Urazole-Bridged Bicyclic Azoalkanes: Generation, Nitroxyl Trapping, and ESR Spectra of the Heterosubstituted 4,5-Diaza-1,3-cyclopentanediyl Diradicals through Direct and Benzophenone-Sensitized Photochemical Deazetation

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The Diels–Alder reaction of isopyrazoles **3** with 4-methyl-1,2,4-triazoline-3,5-dione afforded the azoalkanes **4** in high yields. The stereochemistry of the *syn*- and *anti*-diastereomeric derivatives **4b** was established on the basis of spectral data and an X-ray structure determination for *syn*-**4b**. Photochemical loss of dinitrogen through direct as well as benzophenone-sensitized photolysis led to the corresponding housanes **5**. For the stereolabeled *syn*- and *anti*-**4b** azoalkanes, the respective housanes *anti*- and *syn*-**5b** were obtained as mixtures, the latter in preference (*syn*/*anti* > 90:10). Above −10 °C, the housanes **5b** isomerized thermally to a 96:4 (at −30 °C) thermodynamic mixture of *syn*/*anti*, for which a van't Hoff treatment gave ΔG(243 K) = −4.4 kJ/mol in favor of *syn*-**5b**, ΔH = 4.2 kJ/mol, and ΔS = 36 J/mol K. AM1 calculations confirm that the *syn*-**5b** diastereomer is the preferred one. The triplet-sensitized photolysis at −30 °C of the separate *syn*- and *anti*-**4b** azoalkanes gave the same thermodynamically controlled mixture of housanes **5b** (*syn*/*anti* = 96:4), which speaks for a planar triplet 1,3 diradical **T-IIb** as intermediate. The intervention of triplet diradicals **T-IIa,d** was confirmed by ESR spectroscopy under matrix isolation ($T \leq 77$ K), and the triplet ground state was established by a Curie plot for the dimethyl derivative **T-IIa**. Since in the direct photolysis of the separate *syn*- and *anti*-**4b** azoalkanes also predominantly the *syn*-**5b** housane was obtained, fast intersystem crossing of the singlet 1,3 diradical **S-IIb** to the triplet species **T-IIb** is proposed. The small *memory effect* (retention) in the direct photolysis in solution implies a puckered conformation for the singlet 1,3 diradical **S-IIb**. Indeed, in the direct deazetation under matrix conditions at −78 °C, the *memory effect* (retention) is unequivocally established, i.e. *syn*/*anti*-**5b** = 24:76 for azoalkane *syn*-**4b** and *syn*/*anti* > 99:1 for *anti*-**4b**. In the presence of the nitroxyl radical scavenger 1,1,3,3-tetramethylisoindolin-2-yloxyl, the 1,3 diradicals were efficiently trapped in form of the isomeric bis-alkoxyamines **7** in the triplet-sensitized as well as direct photolyses of azoalkanes **4a,d**. These unprecedented results imply that heteroatom substitution does not generally reduce the lifetime of triplet diradicals.

Introduction

The importance of diradicals in chemical reactions, particularly photochemical transformations,[1] is reflected in the vast number of recent studies on these short-lived intermediates. The current interest concerns especially 1,3 diradicals, which are usually generated from cyclic azoalkanes as precursors.[1,2] The lifetimes and chemical reactivity of triplet diradicals depend generally on the rate of intersystem crossing (ISC) to the singlet states; the latter rapidly cyclize to the products.[1,2] Nevertheless, given sufficiently long lifetimes (in the nanosecond range), both triplet and singlet diradicals can be spectroscopically observed and/or chemically trapped, which provides valuable insight into the factors which affect diradical lifetimes and, hence, the chemical reactivity of such transients in solution.[2] The first case of O_2 trapping of a localized singlet 1,3 diradical, i.e. not of the non-Kekule type, constitutes the 1,3-diphenylcyclopentane-1,3-diyl, which has a singlet lifetime of ca. 22 ps compared to its triplet lifetime of ca. 25 μs and is, thus, by millionfold shorter lived.[3]

Ever since the deazetation of azoalkanes to the 1,3-cyclopentanediyls has been investigated, the question of one-bond *versus* two-bond cleavage has been of paramount interest in the examination of their photochemical and thermal nitrogen extrusion.[4] The consensus of opinion is that the stepwise mechanism prevails,[5] but the resulting diazenyl radicals are usually too short-lived for detection. ESR spectroscopy under matrix isolation conditions provides the most direct information on the spin ground state, on the distance of separation between the two unpaired electrons, and on the symmetry and therewith the preferred conformation of the denitrogenated 1,3-cyclopentanediyl.[6] Additionally, comparative product studies of the thermolysis and triplet-sensitized

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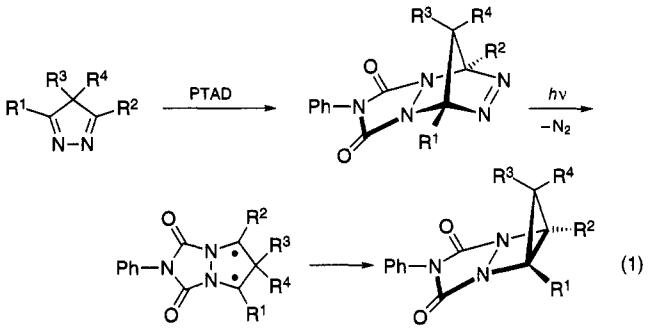
photolysis offer valuable but indirect insight into the reaction mechanism.[2]

Among the chemical trapping methods, dioxygen has proven useful in scavenging triplet diradicals;[2] however, frequently thermally unstable peroxides are obtained, which encumbers quantitative analysis. Recently, nitroxides have been successfully applied for the trapping of diradicals.[7] The oxygen site of the nitroxide radicals binds to carbon-centered radicals at rates in the range of 10^8–10^9 M^{-1} s^{-1}; the actual value depends on the structure of the radical and the solvent used.[8] Fortunately, the alkoxyamine adducts are usually persistent enough for isolation and characterization.[7,9] Especially the nitroxide 1,1,3,3-tetramehylisoindolin-2-yloxyl (TMIO)[10] is advantageous for this purpose because it contains a UV chromophore which facilitates detection and structural elucidation of the alkoxyamine products. Scaiano et al.[11] reported that nitroxides also enhance intersystem crossing in triplet diradicals, which may affect their scavenging efficiency.

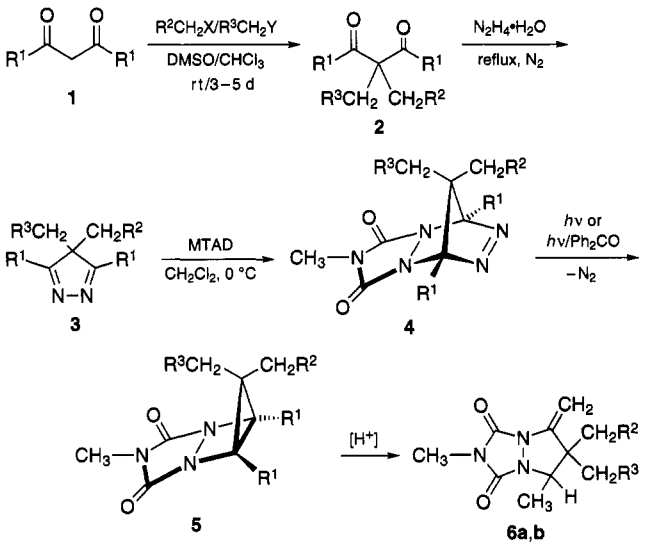
While such spectroscopic and trapping studies have generated a rather elaborate picture on the structure and reactivity of triplet 1,3-cyclopentanediyl diradicals, surprisingly little is known to date on heterocyclic analogs. Fundamental studies in this area were first reported by Arnold and co-workers[12] during the late 1960's, who generated the urazole-bridged 1,3 diradicals by direct photolysis of the corresponding azoalkanes. The latter were readily accessible by Diels–Alder reaction of isopyrazoles with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), as displayed in eq 1. By means of ESR spectroscopy, the



triplet ground state of these first heterocyclic 1,3 diradicals was established and intersystem crossing led to the expected housanes. Unfortunately, only little if any information is available on the triplet lifetimes of such heterosubstituted 1,3-cylopentanediyl diradicals in solution.[12]

Caldwell[13] has shown that oxygen atom substitution for a methylene group in 1,4 diradicals, derived from Norrish Type II photochemistry of aryl ketones, enhances intersystem crossing significantly and thereby drastically shortens the lifetime of these triplet species.[14] Therefore, it was our interest to assess the effect of nitrogen atoms on the reactivity of the urazole-bridged triplet diradicals given in eq 1. It was anticipated that dioxygen trapping would be complicated by the labile nature of the resulting aza-substituted endoperoxides. For this reason nitroxyl radicals were to be employed as scavengers of the triplet diradicals;[7,8] the latter were to be generated by the hitherto not investigated benzophenone-sensitized deazetation of the urazole-bridged azoalkanes.[12] Herein we present the full details of this mechanistic study, in which we demonstrate that, contrary to expectations,[13] such urazole-bridged diradicals are quite persistent.

Scheme 1. Synthesis of Azoalkanes 4 and Their Photochemical Denitrogenation to Housanes 5



a: $R^1 = CH_3$, $R^2 = R^3 = H$
b: $R^1 = CH_3$, $R^2 = Ph$, $R^3 = H$ (*syn*-**4b**, *anti*-**5b**)
$R^1 = CH_3$, $R^2 = H$, $R^3 = Ph$ (*anti*-**4b**, *syn*-**5b**)
c: $R^1 = CH_3$, $R^2 = R^3 = Ph$
d: $R^1 = Ph$, $R^2 = R^3 = H$

Results

Synthesis and Properties of the Urazole-Bridged Bicyclic Azoalkanes. The unknown azoalkanes **4a–d** were prepared in yields above 90% by the known Diels–Alder reaction of the corresponding isopyrazoles **3a–d** with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD), as shown in Scheme 1.[12] MTAD was chosen instead of PTAD[12] to increase the solubility of the urazole-bridged azoalkanes **4**. The *syn*/*anti* isomers of azoalkane **4b** were separated and purified by fractional recrystallization, and their

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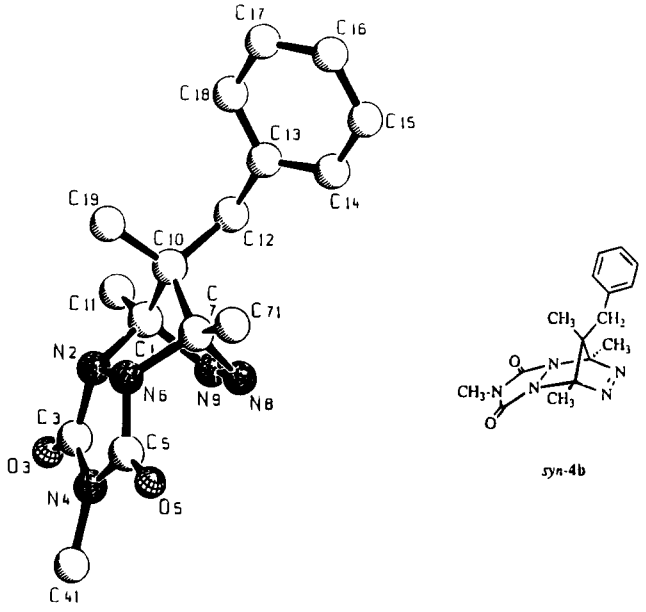


Figure 1. X-ray structure of azoalkane *syn*-**4b**.

stereochemistry was determined by NMR spectroscopy. The absolute configuration of the isomer *syn*-**4b**, which crystallizes in the orthorhombic system, was confirmed by an X-ray analysis (Figure 1, space group *Pbca*; a = 1265.8(3), b = 2612(1), and c = 960.9(3) pm).

The azoalkanes **4** were stored at room temperature in the dark, except **4d**, which was thermally too labile and had to be kept below −20 °C.

Photolyses. Direct as well as triplet-sensitized (benzophenone) photolyses of the azoalkanes **4a−d** led exclusively to the corresponding housanes **5a−d** (Scheme 1, Table 1). The triplet-sensitized photolyses (3-fold molar excess of Ph_2CO) were conducted in sealed Griffin−Worden tubes by irradiation with the 333-nm line of the argon ion laser in order to excite exclusively the benzophenone sensitizer. The housane **4a** is extremely acid labile and decomposed slowly to the olefinic bicycle **6a** even in rigorously purified chloroform (Scheme 1).

Direct and triplet-sensitized photolyses of the two separate azoalkanes *syn*- and *anti*-**4b** both led to similar diastereomeric mixtures of the housanes *syn*/*anti*-**5b** in the range 90:10 to 98:2 in favor of the *syn* isomer (Table 1, entries 3 to 9). Analogous to housane **5a**, both housanes *syn*- and *anti*-**5b** also rearranged to the corresponding olefin **6b** (Scheme 1) under acid catalysis.

The stereochemistry of the *syn*/*anti*-**5b** isomers was determined by NOE experiments. In contrast to the literature,[12] for analogous derivatives the *syn* isomer was the main product. A control experiment by ^{1}H NMR monitoring of the *syn*/*anti*-**5b** ratio revealed that *syn*/*anti* isomerization took place at temperatures above −10 °C; hence, all photolyses of the azoalkanes *syn*/*anti*-**4b** (Table 1, entries 3 to 9) were conducted at low temperatures in order to assure that the results of the quantitative product studies of the direct and sensitized photolyses were not altered by thermal equilibration of the housanes.

The equilibrium composition of the *syn*/*anti*-**5b** housanes (Scheme 2) was determined by ^{1}H NMR spectroscopy over the temperature range from −60 to +25 °C; the *syn*/*anti* ratio varied from 88:12 to 94:6 in this temperature range. A van't Hoff treatment of the above equilibrium data gave molar enthalpy and entropy values of 4.2 ± 0.4 kJ/mol and 36 ± 4 J/mol·K in favor of the *syn* isomer. The molar free energy (ΔG) at −30 °C for the *syn*/*anti* isomerization of housane **5b** was determined to be −4.4 ± 0.5 kJ/mol in favor of the *syn* isomer. From the latter, the equilibrium *syn*/*anti* ratio was estimated to be 97:3 at −30 °C, which is in very good agreement with the ratio of 96:4 assessed by ^{1}H NMR measurements in the sensitized photolyses of both diastereomeric azoalkanes *syn*/*anti*-**4b** at −30 °C (Table 1, entries 5 and 8).

Direct and triplet-sensitized photolyses of azoalkane **4c** led exclusively to the stable housane **5c**, whereas azoalkane **4d** gave the housane **5d**, which was persistent only below −10 °C. For the latter, already above −50 °C coalescence of the methyl signals of the methano bridge was observed by ^{1}H NMR measurements.

Trapping Experiments of the 4,5-Diaza-1,3-cyclopentanediyl Diradicals T-IIa,d by the Nitroxide TMIO. The conditions of the direct and sensitized photolyses and the nitroxide trapping products of the azoalkane **4a** and its housane **5a** are given in Scheme 3, the results of the quantitative product studies in Table 1. Benzophenone sensitization of azoalkane **4a** in the presence of a 6-fold molar excess of the nitroxide TMIO gave the bis-alkoxyamine **7a** in 60% yield (Table I, entry 14); the remainder was undefined higher-molecular-weight material. The corresponding housane **5a** was not stable under the sensitized photolysis conditions. When authentic housane **5a** was submitted to these conditions (control experiment), the adduct **7a** was obtained in 31% yield, besides undefined decomposition products of the housane (Table 1, entry 17). In view of these complications, unfortunately, it was not possible to conduct a quantitative trapping study[2,7,8] to estimate the triplet lifetime of the urazole-bridged 1,3 diradical.

The two stereoisomeric nitroxide adducts *cis*- and *trans*-**7a** were separated by MPLC, but it was not possible to distinguish them by spectral means. Furthermore, attempts to grow suitable crystals for X-ray analysis failed.

The direct photolysis of azoalkane **4a** at 350 nm (Rayonet photoreactor) in the presence of the nitroxide TMIO led on complete conversion of the azo compound to the housane **5a** and the bis-adduct **7a** in a ratio of 80:20 (mass balance >90%), cf. Table 1 (entry 15). Irradiation at the 333-nm laserline afforded the housane **5a** and bis-adduct **7a** in a 70:30 ratio (Table 1, entry 16). When the authentic housane **5a** was photolyzed at 350 nm (Rayonet photoreactor) with TMIO present, partial conversion (15−20%) to the bis-alkoxyamine **7a** was observed (Table 1, entry 18). This control experiment establishes that the housane **5a** is as well quite labile under the direct photolysis conditions. Additional control experiments proved that the azoalkane **4a** does not react with the radical scavenger in the dark, whereas the housane **5a** decomposed slowly in the presence of the radical scavenger.

When the azoalkane **4d** was photolyzed at −20 °C under sensitized conditions in the presence of TMIO, the bis-adduct **7d** precipitated from the crude reaction mixture and was unequivocally characterized by spectral means. All efforts to purify the bis-adduct **7d** failed because it was thermally too labile.

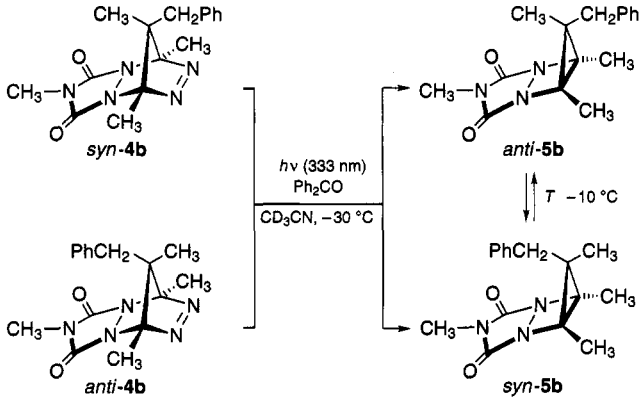
ESR Spectroscopy. Direct photolysis of azoalkane **4a** in an argon matrix at 12 K led to the persistent triplet diradical **T-IIa**. A Curie plot confirmed a triplet ground state for this diradical, but the D and E parameters could not be determined because the ESR spectrum was

Table 1. Product Studies[a] of the Direct and Sensitized Photolyses of the Azoalkanes 4a–d and of Housane 5a in the Absence and Presence of Nitroxide

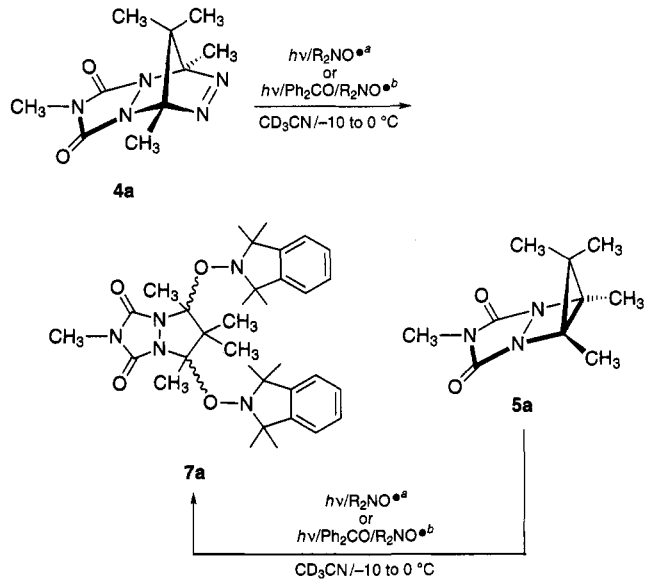
entry	azoalkane[c]	photolysis conditions[b] mode,[d] λ (nm) (W), TMIO (molar excess)	solvent	temp[e] (°C)	time (min)	products[f]
1	**4a**	direct, 350	CD_3CN	−20 (−20)	60	**5a**
2	**4a**	sens., 333 (1.1)	CD_3CN	10 (25)	10	**5a**
3	*syn*-**4b**	direct, 350	CD_2Cl_2	−60 (−60)	60	*syn/anti*-**5b** (88:12)
4	*syn*-**4b**	direct, 350	CD_3CN	−20 (−30)	60	*syn/anti*-**5b** (90:10)
5	*syn*-**4b**	sens., 333 (0.2)	CD_3CN	−30 (−30)	15	*syn/anti*-**5b** (97:3)
6	*syn*-**4b**	matrix,[g] direct, MLUV (2.0)	CD_3CN	−78 (−30)	15	*syn/anti*-**5b** (24:76)
7	*anti*-**4b**	direct, MLUV(0.8)	CD_3CN	−30 (−30)	10	*syn/anti*-**5b** (98:2)
8	*anti*-**4b**	sens., 333 (0.2)	CD_3CN	−30 (−30)	15	*syn/anti*-**5b** (96:4)
9	*anti*-**4b**	matrix,[g] direct, MLUV (0.8)	CD_3CN	−78 (−30)	10	*syn/anti*-**5b** (>99:1)
10	**4c**	direct, 350	CD_3CN	−15 (25)	60	**5c**
11	**4c**	sens., 333 (0.9)	CD_3CN	5 (25)	10	**5c**
12	**4d**	direct, 350	CD_2Cl_2	−78 (−78)	75	**5d**
13	**4d**	sens., 333 (0.4)	CD_2Cl_2	−30 (−30)	20	**5d**
14	**4a**	sens., 333 (3.0), TMIO (6.0)	CH_3CN	−10 (25)	145	**7a**
15	**4a**	direct, 350, TMIO (2.0)	CD_3CN	0 (25)	90	**5a/7a** (80:20)
16	**4a**	direct, 333 (3.0), TMIO (2.0)	CD_3CN	0 (25)	50	**5a/7a** (70:30)
17	**5a**	sens., 333 (3.0), TMIO (6.0)	CD_3CN	−10 (25)	60	**7a**
18	**5a**	direct, 350, TMIO (6.0)	CD_3CN	−5 (25)	300	**5a/7a** (85:15)

[a] Conversions were always >98% and the mass balances (MB) >95%, except entry 12 (convn 87%, MB = 87%) and entry 13 (MB = 70 ± 10%), as determined by ^1H NMR spectroscopy (error ca. 5% of the stated values). [b] All photolyses were carried out under an argon gas atmosphere; photolyses at 350 nm were conducted in a Rayonet photoreactor, for all other entries the argon ion laser was used. [c] [4] ca. 0.013 to 0.26 M (cf. Experimental Section). [d] The molar ratio of benzophenone (sensitizer) to azoalkane varied between 2.0 and 3.5 in the triplet-sensitized photolyses. [e] In parentheses are given the temperatures at which the NMR measurements were conducted. [f] In parentheses are given the relative product ratios normalized to 100%. [g] Solvent matrix.

Scheme 2. Triplet-Sensitized Photolysis of the Diastereomeric Azoalkanes *syn/anti*-4b and the Thermal Equilibration of the Housanes *syn/anti*-5b



Scheme 3. Photolyses of the Azoalkane 4a and Its Housane 5a in the Presence of the Nitroxide TMIO



[a] Direct photolysis at 350 nm (Rayonet photoreactor) or 333 nm (argon ion laser). [b] Triplet-sensitized photolysis with benzophenone at 333 nm.

severely contaminated by the signals of an unknown monoradical. Direct photolysis of azoalkane **4d** in an ethanol/methylene chloride matrix at 77 K gave the corresponding triplet diradical **T-IId** which persisted up to 120 K. From the ESR spectrum, the D and E parameters[15] were calculated as $D/hc = 0.046 \pm 0.001$ cm^{-1} and $E/hc = 0.0004 \pm 0.0001$ cm^{-1}.

Discussion

The present ESR studies of the urazole-bridged 1,3 diradicals derived from the azoalkanes **4a,d**, like the previous ones for the *N*-phenyl derivatives,[12] confirm a triplet ground state for these species. The nearly zero symmetry parameter, i.e. $E/hc = 0.0004 \pm 0.0001$ cm^{-1}, for the triplet diradical **T-IId** of the diphenyl azoalkane **4d** establishes a planar conformation. In analogy, we expect planar triplet ground states for the remaining derivatives. Thus, the same 97:3 ratio of the diastereomeric housanes *syn*- and *anti*-**5b** (Table 1, entries 5 and 8) obtained in the triplet-sensitized photolysis of the separate pure *syn*- and *anti*-**4b** azoalkane isomers reflects the thermodynamic mixture of these photolysis products. Equilibration studies by ^1H NMR spectroscopy on the housanes **5b** in the temperature range −60 to 25 °C substantiated thermodynamic control, for which a van't Hoff treatment gave $\Delta H = 4.2 \pm 0.4$ kJ/mol, $\Delta S = 36 \pm 4$ J/mol K, and ΔG (at 243 K) = − 4.4 ± 0.5 kJ/mol in favor of the *syn* isomer. MO calculations (AM1 method)[16] also suggest that the *syn*-**5b** housane is the thermodynamically preferred diastereomer by at least 3–4 kcal/mol compared to the *anti*-**5b**. Expectedly, the steric crowding between the bridgehead methyl and benzyl

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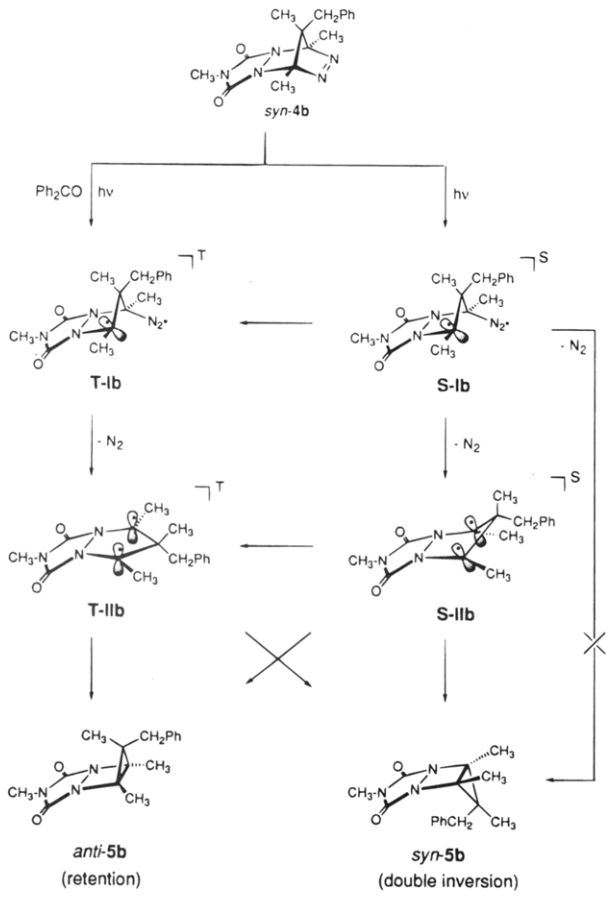
(16) For the help with the AM1 calculations, we thank H. M. Harrer.

Scheme 4. Reaction Pathways of the Singlet Diradical S-4b

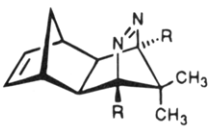


groups is more severe than for the methyl substituent at the methano bridge.

In analogy to previous triplet-sensitized photolyses of related diazabicyclo[2.2.1]hept-2-enes (DBH),[4] the mechanism in Scheme 4 (left-hand branch) rationalizes the above stereochemical results, as exemplified for the *syn*-**4b** azoalkane. The initial triplet diazenyl diradical **T-Ib** eliminates molecular nitrogen to afford the planar triplet 1,3 diradical **T-IIb**, which preferentially cyclizes on intersystem crossing to the *syn*-**5b** housane. Thus, irrespective whether one starts from the *syn*- or *anti*-**4b** azoalkane, the triplet-sensitized deazetation affords with large predominance (dr 97:3) the *syn*-**5b** housane.

The direct photolysis, which initially generates on one-bond C−N cleavage the singlet diazenyl diradical **S-Ib** (Scheme 4, right-hand branch), leads also predominantly to the *syn*-**5b** housane, irrespective of whether one starts from the *syn*- or *anti*-**4b** azoalkane (Table 1, entries 4 and 7). Thus, the usually observed inversion process for the DBH-type azoalkanes[17,18] does not apply, because *syn*-**4b** should have led mainly to *syn*-**5b** and *anti*-**4b** to *anti*-**5b**. *Note that on account of the change in the substituent priorities, the transformation syn-**4b** → syn-**5b** represents double inversion and syn-**4b** → anti-**5b** retention (Scheme 4)!* Clearly, the respective singlet diazenyl diradicals **S-Ib** cannot function as the immediate precursors to the housanes since dinitrogen expulsion[4,17,19] should dictate inversion. Consequently, also in the direct photolysis a common equilibrating planar intermediate must intervene to explain the dominance of the thermodynamically preferred *syn*-**5b** diastereomer from both azoalkane diastereomers. We propose that the triplet 1,3 diradical **T-IIb**, whose planar geometry is established, intervenes as principal intermediate also in the direct photolysis. Two pathways are feasible (Scheme 4), namely intersystem crossing at the diazenyl diradical stage and N_2 loss, i.e. **S-Ib** → **T-Ib** → **T-IIb**, or first denitrogenation followed by intersystem crossing of the 1,3 diradical, i.e. **S-Ib** → **S-IIb** → **T-IIb**. The latter alternative appears to us as the more likely one in view of the established triplet ground state of the urazole-bridged 1,3 diradicals **T-IIa,d** by ESR.

A closer look at the diastereomeric ratios of the housanes **5b**, obtained in the direct photolysis, i.e. *syn*/*anti*-**5b** 90:10 from *syn*-**4b** and 98:2 from *anti*-**4b** (Table 1, entries 4 and 7), reveals a small memory effect in favor of retention (the thermodynamically controlled *syn*/*anti* ratio in the triplet photolysis from both diastereomeric azoalkanes is 96:4, cf. entries 5 and 8 in Table 1). This small but real *memory effect* implies a puckered conformation for the singlet 1,3 diradical, the first experimental evidence of this kind. Apparently, the puckered singlet 1,3 diradical **S-IIb** relaxes on intersystem crossing mainly to the planar triplet species **T-IIb**, but a small fraction cyclizes to the housane with conservation of the original azoalkane configuration. Complete retention of configuration has been previously observed in the direct as well as triplet-sensitized photolyses of the related azoalkanes **8**[20] and **9**,[21] but the stereolabeled urazole-bridged azoalkanes *syn*- and *anti*-**4b** are the first sufficiently flexible representatives to probe the mechanistic details of the spin state-dependent dynamics of retention *versus* double inversion.



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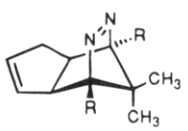

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In this context it was of interest to examine the stereochemistry of the direct photolysis of the separate azoalkanes *syn*- and *anti*-**4b** under matrix isolation (Table 1, entries 6 and 9). Indeed, now a pronounced *memory effect* (retention) prevails, in that from azoalkane *syn*-**4b** the major isomer is housane *anti*-**5b** (dr 24:76) and from *anti*-**4b** it is exclusively *syn*-**5b** (dr > 99:1). Two factors may be responsible, namely temperature-dependent intersystem crossing **S-IIb** → T-**IIb** at the 1,3 diradical stage[22] and/or restricted motion for planarization.[23] Whichever factor dominates is difficult to assess from this data, but clearly the singlet 1,3 diradical **S-IIb** is puckered. That some intersystem crossing to the planar triplet diradical **T-IIb** takes place at very low temperatures should be evident from the fact that triplet

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ESR spectra were observed at 12–30 K for **T-IIa**; moreover, for the *syn*-**4b** azoalkane appreciable amounts (24%) of *syn*-**5b** housane (double inversion) were detected (Table 1, entry 6), which mandates planarization.

The fact that the ESR spectrum of the 1,3 diradical **T-IId** could be measured at all at a temperature as high as 120 K implies that the urazole-bridged 1,3 diradicals are relatively long-lived. It was, therefore, of interest to estimate their triplet lifetime in solution through the established quantitative trapping techniques.[2,7,8] Unfortunately, trapping by dioxygen[2] was encumbered by the fact that the resulting heterosubstituted endoperoxides were too labile for isolation, characterization, and quantification. For this reason we resorted to the nitroxide tetramethylisoindolin-2-yloxyl (TMIO) as scavenger.[8]

As the results for the azoalkane **4a** show (Table 1, entries 14–16), in its triplet-sensitized photolysis exclusively the bis-alkoxyamine **7a** was observed as trapping product. In the direct photolysis substantial amounts of the latter were obtained as well, besides the expected housane **5a**. Clearly, these results manifest that scavenging of the triplet diradical **T-IIa** by the nitroxide TMIO is feasible; moreover, the fact that the bis-alkoxyamine **7a** was obtained in the direct photolysis of azoalkane **4a** corroborates that the intersystem crossing **S-IIa** → **T-IIa** is quite effective.

Unfortunately, the triplet-sensitized as well as the direct photolysis of the housane **5a** also led to the trapping product **7a** (Table 1, entries 17 and 18). Consequently, a quantitative product analysis was forfeited and it was not possible to estimate the triplet lifetimes of the urazole-bridged 1,3 diradicals **T-II** by our trapping techniques.[2,7] Nonetheless, the fact that these transients can be trapped so efficiently by O_2 and nitroxide implies that their triplet lifetimes must be appreciable, certainly at least hundreds of nanoseconds.[2,8] Consequently, heteroatom substitution does not necessarily shorten the lifetime of such triplet species.[13] In view of the importance of triplet diradicals and high-spin polyradicals in connection with organic ferromagnetic materials,[24] we contend that a broad-scale testing of the effect of heteroatom substitution[13,24c] should be valuable in understanding the reactivity of such transients. For a rational design of these high-spin systems, complete knowledge of the factors that determine their lifetimes and thus their persistence seems mandatory.

Experimental Section

General Aspects. Melting points are uncorrected and were measured in glass capillaries on a Büchi SMP-20 melting point apparatus. Direct photolyses were performed under an argon gas atmosphere in Griffin–Worden tubes with the 333-, 351-, and 364-nm lines (MLUV) of a Coherent Innova 100 CW argon ion laser or by irradiation in Pyrex vessels in a Rayonet photoreactor RPR-100, by using a 350-nm lamp as light source. Infrared spectra were recorded on a Perkin-Elmer 1420 infrared ratio recording spectrophotometer. The ultraviolet absorption spectra were measured on a Hitachi U 3200 spectrophotometer. The NMR spectra were run on Bruker WM 400, AC 250, or AC 200 spectrometers with TMS or $CDCl_3$ as internal standards. For low-temperature spectra a Bruker WM 400 or AC 200 instrument was used. ESR spectra were measured on a Bruker ER 420 by irradiation with a Hannovia 977 B-1 1000 W Hg/Xe high-pressure lamp, equipped with UV optics, directly in the ESR cavity.

Benzophenone, commercially available material, was recrystallized twice from ethanol (mp 49–51 °C). 1,1,3,3-Tetramethylisoindolin-2-yloxyl, mp 125–128 °C, was prepared according to the literature.[10] The 4,4-disubstituted isopyrazoles **3** were prepared in two steps according to known procedures[12,25] by starting with the appropriate 1,3-diketones **1**. The latter were dialkylated in DMSO and the dialkylated dione **2** was then condensed with $N_2H_4{\cdot}H_2O$ to the corresponding isopyrazoles **3** in yields from 63 to 74%.

Synthesis of Azoalkanes 4. Analogous to the literature procedure,[12] to a solution of the isopyrazole **3** in 20 mL of dry methylene chloride was added an equimolar amount of MTAD in 30 mL of methylene chloride at 0 °C. The reaction mixture was stirred at ca. 20 °C, except **4d** (0 °C), in the dark until a clear, yellow solution was formed. The solvent was removed at 0 °C/20 Torr, and the crystalline crude product was purified by column chromatography [silica gel, 3:1 petroleum ether (bp 30–50 °C)/ethyl acetate except for **4d**, for which methylene chloride was used]. Yields around 90% were obtained for each of the azoalkanes. The two stereoisomers *syn*-**4b** and *anti*-**4b** were separated by fractional crystallization in toluene and petroleum ether (bp 30–50 °C).

1,4,7,10,10-Pentamethyl-2,4,6,8,9-pentaazatricyclo-[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (4a): 2.22 g (94%), yellow needles, mp 111.5–112.5 °C; IR (KBr) ν 3010, 2940, 1785, 1740, 1440, 1400, 1270, 1190, 1105, 1025, 885, 810, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.50 (s, 3H), 1.02 (s, 3H), 2.11 (s, 6H), 2.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 10.1 (q), 14.8 (q), 16.3 (q), 25.8 (q), 53.4 (s), 101.4 (s), 157.0 (s); UV (CCl_4) λ_{max} (log ϵ) 397 (2.671), 262 nm (2.893); MS (70 eV) *m/z* 209 (1) [$M^+ - N_2$], 195 (8), 194 (76), 138 (8), 137 (100), 83 (6), 68 (8), 42 (39), 41 (19), 39 (8). Anal. Calcd for $C_{10}H_{15}N_5O_2$ (237.3): C, 50.62; H, 6.37; N, 29.52. Found: C, 50.96; H, 5.98; N, 29.01.

***syn*-1,4,7,10-Tetramethyl-10-(phenylmethyl)-2,4,6,8,9-pentaazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (*syn*-4b):** 2.20 g (54%), yellow prisms, which crystallized in the orthorhombic system, space group *Pbca*; a = 1265.8(3), b = 2612-(1), and c = 960.9(3) pm, mp 129–132 °C; IR (KBr) ν 3040, 2960, 1800, 1755, 1740, 1725, 1450, 1395, 1190, 1100, 1020, 780, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.14 (s, 3H), 1.93 (s, 6H), 2.12 (s, 2H), 2.82 (s, 3H), 6.93–7.04 (m, 2H), 7.15–7.29 (m, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 10.8 (q), 14.4 (q), 25.7 (q), 35.8 (t), 56.3 (s), 101.8 (s), 127.3 (d), 128.4 (d), 130.4 (d), 134.6 (s), 156.8 (s); UV (CH_2Cl_2) λ_{max} (log ϵ) 397 (2.815), 245 nm (3.745); MS (70 eV) *m/z* 285 (0.2) [$M^+ - N_2$], 195 (11), 194 (100), 137 (83), 115 (6), 91 (36), 65 (12), 42 (10), 41 (8), 39 (7). Anal. Calcd for $C_{16}H_{19}N_5O_2$ (313.4): C, 61.33; H, 6.11; N, 22.35. Found: C, 60.94; H, 5.85; N, 22.45.

***anti*-1,4,7,10-Tetramethyl-10-(phenylmethyl)-2,4,6,8,9-pentaazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (*anti*-4b):** 570 mg (14%), yellow powder, mp 130–132 °C; IR (KBr) ν 2980, 2955, 1820, 1770, 1760, 1455, 1400, 1175, 1100, 1025, 760, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.52 (s, 3H), 1.92 (s, 6H), 2.74 (s, 2H), 2.87 (s, 3H), 7.08–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 10.8 (q), 12.5 (q), 25.8 (q), 36.8 (t), 56.2 (s), 101.7 (s), 127.2 (d), 128.3 (d), 130.8 (d), 135.1 (s), 157.0 (s); UV (CH_2Cl_2) λ_{max} (log ϵ) = 395 (2.720), 244 nm (3.742); MS (70 eV) *m/z* 285 (1) [$M^+ - N_2$], 195 (11), 194 (100), 137 (91), 91 (27), 79 (5), 65 (10), 42 (9), 41 (7), 39 (s). Anal. Calcd for $C_{16}H_{19}N_5O_2$ (313.4): C, 61.33; H, 6.11; N, 22.35. Found: C, 61.38; H, 6.03; N, 22.07.

1,4,7-Trimethyl-10,10-bis(phenylmethyl)-2,4,6,8,9-pentaazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (4c): 1.91 g (69%), yellow powder, mp 129–132 °C; IR (KBr) ν 3070, 3040, 2950, 1780, 1730, 1495, 1445, 1390, 1275, 1180, 1015, 750, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.58 (s, 6H), 2.38 (s, 2H), 2.84 (s, 3H), 3.00 (s, 2H), 7.04–7.24 (m, 10H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 11.0 (q), 25.7 (q), 32.1 (t), 33.6 (t), 59.4 (s,), 101.8 (s), 127.4 (d), 127.6 (d), 128.5 (d), 128.8 (d), 130.2 (d), 131.2 (d), 134.9 (s), 135.0 (s), 156.8 (s); UV (CCl_4) λ_{max} (log ϵ) 398

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(2.728), 300 nm (1.965); MS (70 eV) *m/z* 361 (1) [$M^+ - N_2$], 270 (100), 269 (36), 268 (29), 254 (19), 213 (40), 141 (23), 115 (22), 91 (64) 28 (67). Anal. Calcd for $C_{22}H_{23}N_5O_2$ (384.5): C, 67.85; H, 5.95; N, 17.98. Found: C, 68.05; H, 5.81; N, 18.19.

4,10,10-Trimethyl-1,7-diphenyl-2,4,6,8,9-pentaazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (4d): 1.02 g (94%), yellow, amorphous powder, mp ca. 100 °C dec; IR (KBr) ν 2960, 1800, 1745, 1470, 1440, 1380, 1340, 1330, 1270, 1160, 1060, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.33 (s, 3H), 1.14 (s, 3H), 2.90 (q, 3H), 7.50–7.66 (m, 6H), 7.82–7.98 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.8 (q), 16.1 (q), 26.0 (q), 59.3 (s), 106.3 (s), 127.0 (d), 127.6 (d), 128.6 (d), 130.2 (s), 156.7 (s); UV (CH_2Cl_2) λ_{max} (log ϵ) 400 (2.720), 318 (2.040), 239 nm (3.986); MS (70 eV) *m/z* 333 (28) [$M^+ - N_2$], 318 (100), 261 (68), 256 (45), 145 (61), 104 (50), 103 (45), 77 (52), 57 (42), 44 (61). Anal. Calcd for $C_{20}H_{19}N_5O_2$ (361.4): C, 66.47; H, 5.30; N, 19.38. Found: C, 66.37, H, 5.25; N, 19.63.

General Procedure for the Preparative Direct Photolysis of Azoalkanes 4a–c. Samples (15 mL) of a 0.01–0.03 M solution of the azoalkanes **4a–c** in methylene chloride were irradiated under an argon gas atmosphere at 0 °C in the Rayonet photoreactor ($300 < \lambda < 370$ nm) for 60 to 70 min until the yellow color of the azoalkane was gone (negative azo test[26]). The solvent was evaporated at 0 °C/20 Torr, and the residue was recrystallized from methylene chloride/*n*-pentane mixtures under an argon gas atmosphere. The housanes **5** are air-, acid-, and moisture-sensitive.

1,4,7,8,8-Pentamethyl-2,4,6-triazatricyclo[5.1.0.0^{2,6}]-octane-3,5-dione (5a): 80.9 mg (84%), colorless needles, mp 104–104.5 °C; IR (CCl_4) ν 2950, 2920, 1780, 1710, 1435, 1385, 1255, 1245, 1215, 1170, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.97 (s, 3H), 1.36 (s, 3H), 1.56 (s, 6H), 3.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 7.9 (q), 12.7 (q), 17.4 (q), 26.1 (q), 28.3 (s), 61.4 (s), 162.0 (s); UV (CH_2Cl_2) λ_{max} (log ϵ) 229 (3.461); MS (70 eV) *m/z* 209 (9) [M^+], 194 (59), 138 (8), 137 (100), 96 (10), 81 (15), 68 (10), 67 (8), 42 (30), 41 (18), 39 (8). Anal. Calcd for $C_{10}H_{15}N_3O_2$ (209.3): C, 57.40; H, 7.23; N, 20.08. Found: C, 57.61; H, 7.28; N, 20.00.

***syn*- and *anti*-1,4,7,8-Tetramethyl-8-(phenylmethyl)-2,4,6-triazatricyclo[5.1.0.0^{2,6}]octane-3,5-dione (*syn/anti*-5b):** 60.4 mg (83%), colorless plates, mp 106.5–109.5 °C. Because of facile *syn/anti* isomerization already above −10 °C, separation of the diastereomers was not possible. The following spectral data are for a mixture of both isomers [dr (*syn/anti*) 94:6]: IR (CCl_4) ν 2965, 2939, 1790, 1720, 1440, 1390, 1260, 1210, 1100, 1000; UV (CH_2Cl_2) λ_{max} (log ϵ) 230 (3.512); MS (10 eV) *m/z* 285 (10) [M^+], 270 (16), 194 (100), 193 (89), 137 (53), 108 (17), 91 (41), 80 (33), 79 (28), 65 (13). ***syn*-5b**: ^{1}H NMR (CD_3CN, 250 MHz) δ 0.75 (s, 3H), 1.48 (s, 6H), 2.97 (s, 3H), 3.09 (s, 2H), 7.18–7.39 (m, 5H); ^{13}C NMR (CD_3CN, 63 MHz) δ 8.1 (q), 14.6 (q), 26.6 (q), 32.3 (t), 34.1 (s), 63.6 (s), 127.1 (d), 129.4 (d), 130.1 (d), 141.3 (s), 162.9 (s). ***anti*-5b**: ^{1}H NMR (CD_3CN, 250 MHz) δ 1.21 (s, 3H) 1.60 (s, 6H), 2.60 (s, 2H), 2.95 (s, 3H), 7.18–7.39 (m, 5H); ^{13}C NMR (CD_3CN, 63 MHz) δ 8.8 (q), 9.9 (q), 26.6 (q), 31.6 (s), 35.8 (t), 62.2 (s), 126.9 (d), 129.1 (d), 129.6 (d), 138.4 (s), 162.7 (s). Anal. Calcd for $C_{16}H_{19}N_3O_2$ (285.4): C, 67.35; H, 6.70; N, 14.73. Found: C, 67.23; H, 6.50; N, 14.42.

1,4,7-Trimethyl-8,8-bis(phenylmethyl)-2,4,6-triazatricyclo[5.1.0.0^{2,6}]octane-3,5-dione (5c): 54.0 mg (73%) colorless powder, mp 103–103.5 °C; IR (CCl_4) ν 2930, 1790, 1730, 1540, 1440, 1390, 1265, 1200, 1010, 720, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.71 (s, 6H), 2.37 (s, 2H), 3.19 (s, 3H), 3.22 (s, 2H), 7.02–7.41 (m, 10H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 9.2 (q), 26.2 (q), 27.7 (t), 32.8 (t), 37.0 (s), 62.4 (s), 126.2 (d), 126.5 (d), 128.3 (d), 128.6 (d), 128.9 (d), 129.3 (d), 136.1 (s), 139.2 (s), 161.6 (s); UV (CH_2Cl_2) λ_{max} (log ϵ) 259 nm (2.487); MS (70 eV) *m/z* 361 (0.3) [M^+], 182 (8), 92 (24), 91 (100), 89 (4), 65 (24), 53 (7), 51 (6), 50 (4), 39 (12). Anal. Calcd for $C_{22}H_{23}N_3O_2$ (361.4): C, 73.11; H, 6.41; N, 11.63. Found: C, 73.29; H, 6.23; N, 11.73.

General Procedure for the NMR Studies of the Direct Photolysis of Azoalkanes 4a–d. In a NMR tube was placed 0.5 mL of a 0.1–0.5 M solution of the azoalkane **4a–d**; it was then degassed and irradiated under argon gas until complete conversion (negative azo test[26]). Low-temperature ^{1}H NMR spectroscopy was used for identification of the products, and the results are summarized in Table 1.

4,8,8-Trimethyl-1,7-diphenyl-2,4,6-triazatricyclo-[5.1.0.0^{2,6}]octane-3,5-dione (5d): ^{1}H NMR (CD_2Cl_2, −78 °C, 400 MHz) δ 0.74 (s, 3H), 1.80 (s, 3H), 3.10 (s, 3H), 7.26–7.58 (m, 10H); ^{13}C NMR (CD_2Cl_2, −78 °C, 100 MHz) δ 12.5 (q), 19.0 (q), 26.2 (q), 31.0 (s), 69.7 (s), 128.6 (d), 128.8 (d), 130.2 (d), 130.3 (d), 131.2 (d), 131.6 (d), 161.7 (s). The housane **4d** is thermally labile above −10 °C and decomposes to undefined higher-molecular-weight material.

General Procedure for the Triplet-Sensitized Photolyses of the Azoalkanes 4a–d. In a NMR tube was placed a 0.07–0.13 M solution (0.5 mL) of the particular azoalkane **4a–d** in CD_3CN or CD_2Cl_2, and a 2.6–3.5-fold molar excess of benzophenone as sensitizer was added. The solution was degassed and irradiated with the 333-nm line of the argon ion laser. After total conversion (TLC, negative azo test[26]), the photolysate was analyzed by low-temperature ^{1}H NMR spectroscopy. The results are summarized in Table 1.

Control Experiments on the Stability of the Housanes 5. (a) Housane 5a in the Presence of Acids. In a NMR tube, a sample (10.0 mg, 48.0 μmol) of the housane **5a** in $CDCl_3$ (0.7 mL) was kept at room temperature under an argon gas atmosphere. After 1 d, ^{1}H NMR spectroscopy showed decomposition to the olefinic product **6a** in a ratio of **5a**:**6a** = 82:18. When repeated on a preparative scale, the olefinic product **3,7,7,8-tetramethyl-6-methylene-1,3,5-triazabicyclo[3.3.0]-octane-2,4-dione (6a)** was isolated in 70% yield by column chromatography [3:1 petroleum ether (bp 30–75 °C)/ethyl acetate as eluent], and recrystallization from petroleum ether (bp 30–75 °C) gave colorless prisms, mp 68–69 °C; IR (KBr) ν 2970, 1750, 1710, 1645, 1460, 1395, 1375, 1260, 1010, 850, 760, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.11 (s, 3H), 1.16 (s, 3H), 1.30 (d, J = 6.5 Hz, 3H), 3.01 (s, 3H), 3.59 (q, J = 6.5 Hz, 1H), 4.42 (d, J = 2.0 Hz, 1H), 5.21 (d, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 12.7 (q), 21.7 (q), 24.5 (q), 25.1 (q), 48.2 (s), 62.8 (d), 87.6 (t), 145.7 (s), 148.7 (s), 153.9 (s); UV (*n*-pentane) λ_{max} (log ϵ) 246 nm (3.901); MS (70 eV) *m/z* 210 (12) [$M^+ + 1$], 209 (100), 152 (15), 124 (11), 96 (8), 82 (14), 81 (69), 68 (6), 67 (10), 41 (9). Anal. Calcd for $C_{10}H_{15}N_3O_2$ (209.3): C, 57.40; H, 7.23; N, 20.08. Found: C, 57.59; H, 7.18; N, 20.01.

(b) Housane 5a in the Presence of Oxygen Gas. A sample (10.0 mg, 48.0 μmol) of housane **5a** was kept in CD_3CN (0.7 mL) for 2 d at room temperature in the presence of oxygen gas. ^{1}H NMR spectroscopy showed decomposition to several products which could not be identified spectroscopically. Formation of the olefinic product **6a** was not observed, but a peroxidic spot was detected by TLC [3:1 petroleum ether (bp 30–75 °C)/ethyl acetate].

(c) High-Temperature NMR Study of Housane 5a. Into a NMR tube was placed 0.5 mL of a 0.1 M solution of the housane **5a** in C_6D_6 under an argon gas atmosphere. Line-broadening of the methyl signals, accompanied by decomposition to the olefinic product **6a**, was observed by ^{1}H NMR spectroscopy above ca. 70 °C.

(d) Housane *syn/anti*-5b in the Presence of Oxygen Gas. After 5 d at room temperature in the presence of oxygen gas, a sample (10.0 mg, 35.0 μmol) of the housane *syn/anti*-**5b** in CD_3CN (0.7 mL) showed, besides higher-molecular-weight material, a peroxidic spot by TLC [3:1 petroleum ether (bp 30–75 °C)/ethyl acetate].

(e) Housane *syn/anti*-5b in the Presence of Acids. To a solution of 110 mg (0.352 mmol) of an isomeric mixture of *syn/anti*-**5b** in 10 mL of methylene chloride was added 0.5 mL of CF_3COOH. After the solution was stirred for 15 min at 20 °C and neutralized with saturated, aqueous K_2CO_3 solution, the organic layer was washed twice with 5 mL of water, and evaporation of the solvent at 25 °C/20 Torr, followed by column chromatography on silica gel [3:1 petroleum ether (30–75 °C)/ethyl acetate], led to 67.0 mg (61%) of **3,7,8-trimethyl-6-methylene-7-(phenylmethyl)-1,3,5-triazabicyclo[3.3.0]-octane-2,4-dione (6b):** colorless needles, mp 108.5–109 °C

(26) Adam, W.; Platsch, H. *Chem. Ber.* **1987**, *120*, 251.

from methyl *tert*-butyl ether/*n*-pentane; IR (KBr) ν 2980, 2950, 1765, 1710, 1645, 1450, 1395, 1385, 1250, 850, 770, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.07 (s), 1.61 (d, J = 6.6 Hz, 3H), 2.60 (d, J = 13.1 Hz, 1H), 2.76 (d, J = 13.1 Hz, 1H), 3.05 (s, 3H), 3.67 (q, J = 6.6 Hz, 1H), 3.72 (d, J = 2.0 Hz, 1H), 5.23 (d, J = 2.0 Hz, 1H), 7.00–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 12.1 (q), 19.5 (q), 25.2 (q), 38.7 (t), 51.7 (s), 64.6 (d), 91.2 (t), 126.7 (d), 128.2 (d), 131.0 (d), 135.8 (s), 141.8 (s), 149.4 (s), 155.0 (s); UV (CH_2Cl_2) λ_{max} (log ϵ) 249 nm (3.794); MS (70 eV) *m/z* 285 (49) [M^+], 271 (17), 270 (97), 213 (14), 144 (12), 143 (12), 129 (14), 105 (13), 91 (100), 65 (15), 53 (14), 42 (12). Anal. Calcd for $C_{16}H_{19}N_3O_2$ (285.4): C, 67.35; H, 6.71; N, 14.73. Found: C, 66.86; H, 6.53; N, 14.58.

(f) Low-Temperature NMR Study of the *syn/anti*-5b Housane Isomerization. A sample (28.0 mg, 98.0 μmol) of the isomers *syn/anti*-**5b** (88:12) in ca. 0.7 mL of CD_3CN at −60 °C was slowly warmed up in 10° steps directly in the NMR spectrometer. The *syn/anti* ratio changed from 88:12 at −60 °C to 89:11 at −40 and −20 °C. At −10 °C the ratio was 90:10 and changed to a 91:9 ratio at 0 °C to 94:6 at 25 °C in favor of the *syn* isomer.

(g) Dynamic ^1H NMR Spectroscopy of Housane 5d. A sample (18.4 mg, 55.0 μmol) of the housane **5d** in ca. 0.5 mL of CD_2Cl_2 at −78 °C was slowly allowed to warm up under an argon gas atmosphere. Above −50 °C, line broadening of the methyl signals at the methano bridge was observed and at 25 ± 10 °C coalescence was reached. Simultaneously, decomposition of the housane **5d** to higher-molecular-weight material occurred, as confirmed by TLC.

General Procedure for Nitroxide Trapping. In a sealed Griffin–Worden tube were placed 0.40–0.50 mmol of the azoalkane **4a** or **4d** in 10 mL of dry acetonitrile or methylene chloride. An up to 2-fold molar excess of benzophenone (sensitizer) and a 6-fold molar excess of the trapping agent TMIO were added. The solution was degassed by applying four freeze–pump–thaw cycles and afterward irradiated with the 333-nm line of the argon ion laser at −10 or −20 °C under an argon gas atmosphere. After complete consumption of the azoalkane (negative azo test[26]), the trapping product was purified by low-temperature flash chromatography [3:1 petroleum ether (30–75 °C)/ethyl acetate as eluent].

***cis/trans*-6,8-Bis((1′,1′,3′,3′-Tetramethylisoindolin-2′-yl)oxy)-3,6,7,7,8-pentamethyl-1,3,5-triazabicyclo[3.3.0]-octane-2,4-dione (7a).** An acetonitrile (10 mL) solution of azoalkane **4a** (100 mg, 0.420 mmol), benzophenone (100 mg, 0.550 mmol), and TMIO (481 mg, 2.53 mmol) gave after 145 min of irradiation 149 mg (60%) of the bis-adduct **7a** as a colorless powder, mp 184–186 °C. The two stereoisomers were separated by MPLC on silica gel, but the two fractions (ratio 9:1) could not be distinguished by NMR spectroscopy; the following spectral data are for a mixture of both isomers: IR (CCl_4) ν 2980, 2930, 1765, 1710, 1455, 1395, 1195, 1115, 1090, 1010, 965, 885 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.85 (s, 3H), 1.32 (s, 6H), 1.38 (s, 6H), 1.45 (s, 3H), 1.48 (s, 6H), 1.62 (s, 6H), 1.88 (s, 6H), 3.00 (s, 3H), 6.95–7.05 (m, 4H), 7.08–7.20 (m, 4H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 17.6 (q), 18.9 (q), 25.2 (q), 25.5 (q), 26.5 (q), 26.7 (q), 28.8 (q), 29.8 (q), 59.8 (s), 67.9 (s), 68.2 (s), 99.7 (s), 120.9 (d), 121.6 (d), 127.0 (d), 144.3 (s), 145.1 (s), 150.6 (s); UV (CH_3CN) λ_{max} (log ϵ) 270 (3.34), 264 (3.33), 224 nm (3.85). Anal. Calcd for $C_{34}H_{47}N_5O_4$ (589.8): C, 69.23; H, 8.03; N, 11.87. Found: C, 69.11; H, 8.35; N, 11.68.

***cis/trans*-6,8-bis((1′,1′,3′,3′-Tetramethylisoindolin-2′-yl)oxy)-6,8-diphenyl-3,3,7-trimethyl-1,3,5-triazabicyclo-[3.3.0]octane-2,4-dione (7d).** In 10 mL of dry methylene chloride were dissolved 200 mg (0.550 mmol) of azoalkane **4d**, 200 mg (1.10 mmol) of benzophenone (sensitizer), and 631 mg (3.32 mmol) of TMIO. Complete consumption of the azoalkane was achieved after 6 h of irradiation at −20 °C. On addition of 5 mL of dry methanol, 351 mg (89%) of the bis-adduct **7d** precipitated as colorless powder, mp >200 °C dec. The latter could not be further purified by silica or alumina chromatography without decomposition to undefined high-molecular-weight material. The bis-adduct **7d** was essentially insoluble in most common solvents; in halogenated solvents it was slightly soluble, but dissolution was accompanied by slow decomposition.

7d: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.64 (s, 6H), 1.06 (s, 6H), 1.34 (s, 6H), 1.42 (s, 6H), 1.53 (s, 6H), 3.00 (s, 3H), 6.90–7.00 (m, 4H), 7.10–7.30 (m, 4H), 7.40–8.10 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 24.4 (q), 25.6 (q), 25.9 (q), 26.1 (q), 26.5 (q), 27.6 (q), 63.1 (s), 67.7 (s), 68.9 (s), 98.5 (s), 120.1 (d), 120.7 (d), 126.0 (d), 126.2 (d), 126.5 (d), 127.0 (d), 127.9 (d), 128.1 (d), 128.6 (d), 137.6 (s), 142.8 (s), 145.2 (s), 148.7 (s).

Control Experiments for the Trapping Reactions. Stability of the Bis-alkoxyamine 7a in the Presence of Acids. To 0.7 mL of a 0.010 M solution of the bis-adduct **7a** in toluene-d_8 was added ca. 0.1 mL of CF_3COOH. After 30 min ^1H NMR spectroscopy showed complete decomposition of **7a** to undefined products.

Stability of the Azoalkane 4a and Its Housane 5a in the Presence of TMIO and Light. (a) Direct Photolysis of Azoalkane 4a at 350 nm (Rayonet). In a Schlenck tube, equipped with a cold finger, were placed 50.0 mg (0.210 mmol) of azoalkane **4a** and 80.2 mg (0.420 mmol) TMIO in 3 mL of CD_3CN. The solution was degassed and irradiated under a nitrogen gas atmosphere at 0 °C in the Rayonet photoreactor for 90 min until complete consumption (negative azo test[26]). NMR spectroscopy showed that the housane **5a** and the bis-adduct **7a** were formed in a ratio of 80:20. Prolonged irradiation (4 h) under these conditions led to further formation of the bis-adduct **7a**, which was the only product after removal of the solvent (20 °C/20 Torr).

(b) Direct Photolysis of Azoalkane 4a at 333 nm (Laser). In a sealed Griffin–Worden tube were placed 25.0 mg (0.110 mmol) of azoalkane **4a** and 40.0 mg (0.210 mmol) of the nitroxide TMIO in 2.5 mL of CD_3CN. The degassed solution was photolyzed under an argon gas atmosphere with the 333-nm line of the argon ion laser. After complete consumption of the azo compound, NMR spectroscopy showed the formation of the housane **5a** and the bis-adduct **7a** in a ratio of 75:25 (mass balance >90%).

(c) Sensitized Photolysis of the Housane 5a. A solution of 50.0 mg (0.210 mmol) of azoalkane **4a** and 80.0 mg (0.430 mmol) benzophenone in 3 mL of CD_3CN was degassed and placed into a sealed Griffin–Worden tube under an argon gas atmosphere. Irradiation at −10 °C by the 333-nm line of the argon ion laser led to complete consumption of the azo compound within 60 min. ^1H NMR spectroscopy showed only the presence of housane **5a**. After addition of 242 mg (1.27 mmol) of TMIO in 5 mL of degassed CH_3CN, the solution was further irradiated for 240 min. TLC showed total conversion of the housane and low-temperature flash chromatography (−20 °C) on silica gel [3:1 petroleum ether (bp 30–75 °C)/ethyl acetate] yielded 31% of the bis-adduct **7a**, besides undefined high-molecular-weight material.

(d) Direct Photoysis of Housane 5a at 350 nm. A solution of 44.1 mg (0.210 mmol) of housane **5a** and 80.1 mg (0.420 mmol) of TMIO in 2.5 mL of CD_3CN was degassed, placed into a Schlenck tube, and sealed under an argon gas atmosphere. Irradiation at −5 °C in the Rayonet photoreactor led after 5 h to partial consumption (15–20%) of the housane **5a**, and by means of ^1H NMR spectroscopy the bis-adduct **7a** was detected as the only product.

Stability of Azoalkane 4a and Housane 5a in the Presence of TMIO in the Dark. (a) Azoalkane 4a. A ca. 0.03 M solution of the azoalkane **4a** and a 6-fold molar excess of the nitroxide in chlorobenzene (1.0 mL) were stirred for 2 d under an argon gas atmosphere in the dark at room temperature. No consumption of azoalkane **4a** could be detected by TLC.

(b) Housane 5a. To 5 mL of a ca. 0.020 M solution of housane **5a** in methylene chloride was added a 6-fold molar excess of TMIO, and the solution was stirred at 10 °C for 2 d in the dark under an argon gas atmosphere. Besides undefined high-molecular-weight material, TLC showed the formation of bis-adduct **7a**.

ESR Studies of the Triplet Diradicals T-IIa,d. Triplet Diradical T-IIa. A sample of azoalkane **4a** was sublimed at 70 °C/10^{-6} Torr together with argon gas on a Saphire rod, which was cooled to 12 K. The matrix sample was irradiated for 10 s with a Hg/Xe lamp directly in the ESR cavity, and the spectrum of the triplet diradical was measured at 12–32

K. The 1,3 diradical persisted below 30 K for several hours, but on account of strong overlap of the triplet diradical signal by a monoradical, the D and E parameters could not be determined. Nevertheless, a Curie plot showed a linear dependence between the signal intensity and the reciprocal temperature.

Triplet Diradical T-IId. A ca. 0.060 M solution of the azoalkane **4d** in a 1:1 methylene chloride/ethanol mixture was placed into a sealed Pyrex tube and degassed. The sample was irradiated with all UV lines (1.0 W) of the argon ion laser for 30−60 s (1.0 W) at 77 K and inserted into the ESR cavity and its spectrum recorded at 77 K. The triplet diradical **T-IId** persisted at 77−120 K for several hours. The zero-field parameters were determined to be $D/hc = 0.046 \pm 0.001$ cm^{-1} and $E/hc = 0.0004 \pm 0.0001$ cm^{-1}.

Supplementary Material Available: X-ray crystallographic data and tables (5 pages) for azoalkane *syn*-**4b**, which includes atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, H atom coordinates, and isotropic displacement parameters. This material is available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, by quoting the depository number CSD-400459, the names of the authors, and the journal citation. The authors have deposited atomic coordinates structure *syn*-**4b** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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