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Photolysis and Thermolysis of a Tetracyclic Bisazoalkane; Nitrogen Extrusion Induced by β Cleavage

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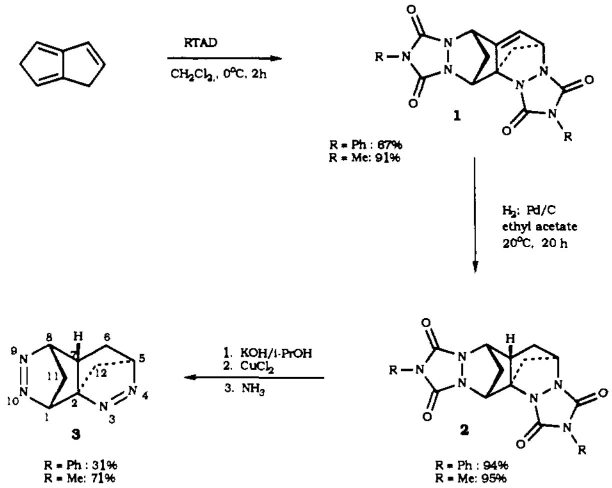
Abstract: The thermolysis and the direct and benzophenone-sensitized photolyses of the tetracyclic bisazoalkane **3** were examined. The product studies of the thermal and the direct and triplet-sensitized photochemical denitrogenations as well as the quantum yields for the photolyses show that the second nitrogen extrusion is induced by β cleavage at the primary diazenyl diradical stage to form 2-allylcyclopentadiene (**6**) by a one-photon process. Whereas this is the exclusive pathway for the benzophenone-sensitized photolysis and the thermolysis, the direct photolysis at −78 °C also gives the monoazoalkanes **4** and **4′**, which undergo further photochemical denitrogenation (two-photon process) to give the bis bicyclopentanes **5** and **5′** (tetracyclo[5.1.0.0^{1,5}.0^{2,4}]octanes) or by cyclopropylcarbinyl (CPC) rearrangement the 2-allylcyclopentadiene (**6**) by fragmentation of a 1,4-diradical.

The β fragmentation of monoradicals (eq 1) is a well-documented process in radical chemistry with a variety of synthetic applications.[1] Particularly, the nature of the leaving group X dictates the reaction rate of this transformation.[2] Recent work of Engel[3] demonstrates that the azo group effectively functions as leaving group in the β fragmentation of azoalkanes with a radical center at the β carbon. An *acyclic* bisazoalkane was used as starting material for the generation of the acyclic β-azo carbon-centered radical which could be trapped with thiophenol; this proves the existence of such short-lived species and excludes the simultaneous cleavage of all four C–N bonds.[3] Contrary to these results, two bisazoalkanes, one tricyclic[4] and one bicyclic,[5] are known not to undergo β fragmentation either under thermal or under photolytic decomposition. Under all conditions reported, only products were formed, which exclude a long-lived primary diradical species which could react by β fragmentation.

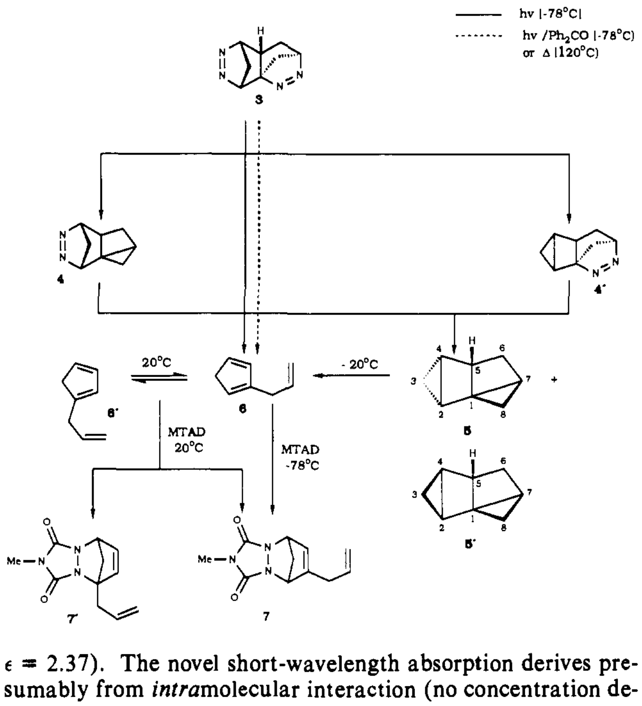
(1)

We have gathered extensive information on the structures and lifetimes of cyclic triplet[6] and singlet[7] 1,3-diradicals, and we felt motivated to investigate the denitrogenation behavior of a bisazoalkane closely related to the exceedingly well-known DBH[8] (diazabicyclo[2.2.1]heptene). As a building block for the synthesis of this model compound, we chose 1,5-dihydropentalene, conveniently available from norbornene-5-carboxaldehyde.[9]

Scheme I



Scheme II



Results

Synthesis of the Bisazoalkane 3. The bisazoalkane **3** was prepared according to the reaction pathway shown in Scheme I. Addition of 2 equiv of *N*-methyltriazolinedione (MTAD) to 1,5-dihydropentalene gave the diastereomerically pure bisurazole **1**. Catalytic hydrogenation under conventional conditions afforded the saturated bisurazole **2**, which was isolated in nearly quantitative yield in pure form. Saponification and oxidation of **2** led to the bisazoalkane **3** in an overall yield of 61% based on the parent 1,5-dihydropentalene. The relative configuration of **3** was assigned on the basis of 2D-COSY and NOE ^{1}H NMR spectroscopy. Most important for the assignment of the stereochemistry of **3** were the NOE experiments. Saturation of the 11-H$_b$ proton resulted in an enhancement (3.2%) of 7-H and vice versa (3%), while irradiation of the 12-H$_a$ proton left the 7-H proton unaffected. Thus, the addition of the second MTAD molecule proceeded anti to the first, and the hydrogenation took place syn to the C-11 methylene group. The UV spectrum of bisazoalkane **3** is unusual in that it exhibits two absorption maxima, one at 340 nm (log ϵ = 2.27, corresponding to the λ_{max} of DBH) and the other at 271 nm (log ϵ = 2.37). The novel short-wavelength absorption derives presumably from *intra*molecular interaction (no concentration de-

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Table I. Product Distribution in the Thermolysis and Photolyses of the Bisazoalkane **3**

		conditions				distribution (%)			
entry	mode	solvent	temp (°C)	time (min)	conversion[a] (%)	**4**	**5,5′**	6	6′
1	thermolysis[b]	CH_3CN	120	60	100	0	0	50[c]	50[c]
2	direct photolysis[b,d] $\phi = 1.5 \pm 0.1$[e]	CH_3CN	20	240	100	0	0	50[c]	50[c]
3	direct photolysis[d,f]	CD_2Cl_2	−78	240	100	0	25	75	0
4	direct photolysis[f,g]	CD_2Cl_2	−78	1.8	62	19	25	56	0
				2.5	84	12	20	69	0
				5.3	100	0	25	75	0
5	sens photolysis[b,h] $\phi = 1.9 \pm 0.1$[e]	CH_3CN	20	3	70	0	0	50[c]	50[c]
6	sens photolysis[f,h]	CD_2Cl_2	−78	1	18	0	0	100	0
				3	41	0	0	100	0
				6	56	0	0	100	0
				12	80	0	0	100	0

[a] The product balance was >90% in all experiments. [b] Detected by capillary GC, error ca. 3% of the stated value. [c] Equilibrium ratio of 1- and 2-allylcyclopentadiene (**6**,**6′**). [d] Rayonet photoreactor ($\lambda_{max} = 350$ nm). [e] Quantum yield of azoalkane disappearance based upon 2,3-diazabicyclo[2.2.1]hept-2-ene as actinometer ($\Phi = 1.0$). Φ_{fl} of **3** was 0.004 ± 0.001 at $\lambda_{ex} = 330$ nm and $\lambda_{em} = 411$ nm using anthracene as a standard ($\Phi_{fl} = 0.27$). [f] Detected by ^1H NMR spectroscopy (−60 °C), error ±5%. [g] Argon ion laser (333-, 351-, and 364-nm lines). [h] Ph_2CO was used as sensitizer; argon ion laser (364-nm line).

pendence) of the two azo chromophores and the long-wavelength absorption from the more normal $n\pi^*$ excitation of the isolated N═N chromophore.

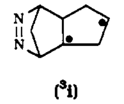
Thermolysis and Photolysis of the Bisazoalkane 3. The 2-allylcyclopentadiene (**6**) was the only primary product (Scheme II) in the thermolysis at 120 °C in CH_3CN, in the direct photolysis at 20 °C by irradiation with all of the UV lines of the argon ion laser (333, 351, and 364 nm) or at 350 nm in CH_3CN in the Rayonet photoreactor, and in the triplet-sensitized photolysis at 20 °C with benzophenone by irradiation with only the 364-nm line of the argon ion laser. In all experiments (Table I), a mixture of the two cyclopentadiene isomers **6** and **6′** was obtained, which were identified by ^1H NMR spectroscopy and/or by coinjection of an authentic sample in the capillary GC. That isomer **6** was the primary product of the denitrogenation was proved by a trapping experiment with MTAD. The bisazoalkane **3** was irradiated with all of the UV lines of the argon ion laser at 0 °C until total conversion (5 min) and addition of MTAD in dichloromethane to the photolysate led exclusively to the urazole **7**. Clearly, at elevated temperatures the isomer **6′** was formed from the primary **6** by a subsequent 1,5-hydrogen shift. Also, the benzophenone-sensitized photolysis (364-nm line of the argon ion laser) of the bisazoalkane **3** in dichloromethane-d_2 at −78 °C led only to 2-allylcyclopentadiene (**6**), as detected by ^1H and ^{13}C NMR spectroscopy (400 MHz, −60 °C).

The direct photolysis at 350 nm in the Rayonet photoreactor or irradiation with all of the UV lines (333, 352, and 364 nm) of the argon ion laser in dichloromethane-d_2 at −60 °C revealed (^1H and ^{13}C NMR) that 75% of 2-allylcyclopentadiene (**6**) and 25% of the two isomeric bisbicyclopentanes **5**,**5′** (80/20 mixture) were formed. Above −20 °C, the strained tetracyclic hydrocarbons **5**,**5′**, the first detected annelated bishousanes, exclusively decomposed into **6** (Scheme II). Careful monitoring of the time dependence on the product composition by ^1H and ^{13}C NMR directly in the 400-MHz spectrometer at −60 °C showed that also the monoazoalkanes **4** and **4′** (cf. the Experimental Section) were formed during irradiation. The monoazoalkanes **4** and **4′**, also detected by TLC (azo test) and by HPLC (UV maxima at 340 nm), as well as the bisbicyclopentanes **5**,**5′** could not be isolated in substance because of their thermal instability. Only the monoazoalkane **4** could be isolated by chromatography as a mixture with the 1- and 2-allylcyclopentadienes (**6**,**6′**), characterized by ^1H and ^{13}C NMR spectroscopy.

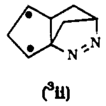
In Table I are summarized, besides the quantitative product distributions, the quantum yields of the direct and the benzophenone-sensitized denitrogenations of the bisazoalkane **3** and its fluorescence quantum yield. These data shall now be mechanistically rationalized.

Discussion

In the benzophenone-sensitized photolysis of **3** a quantum yield of $\Phi = 1.9 \pm 0.1$ was determined for the disappearance of the azoalkane chromophore. Therefore, *both* nitrogen molecules are extruded after the absorption of only *one* photon. Two photons would be required to photodenitrogenate the bisazoalkane **3** by way of the monoazoalkanes **4**,**4′**, and the quantum yield would be unity in that limit (cf. direct photolysis). Consequently, no significant amounts of monoazoalkanes **4**,**4′**, which are thermally stable at −78 °C, are formed during the sensitized denitrogenation (one-photon process). The second denitrogenation is, therefore, induced at the 1,3-triplet (diradical by β fragmentation, which is independent of the primary denitrogenation mode (formation of ^{3}**i** or ^{3}**ii**). The key triplet 1,4-diradical intermediate **D** (Scheme III) suffers C–C bond fission to afford **6**, as is known for other cyclic 1,4-diradicals.[10] An identical product composition was determined for the thermolysis of **3**. In this case, the intermediary monoazoalkanes **4**,**4′** or bisbicyclopentanes **5**,**5′** may intervene, but they are too labile for detection under the thermolysis conditions.



(^{3}**i**)



(^{3}**ii**)

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(1) For example: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986. (b) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829. (c) Webb, R. R.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 1357.

(2) (a) Kerr, J. A.; Lloyd, A. C. *Q. Rev. Chem. Soc.* **1968**, *22*, 549. (b) Boothe, T. E.; Greene, J. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1976**, *98*, 951. (c) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079.

(3) Engel, P. S.; Chen, Y.; Wang, C. *J. Am. Chem. Soc.* **1991**, *113*, 4355.

(4) (a) Allred, E. L.; Hinshaw, J. C. *J. Am. Chem. Soc.* **1968**, *90*, 6885. (b) Allred, E. l.; Hinshaw, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 3382. (c) Hinshaw, J. C.; Allred, E. L. *Chem. Commun.* **1969**, 72.

(5) (a) Gassman, P. G.; Greenlee, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 980. (b) Franck-Neumann, M.; Buchecker, C. *Tetrahedron Lett.* **1969**, 2659. (c) Schneider, M.; Csacsko, B. *Angew. Chem.* **1977**, *89*, 905. (d) Eaton, D. F.; Bergman, R. G.; Hammond, O. S. *J. Am. Chem. Soc.* **1972**, *94*, 1351. (e) Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1980**, 671.

(6) Adam, W.; Wilson, R. M.; Grabowski, S. *Acc. Chem. Res.* **1990**, *23*, 165.

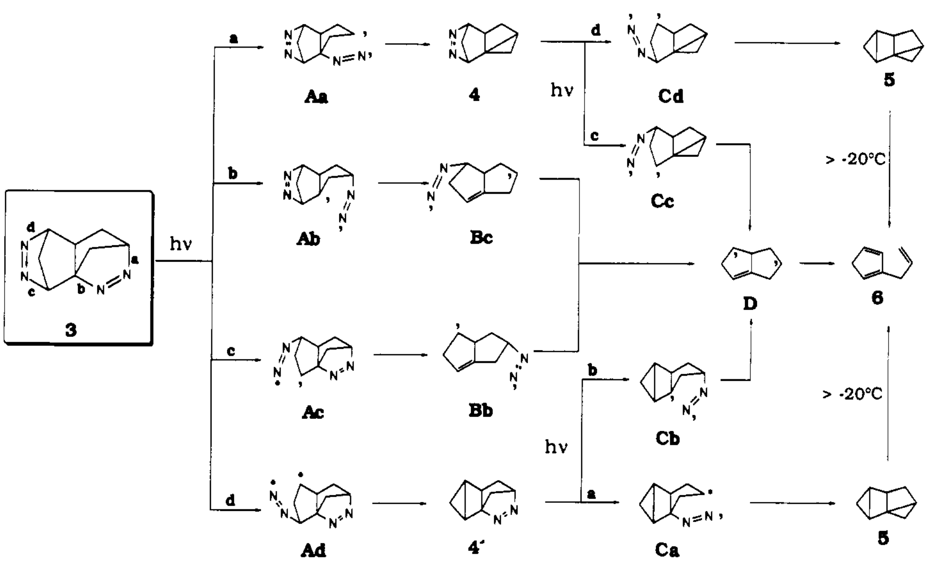
(7) Adam, W.; Platsch, H.; Wirz J. *J. Am. Chem. Soc.* **1989**, *111*, 6896.

(8) (a) Buchwalter, S. L.; Closs G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857. (b) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. (c) Wilson, R. M.; Geiser, F. *J. Am. Chem. Soc.* **1978**, *100*, 2225. (d) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303.

(9) (a) Griesbeck, A. G. *J. Org. Chem.* **1989**, *54*, 4981. (b) Griesbeck, A. G. *Synthesis* **1990**, 144.

(10) (a) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860. (b) Adam, W.; Grabowski, S.; Wilson, R. M.; Hannemann, K.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 7572.

Scheme III



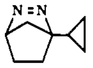
A much more complex situation is found in the direct photolysis of **3** (see Table I and Scheme III). If we assume bond cleavage of the four possible C–N single bonds (a–d) to be equally probable, ca. 50% of the diazenyl diradicals[11,12] which are formed may undergo β fragmentation (**Ab** and **Ac**), whereas the remaining ca. 50% (**Aa** and **Ad**) may lose dinitrogen with simultaneous monoazoalkane **4,4′** formation. Subsequently, the latter may absorb a second photon and eject another molecule of dinitrogen. In this train of thought, by assuming again that all possible C–N bond fissions (a–d) are equally probable, ca. 50% of the diazenyl diradicals (**Cc** and **Cb**) which are formed may undergo cyclopropylcarbinyl (CPC) rearrangement to generate the key 1,4-diradical **D** as an intermediate. The latter cleaves further at the central C–C bond to give 2-allylcyclopentadiene (**6**), and the remaining ca. 50% (**Cd** and **Ca**) may produce the bisbicyclopentanes **5,5′**.

At first sight, an effective competition between C–C bond formation by N_2 loss to give directly the bishousanes **5,5′** and CPC rearrangement at the **Cb,c** diradical stage to give 1,4-biradical **D** seems unlikely, because CPC rearrangements require appreciable thermal activation energy (ca. 6 kcal/mol). Engel and Culotta[13] determined the CPC rearrangement rate of 1-cyclopropylcyclopentyl radical (**iii**) to be 1.45×10^7 s^{-1} at 24.7 °C.


(**iii**)


(**iv**)


(**v**)


(**vi**)

The authors assume that the CPC rearrangement rate of the corresponding *triplet* 1,3-diradical (**iv**) is of the same order of magnitude, which is thus much too slow to compete with cyclization of the *singlet* 1,3-diradical into the corresponding housane. However, recent work of Ingold et al.[14] showed that the rapid ring-opening of the bicyclo[2.1.0]pent-2-yl radical (**v**) makes it one of the fastest radical clocks (2.4×10^9 s^{-1}). Therefore, the rate of CPC rearrangement at the singlet diradical stage **Cb,c** should be at least as fast, whereas loss of N_2 with concomitant cyclization into the bishousanes **5,5′** should be disfavored because of additional strain.[15]

Purely on qualitative grounds (statistical cleavage of the available azo C–N bonds) we expect ca. 25% of the bisazoalkane **3** to be converted to the bisbicyclopentanes **5,5′** following the two-photon process **3** → **Aa,d** → **4,4′** → **Cd,a** → **5**. The β fragmentation route of the diazenyl diradicals **Ab,c** involves a one-photon process to **6** by way of the denitrogenated 1,4-diradical **D** and accounts for 50% of decomposed bisazoalkane **3**. Finally, the two-photon pathway **3** → **Aa,d** → **4,4′** → **Cb,c** → **6** provides the missing 25% of allylcyclopentadiene **6**.

The facts that after complete denitrogenation the product ratio **5**/**6** is 25/75 and the quantum yield of the direct photolysis $\Phi_{\text{direct}} = 1.5 \pm 0.1$ nicely corroborate our mechanistic analysis. Additional evidence comes from the time dependence of the product composition for the direct photolysis. At 62% conversion, the amount of 2-allylcyclopentadiene (**6**) is only 56% (normalized to 100%) in the product distribution and thus has not reached its maximum yield. At this stage, the sum of the relative amounts of monoazoalkanes **4,4′** and bisbicyclopentanes **5,5′** is higher than the amount of **5,5′** at complete conversion. This demonstrates that there must be an additional route from **4** and **4′** to **6**. Under the reaction conditions of the low-temperature direct photolysis, the highly strained tetracyclic bishousanes **5,5′** are thermally stable, as control experiments reveal. In spite of the rather large error (±5%) in the quantitative determination of the product composition in the direct laser photolysis (Table I, entry 4), the data are within acceptable limits for the proposed mechanism.

The mechanistic panorama in Scheme III for the direct photolysis of bisazoalkane **3** constitutes an assembly of β fragmentation, CPC rearrangements, and competing cyclizations of the diverse diazenyl diradicals formed on denitrogenation. The mechanistic course of the direct as well as sensitized photolysis of the bisazoalkane **3** can be explained mainly on statistical cleavage of the available azo C–N bonds. We consider these novel results as encouragement for investigating polyazoalkanes in greater detail.

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(11) Recent literature substantiated the participation of these species in the direct photolysis of azoalkanes: (a) Adam, W.; Carballeira, N.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 5473. (b) Adam, W.; Gillaspey, W. D.; Peters, E.-M.; Peters, K.; Rosenthal, J. R.; von Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 580, 587. (c) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303. (d) Adam, W.; De Lucchi, O.; Dörr, M. *J. Am. Chem. Soc.* **1989**, *111*, 5209. (e) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115. (f) Adam, W.; Zang, G. *J. Org. Chem.* **1991**, *56*, 3315.

(12) The legitimate question may be raised as to why we argue exclusively in terms of diazenyl diradicals A and C and ignore the corresponding nitrogen-free 1,3-cyclopentanediyl intermediates. We assume that singlet 1,3-diyls are much too short lived (for the singlet diradical 1,3-diphenyl-1,3-cyclopentanediyl a lifetime of 22 ps has been determined[7]) to allow any competing radical fragmentation or rearrangement reactions.

(13) Engel, P. S.; Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686.

(14) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 1927.

(15) As CARS analysis[11e] of the primary photoproducts after direct excitation of azoalkanes showed, triplet 1,3-diyls are formed to a certain extent also under such conditions. Similary, the direct photolysis of 1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (vi)[13] gave the CPC rearrangement in detectable amounts through the triplet diradicals. Comparison of the product composition between the direct and the sensitized photolysis of DBH[16] allows one to estimate that a maximum of ca. 10% of all 1,3-diradicals could be formed in the *triplet* manifold during *direct* irradiation.

(16) Adam, W.; Bottle, S. F.; Finzel, R.; Kammel, T.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *J. Org. Chem.*, in press.

Experimental Section

The IR spectra were taken on a Perkin-Elmer 1420 infrared spectrometer in CCl$_4$. UV spectra were recorded on a Hitachi U-3200 spectrometer, fluorescence spectra on a Perkin-Elmer LS 50 luminescence spectrometer, and mass spectra on a Varian MAT CH 7 mass spectrometer. The ^{1}H and ^{13}C NMR spectra were run on the following spectrometers: Bruker AW 80 (80 MHz), AC 200, AC 250, and WM 400, with tetramethylsilane, deuteriodichloromethane, or deuteriochloroform as internal standards. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg, Würzburg, Germany. All melting points were not corrected and were taken on a Reichert Thermovar apparatus. Silica gel (60–230 mesh; Woelm) was used for the column chromatography. TLC analyses were run on silica gel foils Polygram SIL GC/UV$_{254}$ (40 × 80 mm) from Macherey & Nagel. The photochemical reactions were carried out in a Rayonet RP-100 photochemical reactor equipped with 350-nm lamps. The UV lines 363.8, 351.4, 351.1, 335.5, and 333.6 nm of the Coherent INNOVA-100 argon ion laser were used in the laser photolyses. Quantitative gas chromatographic analyses were carried out on a Carlo Erba Strumentazione 4100 (FID); as integrator a Shimadzu C-R1B Chromatopac was used. For HPLC analyses, a KONTRON LC pump T-414, supplied with a detector UVIKON 720 LC micro, was employed.

1,5-Dihydropentalene is known and was prepared accordingly.[9]

***anti*-3,5,7,12,14,16-Hexaaza-5,14-diphenylhexacyclo[9,5,1,1^{1,9},0^{2,8},0^{3,7},0^{12,16}]octadec-9-ene-4,6,13,15-tetraone (1).** To a solution of 3.30 g (31.6 mmol) of 1,5-dihydropentalene in 50 mL of dry dichloromethane was added at 0 °C a solution of *N*-phenyltriazolinedione (10.7 g, 63.0 mmol) in 100 mL of dry dichloromethane. The resulting mixture was stirred for 2 h at 20 °C, and the solvent was removed by rotary evaporation (20 °C/17 Torr). The crude product mixture was chromatographed on silica gel by eluting with a 1/1 mixture of petroleum ether and ethyl acetate ($R_f = 0.55$) to yield **1** (6.45 g, 67%) as a colorless powder: mp 212–213 °C dec; IR (CCl$_4$) ν 1785, 1722, 1640, 1630, 1500, 1485, 1450, 1390, 1125, 1085 cm^{-1}; UV (CH$_3$CN) λ (log ϵ) 268 nm (2.789); ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.08–2.20 (m, 2 H, 18-H), 2.70 (d, J = 11.5 Hz, 1 H, 17-H), 3.31 (d, J = 11.5 Hz, 1 H, 17-H), 5.21 (s, 1 H, 1-H or 11-H), 5.30 (t, J = 1.4 Hz, 1 H, 8-H), 5.66 (s, 1 H, 1-H or 11-H), 6.41 (dd, J = 3.0, 1.0 Hz, 1 H, 9-H), 7.36–7.53 (m, 10 H, aromatic H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 44.4 (t, C-18), 48.6 (t, C-17), 57.5 (d, C-1 or C-12), 59.3 (d, C-1 or C-12), 69.1 (d. C-8), 77.2 (s, C-2), 124.0 (d, C-9), 125.1 (d), 128.8 (d), 129.3 (d), 131.2 (s), 152.0 (s, C-10), 156.8 (s), 157.5 (s), 158.8 (s), 159.1 (s); MS (70 eV) *m/z* 454 (0.3, M$^+$), 279 (9), 177 (79), 119 (100), 103 (34), 91 (32), 77 (22). Anal. Calcd for C$_{24}$H$_{18}$N$_6$O$_4$: C, 63.43; H, 3.99; H, 18.49. Found: C, 63.13; H, 3.96; N, 18.24.

***anti*-3,5,7,12,14,16-Hexaaza-5,14-dimethylhexacyclo[9,5,1,1^{1,9},0^{2,8},0^{3,7}.0^{12,16}]octadec-9-ene-4,6,13,15-tetraone (1′).** Analogous to the above procedure, 2.50 g (24.0 mmol) of 1,5-dihydropentalene and 5.43 g (48.0 mmol) of *N*-methyltriazolinedione gave, after column chromatography (silica gel, gradient elution with a 1/1 mixture of petroleum ether/ethyl acetate), 7.20 g (91%) of **1′** as colorless rhombic crystals: mp 107–108 °C dec; IR (CCl$_4$) ν 2940, 1740, 1680, 1450, 1395, 1250, 1210, 1140, 1020 cm^{-1}; UV (CH$_3$CN) λ (log ϵ) 229 nm (3.830); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.82 (d, J = 9.4 Hz, 1 H, 18-H), 1.90 (d, J = 9.4 Hz, 1 H, 18-H), 2.48 (d, J = 11.5 Hz, 1 H, 17-H), 2.98 (s, 3 H, CH$_3$), 3.11 (d, J = 11.5 Hz, 1 H, 17-H), 5.01 (s, 1 H, 11-H), 5.07 (s, 1 H, 8-H), 5.40 (s, 1 H, 1-H or 11-H), 6.22 (d, J = 2.0 Hz, 1 H, 9-H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 25.9 (q, CH$_3$), 44.2 (t, C-17), 48.3 (t, C-18), 57.3 (d, C-1 or C-11), 59.0 (d, C-1 or C-11), 68.7 (d, C-8), 81.8 (s, C-2), 123.5 (d, C-9), 151.6 (s, C-10), 156.8 (s), 157.1 (s), 158.9 (s), 159.1 (s); MS (70 eV, NH$_3$) *m/z* 348 (1) [M$^+$ + 18], 332 (6) [M$^+$ + 2], 331 (29) [M$^+$ + 1], 330 (2) [M$^+$], 284 (11), 218 (21), 180 (6), 172 (6), 130 (6), 116 (100), 113 (16), 105 (12), 73 (14), 71 (10), 70 (6), 69 (8). Anal. Calcd for C$_{14}$H$_{14}$N$_6$O$_4$: C, 50.91; H, 4.27; N, 25.44. Found: C, 51.13; H, 4.44; N, 25.31.

***anti*-3,5,7,12,14,16-Hexaaza-5,14-diphenylhexacyclo[9.5,1,1^{1,9},0^{2,8}.0^{3,7},0^{12,16}]octadecane-4,6,13,15-tetraone (2).** The bisurazole **1** (1.38 g, 3.04 mmol) and 100 mg of 10% Pd/C in 250 mL of ethyl acetate were vigorously stirred at 20 °C for 120 h under a hydrogen gas atmosphere. Removal of the catalyst by filtration and the solvent by distillation (30 °C/20 Torr) gave 1.31 g (94%) of **2** which, after recrystallization from ethyl acetate, was obtained as a colorless powder: mp 219–220 °C; IR (CCl$_4$) ν 2970, 1770, 1710, 1500, 1390, 1250, 1230, 1120, 1090, 1070, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.90–2.34 (m, 6 H, 17-H, 18-H, 9-H, 10-H), 2.55 (d, J = 11.6 Hz, 1 H, 17-H), 4.64 (br s, 2 H, 8-H, 11-H), 5.36 (s, 1 H, 1-H), 7.32–7.58 (m, 10 H, aromatic H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 31.3 (t, C-9), 40.7 (t, C-18), 43.2 (t, C-17), 51.3 (d, C-10), 58.8 (d, C-1 or C-11), 62.6 (d, C-1 or C-11), 64.2 (d, C-8), 78.0 (s, C-2), 125.3 (d), 125.4 (d), 128.5 (d), 128.7 (d), 129.3 (d), 131.1 (s), 131.2 (s), 156.3 (s), 156.5 (s); MS (70 eV) *m/z* 457 (18) [M$^+$ + 1], 456 (64) [M$^+$], 337 (17), 281 (11), 280 (43), 279 (93), 178 (21), 177 (35), 161 (40), 133 (13), 132 (10), 120 (20), 119 (100), 118 (16), 105 (21), 104 (38), 103 (28), 92 (10), 91 (51), 78 (11), 77 (20), 64 (16). Anal. Calcd for C$_{24}$H$_{20}$N$_6$O$_4$: C, 63.10; H, 4.42; N, 18.41. Found: C, 63.41; H, 4.24; N, 18.62.

***anti*-3,5,7,12,14,16-Hexaaza-5,14-dimethylhexacyclo[9,5,1,1^{1,9},0^{2,8},0^{3,7},0^{12,16}]octadecane-4,6,13,15-tetraone (2′).** According to the above procedure, the bisurazole **1′** (2.80 g, 8.48 mmol) and 200 mg of 10% Pd/C in 500 mL of ethyl acetate at 20 °C for 55 h gave 2.68 g (95%) of **2′** as colorless powder, after recrystallization from ethyl acetate: mp 168 °C; IR (CCl$_4$) ν 2960, 2930, 1745, 1455, 1400, 1260, 1230, 1210, 1150, 1030 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.85 (d, J = 12.2 Hz, 1 H, 17-H), 1.98–2.20 (m, 5 H, 9-H, 10-H, 18-H), 2.42 (d, J = 11.6 Hz, 1 H, 17-H), 2.98 (s, 3 H, CH$_3$), 3.00 (s, 3 H, CH$_3$), 4.48 (br s, 2 H, 8-H, 11-H), 5.19 (s, 1 H, 1-H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 25.8 (s, CH$_3$), 26.0 (s, CH$_3$), 31.2 (t, C-9), 40.4 (t, C-18) 42.9 (t, C-17), 51.0 (d, C-10), 58.4 (d, C-1 or C-11), 62.2 (d, C-1 or C-11), 63.8 (d, C-8), 77.8 (s, C-2), 158.0 (s), 158.2 (s), 160.5 (s); MS (70 eV) *m/z* 333 (5) [M$^+$ + 1], 332 (27) [M$^+$], 219 (9), 218 (45), 217 (100), 179 (10), 178 (16), 161 (34), 133 (25), 132 (13), 118 (27), 116 (18), 105 (27), 104 (47), 103 (52), 102 (15), 91 (32), 77 (19), 69 (26), 65 (16), 53 (13), 41 (20). Anal. Calcd for C$_{14}$H$_{16}$N$_{O4}$: C, 50.60; H, 4.85; N, 25.29. Found: C, 50.44; H, 5.02; N, 24.99.

3,4,9,10-Tetraazatetracyclo[6,2,1,1^{1,6},0^{2,5}]dodeca-3,9-diene (3). A sample of 1.50 g (4.51 mmol) of the bisurazole **2′** was added to a solution of 1.60 g (28.5 mmol) of potassium hydroxide in 100 mL of isopropyl alcohol and refluxed under nitrogen gas for 15 h. The reaction mixture was diluted with 100 mL of ice water, and concentrated HCl was added to adjust the pH to ca. 1–2 and subsequently to pH ca. 5–6 with 12% aqueous NH$_3$. To the solution was added dropwise 10 mL of a saturated copper(II) chloride solution, and the solution became dark, but no complex precipitated. Another 50 mL of 12% aqueous NH$_3$ was added, and after 15 min the NH$_3$ solution was extracted with dichloromethane (5 × 60 mL). The combined organic layers were washed with 2 × 50 mL of water, dried over MgSO$_4$, and concentrated by rotary evaporation (0 °C/20 Torr). The crude product was purified by column chromatography (silica gel, 9/1 dichloromethane/ethyl acetate, $R_f = 0.34$). This produced 520 mg (71%) of colorless pellets: mp 67–68 °C dec; IR (CCl$_4$) ν 3040, 2980, 2940, 1470, 1450, 1370, 1290, 1250, 1225, 1150 cm^{-1}; UV (CH$_3$CN) λ_{max} (log ϵ) 340 (2.267), 271 nm (2.367); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.78 (d, J = 10.9 Hz, 1 H, 12$_b$-H), 1.01 (t, J = 9.8 Hz, 1 H, 7-H), 1.09 (dt, J = 10.9, 1.6 Hz, 1 H, 12$_a$-H), 1.30 (dt, J = 9.3, 1.8 Hz, 2 H, 6-H), 1.76 (dd, J = 10.9, 1.9 Hz, 1 H, 11$_a$-H), 1.99 (d, J = 10.9 Hz, 1 H, 11$_b$-H), 5.05 (br s, 1 H, 5-H), 5.35 (br s, 1 H, 8-H), 5.64 (d, J = 1.9 Hz, 1 H, 1-H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 22.5 (t, C-6), 41.9 (t, C-12), 43.2 (d, C-7), 47.8 (t, C-11), 75.9 (d, C-1), 77.8 (d, C-5), 78.8 (d, C-8), 92.4 (s, C-2); MS (70 eV) *m/z* 134 (6) [M$^+$ − N$_2$], 119 (14), 106 (17) [M$^+$ − 2N$_2$], 105 (47), 91 (100), 78 (50), 65 (18), 51 (12), 39 (27). Anal. Calcd for C$_8$H$_{10}$N$_4$: C, 59.24; H, 6.21; N, 34.54. Found: C, 59.34; H, 6.39; N, 34.41.

Thermolysis of the Bisazoalkane 3. A solution of the bisazoalkane **3** (30.0 mg, 0.185 mmol) in 2 mL of acetonitrile was heated to 120 °C in a sealed tube for 1 h. After cooling, the reaction mixture was analyzed by capillary GC [30 m, OV 1, glass capillary column; temperature programmed at 40 °C (15 min) and then 10 °C/min up to 140 °C]. The 1- and 2-allylcyclopentadienes (**6** and **6′**) with R_f = 5.5 min were the only products detected (Table I).

Direct Photolysis of the Bisazoalkane 3 at 20 °C. A solution of the bisazalkane **3** (26.0 mg, 0.160 mmol) in 0.6 mL of acetonitrile-d_3 was degassed and photolyzed under nitrogen gas at 20 °C in the Rayonet photoreactor at 350 nm. The photolysis was monitored by TLC and capillary GC. Upon total conversion of **3**, the ^{1}H NMR spectrum showed the production of a 50/50 mixture of 1- and 2-allylcyclopentadienes (**6** and **6′**) (cf. Table I). The ^{1}H NMR spectrum was in agreement with that in the literature.[17]

Benzophenone-Sensitized Photolysis of the Bisazoalkane 3 at 20 °C. A 9.25 × 10^{-3} M acetonitrile solution of the bisazoalkane **3** and 1 × 10^{-2} M benzophenone was irradiated under nitrogen gas with the 364-nm line of the argon ion laser (0.5 W). The progress of the reaction was monitored by capillary GC. Only 1- and 2-allylcyclopentadienes (**6** and **6′**) were detected and identified by coinjection with the authentic samples (Table I).

MTAD Trapping in the Direct Photolysis of the Bisazoalkane 3. A solution of the bisazoalkane **3** (30.0 mg, 0.185 mmol) in 2 mL of dichloromethane was degassed and, under nitrogen gas, photolyzed at 0 °C with the 333-, 352-, and 364-nm lines of the argon ion laser (1.5 W).

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[17] Liu, Z. J.; Rong, G. *Synth. Commun.* **1986**, *16*, 871.

After total conversion of **3**, a solution of MTAD (20.3 mg, 0.180 mmol) in dichloromethane was added dropwise until the red color persisted. Evaporation of the solvent (20 °C/20 Torr) yielded 38.5 mg (98%) of a colorless oil: IR (CCl_4) ν 3100, 3040, 2980, 1790, 1740, 1720, 1640, 1460, 1410, 1270, 1200, 1080, 1030, 930 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.87 (dt, J = 9.0, 1.4 Hz, 1 H, 10-H), 2.09 (dt, J = 9.0, 1.4 Hz, 1 H, 10-H), 2.88 (s, 3 H, CH_3), 2.92–3.05 (m, 2 H, 11-H), 4.77 (t, J = 1.3 Hz, 1 H, 1-H or 7-H), 4.94 (br s, 1 H, 1-H or 7-H), 5.00–5.18 (m, 2 H, 13-H, 13′-H), 5.67 (dddd, J = 16.5, 10.3, 6.7 Hz, 1 H, 12-H), 5.77 (t, J = 1.8 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 24.6 (q, CH_3), 33.6 (t, C-11), 47.5 (t, C-10), 64.6 (d, C-1 or C-7), 65.8 (d, C-1 or C-7), 116.8 (t, C-13), 121.4 (d, C-8), 132.0 (d, C-12), 144.9 (s, C-9), 159.3 (s), 159.7 (s); MS (70 eV, 2-methylpropane) m/z 276 (4) [$M^+ + 57$], 221 (14) [$M^+ + 2$], 220 (100) [$M^+ + 1$], 219 (5) [M^+], 217 (100), 179 (10), 178 (16), 161 (34), 133 (25), 132 (13), 118 (27), 114 (9), 113 (30), 112 (10), 101 (26), 85 (10), 81 (8), 75 (7), 73 (30), 71 (17), 70 (10), 69 (10). Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.22; H, 5.93; N, 19.17. Found: C, 60.44; H, 6.06; N, 18.93.

Direct Photolysis of Bisazoalkane 3, Detection of Tetracyclo[5,1,0,$0^{1,5}$,$0^{2,4}$]octanes (5,5′) at −78 °C, A sample of 25.0 mg (0.155 mmol) of the bisazoalkane **3** was dissolved in 0.8 mL of dichloromethane-d_2, degassed, and irradiated under nitrogen gas at 350 nm and −78 °C directly in an NMR tube. The progress of the reaction was monitored by TLC (azo test[18]). After total conversion of **3**, the NMR tube was cooled to −196 °C, and the ^1H and ^{13}C NMR spectra at −60 °C showed that besides **6** and **6′** two other products were formed, namely the tetracyclo[5.1.0.$0^{1,5}$.$0^{2,4}$]octanes (**5**,**5′**) in a ratio of 80/20 (cf. Table I): ^1H NMR (CD_2Cl_2, 400 MHz) of the major diastereomer **5** δ 0.70 (ddd, $J_{3s,3a}$ = 5.0 Hz, $J_{3s,2}$ = $J_{3s,4}$ = 1.6 Hz, 1 H, 3-H_s), 0.76 (ddddd, $J_{7,8a}$ = 6.0 Hz, $J_{7,6x}$ = 4.8 Hz, $J_{7,8s}$ = 2.4 Hz, $J_{7,5}$ = 2.2 Hz, $J_{7,6n}$ = 1.5 Hz, 1 H, 7-H), 0.88 (ddd, $J_{3a,3s}$ = 5.0 Hz, $J_{3a,2}$ = 5.0 Hz, $J_{3a,4}$ = 5.3 Hz, 1 H, 3-H_a), 0.98 (dd, $J_{8s,8a}$ = 6.0 Hz, $J_{8s,7}$ = 2.4 Hz, 1 H, 8-H_s), 1.07 (dd, $J_{8a,8s}$ = $J_{8a,7}$ = 6.0 Hz, 1 H, 8-H_a), 1.51 (dddd, $J_{5,6n}$ = 5.3 Hz, $J_{5,6x}$ = $J_{5,7}$ = 2.2 Hz, $J_{5,4}$ = 2.0 Hz, 1 H, 5-H), 1.72 (ddd, $J_{6n,6x}$ = 12.7 Hz, $J_{6n,7}$ = 1.5 Hz, $J_{6n,5}$ = 5.3 Hz, 1 H, 6-H_n), 1.85 (dddd, $J_{4,3a}$ = 5.3 Hz, $J_{4,2}$ = 4.0 Hz, $J_{4,5}$ = 2.0 Hz, $J_{4,3s}$ = 1.6 Hz, 1 H, 4-H), 1.94 (ddd, $J_{2,3a}$ = 5.0 Hz, $J_{2,4}$ = 4.0 Hz, $J_{2,3s}$ = 1.6 Hz, 1 H, 2-H), 2.17 (ddd, $J_{6x,6n}$ = 12.7 Hz, $J_{6x,7}$ = 4.8 Hz, $J_{6x,5}$ = 2.2 Hz, 1 H, 6-H_x); ^1H NMR signals of the minor diastereomer **5′** δ 1.03 (m, 1 H), 1.15 (ddd, 1 H), 1.34 (dd, 1 H), 1.46 (m, 1 H), 1.61–1.72 (m, 2 H), 2.02 (d, 1 H), the remaining signals could not be assigned due to overlap; ^{13}C NMR (CD_2Cl_2, 100 MHz) of the major diastereomer **5** δ 7.00 (C-2 or C-4 or C-7), 12.2 (C-2 or C-4 or C-7), 16.2 (C-2 or C-4 or C-7), 18.6 (C-3 or C-8), 23.6 (C-3 or C-8), 30.9 (C-6), 33.9 (C-1 or C-5), 34.4 (C-1 or C-5); ^{13}C NMR of the minor diastereomer **5′** δ 11.7 (C-2 or C-4 or C-7), 13.6 (C-2 or C-4 or C-7), 15.5 (C-2 or C-4 or C-7), 18.2 (C-3 or C-8), 20.6 (C-3 or C-8), 22.8 (C-6), 31.5 (C-1), 32.6 (C-5).

When the above photolysate of bisazoalkane **3** was allowed to warm up directly in the NMR tube to −30 °C, the bishousanes **5**,**5′** decomposed into the 2-allylcyclopentadiene (**6**). After 2 h at 20 °C all bishousane was consumed, and the ^1H NMR spectrum showed 90% 2-allylcyclopentadiene (**6**) and 10% 1-allylcyclopentadiene (**6′**).

Benzophenone-Sensitized Photolysis of the Bisazoalkane 3 at −78 °C, A sample of 28.0 mg (0.173 mmol) of the bisazoalkane **3** and 12.4 mg (68.1 mmol) of benzophenone in 0.8 mL of dichloromethane-d_2 was degassed and under nitrogen gas irradiated with the 364-nm line of the argon ion laser at −78 °C directly in an NMR tube. The progress of the reaction was monitored by TLC (azo test[18]). After 85% conversion, the NMR tube was cooled to −196 °C, and the ^1H NMR ^{13}C NMR spectra at −60 °C showed only the presence of 2-allylcyclopentadiene (**6**) (cf. Table I).

Direct Photolysis of the Bisazoalkane 3 at −78 °C followed by NMR Analysis, A solution of the bisazoalkane **3** (26.3 mg, 0.162 mmol) in 0.8 mL of dichloromethane-d_2 was degassed and photolyzed with the argon ion laser (total UV output of the 333-, 352-, and 364-nm lines was 1.5 W) under nitrogen gas at −78 °C. The reaction was monitored by ^1H and ^{13}C NMR at −60 °C (400 MHz). Besides the 2-allylcyclopentadiene (**6**) and the bisbicyclopentanes **5**,**5′**, the monoazoalkanes **4** and **4′** were detected. TLC (9/1 dichloromethane/ethyl acetate) showed (azo test[18]), besides the bisazoalkane **3** (R_f = 0.32), another spot (R_f = 0.53). HPLC (reversed-phase RP 18, MeOH/H_2O 60/40, flow 0.5 mL/min, p = 125 bar, detection 254 nm) of the mixture showed three peaks at 6.5, 7.8, and 43.0 min, which were assigned as bisazoalkane **3**, monoazoalkane **4** (λ_{max} = 340 nm), and 2-allylcyclopentadiene (**6**) (cf. Table I).

In a preparative run, 100 mg (0.617 mmol) of the bisazoalkane **3** in 5 mL of dichloromethane was irradiated under nitrogen gas for 3 min at 0 °C with the 333-, 352-, and 364-nm lines of the argon ion laser, monitoring with TLC. The reaction mixture was separated by column chromatography to afford 18.4 mg (0.17 mmol) of **6** and **6′**, 23.7 mg of a mixture of **6**,**6′** and **4**, and 21.9 mg (0.13 mmol) of **3**. The products were identified by ^1H and ^{13}C NMR spectroscopy.

3,4-Diazatetracyclo[6,1,$1^{2,5}$,$0^{2,7}$,0]dec-3-ene (4): ^1H NMR ($CDCl_3$, 250 MHz) δ 0.7–2.3 (m, 8 H), 4.77 (br s, 1 H, 2-H or 5-H), 5.32 (br s, 1 H, 2-H or 5-H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 8.74 (d, C-8), 15.8 (t, C-7 or C-9), 19.7 (t, C-7 or C-9), 33.7 (d, C-6), 42.9 (t, C-10), 74.7 (d, C-2 or C-5), 80.4 (d, C-2 or C-5) (because of the small amount of material, the C-1 signal could not be detected). Characteristic ^1H and ^{13}C NMR signals of the monoazoalkane **4′**: ^1H NMR ($CDCl_3$, 250 MHz) δ 4.92 (d, αN-bridgehead H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 77.7 (d, αN-bridgehead C).

Determination of Quantum Yields of Denitrogenation for Bisazoalkane 3, Direct Photolysis, The quantum yield in the direct photolysis at 20 °C was measured relative to 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH, $\Phi^S = 1.0$) by following the literature procedure.[19] For this purpose, 3.5 mL of a dichloromethane solution of 10^{-2} M in DBH was irradiated with the 333-nm line of the argon ion laser (0.7 W) at different time intervals. The plot of azo concentration against time gave a straight line with slope 1.69×10^{-3} mol L^{-1} s^{-1}. By following the same procedure, a 10^{-2} M solution of the bisazoalkane **3** in CH_2Cl_2 gave a line with slope 1.23×10^{-3} mol L^{-1} s^{-1}. The quantum yield for direct photolysis of the bisazoalkane **3** was calculated to be $\Phi = 1.5 \pm 0.1$.

Benzophenone-Sensitized Photolysis of Bisazoalkane 3, The quantum yield in the benzophenone-sensitized photolysis at 20 °C was measured as described above. For this purpose, 3.5 mL of a dichloromethane solution 10^{-2} M in DBH and 2×10^{-3} M in benzophenone was irradiated with the 364-nm line of the argon ion laser (0.3 W). The plot of azo concentration against time gave a straight line with slope 2.81×10^{-3} mol L^{-1} s^{-1}. By following the same procedure, a 10^{-2} M CH_2Cl_2 solution of the bisazoalkane **3** gave a straight line with slope 2.68×10^{-3} mol L^{-1} s^{-1}. The quantum yield for sensitized photolysis of the bisazoalkane **3** was calculated to be $\Phi = 1.9 \pm 0.1$.

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Registry No. **1**, 140438-53-5; **1′**, 140438-55-7; **2**, 140438-54-6; **2′**, 140438-56-8; **3**, 140438-57-9; **4**, 140438-60-4; **4′**, 140438-61-5; **5**, 140438-59-1; **5′**, 140630-89-3; **6**, 21115-31-1; **6′**, 29378-03-8; **7**, 140438-58-0; Ph_2CO, 119-61-9; 1,5-dihydropentalene, 33284-11-6; *N*-phenyltriazolinedione, 4233-33-4; *N*-methyltriazolinedione, 13274-43-6.

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