Wavelength-Selective Photodenitrogenation of Azoalkanes to High-Spin Polyradicals with Cyclopentane-1,3-diyl Spin-Carrying Units and Their Photobleaching: EPR/UV Spectroscopy and Product Studies of the Matrix-Isolated Species

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The photolysis of the mono-, bis-, and trisazoalkanes **1**, **2**, and **3** in a toluene matrix at 77 K has been studied by EPR and UV spectroscopy. The purpose was to find the optimal conditions for the generation of the corresponding organic high-spin polyradicals (the triplet diradicals **D-1**, **D-2**, and **D-3**, the tetraradicals **T-2** and **T-3**, and the hexaradical **H-3**) all with localized cyclopentane-1,3-diyl spin-carrying units, connected by *m*-phenylene (except **D-1**) as ferromagnetic coupler. Irradiation of these azoalkanes at 333, 351, or 364 nm gave different polyradical compositions. This observed wavelength dependence is due to the secondary photoreaction (photobleaching) of the polyradical intermediate. The photobleaching process has been examined in detail for the triplet diradical **D-1**, for which π,π^* excitation affords the cyclopentenes **5** instead of the housane **4** (the usual product of the diradical **D-1** on warm-up of the matrix). The π,π^*-excited diradical **D-1** fragments into a pair of allyl and methyl radicals (the latter was observed by EPR spectroscopy of a photobleached sample), and recombination affords the cyclopentene. Similar photochemical events are proposed for the photobleaching of the tetraradical **T-2** and hexaradical **H-3**, derived from the respective azoalkanes **2** and **3**. Thus, photobleaching of the polyradicals competes effectively with their photogeneration from the azoalkane. This unavoidable event is the consequence of spectral overlap between the cumyl-radical π,π^* chromophore of the polyradical and the n,π^* chromophore of the azoalkane at the wavelength (364 nm), at which the latter is photoactive for the required extrusion of molecular nitrogen.

Introduction

The synthesis and EPR characterization of the high-spin tetraradical **T-2** (quintet) and hexaradical **H-3** (septet) has recently been achieved,[1] to date being the most persistent localized polyradicals, with the cyclopentane-1,3-diyl diradical as spin-carrying unit (Scheme 1), connected by the *m*-phenylene ferromagnetic coupler. Analogous to the parent diradical **D-1** derived from the monoazoalkane **1**, the polyradicals **T-2** and **H-3** are also accessible from the corresponding azoalkane precursors **2** and **3** by direct photolysis in a toluene matrix at 77 K. Irrespective of the photolysis conditions (wavelength, time, conversion), for the denitrogenation of the azoalkanes **2** and **3**, the corresponding polyradicals **T-2** and **H-3** could not be generated without contamination by the partially denitrogenated polyradicals, i.e., **T-2** by **D-2** and **H-3** by **D-3** and **T-3**. In fact, EPR-spectral monitoring of the photolysis revealed that on prolonged irradiation of the matrix sample, the intensity of the polyradical signals decreased. Moreover, the efficacy of this photobleaching depended on the irradiation wavelength; namely, it was more effective at the 333-nm than at the 351-nm and 364-nm laser lines.

Such photochemically induced transformations of diradicals are known to occur in rigid solvent matrixes at 77 K.[2] For example, the 2-methylenecyclopentane-1,3-diyl diradical fragments into an enyne upon irradiation at 77 K,[2a] while the 1,3-perinaphthalene diradical undergoes a photoinduced 1,3-hydrogen shift.[2b] The related 1,4-perinaphthalene diradical photocleaves quantitatively to 1,8-divinylnaphthalene.[2c]

Evidently similar photochemical reactions compete with the generation of the desired polyradicals derived from the azoalkanes **1**−**3** (Scheme 1). An in-depth understanding of the photophysical and photochemical properties of the diradical **D-1**, as well as **D-2** and **D-3**, which are the precursors to the polyradicals **T-2** and **T-3** (**H-3**) appears essential to improve the conditions for the clean and efficient generation of high-spin systems. For this purpose, besides detailed EPR studies, particularly informative should be concurrent UV spectroscopy of the matrix-isolated species, generated in the photolysis of the azoalkane **1**−**3** as a function of time and irradiation wavelength. In conjunction with these spectral studies,

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Scheme 1. Polyradicals Obtained on Irradiation of the Monoazoalkane 1, Bisazoalkane 2, and Trisazoalkane 3
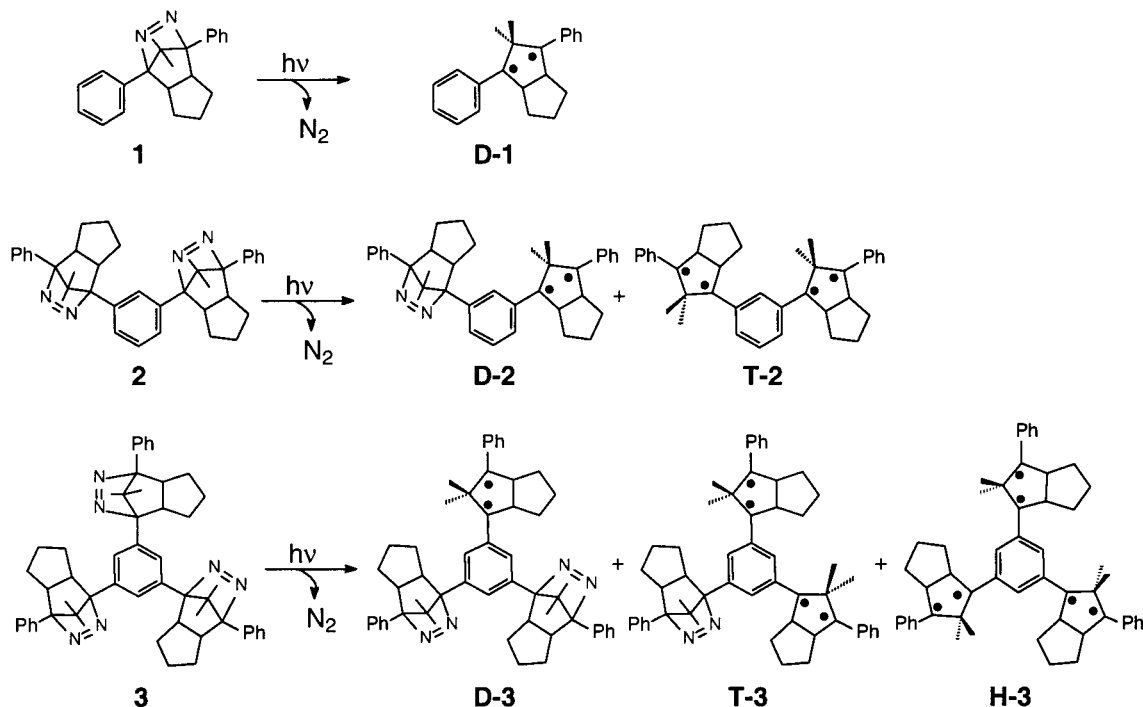
the products should be determined after warm-up of the photolyzate to assess the photochemical reactions of the polyradicals upon excitation.
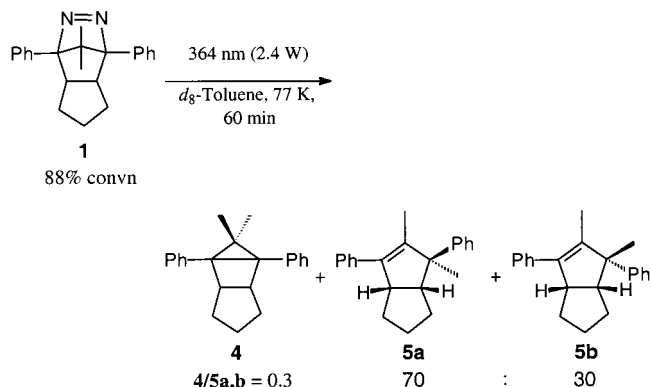
Herein we present the results of these investigations. They clearly demonstrate that the spectral overlap between the cumyl-radical π,π^* chromophore of the polyradicals and the azo n,π^* chromophore of the azoalkanes is responsible for the competitive photodenitrogenation versus photobleaching of the high-spin species.

Results

Photolysis of Monoazoalkane. On irradiation of the monoazoalkane **1** in the toluene matrix at 77 K, the triplet diradical **D-1** is formed (Scheme 1), as manifested by its intense and well-resolved EPR spectrum. Prolonged photolysis led to reduction of the EPR signal, which substantiates photobleaching, i.e., destruction of the triplet diradical **D-1**. It was, therefore, of mechanistic import to assess the products of the photobleaching process and determine a time profile for the **D-1** species and its photoproducts.

After photolysis of the monoazoalkane **1** until total depletion of the EPR signal and warm-up to room temperature, NMR spectroscopy of the photolyzate revealed that the housane **4** (the exclusive photoproduct in the solution photolysis at room temperature)[3] is only formed in minor amounts in the matrix photolysis at 77 K (Scheme 2), while the unknown cyclopentene **5a** and its known diastereomer **5b** (dr 70:30) are the major products.[4] A time profile (expressed as % conversion of azoalkane **1**) is given in Figure 1, in which the amount of the diradical **D-1** was monitored at 77 K by EPR

(3) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis* **1995**, 1163–1170.

(4) At a conversion of <90% under the matrix conditions and a product balance of >90% only traces of other products are expected, which go undetected by ^{1}H NMR spectroscopy.

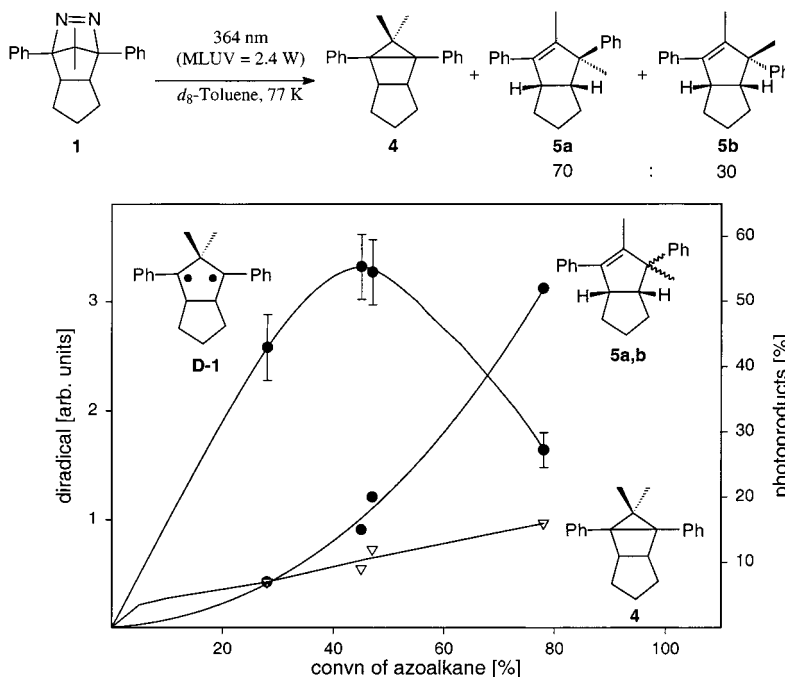**Scheme 2. Photoproducts of the Monoazoalkane 1 in the Toluene Matrix at 77 K**

spectroscopy, while the amounts of the photoproducts housane **4** and cyclopentene **5** (after warm-up of the matrix) were determined at ca. 20 °C by ^{1}H NMR spectroscopy. After about 5 min irradiation time (50% conversion of **1**), a maximal concentration of the diradical **D-1** was reached. Further irradiation (20–60 min) led to a decrease of the EPR signal intensity, accompanied with a strong increase of the amount of cyclopentene **5**, while the amount of housane **4** essentially leveled off. The time profile in Figure 1 unequivocally demonstrates that photobleaching of the triplet diradical **D-1** affords principally the cyclopentene **5**. Mechanistically significant is the observation that in all the photolysis experiments, especially on extensive photobleaching, strong EPR signals for the methyl radical ($g = 2.001$, $a_H = 23$ G) were observed (see Figure 3 in the Supporting Information), which disappeared on melting of the matrix.

The height of the maximal EPR signal of the diradical **D-1** depends on the photolysis wavelength, as shown in Table 1 (second column), i.e., by changing the irradiation wavelength from 364 to 333 nm, the relative amount of

Figure 1. Amount of the diradical **D-1** (solid squares), housane **4** (open triangle), and cyclopentenes **5a,b** (open circle) versus the conversion of the azoalkane **1** on irradiation at 364 nm in a d_8-toluene matrix at 77 K.

Table 1. Relative EPR-Signal Intensities of the Diradicals D-1, D-2, and D-3 and the Polyradicals T-2, T-3, and H-3 for the Photolysis of the Monoazoalkane 1, Bisazoalkane 2, and Trisazoalkane 3

λ^a (nm)	monoazo 1	bisazo 3			trisazo 3		
	rel amount^b	rel amounts^b		ratio	rel amounts^b		ratio
	D-1	D-2	T-2	T-2/D-2	D-3	T-3+H-3	(T-3+H-3)D-3
333	0.35	0.18	0.46	2.55	0.29	1.05	3.62
351	0.94	0.54	0.26	0.48	0.50	1.09	2.18
364	1.00	1.00	0.00	0.00	1.00	0.23	0.23

^{a} Degassed samples of the mono-, bis-, and trisazoalkanes **1**, **2**, and **3** were irradiated in a toluene matrix at 77 K for 20 min (30–50% conversion of azoalkane); the light intensity of the argon-ion laser was adjusted to 0.48 W for each wavelength. ^{b} Determined by double integration of the diradical **D-1**, **D-2**, and **D-3** signals in the 3027–3157 and 3564–3695 G regions and the polyradical **T-2**, **T-3+H-3** signals in the 3159–1561 G region; error ±10% of the stated values, the value obtained on 364-nm photolysis was normalized to unity.

diradical decreases.[5] A wavelength dependence was also found for the relative amounts of the photoproducts housane **4** and cyclopentene **5**. Thus, continuous irradiation of the monoazoalkane **1** at 77 K with 333-nm light gave a product ratio **4/5** of 0.3 (33% conversion of the azoalkane **1**) versus 0.6 (44% conversion) on 364-nm photolysis (data not shown). When the azoalkane **1** was irradiated as a matrix sample for 30 s, allowed to warm to room temperature, refrozen, and irradiated again for 30 s, after 10 repetitions of this intermittent irradiation/warm-up cycle, a product ratio **4/5** of 1 (50% conversion of the azoalkane **1**) was obtained on ¹H NMR analysis of the final photolyzate. A control experiment showed that on irradiation of the housane **4** in a toluene matrix at 77 K, no conversion to the cyclopentene **5** or to any other photoproduct took place. Thus, short irradiation time

(30 s) resulted in less photobleaching of the triplet diradical **D-1** and, consequently, proportionally more housane **4** was formed.

The photolysis of the monoazoalkane **1** was also monitored in matrix at 77 K by UV spectroscopy (Figure 2a). From time-resolved laser-flash experiments, we know already that the cumyl-radical chromophore in such triplet diradicals absorbs around 320 nm;[6] consequently, the intensive new signals at 316 and 328 nm were assigned to the triplet diradical **D-1**. The fact that these UV absorptions also level off in their growth, as observed for the triplet EPR signals of **D-1**, supports their assignment to the **D-1** diradical.

The conversion of the monoazoalkane **1** under the conditions of the UV spectroscopy (in matrix at 77 K) was found to be below 5% by ¹H NMR analysis of the photolyzate. With this value as upper limit and the measured UV absorbance, we estimate the extinction coefficient (ϵ) at 316 and 328 nm to be log $\epsilon \sim 3.5$–4, which is in the same order of magnitude as the reported value for the benzyl radical (log $\epsilon = 3.9$).[7,10b] This means that the absorption of the cumyl-radical π,π^* chromophore of the triplet diradical **D-1** at 328 nm (log $\epsilon = 3.5$–4) is 100–300 times more intensive than that of the azo n,π^* chromophore (Figure 2a) at 333 nm (log $\epsilon = 1.5$). Thus, these ϵ values imply that the triplet diradical **D-1** is not only well detectable by UV spectroscopy, even when

(5) For the experiments in Table 1, the amount of the diradical maximum was obtained after 20 min, because different conditions were used than in the product study.

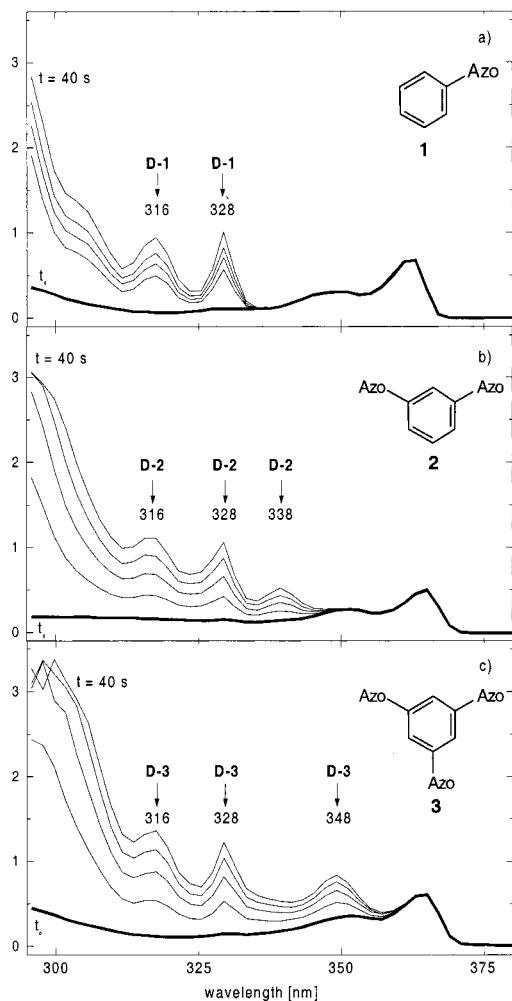(6) Adam, W.; Fröhlich, L.; Nau, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 9824–9825.

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Figure 2. Absorption spectra of the photolysis of monoazoalkane **1** (a), bisazoalkane **2** (b), and trisazoalkane **3** (c), recorded at regular time intervals of irradiation with a Hg lamp by using a cutoff filter ($\lambda > 330$ nm); the lowermost spectrum at 40 s irradiation time; the marked new absorptions between 290 and 350 nm correspond to the triplet diradicals **D-1**, **D-2**, and **D-3**.

the monoazoalkane-to-diradical ratio **1/D-1** is ≤95:5, but it competitively absorbs the incident UV light and is photobleached already at these low conversions of the monoazoalkane **1**.

Photolysis of the Bis- and Trisazoalkanes. A similar wavelength-dependent photolysis was also previously observed[1] for the polyradicals generated in the UV irradiation of the bis- and trisazoalkanes **2** and **3**, which merited a more detailed investigation. Thus, as for the **D-1** diradical, the photobleaching of the polyradicals was examined by EPR and UV spectroscopy at the wavelengths 333, 351, and 364 nm. Unfortunately, a product study was not feasible for the azoalkanes **2** and **3** because the complex product mixtures were not amenable to ^{1}H NMR spectroscopic analysis in view of severe overlap of the characteristic signals.

The relative EPR-signal intensities of the diradicals **D-1**, **D-2**, and **D-3**, and the polyradicals **T-2** and **T-3**+**H-3** are given in Table 1, which have been measured when prolonged irradiation did not change the EPR spectrum anymore. Since the EPR signals of the triplet diradical **D-2** (third column) and quintet tetraradical **T-2** (fourth column) are sufficiently well separated, their amounts

were determined by double integration of the respective EPR signals (Table 1); their relative amounts are compared in terms of their **T-2/D-2** ratio (fifth column) at the three wavelengths. Unfortunately, the EPR signals of the tetraradical **T-3** and hexaradical **H-3** overlap severely and only their total amount, **T-3**+**H-3**, could be determined (column 7); their relative amounts are compared with that of the diradical **D-3** (sixth column) in terms of their (**T-3**+**H-3**)/**D-3** ratio (eighth column) at the three wavelengths.

The data in Table 1 disclose that the ratios of polyradicals (**T-2**, **T-3**+**H-3**) to the corresponding diradicals (**D-2**, **D-3**), i.e., **T-2/D-2** and (**T-3**+**H-3**)/**D-3**, which is a measure for the purity of the high-spin system, are strongly influenced by the photolysis wavelength. Thus, the **T-2/D-2** and (**T-3**+**H-3**)/**D-3** ratios decrease as the irradiation wavelength is changed from 333 to 364 nm. Notice that the decrease of these ratios arises not only from the reduction of the amount of polyradicals **T-2** and **T-3**+**H-3** (columns 4 and 7), but also from the increase of the amount of diradicals **D-2** and **D-3** (columns 3 and 6).

As for the diradical **D-1**, the UV absorption characteristics of the triplet diradicals **D-2** and **D-3** at 77 K were also investigated (Figure 2). From EPR experiments we know that irradiation of the azoalkanes **2** or **3** for 2 min at 364 nm produces only the triplet diradicals **D-2** and **D-3** without contamination of higher spin states. These conditions were used to generate the triplet diradicals **D-2** and **D-3** for the UV spectroscopic study in matrix. Identical absorption spectra were obtained on irradiation with a Hg lamp (150 W), equipped with a cutoff filter ($\lambda > 330$ nm). The resulting UV absorption spectra of the diradicals **D-2** and **D-3** resemble those of **D-1**, except additional signals appear at 338 nm for the bisazoalkane **2** (Figure 2b) and 348 nm for the trisazoalkane **3** (Figure 2c).

The chromophore of the diradical **D-1** possesses a λ_{max} of 328 nm, which corresponds well to the near-UV absorption of the cumyl radical at 324 nm.[8a] For the cumyl-radical chromophore of the triplet diradicals **D-2** (and **D-3**), one of the aryl groups at the radical centers bears a 3-monoazo (and 3,5-bisazo) substituent. Azo-substituted cumyl radicals are not known, but the assignment of the signals at 338 nm (and 348 nm) to the azo-substituted cumyl-radical fragments of **D-2** (and **D-3**) seems reasonable, because alkyl-substituted derivatives of known cumyl radicals[8] display similar trends (Table 2), i.e., higher *meta* substitution on the benzylic ring causes a bathochromic shift. That this bathochromic shift of the near-UV transition caused by alkyl substitution is not fortuitous is documented by CNDO calculations of methyl-substituted benzyl radicals.[9] This theoretical analysis predicts a small influence of the methyl group on the strongly allowed transitions around 260 nm, but an appreciable effect on the near-UV transitions around 325 nm, because the methyl group effectively perturbs these weakly allowed transitions.[9]
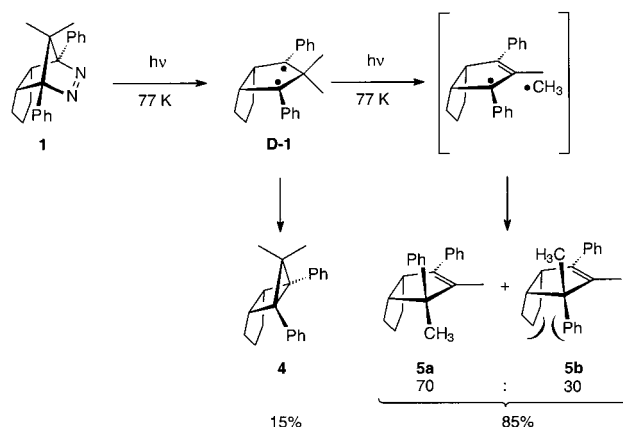
Discussion

The product study for the matrix photolysis of the monoazoalkane **1** (Scheme 1) has revealed that mainly the diastereomeric cyclopentenes **5** and some housane **4** have been formed. The cyclopentene **5** is evidently a product of the photoexcited diradical **D-1** (photobleach-

Table 2. Near-UV Absorptions of the Triplet Diradicals D-1, D-2, and D-3 and Related Cumyl Monoradicals

	Ar	λ [nm]	λ [nm]	Ar
D-1	Ph	328	324 (ref 8a)	Ph
D-2	Azo (meta)	338	330 (ref 8b)	isopropyl-meta
D-3	Azo (3,5)	348	334 (ref 8c)	diisopropyl-3,5

Scheme 3. Proposed Mechanism for the Photobleaching of the Diradical D-1

ing), since the cyclopentene appears after a certain lag time, apparently when enough of the diradical **D-1** has accumulated (Figure 1). In contrast, the amount of the housane **4** increases independently of the amount of diradical **D-1** that is present. Thus, although we cannot exclude that excitation of the diradical **D-1** leads also to some housane **4**, the latter is mainly obtained from the ground-state diradical **D-1**, when the matrix is allowed to warm to room temperature, through intersystem crossing to the singlet diradical and subsequent cyclization.[10] That the housane **4** results directly from the ground-state diradical **D-1** and the cyclopentene **5** from the photoexcited diradical is also supported by the intermittent "freeze-warmup-refreeze" photolysis experiment. As expected under these short-time (30 s) photolysis conditions, the temporary diradical **D-1** concentration is low and, thus its photobleaching diminished; consequently more housane **4** and less cyclopentene **5** are obtained in the intermittent (**4/5** ca. 1) versus continuous irradiation (**4/5** ca. 0.6).

The rearrangement of the diradical **D-1** to the cyclopentene **5** is quite unusual, since 1,3-cyclopentene-1,3-diyl triplet diradicals normally cyclize to form the corresponding housanes. If at all, such rearrangement products have been observed only in small amounts; for example, the parent cyclopentane-1,3-diyl triplet diradical gave only 4% of cyclopentene by 1,2-H shift and mainly the housane.[11] Although structurally different, the 1,4-perinaphthalene triplet diradical behaves similarly to the diradical **D-1**, because it cyclizes at room temperature to the naphthocyclobutane, but photorearranges at 77 K by C−C bond cleavage to the 1,8-divinylnaphthalene.[2c] In contrast to the diradicals of the cyclopentane-1,3-diyl type, the rearrangement of their radical cations is well established.[12] Thus, the cyclopentane-1,3-diyl radical cation of the diradical **D-1**, generated from the housane **4** by chemical electron transfer (CET) with tri(aryl)aminium salts, affords quantitatively the cyclopentene **5**.[13] Mechanistically significant, in contrast to the photolysis of the diradical **D-1**, which affords mainly

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the **5a** diastereomer, the Wagner−Meerwein-type rearrangement of the radical cation leads exclusively to the cyclopentene **5b**!

How can this dichotomy in the stereochemical results for two apparently similar processes, i.e., the same product but of different configurations, be mechanistically reconciled? The clue gives the strong EPR signal of the methyl radical (see Figure 3 in the "Supporting Information" section), which was observed in matrix especially in prolonged irradiated samples of the monoazoalkane **1** (extensive photobleaching). Clearly, the electronically excited triplet diradical **D-1** fragments into a pair of methyl and allyl radicals (Scheme 3). Thus, the photolysis of the triplet diradical **D-1** to the cyclopentene **5** is not a bona fide rearrangement by 1,2-methyl shift, but rather a photofragmentation—the less sterically hindered product, namely the cyclopentene **5a**, is formed preferentially in the photobleaching process.[4] Evidently, thermodynamically controlled conditions prevail in the recombination step of the methyl−allyl radical pair.

Since the diradical **D-1** absorbs quite intensively at 333 nm (Figure 2a), this triplet species is bleached efficiently at this wavelength. Although no definite UV absorption at 364 nm is displayed by the diradical **D-1** (Figure 2a), the observed photoreactivity at this wavelength (Table 1) suggests that its absorption is covered by that of the azoalkane in this region. Thus, the increase of the diradical **D-1** (Table 1) and decrease of cyclopentene **5** amount (product ratio **4/5** at 333 nm is 0.3 and 0.6 at 364 nm) is due to the higher absorption at 333 nm than at 364 nm. Since the UV absorption of the diradical **D-1** overlaps with the absorption of the azoalkane chromophore, the irradiation of the monoazoalkane **1** is always accompanied by photobleaching of the diradical. Thus, unfortunately, the diradical **D-1** amount goes through a maximum (Figure 1), since as it builds up through photodenitrogenation of the monoazoalkane **1**, it is consumed by photobleaching to the cyclopentene **5**.

As in the case of the diradical **D-1** generated from the monoazoalkane **1**, the UV absorption of the diradicals **D-2** derived from the bisazoalkane **2** also overlaps with that of the azo chromophore (Figure 2b). Thus, what has been said above for the diradical **D-1** applies also to **D-2**, i.e., photoexcitation of the diradical competes with that of the azo functionality. However, the **D-2** diradical possesses two chromophores, namely the strongly absorbing chromophore (π,π^* type) of the cumyl radical and the weakly absorbing one (n,π^* type) of the azo group at the *meta*

Scheme 4. Mechanism of the Stepwise Nitrogen Extrusion of the Bisazoalkane 2 and Trisazoalkane 3 and Photobleaching of the Polyradicals

2 (X = H)
3 (X = Azo)

2*, 3*

D-2, D-3

D-2*, D-3*

T-2, T-3

H-3

Photobleaching

Photobleaching
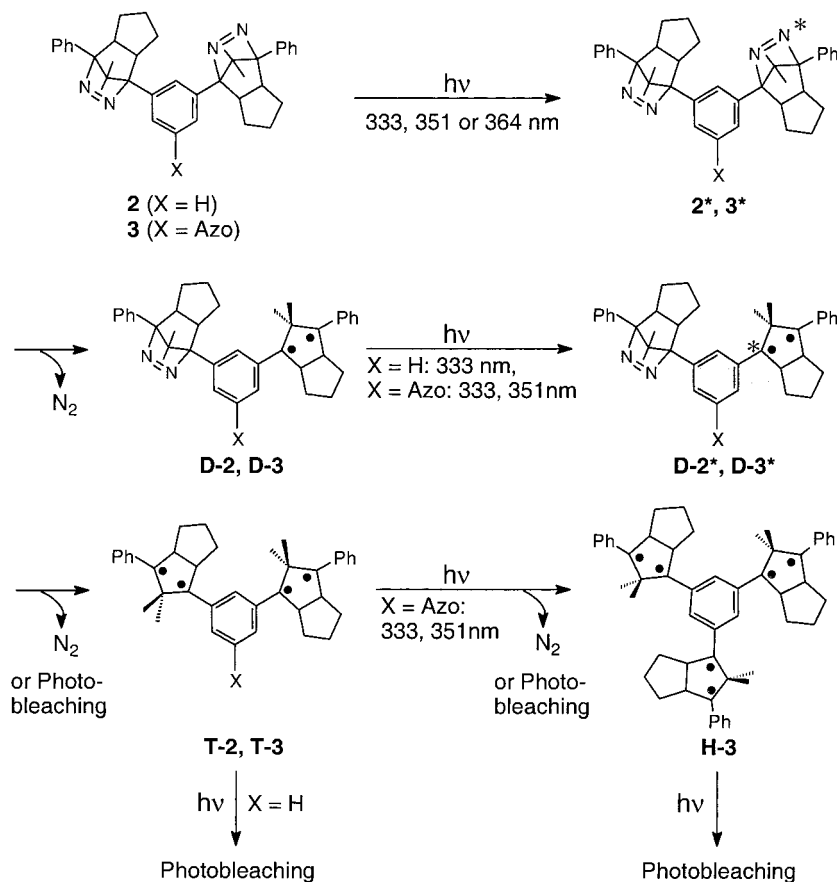
position of one of the phenyl rings. Especially at 328 nm (338 nm), the cumyl-radical chromophore absorbs 100–300 times more intensively than the azo chromophore at 333 nm (it is supposed that the **D-1** and **D-2** diradicals have the same extinction coefficients). Accordingly, the cumyl-radical chromophore of the diradical **D-2** at 328 nm (338 nm) is already well detectable, even when little of the bisazoalkane has been converted to the diradical, i.e., when the **D-2/2** ratio is only 5:95. Thus, we expect that also the absorbance of the azo chromophore (333–365 nm) within the **D-2** diradical is not only negligible compared to its cumyl-radical chromophore, but also compared to the surplus amount of unconverted bisazoalkane **2** (Figure 2b). Consequently, further irradiation of the mixture of the bisazoalkane **2** and the diradical **D-2** at 364 nm (351 nm) leads exclusively to n,π^* excitation of the azo chromophore of the bisazoalkane **2** with formation of more diradical **D-2**. As argued above, no n,π^* excitation of the azo chromophore in the diradical **D-2** takes place on 364 nm irradiation and, thus no tetraradical **T-2** is formed. Accordingly, the amount of diradical **D-2** increases, but the **T-2/D-2** ratio is small, actually zero at 364 nm (Table 1, columns 3 and 5). In contrast, on 333-nm photolysis, the cumyl-radical π,π^* chromophore of **D-2**, which is at this wavelength more intense than all azo n,π^* chromophores (Figure 2b), absorbs preferentially the 333-nm light (Scheme 4). The fate of this π,π^* excitation of the diradical **D-2** is that the amount of the tetraradical **T-2** increases through denitrogenation (**D-2*** → **T-2**), while the amount of **D-2** decreases, additionally due to photobleaching, as is evident from the **T-2/D-2** ratio in Table 1 (column 5) for

Scheme 5. Photolytic Generation of the 1,8-Dimethylenenaphthalene Diradical
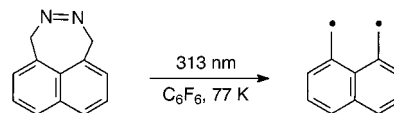
the 333-nm photolysis. This implies that π,π^* excitation of the diradical **D-2** induces the extrusion of the second nitrogen molecule to afford the tetraradical **T-2**. The extrusion of molecular nitrogen by excitation of a neighboring π,π^* chromophore has already been reported for the photolysis of 1,4-dihydronaphtho[1,8-*de*][1,2]-diazepine to the 1,8-dimethylenenaphthalene diradical (Scheme 5).[14]

Since the diradical **D-2** absorbs so well due to π,π^* excitation of the cumyl-radical chromophore and efficiently ejects N_2 from its azo group to afford presumably the tetraradical **T-2**, why is the photochemical generation of the tetraradical **T-2** from the bisazoalkane **2** not more effective? In fact, the **T-2/D-2** ratio remains quite constant after a certain irradiation time. This apparently contradictory behavior may be rationalized again in terms of photobleaching of the tetraradical **T-2** (Scheme 4). Unfortunately, no characteristic UV signals are unambiguously assignable to the tetraradical **T-2**, because the latter cannot be produced without contamination by the bisazoalkane **2** and diradical **D-2**. Since the UV absorptions of the *m*-phenylene diradical (320 nm)

(14) (a) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1976**, *59*, 2273–2277. (b) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972–1973.

and the benzyl monoradical (319 nm) are essentially identical,[15] we assume that the *m*-phenylene diradical fragment in our tetraradical **T-2** absorbs almost in the same region as the cumyl radical of the diradical **D-1** or **D-2**. If now the absorption of the tetraradical **T-2** coincides with that of the diradical **D-2**, the tetraradical **T-2** will be bleached when its absorbance becomes as intensive as that for the diradical **D-2**. Then, diradical **D-2** and tetraradical **T-2** will be photobleached to the same extent, and their ratio remains approximately constant during prolonged irradiation of the bisazo-alkane **2**.

A similar photochemical behavior is expected for the polyradicals **T-3** and **H-3** in the photolysis of trisazoal-kane **3**, as evidenced by the experimental data in Table 1 and Figure 2, except that this case is still more complex because the three polyradicals **D-3**, **T-3**, and **H-3** are involved (Scheme 4). Moreover, the diradical **D-3** absorbs not only at 333 nm, but also significantly at 351 nm (Figure 2c). Consequently, since the π,π^* excitation of the **D-3** diradical is crucial for further nitrogen extrusion, the diradical **D-3** is also efficiently excited by 351-nm light and as much tetraradical **T-3** (and hexaradical **H-3**) is generated as at 333 nm (Table 1, column 7).

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(15) Mirgidicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400–7404.

From this combined EPR- and UV-spectral study, we have learned that for the efficient generation of the polyradicals **D-1**, **T-2**, and **H-3** it is necessary to optimize the photodenitrogenation conditions of the corresponding azoalkanes **1**, **2**, and **3**, such that the photobleaching of the generated polyradicals is minimized. This is quite difficult in the present case, because the azo chromophore (n,π^*), which is responsible for the nitrogen extrusion, overlaps extensively with the π,π^* absorption of cumyl radical within the polyradical, and photobleaching com-petes effectively. Thus, for the rational design of efficient high-spin systems by photochemical means, it is crucial to investigate the photoreactivity of the desired polyradi-cal, as well as of its precursors.

Supporting Information Available: Description for the photolysis of the azoalkanes **1**, **2**, and **3** in matrix at 77 K, monitored by EPR and UV spectroscopy, and the NMR spectral data of the azoalkane **1** and its photoproducts **4** and **5**. This material is available free of charge in the Internet at http://pubs.acs.org.

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