J. Am. Chem. Soc. **1994**, *116*, 7049–7054

Temperature Dependence of the α versus β Bond Cleavage in the Direct and Triplet-Sensitized Photolysis of Azoalkanes of the 2,3-Diazabicyclo[2.2.1]hept-2-ene Type

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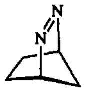
Received March 15, 1993[•]

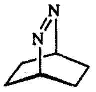
Abstract: On direct irradiation, the azoalkanes *anti*-hexahydro-1,4:5,8-dimethanophthalazines (**5a**, 1,4-H; **5b**, 1,4-Me; **5c**, 1,4-Ph) do not only give the expected housanes **6** through α C–N bond cleavage and subsequent denitrogenation but also yield, in the order **5a** > **5b** > **5c**, the rearranged aziranes **7** through β C–C bond cleavage. The increased formation of the heterocycles **7** on triplet sensitization with benzophenone and the suppression of these rearrangement products by the triplet quenchers *trans*-piperylene and 1,3-cyclohexadiene show that the aziranes **7** are derived from the triplet state of the azoalkanes $^{3}\mathbf{5}^{*}$ by β C–C bond cleavage. The higher amounts of housanes **6** at higher temperatures suggest that intersystem crossing (ISC) to $^{3}\mathbf{5}^{*}$ competes with denitrogenation in the singlet-excited azoalkanes $^{1}\mathbf{5}^{*}$. Since ISC should be relatively temperature independent, the temperature effect is rationalized in terms of an activation barrier for α C–N bond cleavage in the singlet-excited azoalkane $^{1}\mathbf{5}^{*}$, which is more readily overcome at higher temperatures to form increased amounts of housane **6**. From the temperature dependence of the direct and sensitized photoreactions of azoalkane **5a**, the relative activation energies were estimated to be ≥ 3.3 and ≥ 10.5 kcal/mol for α C–N scission from the singlet and triplet states and ≥ 7.9 kcal/mol for the β C–C bond cleavage from the triplet.

Introduction

The majority of bicyclic azoalkanes exhibit a high propensity to extrude molecular nitrogen upon thermal and photochemical excitation.[1] The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) constitutes an exception, whose photoreluctance is still not fully understood.[2] In contrast, 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and its derivatives, which have been intensively investigated,[1,3] denitrogenate photochemically with quantum yields close to unity[1a,d] to yield 1,3 biradicals. The latter usually cyclize to bicyclo[2.1.0]pentanes, and only their triplet states possess sufficiently long lifetimes to allow bimolecular reactions such as scavenging[1c,4] or unimolecular rearrangement such as cyclopropylcarbinyl ring-opening.[3,5]

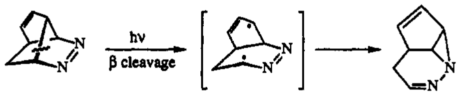


DBH



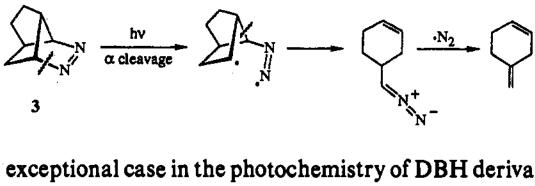
DBO

Chemical transformations of excited DBH derivatives other than denitrogenation were observed only in few cases.[6] When certain prerequisites are met, for example as in 4,5-diazatricyclo-[4.3.0.0^{3,7}]nona-4,8-diene (**1**)[6a] and anellated derivatives,[6b,c] β cleavage is facilitated through increased ring strain due to the additional etheno bridge and simultaneous allylic stabilization of the resulting biradical. Thus, the azirane **2** is formed in significant amounts on direct photolysis and exclusively on triplet-sensitized photolysis[6a] (eq 1).



1 **2** (1)

Although a number of retrocleavages of strained azoalkanes to diazoalkanes have been reported over the years,[7] only few of them are for DBH derivatives. For example, the azoalkane **3**, the dihydro derivative of **1**, gave on direct photolysis traces of methylenecyclohexene, which was derived from secondary photolysis of the diazoalkane (eq 2).[8]



3 (2)

An exceptional case in the photochemistry of DBH derivatives is the reaction of the azoalkanes **4**, which upon excitation afforded exclusively the diazetidines by [2 + 2] cycloaddition rather than denitrogenated products (eq 3). Not surprisingly, this rare [2 + 2] cycloaddition, characteristic for azoalkanes with proximate C=C and N=N double bonds, attracted considerable interest.[9,10]

We have recently examined[11] the photophysical properties of azoalkane **5a** by means of transient absorption spectroscopy, Stern–Volmer analysis of the quantum yields, and product

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[•] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

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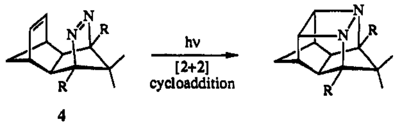
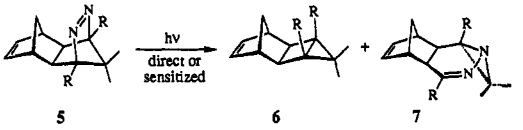


(3)

distributions. Azoalkane **5a** is quite different from other DBH derivatives, since it undergoes efficient $S_1 \rightarrow T_1$ intersystem crossing (ISC) during direct photolysis to form a triplet state (^{3}**5a***) with a remarkably long triplet lifetime (ca. 0.6 μs). This study has been initially motivated by the observation that azoalkanes **5** exhibit pronounced spin-selective β C–C bond cleavage. Thus, on direct and triplet-sensitized photolysis they produce the housane **6** and the azirane **7** (eq 4) in varying amounts.



(4)

a: R = H; b: R = Me; c: R = Ph

Herein, we present the details of our studies on the photochemistry of azoalkanes **5**, in which we corroborate the involvement of the triplet states ^{3}**5*** by quenching and sensitization effects on the product distribution. Moreover, the temperature dependence of the sensitized and direct photoreactions is employed to assess the relative activation energies for α and β photocleavages.

Results

The azoalkanes **5** were synthesized according to literature procedures.[10] Their photoproducts in benzene and deuteriochloroform were the housanes **6** and the aziranes **7** (Table 1). The characterization of housane **6a** was done by comparison with the known spectral data[10] of the housanes **6b** and **6c**. The structures and stereochemistry of the new aziranes **7** were established by NMR spectra and NOE effects. Control experiments showed that the aziranes **7** were stable toward the photolysis conditions. Moreover, aziranes **7** were not observed in the thermolysis of azoalkanes **5**. Instead, only housanes **6** and eventually cyclopentadienes (cycloreversion of the housanes) were formed.

It has been reported[10a] that azoalkane **5a** undergoes photochemical transformations, but no products have been analyzed. We have found[11] that direct near-UV irradiation of azoalkane **5a** in benzene solution at ambient temperature produced the expected housane **6a** and additionally azirane **7a** in a 67:33 ratio (entry 3). For the triplet-sensitized photolysis (entry 9), the fraction of azirane **7a** increased and it was then as large as that of the housane **6a**. The **6a**/**7a** ratios of the direct (entries 1–7) and triplet-sensitized (entries 8–11) photolyses were strongly temperature dependent; in both cases the housane **6a** increased at higher temperatures. Moreover, when the photolyses were carried out at different *trans*-piperylene concentrations[11] (entries 12–14), the product ratio changed in favor of the housane **6a**, and at a 1 M *trans*-piperylene concentration, only traces of the azirane **7a** were detected. When the photolyses were run in $CDCl_3$ (entries 15–16), only a small change was observed for the direct irradiation compared to benzene-d_6 (entries 2 and 15), but a significant solvent dependence became noticeable for the benzophenone-sensitized process (entries 8 and 16), for which now the azirane **7a** product dominated. As a control experiment (not shown in Table 1), the photolyses were carried out at different laser wavelengths (364, 351, and 333 nm), and it was found that the product distribution, within the experimental error, was not dependent on the irradiation wavelength. The absorption spectra in benzene of azoalkanes **5** (λ_{max} = 360–366 nm)[10] are significantly bathochromically shifted[11] compared to DBH (λ_{max} = 342 nm), such that the direct photolyses of azoalkanes **5** can be conducted at the 364-nm laser line.

At 15 °C in deuteriochloroform, the direct photolysis of azoalkane **5b** produced the housane **6b** and the azirane **7b** (entry 17). This result contrasts an earlier study[10c] on the photochemistry of **5b** at comparable reaction conditions, in which only the formation of housane **6b** was reported. Interestingly, while at −60 °C the azirane **7b** was the major product (entry 18), the amount of housane **6b** increased at higher temperature and at 45 °C (entry 19) it was essentially exclusively formed. Thus, the discrepancy between our and the earlier[10c] results is apparently due to the lack of temperature control. Triplet sensitization by benzophenone (entry 20) gave a **6b**/**7b** ratio of 25:75, while for acetone as solvent and sensitizer it was only 40:60 (entry 25). With 1,3-cyclohexadiene as triplet quencher in $CDCl_3$ (entry 21), not even traces of the azirane **7b** were detected. Similarly, when the photolyses were carried out in benzene-d_6 (entries 22–24), addition of *trans*-piperylene as triplet quencher reduced the amount of azirane **7b** effectively. The dependence of the **6b**/**7b** product ratio on the solvent was small for benzene-d_6 and deuteriochloroform (entries 17 and 22), but in deuteriomethanol higher yields of the azirane **7b** were obtained (entry 26). Mechanistically more significant is the fact that the direct photolysis of azoalkane **5b** in deuteriomethanol gave no carbene insertion products.[12] Furthermore, not even traces of diazoalkanes could be detected by IR, UV–vis, and laser-flash spectroscopy (nanosecond resolution) during the photolysis.

As reported previously,[10b] azoalkane **5c** yielded on direct photolysis at ambient temperature exclusively housane **6c** (entry 27). Nevertheless, irradiation at low temperature (entry 28) gave minor amounts (ca. 4%) of the new heterocycle **7c**. Upon triplet-sensitized photolysis with Ph_2CO (entry 29), the latter became the major product (78%). In acetone as conveniently removable solvent and triplet sensitizer, the **6c**/**7c** ratio was 38:62 (entry 30). The lower yields of aziranes **7b** and **7c** in acetone (entries 25 and 30) compared to benzophenone (entries 20 and 29) imply that direct photolysis of **5b** and **5c** takes place concurrently with triplet sensitization. This finding is tentatively attributed to the lower absorption of acetone at the irradiation wavelengths and/or to competing singlet sensitization by acetone.

Discussion

Photoproducts. The formation of housanes **6** as photoproducts of the azoalkanes **5** reveals the typical photoreactivity of DBH derivatives,[1] namely α cleavage of a C–N bond to give the diazenyl biradical **5**(α). This species will readily lose molecular nitrogen to give the 1,3-cyclopentanediyl biradical, which subsequently cyclizes to the housane **6** (Scheme 1).

Since the housanes with inverted geometry are the typical photoproducts of the direct photolysis of DBH and derivatives,[13]

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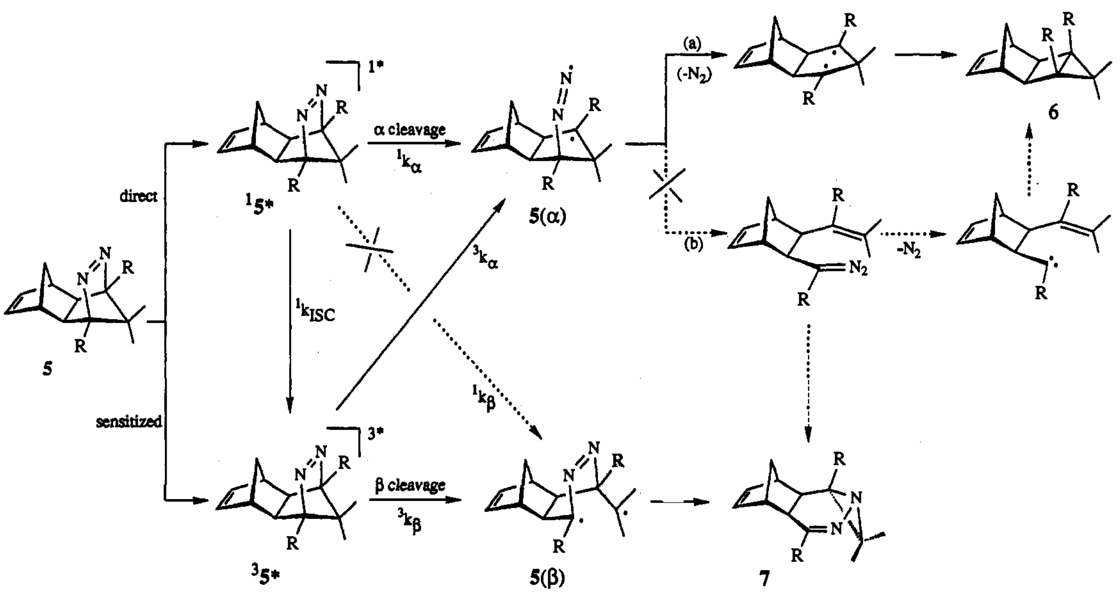
Table 1. Product Studies of the Direct and Triplet-Sensitized Photolyses of Azoalkanes **5**

					product composition[c] (%)	
entry[a]	substrate	T^b (°C)	solvent	additive	**6**	**7**
1	**5a**	2.5	C_6D_6		54.2	45.8
2		12.2	C_6D_6		59.5	40.5
3		25.0	C_6D_6		66.8	33.2
4		37.0	C_6D_6		71.5	28.5
5		52.0	C_6D_6		77.8	22.2
6		64.5	C_6D_6		82.1	17.9
7		75.2	C_6D_6		86.1	13.9
8		17.5	C_6D_6	benzophenone	48.3	51.7
9		23.0	C_6D_6	benzophenone	50.1	49.9
10		46.0	C_6D_6	benzophenone	58.0	42.0
11		70.0	C_6D_6	benzophenone	65.0	35.0
12		27	C_6D_6		67.8	32.2
13		27	C_6D_6	*trans*-piperylene (0.006 M)	76.5	23.5
14		27	C_6D_6	*trans*-piperylene (1.0 M)	>99.5	<0.5[d]
15		15	$CDCl_3$		57.0	43.0
16		15	$CDCl_3$	benzophenone	27.0	73.0
17	**5b**	15	$CDCl_3$		71	29
18		-60	$CDCl_3$		40	60
19		45	$CDCl_3$		>95	<5
20		15	$CDCl_3$	benzophenone	25	75
21		15	$CDCl_3$	1,3-cyclohexadiene (1.0 M)	100	
22		20	C_6D_6		70	30
23		20	C_6D_6	*trans*-piperylene (0.006 M)	86	14
24		20	C_6D_6	*trans*-piperylene (1.0 M)	>99.5	<0.5[d]
25		15	$(CD_3)_2CO$		40	60
26		15	CD_3OD		32	68
27	**5c**	15[e]	$CDCl_3$[e]		100	
28		-60	$CDCl_3$		96	4[f]
29		15	$CDCl_3$	benzophenone	22	78[f,g]
30		15	$(CD_3)_2CO$		38	62[f]

[a] See Experimental Section for details of photolysis conditions. [b] Temperature control was within ±1 °C. [c] Relative yields (normalized to 100%) determined by quantitative ^1H NMR analysis of the appropriate methyl signals; error ±3%; azoalkane consumption and mass balance were >90%, except for entries 14, 21, and 24 (70 ± 10%). [d] Only traces were detected. [e] Same results in C_6D_6 at 20 °C. [f] Also determined by HPLC (error ca. 2%). [g] Traces of 5,5-dimethyl-1,4-diphenylcyclopentadiene (<1%) were detected.

Scheme 1



it is noteworthy that in all cases the bicyclo[2.1.0]pentanes **6** were formed with retention of configuration. Supposedly this is due to severe steric repulsion between the methano bridge and the *gem* dimethyl group. Indeed, semiempirical calculations (AM1 for **5c**) reveal that the experimentally found retention of configuration for the housane is energetically favored by ca. 20 kcal/mol over the inverted housane. The impact of steric constraints in the cyclization of 1,3-cyclopentanediyl biradicals to their housanes has been discussed elsewhere.[14]

More interesting is the formation of aziranes **7** in the direct and triplet-sensitized photolyses of azoalkanes **5**, since this photoreactivity is unusual for DBH derivatives (eq 4). Whereas this photoreaction is precedented for azoalkanes, two possible

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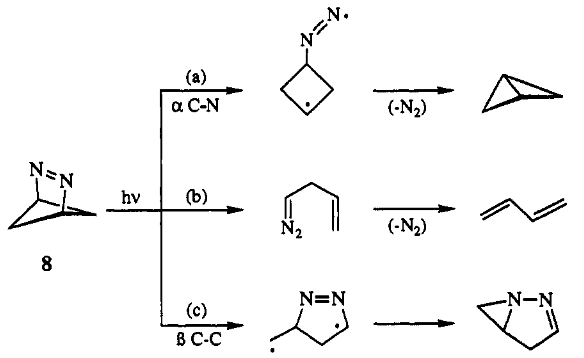
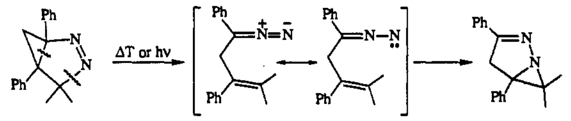
Scheme 2



reaction mechanisms apply, namely the intervention of the corresponding diazoalkane or an open-chain biradical through β cleavage.[15] For example, it is known for cyclic azoalkanes that after photochemical or thermal ring-opening the resulting diazoalkane may undergo nitrene-type intramolecular cycloaddition to aziranes (eq 5).[7,8] Not only direct spectroscopic evidence speaks for such diazoalkane intermediates but the *in situ* denitrogenation of the diazoalkanes is also often accompanied by carbene-derived products.[7d]



(5)

On the other hand (Scheme 2, path c),[15] the photoreaction of 2,3-diazabicyclo[2.1.1]hex-2-ene (**8**) involves β C–C cleavage to result in the azirane 1,2-diazabicyclo[3.1.0]hex-2-ene through the 1,4 biradical. The intermediacy of this biradical was corroborated by deuterium labeling experiments.[15] Besides the expected photoproduct bicyclobutane (Scheme 2, path a), butadiene was produced on photolysis of azoalkane **8**, which again was proposed to be formed from the diazoalkane (Scheme 2, path b).

To establish the mechanism for azirane **7** formation (Scheme 1), the photolysis of azoalkanes **5** was monitored spectroscopically (UV–vis, IR), but no intermediary diazoalkanes were detected. Moreover, direct photolysis of azoalkane **5b** in deuteriomethanol gave no carbene-derived products (entry 26). Thus, on the basis of these results, diazoalkanes (Scheme 1, path b) appear not to intervene in the photolyses of the azoalkanes **5** and β cleavage with 1,3 reclosure of the intermediary hydrazonyl biradical **5**(β) constitutes the reasonable alternative for azirane **7** formation (Scheme 1, path $\mathbf{5}^* \rightarrow \mathbf{5}(\beta) \rightarrow \mathbf{7}$).

Spin-State Selectivity. The suppression of azirane **7** formation by addition of triplet quenchers (entries 12–14 and 21–24) strongly suggests that this photorearrangement occurs predominantly from the triplet state $^3\mathbf{5}^*$ ($^3k_\beta$ in Scheme 1). The latter is thermally populated through significant ISC in the singlet-excited azoalkanes $^1\mathbf{5}^*$ ($^1k_{\mathrm{ISC}}$ in Scheme 1) and must have lifetimes in the microsecond range to allow efficient quenching by dienes. Indeed, this rather unusual behavior for azoalkanes[16] has been rigorously established[11] for compound **5a**. Thus, besides the usual α cleavage of the C–N bond to the diazenyl biradical **5**(α) ($^3k_\alpha$ in Scheme 1), the triplet-excited azoalkane $^3\mathbf{5}^*$ undergoes efficient β cleavage of the C–C bond.

The azirane **7** is *not* produced from the singlet-excited state $^1\mathbf{5}^*$ ($^1k_\beta$ in Scheme 1), since high concentrations of appropriate[17] triplet quenchers suppress this product essentially completely (entries 14, 21, and 24). Thus, besides its predominant radiationless fate ($^1k_{\mathrm{ISC}}$ in Scheme 1), the preferred chemical reaction of the singlet-excited azoalkane $^1\mathbf{5}^*$ is α C–N bond scission ($^1k_\alpha$ in Scheme 1). On account of this spin selectivity, triplet sensitization should change the product ratio in favor of the triplet photoproducts. Indeed, addition of the triplet sensitizer benzophenone (entries 16, 20, and 29) increases the formation of azirane **7** compared to the direct photolysis (entries 15, 17, and 27).

That α cleavage competes with ISC in the singlet-excited azoalkane $^1\mathbf{5}^*$ during the direct photolysis is reflected in the product distribution between housane **6** and azirane **7** (Scheme 1). Thus, the better the carbon radical site in the diazenyl biradical **5**(α) is stabilized by the R substituent, i.e. Ph (**5c**) $\gg$ Me (**5b**) > H (**5a**), the more α cleavage is observed and consequently the more housane **6** is obtained (entries 15, 17, and 27). The benzylic stabilization of radical **5c**(α) is so effective that denitrogenation to the housane **6c** occurs exclusively in the singlet-excited $^1\mathbf{5c}^*$ and ISC cannot compete.

In this context it is of interest to observe that the effect of the bridgehead substituents on the photoreactivity in the triplet manifold is much less pronounced, since the **6**/**7** product ratio is ca. 25:75 for the sensitized photolysis of all three azoalkanes **5** (entries 16, 20, and 29). It should be noted that the stabilization of the incipient radical sites by the bridgehead substituents in azoalkanes $^3\mathbf{5}^*$ operates for both triplet reactions, i.e. for α cleavage ($^3k_\alpha$ in Scheme 1) to form the diazenyl biradical **5**(α) and for β cleavage ($^3k_\beta$ in Scheme 1) to form the hydrazonyl biradical **5**(β) and, thus, no large bridgehead substituent effects on the **6**/**7** ratio should be expected. The major stabilization of the hydrazonyl-type biradical **5**(β) derives unquestionably from the heteroallylic delocalization, which has been estimated[18] to be worth ca. 13–19 kcal/mol.

Temperature Dependence of the Product Distribution. The housanes **6** are favored at higher temperatures (entries 7, 19, and 27) and become the exclusive photoproducts for the direct irradiation mode for the azoalkanes **5b,c**. The aziranes **7** are preferentially formed at low temperatures (entries 1, 18, and 28) and may constitute the major photolysis products even on direct irradiation. It is tempting to attribute the increased formation of azirane **7** at the lower temperatures to slower α cleavage ($^1k_\alpha$ in Scheme 1) from the singlet state $^1\mathbf{5}^*$, which would imply an activation barrier for this reaction.[16a] Thus, the thermal population of $^3\mathbf{5}^*$ through ISC ($^1k_{\mathrm{ISC}}$ in Scheme 1), which should be less sensitive to temperature,[15,19] competes more effectively in the singlet-excited azoalkane $^1\mathbf{5}^*$ and the characteristic triplet reactivity, namely azirane **7** formation through β C–C bond scission ($^3k_\beta$ in Scheme 1), becomes more pronounced. Such arguments have been forwarded to account for the increased formation of azirane[15] in Scheme 2 and other photochemical reactions of singlet-excited azoalkanes.[6c,19] However, when we examined the sensitized photolysis of azoalkane **5a**, a similar temperature dependence was found (entries 8–11).

The question arises whether the observed temperature dependence of the **6**/**7** product ratio in the direct photolyses (entries 1–7, 17–19, and 27/28) was due to a discrimination between α and

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(17) The triplet energies of *trans*-piperylene (E_T = 59.2 kcal/mol) and 1,3-cyclohexadiene (E_T = 52.4 kcal/mol) have been determined from the 0–0 bands of the singlet–triplet transitions in their oxygen-perturbed absorption spectra; cf.: Kellogg, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4230. These values are lower than the triplet energies of DBH-type azoalkanes (ca. 60 kcal/mol),[11,16b] and triplet quenching should be effective from the energy point of view. That 1,3-cyclohexadiene (entry 21) is somewhat more effective than *trans*-piperylene (entry 24) is attributable to its lower triplet energy.

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(19) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 187–188. (b) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388.

β cleavage ($^{3}k_\alpha$ and $^{3}k_\beta$) in the triplet state $^{3}\mathbf{5}^{*}$ rather than between α cleavage and ISC ($^{1}k_\alpha$ and $^{1}k_{\mathrm{ISC}}$) in the excited singlet state $^{1}\mathbf{5}^{*}$ (Scheme 1). To answer this question, the kinetics of the temperature dependence on the **6**/**7** product ratio must be tested for the direct and triplet-sensitized photolyses.

The simpler case is the triplet-sensitized photolysis, for which a kinetic analysis of Scheme 1 leads to the expression in eq 6 for

$$\frac{^{3}[\mathbf{6}]}{^{3}[\mathbf{7}]} = \frac{^{3}k_\alpha}{^{3}k_\beta} \qquad (6)$$

$$\ln\frac{^{3}[\mathbf{6}]}{^{3}[\mathbf{7}]} = \ln\frac{^{3}A_\alpha}{^{3}A_\beta} - \frac{(^{3}E_\alpha - {}^{3}E_\beta)}{R}\frac{1}{T} \qquad (7)$$

the product ratio $^{3}[\mathbf{6}]/^{3}[\mathbf{7}]$. Its temperature dependence is given by eq 7 (Arrhenius theory), which allows one to assess the relative activation parameters for the α and β cleavages in the triplet state $^{3}\mathbf{5}^{*}$, i.e. $^{3}k_\alpha$ and $^{3}k_\beta$ (Scheme 1). On the basis of the temperature-dependent **6**/**7** product ratio for the sensitized photolysis of azoalkane **5a** (entries 8–11), an Arrhenius plot of $\ln(^{3}[\mathbf{6a}]/^{3}[\mathbf{7a}])$ versus $1/T$ according to eq 7 gave the linear relationship $\ln(^{3}[\mathbf{6a}]/^{3}[\mathbf{7a}]) = 4.44 \pm 0.06 - (1310 \pm 20)T^{-1}$ ($r^2 = 0.9996$, $n = 4$), from which the relative activation parameters $^{3}A_\alpha/^{3}A_\beta = 85 \pm 5$ and $^{3}E_\alpha - {}^{3}E_\beta = 2.6 \pm 0.1$ kcal/mol were calculated. Thus, the activation energy for β cleavage ($^{3}E_\beta$) in the triplet state $^{3}\mathbf{5a}^{*}$ is lower than that for α cleavage ($^{3}E_\alpha$), but due to its higher pre-exponential factor ($^{3}A_\alpha$), α cleavage to afford the housane **6a** dominates at higher temperatures.

It is more tedious to assess the temperature dependence for the direct photolysis because singlet ($^{1}k_\alpha$, $^{1}k_{\mathrm{ISC}}$) as well as triplet ($^{3}k_\alpha$, $^{3}k_\beta$) pathways are involved (Scheme 1). From the complex kinetics in Scheme 1 the expression in eq 8 was derived, which requires knowledge of the triplet lifetimes ($^{3}\tau$) of azoalkanes **5**. Algebraic rearrangement of eq 8 and use of the relationship in

$$\frac{[\mathbf{6}]}{[\mathbf{7}]} = \frac{^{3}k_\alpha}{^{3}k_\beta} + \frac{^{1}k_\alpha}{^{3}k_\beta\,{}^{1}k_{\mathrm{ISC}}\,{}^{3}\tau} \qquad (8)$$

$$\mathrm{f}([\mathbf{6}],[\mathbf{7}],{}^{3}\tau) = \left(\frac{[\mathbf{6}]}{[\mathbf{7}]} - \frac{^{3}[\mathbf{6}]}{^{3}[\mathbf{7}]}\right){}^{3}\tau = \frac{^{1}k_\alpha}{^{3}k_\beta\,{}^{1}k_{\mathrm{ISC}}} \qquad (9)$$

$$\ln\{\mathrm{f}([\mathbf{6}],[\mathbf{7}],{}^{3}\tau)\} = \ln\frac{^{1}A_\alpha}{^{3}A_\beta\,{}^{1}A_{\mathrm{ISC}}} - \frac{(^{1}E_\alpha - {}^{3}E_\beta - {}^{1}E_{\mathrm{ISC}})}{R}\frac{1}{T} \qquad (10)$$

eq 6 affords the function in eq 9, and its temperature dependence according to Arrhenius theory is given by eq 10. On the basis of the temperature-dependent product ratios $[\mathbf{6a}]/[\mathbf{7a}]$ for the direct irradiation of azoalkane **5a** (entries 1–7), the explicit $^{3}[\mathbf{6a}]/^{3}[\mathbf{7a}]$ values at the same temperatures, which are obtained from the plot according to eq 7 (see above), and the triplet lifetimes of $^{3}\mathbf{5a}^{*}$, which are fortunately known as a function of temperature,[20] the Arrhenius plot according to eq 10 gave the linear relationship $\mathrm{f}([\mathbf{6a}],[\mathbf{7a}]) = -22.3 \pm 0.3 + (2360 \pm 90)T^{-1}$ ($r^2 = 0.992$, $n = 7$). Since intersystem crossing (ISC) is essentially temperature independent[19a] ($^{1}E_{\mathrm{ISC}}$ ca. 0 kcal/mol), the slope of this plot gives the difference in the activation energies for the α and β cleavages of the singlet $^{1}\mathbf{5a}^{*}$ and triplet $^{3}\mathbf{5a}^{*}$ species, i.e. $^{3}E_\beta - {}^{1}E_\alpha = 4.7 \pm 0.2$ kcal/mol.

The present temperature studies provide the relative order $^{3}E_\alpha > {}^{3}E_\beta > {}^{1}E_\alpha$ in the activation energies for the different photochemical reactions of azoalkane **5a**. The common photoproducts of all three azoalkanes **5** and the similar temperature dependence of the product ratios strongly suggest that this relative order is diagnostic for azoalkanes of this type.

The determination of the absolute activation energies is more difficult. Nevertheless, the slope of the Arrhenius plot for the triplet lifetimes of $^{3}\mathbf{5a}^{*}$ implies an activation energy of 10.5 ± 0.2 kcal/mol.[20] This should constitute a lower limit for the triplet process with highest activation energy, namely α cleavage ($^{3}E_\alpha$).[21] Thus, with this approximation, the absolute activation energies for the photochemical reactions of azoalkane **5a** can be estimated as $^{3}E_\alpha \geq 10.5$ kcal/mol, $^{3}E_\beta \geq 7.9$ kcal/mol, and $^{1}E_\alpha \geq 3.2$ kcal/mol. As already discussed under substituent effects, these values should decrease in the order **5a** > **5b** > **5c**, since methyl and phenyl substituents promote α and β cleavage on account of steric repulsion and conjugative stabilization.

The activation barriers in photochemical reactions of azoalkanes have been subject to discussion.[22,23] The low-temperature reactivities of the parent DBH[24] and derivatives of its next smaller homolog[25] **8**, which extrude molecular nitrogen even at 4 K to form 1,3-cyclopentanediyl and 1,3-cyclobutanediyl triplet biradicals, imply very small activation energies for C–N bond cleavage (ca. 0–0.3 kcal/mol), which have been determined for other photolabile azoalkanes as well.[22] In contrast, the estimated activation energies for α C–N bond cleavage in the singlet- and triplet-excited states of **5a** ($^{1}E_\alpha \geq 3.3$ and $^{3}E_\alpha \geq 10.5$ kcal/mol) are significant and approach the energy barrier for chemical reactivity in the photoreluctant DBO molecules (6–11 kcal/mol).[16a,22] Thus, the efficient population of the triplet states and the observed triplet photochemistry of the DBH derivatives **5** may be due to the higher persistence of their excited singlet state, since other channels for energy dissipation, namely ISC to the energetically lower triplet state, can compete more effectively. However, since DBO-type azoalkanes, despite their photoreluctance, do not show efficient ISC,[16a] the relatively high activation energy for denitrogenation of the excited singlet states $^{1}\mathbf{5}^{*}$ does not account entirely for the preference for this radiationless transition. Additionally, the probability for ISC, as judged by the Arrhenius A factor, must also be quite high in azoalkanes **5**, because this factor will ultimately limit the efficiency of the essentially temperature independent ISC process.

The question arises why β cleavage prevails over α scission in the triplet species $^{3}\mathbf{5}^{*}$ but does not occur in the singlet state $^{1}\mathbf{5}^{*}$. This unusual property is in line with the remarkably long triplet lifetime and the efficient ISC of azoalkanes **5** and renders this type as unusual.[11] Since we suspected that the photochemical reactivity (β cleavage) could be due either to *gem* dimethyl substitution or anellation at the 5,6 positions of the DBH skeleton, we have examined[26] a variety of closely related azoalkanes **9**–**12**.

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(20) The temperature dependence of the triplet lifetimes of $^{3}\mathbf{5a}^{*}$ between 8 and 38 °C, determined by laser-flash spectroscopy,[11] yielded the linear Arrhenius plot $\ln(1/^{3}\tau) = (-32.1 \pm 0.3) - (5300 \pm 80)T^{-1}$ ($r^2 = 0.992$ for six temperatures with 6–7 data points each), from which an activation energy of 10.5 ± 0.2 kcal/mol was calculated for the triplet decay. Adam, W.; Nau, W. M.; Wirz, J. Unpublished results.

(21) This approximation is based on the assumption that the measured activation energy[20] for triplet decay of $^{3}\mathbf{5a}^{*}$ is dominated by chemical reactions and not by radiationless deactivation. Although the latter is significant (ca. 40%)[11] for **5a**, we do not know whether it takes place in the singlet or triplet manifold. The conclusions regarding the absolute quantum yields would only be affected if the radiationless process takes place in the triplet state and if its activation energy is on the order of the measured[20] 10.5 kcal/mol. Note that the *relative* activation energies derived from eqs 6–8 are not dependent on the radiationless deactivation.

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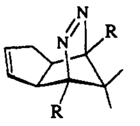
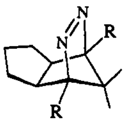
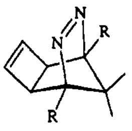


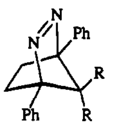
9
(R = H. Me. Ph)



10
(R = H. Me. Ph)



11
(R = Me. Ph)



12
(R = H, Me)

However, no aziranes could be observed. Therefore, we can only rationalize tentatively that the unusual photochemical properties of azoalkanes **5** derive from steric constraints and molecular rigidity. Indeed, it appears to be more than coincidental that azoalkanes **5** and all the other azoalkanes,[2,6–8,15,19] which show unexpected β C–C bond cleavage or for which ISC has been invoked, possess rigid structures.

Be this as it may, in conclusion, the photochemistry of the azoalkanes **5** deviates strongly from the behavior known for most DBH derivatives. In contrast to the latter, the singlet-excited azoalkanes ^{1}**5*** exhibit efficient ISC to the long-lived triplet state ^{3}**5***,[11] which leads to the aziranes **7** by β C–C bond cleavage. This photoreaction competes with denitrogenation by α C–N bond scission to the housanes **6**, as expressed by a pronounced temperature dependence. Unquestionably, seemingly subtle structural changes of the DBH skeleton manifest themselves in unusual and contrasting photochemical behavior.

Experimental Section

Instrumentation and General Aspects. NMR spectra were run on a Bruker AC 200, AC 250, or WM 400 with $CDCl_3$, C_6D_6, and $(CD_3)_2CO$ as internal standards. UV absorption spectra were recorded with a Hitachi U 3200 spectrophotometer, infrared spectra were measured on a Perkin Elmer 1420 Ratio Recording infrared spectrophotometer, and melting points were taken on a Reichert Thermovar Kofler apparatus. Combustion analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry (University of Würzburg). The light output (333, 351, and 364 nm, 2.0 W) of a continuous-wave argon ion laser (INNOVA 100, Coherent Company) and the Rayonet Photochemical Reactor of the Southern New England Ultraviolet Company, fitted with 350- and 300-nm lamps, were used as irradiation source for the direct and triplet-sensitized photolyses of the azoalkanes. Solvents and commercially available chemicals were purified by standard procedures or used as bought (deuterated solvents). Column chromatography was carried out on silica gel (0.032–0.063 μm, Woelm).

Photolyses and Product Studies. For the direct photolyses, a solution of ca. 0.04 mmol of the azoalkanes **5**, dissolved in 0.7 mL of $CDCl_3$, $(CD_3)_2CO$, or C_6D_6 and deaerated with a gentle stream of argon gas for 15 min, were irradiated above 330 nm in NMR tubes, fitted with a cooling jacket to achieve temperature control. For the quenching experiments, either *trans*-piperylene or 1,3-cyclohexadiene was added as the triplet quencher. The triplet-sensitized photolyses were carried out by using 300-nm light and benzophenone (50 mg, 0.28 mmol) as sensitizer. Irradiation times were 60–120 min for the Rayonet photolyses and ca. 3 min for the laser photolyses. The azoalkanes **5** and the housanes **6b,c** are known compounds.[10] To obtain the housane **6a** and the aziranes **7** in preparative amounts for complete characterization, the triplet-sensitized photolyses were conducted by irradiating solutions of ca. 1.5 mmol of the azoalkanes **5** dissolved in 50 mL of degassed acetone at –20 °C for 2–3 h at 300 nm. The solvent was removed by distillation at 20 °C/15 Torr, and the crude material was purified as indicated for the individual cases below.

4,4-Dimethyl-(1-*r*-C^{10},2-*t*-H,3-*c*-H)-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (6a). An analytical sample of the unknown hydrocarbon **6a**, which was separated from the heterocycle **7a** by flash chromatography of the crude product with petroleum ether/ethyl acetate (4:1) as eluent, was further purified by preparative GC (1.5-m glass column packed with 10% SE-30 on Volaspher A2; N_2 flow of 1.8 kp/cm^2, operated at 120 °C isothermally at injector/detector temperatures of 160/160 °C) as a colorless oil (40%). IR (CCl_4): 3050, 2995, 2950, 2905, 2860, 1530, 1455, 1445, 1365, 1330. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.95 (s, 3H, CH_3), 1.06 (br s, 2H, CH), 1.15 (s, 3H, CH_3), 1.23 (d, J = 8.4 Hz, 1H, CH_2), 1.48 (br s, 2H, CH), 2.23 (d, J = 8.4 Hz, 1H, CH_2), 2.63 (br s, 2H, bridgehead H), 6.02 (pseudo t, J = 1.7 Hz, 2H, =CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.8 (q), 24.9 (2 × d), 30.9 (q), 39.6 (2 × d), 41.8 (t), 43.8 (2 × d), 51.2 (s), 136.0 (2 × d). Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.58; H, 10.36.

(1α,2β,5α,7α,8β,9α)-6,6-Dimethyl-4,5-diazatetracyclo[7.2.1.0^{2,8}.0^{5,7}]-dodeca-3,10-diene (7a). Flash chromatography with ethyl acetate/methanol (15:1) as eluent and Kugelrohr distillation at 130 °C/0.1 Torr yielded a colorless oil (33%). IR (CCl_4): 3060, 2920, 2860, 1545, 1245, 1220, 1105, 1060, 1000, 980. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88 (s, 3H, CH_3), 1.03–1.44 (m, 3H, CH_2, 8-H), 1.39 (s, 3H, CH_3), 1.59 (d, J = 9.3 Hz, 1H, 2-H), 1.90 (br s, 1H, 7-H), 2.85 (br s, 2H, bridgehead H's), 6.15 (dd, J = 4.1, 0.9 Hz, 1H, =CH), 6.22 (dd, J = 4.1, 0.9 Hz, 1H, =CH), 7.72 (d, J = 3.5 Hz, 1H, N=CH). ^{13}C NMR (63 MHz, $CDCl_3$): δ 13.9 (q), 26.9 (q), 27.5 (d), 35.0 (d), 45.3 (t), 45.8 (d), 46.7 (d), 47.1 (s), 50.7 (d), 136.0 (d), 137.5 (d), 157.6 (d, H-C=N). Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.79; H, 9.01; N, 14.39.

(1α,2β,5α,7α,8β,9α)-3,6,6,7-Tetramethyl-4,5-diazatetracyclo-[7.2.1.0^{2,8}.0^{5,7}]dodeca-3,10-diene (7b). Flash chromatography with ethyl acetate/petroleum ether (10:1) as eluent and Kugelrohr distillation at 180 °C/0.01 Torr yielded a colorless oil (35%). IR (CCl_4): 3050, 3000, 2960, 2910, 2860, 1620, 1540, 1370, 1330, 1240, 1210. ^{1}H NMR(250 MHz, $CDCl_3$): δ 0.69 (s, 3H, CH_3), 1.05 (d, J = 8.5 Hz, 1H, CH_2), 1.18 (s, 3H, CH_3), 1.28–1.37 (m, 2H, CH_2, 8-H), 1.31 (s, 3H, CH_3), 1.56 (dd, J = 8.3, 2.0 Hz, 1H, 2-H), 2.01 (s, 3H, CH_3), 2.89 (br s, 1H, bridgehead H), 3.01 (br s, 1H, bridgehead H), 6.07 (dd, J = 5.5, 3.0 Hz, 1H, =CH), 6.18 (dd, J = 5.5, 3.0 Hz, 1H, =CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.1 (q), 18.6 (q), 23.2 (q), 24.2 (q), 32.9 (d), 40.2 (d), 40.4 (s), 45.35 (d), 45.44 (d), 45.5 (t), 51.0 (s), 136.2 (d), 138.8 (d), 162.3 (s, C=N). Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.61; H, 9.48; N, 12.80.

(1α,2β,5α,7α,8β,9α)-6,6-Dimethyl-3,7-diphenyl-4,5-diazatetracyclo-[7.2.1.0^{2,8}.0^{5,7}]dodeca-3,10-diene (7c). Flash chromatography of the crude product with petroleum ether/ethyl acetate (4:1) as eluent yielded colorless needles (41%), mp 145–145.7 °C dec. IR (CCl_4): 3050, 2985, 2950, 2905, 2855, 1545, 1485, 1435, 1340, 1245, 1210, 1005, 970. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.01 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.02 (dd, J = 8.9, 1.9 Hz, 1H, CH_2), 1.13 (d, J = 8.9 Hz, 1H, CH_2), 2.2 (dd, J = 9.1, 1.9 Hz, 1H, 8-H), 2.27 (br s, 1H, 9-H), 2.31 (dd, J = 9.1, 1.9 Hz, 1H, 2-H), 2.77 (br s, 1H, 1-H), 6.11 (dd, J = 5.6, 3.1 Hz, 1H, =CH), 6.36 (dd, J = 5.6, 3.0 Hz, 1H, =CH), 7.25–7.85 (m, 10H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.6 (q), 24.9 (q), 33.5 (d), 36.6 (d), 44.6 (t), 46.9 (d), 47.6 (d), 50.3 (s), 53.2 (s), 126.5 (d), 126.76 (d), 126.83 (d), 128.0 (d), 128.2 (d), 128.5(d), 128.60 (d), 128,64 (d), 128.9 (d), 129.5 (d), 136.8 (d), 138.3 (s), 138.5 (d), 142.2 (s), 162.5 (s, C=N). Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.66; H, 7.11; N, 8.23. Found: C, 84.78; H, 7.05; N, 8.12.

Vapor-Phase Pyrolysis of the Azoalkanes 5a–c. The azoalkanes **5** were sublimed at 120 °C/0.1 Torr into a quartz tube heated at 300 °C. The products were collected in a liquid nitrogen-cooled trap. NMR analysis of the crude product showed the corresponding housanes **6**, which were accompanied by varying amounts of the corresponding cyclopentadienes as thermal cycloreversion products of the housanes **6**. No aziranes **7** were detected.

Acknowledgment. We are most grateful for financial support by the Deutsche Forschungsgemeinschaft. W.M.N. and J.S. thank the Fonds der Chemischen Industrie for doctoral fellowships.

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