-state molecular nitrogen and a $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl species. We *postulate* that also in this mode of activation the inward-pyramidalized species is preferentially formed (Scheme I), since analogous to the trimethylene species,[11a] it is expected to be the lowest energy conformer of the singlet 1,3-cyclopentadiyls. Consequently, the significant degree of double inversion in the vacuum flash pyrolysis (fact i) can be rationalized ($^1D_{\sigma,\sigma}$) in terms of faster cyclization of the inward-pyramidalized 1,3-cyclopentadiyl to the *exo*-**2** bicyclopentane than stereoisomerization via planarization. Rearrangement, which is observed only to a small extent at moderate temperatures (fact i), takes place presumably via such planar singlet 1,3-cyclopentadiyls. As pointed out already (Figure 1), the singlet trimethylene experiences an appreciable activation energy (ca. 5 kcal/mol) toward rearrangement into propene compared to cyclization into cyclopropane.[11a] Therefore, in the absence of quantum chemical data, we content that the trimethylene results serve as instructive model for the rearrangement and cyclization of 1,3-cyclopentadiyl into cyclopentene and bicyclopentane, respectively.

An alternative way to rationalize the stereoselective double inversion (fact i) in the bicyclopentane product would be to invoke the backside S_H2 displacement[13e] in the $^1D'_{\sigma,\sigma}$ diazenyl diradical. However, as a competing process, denitrogenation to yield a planar $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl, which predominantly isomerizes into *exo*- and *endo*-bicyclopentenes and to a small degree rearranges into cyclopentene, would have to be invoked. We claim that our mechanistic construct of the inward-pyramidalized $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl as key intermediate provides an inherently more consistent rationalization of the *complete* set of data.

Let us now attempt to rationalize the results of the 350-nm photolysis (n,π^* excitation) of the azoalkanes **1**. In view of the theoretical work[5] on diazene and the published experimental results, we *postulate* that also here the stepwise process (one-bond cleavage) obtains, generating initially a diazenyl diradical. In the triplet-sensitized (benzophenone) photolysis the Salem diagram (Figure 3) reveals that the $^3n_-,\pi^*$ state of the azoalkane **1** correlates with the $^3D'_{\sigma,\pi}$ diazenyl species. Direct denitrogenation into the lowest energy planar $^3D_{\pi,\pi}$ 1,3-cyclopentadiyl is by space symmetry forbidden. Worse yet, n,π^* excited molecular nitrogen must result on cleavage of the remaining C–N bond. A surface jump would be necessary to fulfill this process, and a large activation energy is expected. More probably the $^3D'_{\sigma,\pi}$ diazenyl diradical could by less costly (energywise) surface jump first be converted into the $^3D'_{\sigma,\sigma}$ species. In fact, this species can be directly obtained from the $^3n,\pi^*$ excited azoalkanes by jumping onto the $^3n_-,\sigma_+^*$ $^3D'_{\sigma,\sigma}$ surface (Figure 3). Whatever the origin of the $^3D'_{\sigma,\sigma}$ diazenyl diradical, it can readily lose ground-state molecular nitrogen to give the lowest energy $^3D_{\pi,\pi}$ 1,3-cyclopentadienyl. The latter is expected to cyclize into completely exo- and endo-isomerized bicyclopentanes. However, the small degree (fact d) of double inversion (1.15) in the bicyclopentane product is puzzling. Possibly this could arise from intersystem crossing of the $^3D'_{\sigma,\sigma}$ to the $^1D'_{\sigma,\sigma}$ diazenyl diradical,[12] whose chemical fate has already been discussed in connection with thermolysis of the azoalkanes **1** (Scheme I). That this small degree of

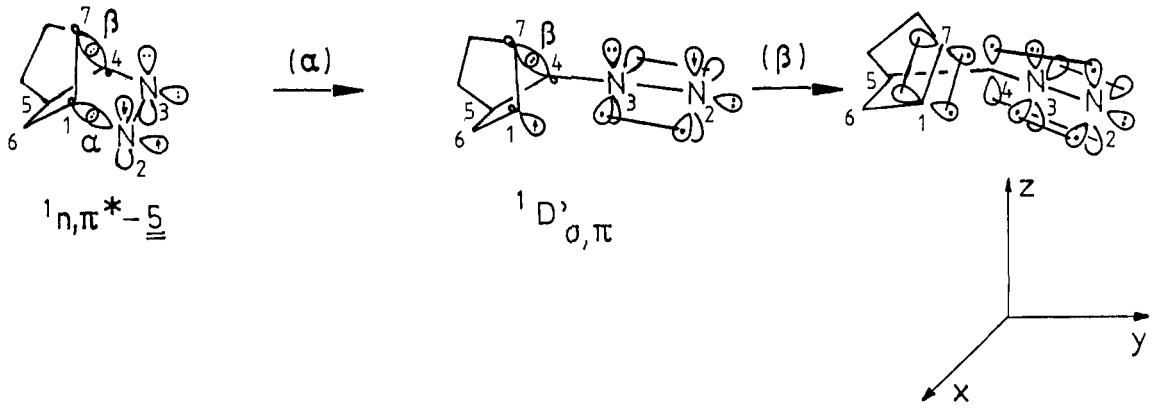


Figure 5. β-Cleavage on $^1n,\pi^*$ excitation of the $^1D'_{\sigma,\pi}$ diazenyl diradical derived from the tricyclic azoalkane **5** leading to diazoalkane.

double inversion cannot be derived from the planar $^3D_{\pi,\pi}$ 1,3-cyclopentadiyl is convincingly demonstrated by the observation that oxygen trapping gives completely exo- and endo-isomerized endo peroxides.[23] Finally, the lack (traces) of rearrangement of the $^3D_{\pi,\pi}$ 1,3-cyclopentadiyl into cyclopentene (fact d) has been rationalized for the parent 1,3-diradical trimethylene[11] in terms of efficient intersystem crossing with concurrent cyclization (Figure 1).

Many of the above speculations also apply to the direct 350-nm photolysis (singlet) of the azoalkanes **1**. The Salem diagram (Figure 3) clearly indicates that initially the $^1D'_{\sigma,\pi}$ diazenyl diradical must result because the $^1n,\pi^*$ excited azoalkane correlates directly with the $^1D'_{\sigma,\pi}$ diradical state. As a competitive mode, the $^1n,\pi^*$ excited azoalkane undergoes surface jump with intersystem crossing to generate the $^3D'_{\sigma,\sigma}$ diazenyl diradical, whose chemical fate has already been discussed in terms of the triplet-sensitized photolysis (Scheme I). This would rationalize the relatively low degree (1.54) of double inversion in the bicyclopentane **2a** (fact a). However, what is the origin of even this notable stereoselectivity, especially in the case of bicyclopentane **2b** (fact c)?

Backside displacement of nitrogen via an S_H2 process[13e] (Scheme I) to give directly doubly inverted *exo*-**2** bicyclopentane would afford $^1n,\pi^*$ excited molecular nitrogen. The activation energy for this highly endothermic process would be inaccessible. In fact, such $^1D'_{\sigma,\pi}$ diazenyl diradicals suffer β-cleavage to result in diazoalkane, as illustrated for the related tricyclic azoalkane **5** (Figure 5).[8] In the $^1D'_{\sigma,\pi}$ diradical the β-bond aligns with the nitrogen π_2-orbital in such a way as to profit from maximal overlap with the incipient 2p orbital at the 4-carbon (norbornane numbering) to form the diazo π-orbital. At the same time the overlap between the incipient 2p orbitals at the 1,7-carbons is optimized for the formation of the C–C double bond. Yet, in the direct 350-nm photolysis of azoalkanes **1** no corresponding diazoalkane is formed. Inspection of molecular framework models suggests that for azoalkanes **1** the incipient 2p orbitals are essentially orthogonal to one another, while the 5,7-ethano bridge in **5** places these 2p orbitals essentially parallel to one another and is thus optimal for C–C double bond formation during β-cleavage.

The point of this discussion is that the $^1D'_{\sigma,\pi}$ diazenyl diradical is obliged to become dissipated along chemical channels other than nitrogen loss or β-cleavage, because both modes are expected to require appreciable activation. Conversion into the $^1D'_{\sigma,\sigma}$ diazenyl diradical, the species

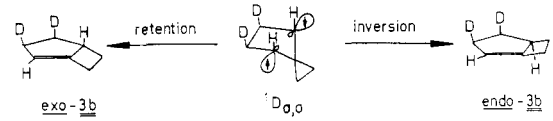


Figure 6. Rearrangement of the inward-pyramidalized $^1D_{\sigma,\sigma}$ 1,3-cyclopentadiyl derived from azoalkane **1b** into the cyclopentenes **3b**.

of the thermal process and thus a means to generate doubly inverted bicyclopentane *exo*-**2** (Scheme I), should also require considerable activation because a surface jump is involved. Even worse, the Salem diagram (Figure 3) provides no direct access to this species, because the $^1D'_{\sigma,\sigma}$ species correlates with the ground state of azoalkane **1**. The pathway $^1D'_{\sigma,\pi} \rightarrow {}^3D'_{\sigma,\sigma} \rightarrow {}^1D'_{\sigma,\sigma}$, involving first surface jump with intersystem crossing, followed by a second intersystem crossing is possible but should be rather inefficient. Since the $^3D'_{\sigma,\sigma}$ diazenyl diradical is presumably formed from the $^1n,\pi^*$ excited azoalkane via surface jump and intersystem crossing, a more likely route to the $^1D_{\sigma,\sigma}$ species is subsequent intersystem crossing and eventual double inversion to give *exo*-**2** bicyclopentane (Scheme I). Of course, most of the $^3D_{\sigma,\sigma}$ leads via the $^3D_{\pi,\pi}$ 1,3-cyclopentadiyl to predominantly (1.54) exo- and endo-isomerized bicyclopentane **2a** (fact b).

A possible reason why the $^3D'_{\sigma,\sigma}$ diazenyl diradical derived from azoalkane **1b** exhibits so much higher (2.32) double inversion (fact c) could be more efficient intersystem-crossing in the $^3D'_{\sigma,\sigma} \rightarrow {}^1D'_{\sigma,\sigma}$ transformation. The spirocyclopropane substituent should promote planarization of the carbon radical site due to cyclopropylcarbinyl interaction (optimized overlap between radical site 2p and cyclopropane Walsh orbitals). This tends to arrange the orbitals on the carbon and nitrogen radical sites of the $^3D'_{\sigma,\sigma}$ diazenyl diradicals in an orthogonal conformation (cf. molecular framework models), a favored condition for efficient spin–orbital intersystem crossing.[12]

Of note (fact c) is also the relatively large (8%) amount of rearrangement product **3b** derived from azoalkane **1b** in the 350-nm photolysis, especially that it is formed with excess (1.55) retention (Figure 6). If planarization takes place competitively with the 1,2-shift, excess retention is expected (cf. molecular framework models). The release of spirocyclopropane strain energy (ca. 30 kcal/mol) should provide the necessary driving force. The much shorter triplet lifetime ($\tau_T < 0.5$ ns) of the 1,3-cyclopentadiyl derived from azoalkane **1b** vs. that of azoalkane **1a** ($\tau_T \sim 600$ ns) clearly brings out the greater reactivity of the former as the result of spirocyclopropanation.[23] Excess double inversion in the cyclization product bicyclopentane **2b** but excess retention in the rearrangement product cyclopentene **3b** *cannot* be reconciled in terms of a pathway in

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which a diazenyl diradical serves as immediate precursor[13e] to these denitrogenated products. For example, backside displacement of nitrogen (S_H2 process) in the diazenyl species with concomitant ring expansion (1,2-shift) would have to afford excess *endo*-**3b** (inversion).

Unquestionably, the photochemical denitrogenation of bicyclic azoalkanes is considerably more complex than the thermal denitrogenation of acyclic ones, and even for the latter a satisfactory and consistent mechanistic framework is lacking.[16c] We hope that the present mechanistic *speculations* provide new food for thought on this perplexing but fascinating problem. Nevertheless, we prefer the mechanistic rationalization of Scheme I to those previously suggested[13-15] because on one hand it accounts satisfactorily for all the experimental facts including the novel 185-nm photolysis results and on the other hand it is consistent with the recent theoretical work on this subject.[3,5,11] The crucial assumptions of our analysis are as follows: (i) stepwise one-bond cleavage leading first to diazenyl diradicals $^1D'_{\sigma,\sigma}$ and $^{1,3}D'_{\pi,\pi}$, respectively, for the thermal and long wavelength ($\lambda > 300$ nm) photolyses, (ii) subsequent denitrogenation of these diazenyl diradicals affording the 1,3-cyclopentadiyl diradicals $^1D_{\sigma,\sigma}$ and $^3D_{\pi,\pi}$, (iii) the singlet 1,3-cyclopentadiyl diradical $^1D_{\sigma,\sigma}$ in its inward-pyramidalized conformation serving as immediate precursor to the cyclization product with double inversion, and (iv) two-bond cleavage leading directly to the 1,3-cyclopentadiyl diradical $^1D_{\sigma,\sigma}$ and the zwitterion Z in the 185-nm photolysis, the latter being responsible for extensive rearrangement via 1,2-shift.

Experimental Section

General Aspects. Melting points are uncorrected and were measured in a sealed capillary on a Buchi SMP-20 apparatus. All photolyses were conducted in a mercury-free apparatus using degassed spectrograde *n*-pentane or *n*-heptane as solvent. The solvents were purified as reported.[20]

Spectroscopic Instrumentation. Infrared spectra were recorded on a Beckmann Acculab 4 spectrometer and are reported in wavenumbers (cm^{-1}). ^1H (400 MHz), ^{13}C (100.6 MHz), and ^2H (61.4 MHz) NMR spectra were measured on a Bruker WM-400 NMR spectrometer in $CDCl_3$ or $CFCl_3$, respectively, with Me_4Si or $CDCl_3$ as reference. The ultraviolet absorption spectra were measured on a Cary 17 spectrophotometer which was flushed with purified nitrogen prior to measurement.

Gas Chromatographic Instrumentation. Preparative gas chromatographic separations were performed on a Carlo Erba, Model 4200 gas chromatograph, equipped with flame-ionization detector (FID), using packed glass columns. Column A: 1.5 m × 8 mm, packed with 10% Apiezon L on Chromosorb WHP (80/100); carrier gas flow (N_2), 25 mL/min; column, injector, and detector temperatures, 50, 180, and 200 °C, respectively. Column B: 1.5 m × 8 mm, packed with 10% β,β'-oxidipropionitril (ODPN) on Volaspher (80/100); carrier gas flow (N_2), 20–40 mL/min; column, injector, and detector temperatures 50, 100, and 100–150 °C, respectively. Column C: Column A but column, injector, and detector temperatures of 40, 100, and 100 °C, respectively. Column D: 1.5 m × 8 mm, packed with 5% $AgNO_3$/20% ethylene glycol on Volaspher (80/100); carrier gas flow (N_2), 30 mL/min; column, injector, and detector temperatures 40, 70, and 80 °C, respectively.

Analytical separations and quantitative product analyses were performed on a Carlo Erba capillary gas chromatograph (CGC) Fractovap 2900, equipped with FID using glass capillary columns. Column E: 86 × 0.8 mm, polypropylene glycol (PPG); carrier gas flow (N_2), 0.56 mL/min; column, injector, and detector temperatures, 20, 150, and 150 °C, respectively. Column F: 50 m × 0.8 mm, OV 101; carrier gas flow (N_2), 1.7 mL/min; column, injector, and detector temperatures, 72, 125, and 125 °C, respectively. Column G: 40 m × 0.8 mm, OV 101; carrier gas flow (N_2), 0.86 mL/min; column, injector, and detector temperatures 72, 100, and 150 °C, respectively.

Light Sources. For quantitative 185-nm photolyses the unfiltered light of a 10-W low-pressure mercury arc (Gräntzel Company, Karlsruhe) was used with an output of 10% at 185 nm, 66% at 254 nm, and the remaining 24% at higher wavelengths. Preparative 185-nm photolyses were performed using the unfiltered light of a low-pressure mercury arc (HNS-10W, Osram Company) with a light output of 12% at 185 nm, 78.5% at 254 nm, and the rest at higher wavelengths. The 350- and 254-nm photolyses were conducted in a Rayonet photoreactor RPR-100, using the appropriate 350- and 254-nm lamps as light sources. Vacuum flash thermolyses (VFT) were performed by distilling the substrate through an electrically heated Quartz tube (20 cm × 1 cm) regulated at the appropriate temperature and pressure.

Materials. Cyclopentene, 1,3-pentadiene, nonane (CGC-standard), and 2-methyl-1,3-butadiene (CGC-standard) were commercially available in purities better than 99%. Methylenecyclobutane and 1,4-pentadiene were obtained from Dr. P. Binger (Max-Planck-Institut für Kohleforschung, Mülheim).

2,3-Diazabicyclo[2.2.1]hept-2-ene (1a), mp 98.5–100 °C, was prepared according to the known procedure[13f] and before use sublimed twice at 40 °C (0.1 torr): UV (*n*-pentane) λ (ϵ) 341 (420), 185 nm (2800).

Bicyclo[2.1.0]pentane (2a), bp 45–46 °C (760 torr), was prepared in purity better than 99.4% (CGC) by thermolysis of azoalkane[13f] **1a** at 260 °C (760 torr): UV (*n*-pentane) λ (ϵ) 185 nm (2500); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.51 (dt, 1 H, syn 5-H), 0.67 (mc, 1 H, anti 5-H), 1.35 (mc, 2 H, endo 2,3-H), 1.51 (mc, 2 H, 1-H, 4-H), 2.11 (mc, 2 H, exo 2,3-H).

***exo*-5,6-Dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (1a-d_2)** was synthesized as reported by Roth and Martin,[15] mp 96–97 °C. Its ^1H NMR and IR coincided with those published.[14a] The ^2H NMR [δ 1.52 (br s)] and ^1H NMR demonstrated that the sample was >95% deuterated in the exo 5,6-positions.

***exo*/*endo*-2,3-Dideuteriobicyclo[2.1.0]pentane (2a-d_2)** was synthesized by thermolysis[13a,15] of azoalkane **1a**-d_2 to yield a mixture of *exo*/*endo*-**2a**-d_2 = (54.3 ± 1.2%)/45.7 ± 0.8%) at 260 °C (760 torr) or *exo*/*endo*-**2a**-d_2 = (74.6 ± 0.5%)/(25.4 ± 0.2%) at 180 °C (140 torr) (Table I): ^2H NMR ($CFCl_3$, 61.4 MHz) δ 1.45 (br s, endo D), 2.19 (br s; exo D).

***cis*-3,4-Dideuteriocyclopent-1-ene (3a-d_2)** was synthesized by pyrolysis[13a] of 1.00 g (10.2 mmol) of azoalkane **1a**-d_2 at 350 °C (760 torr) to yield 0.51 g (71%) of a 80:20 mixture of cyclopentene-3,4-d_2 (**3a**-d_2) and bicyclo[2.1.0]pentane-2,3-d_2 (**2a**-d_2). The pure olefin **3a**-d_2 was collected by preparative GC using Column D: IR ($CFCl_3$) 3050, 2930, 2900, 2850, 2120, 1660, 1365, 910, 830, 735 cm^{-1}; UV (*n*-pentane) λ (ϵ) 185 nm (11 000); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.79 (br m, 1 H, 4-H), 2.24 (br m, 1 H, 3-H), 2.28 (br d, 2 H, 5-H), 5.68 (s, 2 H, 1-H, 2-H). ^2H NMR ($CFCl_3$, 61.4 MHz) δ 1.92 (m, 1 D, 4-D), 2.38 (br m, 1 D, 3-D).

Spiro[cyclopropane-1,7'-[2,3]diazabicyclo[2.2.1]hept-2-ene] (1b) was synthesized in analogy to the literature procedure[14b] using 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) as dienophile: UV (*n*-pentane) λ (ϵ) 342 (161), 185 nm (5320).

Spiro[bicyclo[2.1.0]pentane-5,1'-cyclopropane] (2b) was prepared by 350-nm photolysis of azoalkane **1b**[14b] in 200 mL of *n*-pentane. The pure spirobicyclopentane **2b** was collected by preparative GC using Column B in purity better than 99.5% (CGC): IR (CCl_4) 3070, 3035, 3000, 2970, 2930, 2895, 2860, 1424, 865, 834 cm^{-1}; UV (*n*-pentane) λ (ϵ) 185 nm (1440); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.66–0.76 (m, 2 H), 0.91–1.00 (m, 2 H), 1.49 (mc, 2 H, endo 2,3-H), 1.79 (mc, 2 H, 1-H, 4-H), 2.16 (mc, 2 H, exo 2,3-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 1.91 (t, C-2'), 6.91 (t, C-3'), 21.24 (d, C-1, C-4), 22.60 (s, C-5), 22.84 (t, C-2, C-3).

Bicyclo[3.2.0]hept-1-ene (3b)[14c] was prepared by benzophenone-sensitized 350-nm photolysis of azoalkane **1b**. A solution of 0.50 g (4.1 mmol) of azoalkane **1b** and 5.00 g (27.4 mmol) of benzophenone in 300 mL of *n*-pentane were irradiated for 2 h in the Rayonet photoreactor at 350 nm. The yellow solution was concentrated to 2–3 mL by means of distillation over a 20-cm Vigreux column (35–36 °C). The benzophenone was removed by means of silica gel chromatography (SiO_2/substrate = 25:1) and subsequent preparative GC (Column B) yielded 0.30 g (78%) of the olefin **3b** as a colorless liquid: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.49 (mc, 1 H), 1.66 (mc, 1 H, endo 4-H), 2.17 (mc, 1 H, exo 4-H), 2.22–2.36 (m, 2 H, endo 3-H), 2.46–2.64 (m, 2 H, exo 3-H), 2.68–2.82 (m, 1 H), 3.02 (mc, 1 H, 5-H), 5.27 (br s, 1 H, 2-H) [a

definitive assignment of the cyclobutane protons anti 6-H, anti 7-H, syn 6-H, and syn 7-H, at δ 1.49, 2.22–2.36, 2.46–2.64, and 2.68–2.82, was not possible even with decoupling experiments]; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.6 (t, C-6), 30.4 (t, C-7), 35.4 (t, C-4), 36.4 (t, C-3), 49.7 (d, C-5), 115.8 (:, C-2), 14..8 (s, C-1).

Spiro[cyclopropane-1,7′-*exo*-2′,3′-dideuteriobicyclo-[2.2.1]hept-2-ene][14b] **(1b)** was obtained by reaction of cyclopentadiene with 4-phenyl-1,2,4-triazole-3,5-dione to yield 43% of the unsaturated urazole (mp 150 °C) followed by catalytic deuteration with Pd/C to yield 91% of the corresponding saturated urazole (mp 208–209.5 °C). Saponification and subsequent oxidation with $CuCl_2$ yielded 71% of the azoalkane **1b**-d_2 (mp 26–27 °C). Its ^1H NMR and IR spectra coincided with those published.[14b] The ^2H NMR [($CFCl_3$, 61.4 MHz) δ 1.74 (br s)] and ^1H NMR demonstrated that the sample was >95% deuterated in exo 5,6-positions.

Spiro[bicyclo[2.1.0]pentane-5,1′-cyclopropane-2′,3′-d_2] (**1b-d_2**)[14a,b] was obtained by 350-nm photolysis of azoalkane **1b**-d_2 in 37% yield by preparative GC collection (Column B): IR (CCl_4) 3070, 3035, 2998, 2960, 2920, 2865, 2200, 2185, 1422, 865 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.65–0.77 (m, 2 H), 0.89–1.02 (m, 2 H), 1.49 (br s, 1.4 H, endo 2,3-H), 1.79 (br s, 2 H, 1-H, 4-H), 2.14 (br s, 0.6 H, exo 2,3-H); ^2H NMR ($CFCl_3$, 61.4 MHz) δ 1.56 (br s, 0.6 D, endo 2,3-D), 2.22 (br s; 1.4 D, exo 2,3-D); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 1.88 (t, C-2′), 6.86 (t, C-3′), 21.10 (d, C-1, C-4), 22.34 (m, C-2, C-3), 22.68 (s, C-5).

Bicyclo[3.2.0]hept-1-ene-3,4-d_2 (3b-d_2) was synthesized by 350-nm photolysis of azoalkane **1b**-d_2 in 8% yield after collection by means of preparative GC (Column B): IR (film) 3040, 2960, 2918, 2876, 2832, 2170, 2135, 1651, 1436, 793 cm^{-1}; ^2H NMR ($CFCl_3$, 61.4 MHz) δ 1.70 (br s, 0.39 D, endo 4-D), 2.24 (br s, 0.61 D, exo 4-D), 2.30 (br s, 0.39 D, endo 3-D), 2.60 (br s, 0.61 D, exo 3-D); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.65 (t, C-6), 30.40 (t, C-7), 35.01 (m, C-4), 36.03 (m, C-3), 49.61 (d, C-5), 115.71, 115.76 (d, C-2), 149.43 (s, C-1) [the two doublets for C-2 are due to the deuterium isotope effect,[25] consistent with the fact that a mixture of *exo/endo*-3,4-dideuterated bicycloheptene **3b** was formed].

1-Hydroperoxybicyclo[3.2.0]hept-2-ene-d_2 (4) was prepared in analogy to the undeuterated derivative[14d] by photooxygenation of 0.10 g (1.04 mmol) of the olefin **3b**-d_2 in 25 mL of CH_2Cl_2 and 2 mg of tetraphenylporphine as sensitizer. After 3 h of photooxygenation at −78 °C the solvent was removed by means of destillation at 0 °C (18 torr) and the crude product was purified by silica gel chromatography (SiO_2/substrate = 40:1; CH_2Cl_2) at −20 °C. Final destillation at 20 °C (0.1 torr) yielded 26% hydroperoxide **4** as colorless liquid: IR (film) 3380, 3060, 2996, 2945, 2905, 2860, 2160, 1658, 1435, 1244 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.08–1.28 (m, 1 H, syn 6-H), 2.04–2.17 (m, 2.7 H, endo 4-H, anti 6-H, syn 7-H), 2.44 (mc, 1 H, anti 7-H), 2.67 (mc, 0.4 H, exo 4-H), 2.79–2.94 (m, 1 H, 5-H), 5.75 (mc, 1 H, 2-H), 6.11 (mc, 0.6 H, 3-H), 8.14 (br s, 1 H, OOH); ^2H NMR ($CFCl_3$, 61.4 MHz) δ 2.13 (br s, endo 4-D), 2.72 (br s, exo 4-D), 6.11 (br s, 3-D); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.03 (t, C-6), 30.31 (t, C-7), 38.87 (m, C-4), 39.56 (d, C-5), 96.30 (s, C-1), 130.32, 130.46 (d, C-3), 136.68 (d, C-2) [again the two doublets for C-3 are due to the deuterium isotope effect,[25] consistent with the fact that a mixture of 3-deuterated hydroperoxide **4** was formed].

Apparatus. For analytical and quantitative 185-nm photolysis a low-pressure mercury arc (Gräntzel, Karlsruhe) was used, similar to that described by Sänger and von Sonntag.[26] The sigmoidal light source was mounted on an optical bench. The Suprasil cuvette (Hellma Company, Mülheim) was provided with a three-way stopcock to permit evacuation and nitrogen purging (gas inlet) and thermostated at 25.0 ± 0.1 °C by means of a brass block which was connected to a Lauda model D8/17 thermostat. The cuvette was fixed on the optical bench directly in front of the 185-nm light source. The contents of the suprasil cuvette were stirred magnetically to minimize secondary photolysis and filter effects.

Preparative 185-nm photolyses were conducted on semipreparative scale (25 mL of 0.01 M *n*-heptane solutions) at 25 °C in a reaction vessel bearing a gas inlet and fitted with a Suprasil immersion well. The light source (HNS 10W/UoZ, Osram) was allowed to warm up for 30 min before each run, and the samples were degassed for 15 min by purging with purified nitrogen. During photolysis the lamp was cooled by means of a slow nitrogen stream (ca. 5–10 mL/min).

Product yields were obtained by CGC calibration and are reported in mol %. Calibration curves were constructed for bicyclo[2.1.0]pentane (**2a**), cyclopentene (**3a**), methylenecyclobutane, and 1,4-pentadiene by using 2-methyl-1,3-butadiene as the CGC standard. The calibration factors $f_i = 0.50 \pm 0.01$, $f_i = 1.11 \pm 0.01$, $f_i = 0.92 \bullet 0.01$, and $f_i = 1.14 \pm 0.01$, respectively, were determined on column E. Spirocyclopropane **2b** and olefin **3b** were calibrated on column G by using nonane as the CGC standard, leading to $f_i = 1.02 \pm 0.02$ and $f_i = 0.97 \pm 0.03$, respectively. The azoalkanes **1a** and **1b** were calibrated relative to nonane as the CGC standard, leading to calibration factors $f_i = 1.92 \pm 0.01$ (column F) and $f_i = 1.41 \pm 0.02$ (column E), respectively.

Isolation and Identification of the Photoproducts. Degassed samples (25 mL, 0.01 M) of the azoalkanes **1a** (*n*-pentane) and **1b** (*n*-heptane) were photolyzed at the appropriate wavelength. In the case of azoalkane **1a** the volatile C_5 products were collected by distillation up to 98 °C (760 torr), recovering ca. 1–2 mL of distillate. This fraction was processed by preparative GC on column A, collecting the C_5 fraction (t_R = 2.3 min). The products were characterized by means of ^1H (400 MHz) and ^2H (61.4 MHz) NMR and capillary GC coinjection with authentic samples on column E. By electronic integration of the appropriate resonances in the ^1H and ^2H NMR spectra the exo/endo ratios were determined. In the case of azoalkane **1b** the photolysate was concentrated by distillation [35–36 °C (760 torr)] to 1–2 mL and processed by preparative GC on Column C, collecting spirocyclopropane **2b** (t_R = 5.5 min) and olefin **3b** (t_R = 8.5 min). The products were characterized by ^1H, ^{13}C, and ^{H} NMR and the exo/endo ratios were determined by electronic integration of the appropriate resonances in the ^1H and/or ^2H NMR spectra.

Time-Dependent Photolyses. Solutions of substrate (0.01–0.05 M) in *n*-pentane (**1b, 2b**) or *n*-heptane (**1a, 2a**) were divided into four portions (25 mL). Each portion was photolyzed under the same conditions as function of time. After usual workup, the products were isolated by preparative GC and analyzed by means of ^1H and/or ^2H NMR. The results are summarized in Table I.

254-nm Control Experiments. Samples (4 mL, 0.01 M) in *n*-pentane or *n*-heptane were photolyzed in the Rayonet photoreactor (254-nm lamps) at 25 °C for 30 min. After usual workup, the products were analyzed by ^1H and/or ^2H NMR or CGC.

Sensitized Photolyses. Benzophenone sensitization was performed analogously to the 350-nm photolyses but by adding ca. 3–5 M excess benzophenone. After concentrating the solution by means of distillation to 2–3 mL, the benzophenone was removed by silica gel chromatography (CH_2Cl_2) before processing with preparative GC.

Quantum Yields. The determination of quantum yields of substrate conversion (ϕ_S) was achieved by calibrating the 185-nm light source with the cyclooctene actinometer.[20] Quantum yields of the 350-nm photolyses were measured on an optical bench with a high-pressure Xenon lamp (XBO-1600W, Osram) and a monochromator (Schoeffel Instrument GmbH, Kratos) using Actinochrome R (248/334) as actinometer,[19] kindly provided by Prof. Dr. H.-D. Brauer.

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