Photoreduction of Azoalkanes by Direct Hydrogen Abstraction from 1,4-Cyclohexadiene, Alcohols, Stannanes, and Silanes

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A mechanistic investigation of the photoreduction of the n,π* triplet-excited azo chromophore has been carried out on azoalkanes **1**, which exhibit efficient intersystem-crossing quantum yields (ca. 0.5). The azoalkanes **1a** and **1b** undergo facile photoreduction to the corresponding hydrazines in the presence of a variety of hydrogen donors, which include 2-propanol, benzhydrol, 1,4-cyclohexadiene, tributylstannane, and tris(trimethylsilyl)silane. In contrast, the hydrazine yields derived for the azoalkanes **1c** and **1d** are significantly lower even at high hydrogen donor concentrations due to their lower triplet yields and shorter triplet lifetimes. A clear dependence of the hydrazine yields on the bond dissociation energies of the hydrogen donors has been observed, which is reflected in the quenching rate constants obtained from time-resolved transient absorption spectroscopy. The absolute rate constants for interaction of the triplet azoalkane **1a** with hydrogen donors are generally lower (ca. 10−100-fold) than for benzophenone, in line with the less favorable reaction thermodynamics. The comparison of the rate constants for quenching of the triplet-excited azoalkane **1a** and of the singlet-excited state of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) reveals a similar reactivity of excited azoalkanes toward hydrogen donors; differences can be accounted for in terms of variations in the energies of the excited states. The interactions of the excited azoalkanes with tributylstannane and benzhydrol produce the radicals characteristic for hydrogen abstraction from these substrates, namely tributylstannyl and hydroxydiphenylmethyl radicals, which were detected through their transient absorptions at 390 and 550 nm, respectively. Interestingly, compared to the photoreduction of benzophenone with benzhydrol, for which the quantum yield for conversion to radicals is unity, between the azoalkane **1a** and benzhydrol this efficiency is only ca. 12%. An associative effect through N···H−O bonding is held responsible, which promotes hydrogen transfer versus diffusion out of the caged radical pair. The quenching of the singlet-excited DBO by toluene was also employed to monitor the formation of benzyl radicals (at 317 nm). The photolysis of DBO in tetrahydrofuran as solvent and quencher produced an absorption at ca. 290 nm, which was tentatively assigned to the corresponding hydrazinyl radical.

Introduction

The photochemistry of the azo chromophore has long been the subject of extensive investigation.[1−3] The excited states of most sterically nonhindered acyclic azo compounds are efficiently deactivated by *cis*−*trans* isomerization.[1] In contrast, bicyclic azoalkanes cannot dissipate the excitation energy by such a mechanism. Two prototypes are 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), which serve to exemplify the distinct photophysical and photochemical properties of cyclic azoalkanes in general. The DBH derivatives extrude molecular nitrogen from their short-lived singlet- and triplet-excited states (τ ca. 0.1 and 1.0 ns) with quantum yields close to unity.[2,4] Intersystem crossing (ISC) from the singlet-excited state to the triplet is generally too slow to compete with extrusion of molecular nitrogen.[2] In sharp contrast, singlet-excited DBO derivatives exhibit low decomposition quantum yields and are consequently termed photoreluctant azoalkanes,[5−8] but ISC to the triplet states is also inefficient.

In contrast to the relatively long-lived singlet-excited azoalkanes such as DBO (τ_f ca. 700 ns in acetonitrile),[7] long-lived azoalkane *triplet* states have remained elusive[4,8−10] until the recent detailed examination of the photochemistry of azoalkanes **1** revealed the existence of quite persistent azo triplets.[2] The azoalkanes **1** (Scheme 1) are unique in that spontaneous ISC to the triplet state prevails over the deactivation of singlet-excited states by either rapid nitrogen extrusion or fluorescence.[2,11,12] Direct photoexcitation of azoalkanes **1a** and **1b** affords not only the expected α C−N cleavage products, viz., the housanes **2**, but also the aziranes **3** derived from β C−C bond cleavage. From quenching experiments, the triplet quantum yields for the azoalkanes **1a** and **1b** have been estimated to be as high as

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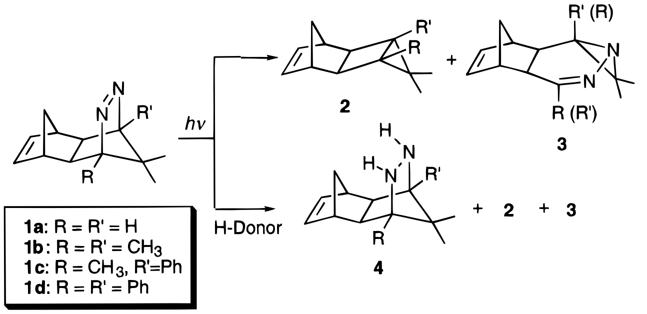
Scheme 1



0.5.[2,11,12] In contrast, the bridgehead phenyl-substituted azoalkane **1d** exhibits significantly lower ISC quantum yields (ca. 0.10),[2] since the benzylic radical stabilization favors nitrogen extrusion in the singlet manifold. Indeed, this trend is qualitatively reproduced in the triplet lifetimes,[2,13] which follow the relative stabilization of the incipient radical site by the substituents, i.e., **1a** (630 ns) > **1b** (440 ns) ⩾ **1c** (⩽ 440 ns) > **1d** (200 ns).

The azoalkanes **1** constitute a promising set of substrates to compare the reactivity of the n,π* triplet-excited azo chromophore with that of the extensively investigated carbonyl chromophore.[14,15] For example, analogous to the carbonyl triplets, the n,π* triplets of azoalkanes are predestined reactive states for hydrogen abstraction from appropriate donors. The present study, which has been carried out to examine this photoreactivity in detail, presents a comprehensive account of our preliminary report[16] and complements our study on the photoreduction by amines.[13] The latter is mediated by charge-transfer interactions and, hence, distinct from the presently examined direct (covalent) hydrogen abstraction to produce the radical pairs and photoreduced products therefrom.

Although scattered reports of the photoreduction of azobenzene[17,18] and of cyclic azoalkanes[19−21] have appeared, there is only one report dealing with hydrogen abstraction by a triplet state in the *triplet-sensitized* DBO photolysis.[7] Moreover, the previous mechanistic study on the photoreduction of *singlet-excited* DBO by cyclohexadienes[21] has focused on deuterium isotope effects and possible charge-transfer contributions in the quenching process. In the present mechanistic investigation on the direct hydrogen abstraction of the n,π* triplet-excited azoalkanes **1** by a variety of hydrogen donors, the efficiency of photoreduction and the spectroscopic characterization of the primary reaction intermediates have been examined. The data reveal several similarities to the reactions of ketones (benzophenone), which allow one to generalize further the photoreactivity of n,π*-excited states. The rate constants for quenching of the triplet-excited azoalkanes **1** by hydrogen donors are also compared with those of the singlet-excited state of DBO, for which some rate constants have already been reported.[21]

Table 1. Quenching Rate Constants for the Singlet-Excited Azoalkane DBO, the Triplet-Excited Azoalkane 1a, and Benzophenone by Hydrogen Donors

	k_q (10^7 M^{-1} s^{-1})		
hydrogen donor	^{3}**1a*** [a]	^{1}DBO* [b]	$^3Ph_2CO$* [c]
tetrahydrofuran	0.09[d]	0.23[e]	0.96[f]
1,4-dioxane	0.008[e]	0.043[e]	0.043[g]
toluene	*h*	0.037[e]	0.030[i]
2-propanol	≤0.064[e,j]	0.49	0.18[k]
benzhydrol	1.9[l]	2.6	0.75[k]
1,4-cyclohexadiene	2.4[j]	1.7[m]	29[n]
tributylstannane	3.5[j]	6.2	29[o]

[a] Values (±15%) determined by laser-flash spectroscopy (λ_{exc} = 355 nm) of the azoalkane triplet **1a** in benzene (λ_{mon} = 450 nm); where neat quenchers were employed, the data have been corrected for the molarity. [b] From fluorescence lifetimes in acetonitrile or in neat quencher (corrected for the molarity); error ±10% of the stated values. [c] Literature data for benzophenone were selected for benzene as solvent. [d] Value from lifetime in neat quencher is 4.4 × 10^5 M^{-1} s^{-1}, cf. ref 27. [e] Value from the lifetime in neat quencher, cf. ref 27. [f] Reference 75. [g] Calculated from the lifetime in neat quencher from ref 76. [h] No significant quenching observed, even in neat quencher. [i] Reference 77. [j] Value refers to the hydrogenated azoalkane **1a-H$_2$** derivative from refs 16, 23. [k] Reference 78. [l] A similar rate constant (±20%) was determined from the growth of the hydroxydiphenylmethyl radical at 550 nm. [m] Reference 21. [n] Reference 62. [o] Reference 25.

Results

Laser Flash Photolysis. Rate constants for bimolecular quenching of the triplet-excited azoalkane **1a** and of the singlet-excited azoalkane DBO by selected hydrogen donors are given in Table 1. The data were obtained by measuring the effects of the additives on the lifetimes of the triplet state of the azoalkane **1a** (transient absorption at 310 or 450 nm) or on the lifetime of the singlet state of DBO (fluorescence emission). While the fluorescence quenching of DBO was performed without complications, the triplet transient absorption measurements of the azoalkane **1a** in the presence of additives required more detailed attention. Linear Stern−Volmer quenching was observed in most cases, but some quenching of the singlet-excited state of **1a** was suggested for 1,4-cyclohexadiene and tributylstannane due to the decreasing intensity of the T−T absorption (top-OD) at high quencher concentrations. This observation is in line with the expected higher reactivity of singlet-excited n,π* states and the singlet lifetime of **1a**, which is long enough to undergo bimolecular interactions (ca. 2.4 ns in benzene);[2,22,23] however, singlet quenching was not higher than 20−30% at the highest quencher concentrations employed in the spectroscopic measurements.

In the case of quenching of triplet **1a** by 1,4-cyclohexadiene, a new transient (attributed to the cyclohexadienyl radical)[24] interfered with the transient absorption measurement at 310 nm; for this quencher the measurement of the rate constant needed to be performed by using the weaker absorption at 450 nm. Tributylstannane as additive (for azoalkane **1a-H$_2$**) also caused the formation of a transient at ca. 390 nm, the expected absorption

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maximum of the tributylstannyl radical.[25,26] However, the kinetics of the 390-nm growth could not be resolved due to the overlap with the more intense absorption of the triplet azoalkane **1a-H$_2$** in this region. Flash photolysis of the azoalkane **1a** in hydrogen donor solvents (2-propanol, tetrahydrofuran, 1,4-dioxane, toluene) resulted generally in shorter triplet lifetimes and weaker signal intensities,[27] but no new transients in the region 280−600 nm were observed, except for some weak absorption of photoproducts at $\lambda < 320$ nm. The weaker triplet signals in these solvents are attributed to solvent-assisted quenching of the singlet-excited state of azoalkane **1a**.[28]

For benzhydrol as additive in the photolysis of azoalkane **1a**, a growth of transient absorption with a maximum at ca. 550 nm was observed, which followed the same kinetics as the decay of the triplet state of **1a**. This growth was assigned to the formation of hydroxydiphenylmethyl radicals, since their transient spectrum is well established.[29] This characteristic absorption was further employed to determine the efficiency of hydroxymethyl radical formation resulting from the reaction of the triplet azoalkane **1a** with benzhydrol; the triplet state of benzophenone was used as reference in this experiment (cf. the Experimental Section). Whereas the reaction of triplet benzophenone with benzhydrol is known to produce the hydroxymethyl radicals with unit efficiency,[30] their yield from the reaction with triplet azoalkane **1a** was determined to be much lower (0.12 ± 0.04).

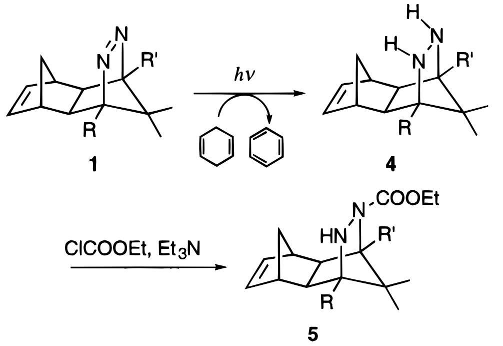
The transient absorption spectra were also monitored for the photolysis of the azoalkane DBO in toluene and tetrahydrofuran as solvents and in the presence of tributylstannane (15 mM) and benzhydrol (50 mM) as additives. Efforts were made to minimize the adverse effects of concomitant fluorescence on the absorption spectra in these experiments. In the case of toluene, evidence for the formation of benzyl radicals ($\lambda_{max} = 317$ nm with a shoulder at 303 nm)[31,32] was obtained by following the fluorescence decay. The identity of the benzyl radicals was also confirmed by comparison with an authentic spectrum obtained by photolysis of *tert*-butyl peroxide in toluene.[33] For tetrahydrofuran, a transient absorption with a maximum at ca. 290 nm was detected after the initial fluorescence had decayed (see Discussion for assignment). Finally, quenching of the DBO fluorescence by benzhydrol and tributylstannane resulted in the formation of absorptions at 550 and 390 nm, which were assigned, in analogy to the observation made for quenching of the triplet state of **1a**, to the hydroxydiphenylmethyl and tributylstannyl radicals.

Table 2. Product Studies[a] for the Photolysis of Azoalkanes 1 in the Presence of Hydrogen Donors

entry	azoalkane	hydrogen donor (M)	product composition (%)[b] **2**	**3**	**4**
1	**1a**	none	54	46	
2		2-propanol-d_8 (13.0)	8	23	69
3		1,4-cyclohexadiene (1.0)	<5		>95
4		benzhydrol (0.9)			>95
5		silane [$(Me_3Si)_3SiH$] (1.0)	<30		>70[c]
6	**1a-H$_2$**	tributylstannane (0.76)			>66[d]
7	**1b**	none	60	40	
8		2-propanol-d_8 (13.0)	18	45	37
9		1,4-cyclohexadiene (0.4)	30		70
10		1,4-cyclohexadiene (1.0)	5		95
11		benzhydrol (1.0)	<5		>95
12		silane [$(Me_3Si)_3SiH$] (1.0)	50		50
13	**1b-H$_2$**	tributylstannane (0.76)			>53[d]
14	**1c**	none	100		
15		2-propanol-d_8 (13.0)	100		
16		1,4-cyclohexadiene (2.0)	72		28
17		benzhydrol (1.0)	60		40
18	**1d**	none	100		
19		2-propanol (13.0)	100		
20		1,4-cyclohexadiene (8.0)	79		21
21		benzhydrol (1.0)	76		24

[a] Photolyses were conducted in a Rayonet photoreactor (350 nm) at 8 °C for 6−8 h in benzene except for 2-propanol as hydrogen donor, which was employed neat. [b] Azoalkane consumption and mass balances were >90%; relative yields (normalized to 100%) were determined by ^1H NMR analysis of the appropriate methyl or olefinic signals of the norbornene moiety; error ±6% of the stated values. [c] Yield refers to the photoreduced silyl derivative **6a**; error ± 10% of the stated value. [d] Absolute yield of the isolated trapping product **5-H$_2$**; the relative yield may be higher, cf. text.

Product Studies. The photoproducts of the azoalkanes **1** in the presence of typical hydrogen donors and under various reaction conditions are, in analogy to our preliminary report for the derivative **1a**[16] and our study on the charge-transfer induced photoreduction by amines,[13] the corresponding hydrazines **4**, which are formed in competition with the unimolecular products, viz., the housanes **2** and the aziranes **3** (Scheme 1). The cyclic hydrazines such as **4** are very sensitive toward oxidation, and hence, their characterization is mainly based on NMR spectral data.[34] However, the autoxidation of the hydrazines **4** to the precursor azoalkanes **1**[13,35] and their trapping with ethyl chloroformate[7,13] to afford the carbamates **5** (eq 1), which have been fully characterized,[13] provide unambiguous structural evidence. Only for the azoalkane **1d**, the thermal as well as acid lability of the carbamate derivative **5d** precluded its isolation for full characterization. Nevertheless, the hydrazine **4d** exhibited ^1H and ^{13}C resonances analogous to those of the hydrazines **4a−c**[13] (cf. the Experimental Section).



(1)

For most hydrogen donors, the product distributions for the photolysis of azoalkanes **1** were determined from the characteristic ^1H NMR signals of the methyl and/or norbornene olefinic protons (Table 2). However, tribu-

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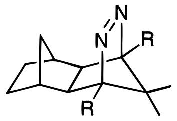
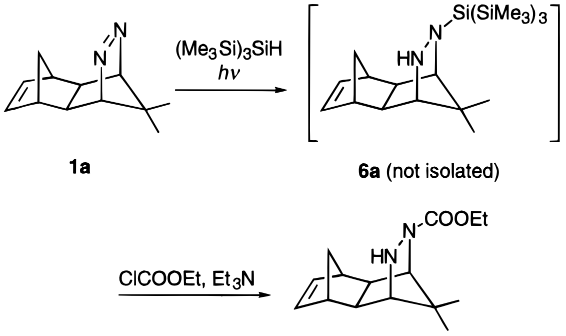
tylstannane was found to react *thermally* with the norbornene C=C double bond of azoalkanes **1**.[36−39] Hence, the C=C saturated derivatives **1-H$_2$** needed to be employed in the spectroscopic and preparative experiments (Tables 1 and 2). Furthermore, since the spectral complexity of the tributylstannane photolyzates precluded ^{1}H NMR monitoring, the photoreductions were performed on a preparative scale and the hydrazines were trapped with ethyl chloroformate (eq 1). Thus, the yields of isolated azoalkane reduction products (Table 2, entries 6 and 13) represent only the lower limits; the deficit presumably corresponds to the unimolecular photoproducts, cf. Scheme 1, or material lost during workup. Control experiments established that the azo linkage in the azoalkanes **1-H$_2$** was not thermally reduced by tributylstannane.



1a–H$_2$: R = H
1b–H$_2$: R = CH$_3$

In the presence of 1.0 M of the silane (Me$_3$Si)$_3$SiH as hydrogen donor,[36] the photolysis of azoalkane **1b** led to the corresponding hydrazine **4b** and the housane **2b** in nearly equal yields (Table 2, entry 12). The photolysis of azoalkane **1a** led to a new product (70%, entry 5), but treatment of the photolyzate with ethyl chloroformate followed by triethylamine led again to the known carbamate derivative **5a**, as revealed by ^{1}H NMR spectroscopy. From the derivatization and the NMR resonances, which resembled those of the carbamate **5a**, the new (not isolated) product is assigned to the *N*-silyl adduct **6a** (eq 2). Since this adduct arises presumably from trapping of the intermediary hydrazinyl radical after hydrogen abstraction (cf. Discussion), it is also entered as a photoreduction product in Table 2. That such silylation did not occur for the azoalkane **1b** may be due to the steric encumbrance posed by the bridgehead methyl substituents toward the bulky silane.



1a **6a** (not isolated) (2)

5a

Discussion

Quenching Rate Constants. In Table 1 are compared the rate constants for quenching by the various hydrogen donors of the triplet azoalkane **1a** (a representative case) with those of triplet benzophenone; also shown are the rate constants for quenching of the singlet-excited azoalkane DBO. The comparison of the singlet reactivity of DBO with that of triplet **1a** reveals similar variations with hydrogen donors, which can be roughly accounted for in terms of reaction energetics, i.e., hydrogen abstraction from the weaker C−H bonds (e.g., 1,4-cyclohexadiene) is faster than from the stronger ones (e.g., tetrahydrofuran). The reactivity of the singlet-excited state of DBO is generally higher, with the exception of 1,4-cyclohexadiene as donor, than for the triplet state of azoalkane **1a**. This difference can be accounted for in terms of the higher excited-state energy of singlet DBO (ca. 76 kcal/mol)[2] compared to triplet **1a** (ca. 62 kcal/mol).[2] Despite the very similar reactivities of singlet- and triplet-excited azoalkanes (Table 1), it seems noteworthy that the efficiency for photoreduction (product formation) may be significantly lower for the singlet reaction on account of competitive deactivation to the reactant molecules (see below).[23]

The photoreduction of triplet-excited azoalkanes is of prominent interest for comparison with ketone triplets. For triplet benzophenone, a clear dependence of the rate constants on the bond dissociation energy (BDE) of the hydrogen donor has been established long ago,[15,40−42] cf. data in Table 1. Hence, it is reassuring that a similar trend is observed for the triplet-excited azoalkane **1a** (Table 1). For example, one observes for benzophenone a ca. 100-fold enhancement in the quenching rate of 1,4-cyclohexadiene *versus* 2-propanol as hydrogen donor, and a similar trend (ca. 40-fold) is observed for quenching of the triplet azoalkane **1a**. In general, rate constants lower than for benzophenone apply for the azoalkane **1a**. This is presumably a consequence of the less favorable energetics for azoalkane photoreduction, which has been exemplified previously.[23,28] In particular, the triplet energy of the azoalkane **1a** (ca. 62 kcal mol^{-1})[2] is lower than that of benzophenone (69.0 kcal mol^{-1})[43] and the strength of the N−H bond formed in the hydrogen abstraction by azoalkanes (ca. 80 kcal/mol in alkylhydrazines)[44] falls below that of the O−H bond formed in ketone photoreduction (ca. 104 kcal/mol).[42,45] Regardless of these energy trends, the quenching rate constant for benzhydrol is actually ca. 2 times that for the azoalkane, which indicates that structural characteristics may also become important (see below).

Intermediate Radicals Derived from Hydrogen Abstraction. Evidence for hydrogen abstraction as a mechanism of quenching of the triplet state **1a** was obtained not only from the examination of the photoproducts (hydrazines) but also by monitoring the formation of the primary radicals derived from hydrogen abstraction, which could be identified through their characteristic absorptions. In this manner, hydrogen abstraction as a mechanism of quenching of excited azoalkanes, either the singlet state of DBO or the triplet state of **1a**, was established for benzhydrol, tributylstan-

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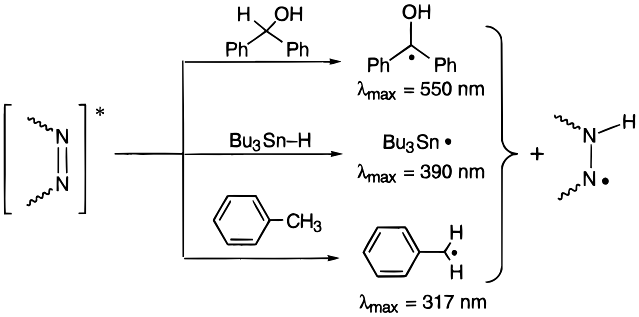
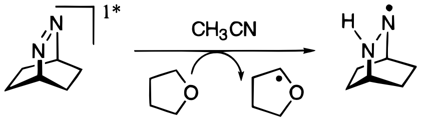
Scheme 2



nane, and toluene; the corresponding hydroxydiphenylmethyl, tributylstannyl and benzyl radicals displayed characteristic absorptions at 550, 390, and 317 nm,[25,26,29,31,32] which resulted from the reaction of the excited azoalkanes (Scheme 2). In the case of benzhydrol, the kinetics of the growth of the hydroxymethyl radical absorption matched the kinetics of the decay of the triplet azoalkane **1a**, which corroborated hydrogen abstraction as the quenching mechanism.

Additional efforts were made to observe the accompanying hydrazinyl radicals produced from the excited azoalkanes by hydrogen abstraction, cf. Scheme 2. For this purpose, a quencher, whose resultant radical (after hydrogen abstraction) does not absorb in the wavelength range accessible for UV transient detection (>280 nm), needed to be chosen. Tetrahydrofuran and 1,4-dioxane are candidates with the desired properties, but attempts to observe the hydrazinyl radicals by flash photolysis of azoalkane **1a** in these solvents met with failure due to the low triplet quantum yields in these solvents (efficient singlet-state deactivation),[28] a small fraction of the intercepted triplets (Table 1), and the absence of discernible new characteristic transient absorption. Conditions for the observation of the hydrazinyl radical were optimized by choosing DBO as a reactant and tetrahydrofuran as the solvent, which causes nearly quantitative (ca. 95%) quenching of the DBO fluorescence, cf. τ_f ca. 700 ns in acetonitrile[7] versus τ_f ca. 30 ± 15 ns in tetrahydrofuran (this work). The strong fluorescence of DBO precluded the observation of a time-resolved growth in transient absorption immediately after laser photolysis. However, after the fluorescence had decayed, a transient absorption with a maximum at 290 nm remained, which is tentatively assigned to the hydrazinyl radical derived from DBO photoreduction (eq 3). For comparison, the parent hydrazinyl radical (•NHNH$_2$) has been reported to absorb at 230 nm.[46]



(3)

Product Studies. The photoproduct distributions have been determined for differently substituted azoalkanes **1** for various hydrogen donors and reaction conditions (Table 2). In the presence of 1,4-cyclohexadiene as a prototypal hydrogen donor, the photolysis of azoalkanes **1a** and **1b** leads to the hydrazines **4a** and **4b** in a quantitative (> 95%) yield at a 1.0 M concentration (Table 2, entries 3 and 10). In contrast, the azoalkanes **1c** and **1d** afford significantly lower (<30%) yields of the respective hydrazines **4c** and **4d** even at higher 1,4-cyclohexadiene concentrations (entries 16 and 20). Since the triplet states are held responsible for the observed photoreduction, this trend in the hydrazine yields on going from the azoalkanes **1a**,**b** to the phenyl-substituted derivatives **1c**,**d** presumably reflects the differences in their triplet quantum yields and their triplet lifetimes.[2] In fact, azoalkanes with very short triplet lifetimes (<30 ns), e.g., derivatives of **1** without the norbornene moiety,[2] do not undergo photoreduction even at hydrogen donor concentrations of ca. 1.0 M. Photoreduction of benzophenone by 2-propanol and benzhydrol constitutes the classical example for photoreduction of ketones in general.[47,48] Hence, the photoreduction of azoalkanes **1** by these alcohols was also explored. The photolysis of azoalkanes **1a** and **1b** in neat 2-propanol (deuterated for NMR-spectroscopic purposes) led to significant amounts of the hydrazines **4a** and **4b** in competition with the unimolecular products (Table 2, entries 2 and 8), but the phenyl-substituted azoalkanes **1c** and **1d** afforded exclusively the housanes **2c** and **2d** (entries 15 and 19). In contrast, when the more reactive benzhydrol was employed (cf. rate constants in Table 1) as the hydrogen donor, the hydrazines **4a** and **4b** were again formed quantitatively (>95%) from the azoalkanes **1a** and **1b** even at a lower hydrogen donor concentration (entries 4 and 11). Interestingly, appreciable yields of the corresponding hydrazines were also observed for the photolysis of the azoalkanes **1c** and **1d** at 1.0 M concentration of benzhydrol (entries 17 and 21). Thus, analogous to benzophenone,[15,41,42] the enhanced reactivity toward alcohols with weaker α C−H bonds is evident.

To establish the generality of the hydrogen abstraction by n,π* triplet-excited azoalkanes, the photoreduction of **1** or **1-H$_2$** by tributylstannane and the silane [(Me$_3$Si)$_3$]SiH as hydrogen donors was also examined; the BDEs for SnH and SiH bonds (ca. 74 and 79 kcal/mol)[36,49] are quite similar to the BDE of the C−H bond in benzhydrol (75 kcal/mol).[50] For comparison, triplet benzophenone is known to abstract hydrogen from stannanes (Table 1) and silanes, e.g. the rate constant is ca. 10^7 M^{-1} s^{-1} for triethylsilane.[51] Although some complications were encountered for these hydrogen donors (cf. Results), efficient photoreduction was nonetheless observed (Table 2).

Involvement of the Singlet-Excited States. In the preparative experiments significant quenching (up to 75%) of the singlet-excited azoalkanes is expected due to the high hydrogen donor concentrations (1.0 M) that are employed, relatively long singlet lifetimes ($^1\tau$ ca. 3 ns),[23] and high fluorescence quenching rate constants for some hydrogen donors (^1k_q ca. 10^9 M^{-1} s^{-1}).[23] Hence, some of the photoreduction products may originate from the singlet state even if it is well recognized that the major fate of the singlet encounters with hydrogen donors is radiationless deactivation back to the ground-state reactants (75−100%) rather than the chemical reaction (photoreduction).[23,28] Indeed, from the known rate con-

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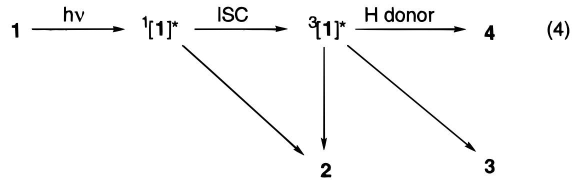
stants and quantum yields[21] for the photoreduction of singlet-excited DBO by 1,4-cyclohexadiene, we have calculated the maximum efficiency for singlet photoreduction to be only 8%. Thus, even in the extreme case of 75% singlet quenching, the remaining 25%, which undergo intersystem crossing to the triplet and may then react with the hydrogen donor, may still contribute 4 times more (25%) to the photoreduction products than the singlet pathway (75% × 8% = 6%), if the latter is, indeed, inefficient (e.g., 8%) and the former is assumed to be 100% efficient. Regardless of the possibility of singlet quenching in the preparative runs, compelling mechanistic evidence for the involvement of the azo triplet states, which is of prominent interest in relation to the photoreactivity of triplet ketones, has been accumulated in our preliminary study.[16]

Efficiency of Photoreduction. Experimental attempts to determine the absolute quantum yields of the azoalkane photoreduction by the various hydrogen donors were made, but a number of problems precluded a reliable quantitative analysis. These comprised (i) competitive and solvent-dependent quenching of the singlet-excited azoalkanes at the high alcohol concentrations used in the preparative runs, in particular for 2-propanol,[28] (ii) concomitant absorption (and photoreactions) of benzophenone formed as an oxidation product in the preparative photoreductions with benzhydrol, (iii) the possibility of quenching of the excited azoalkanes by the hydrazine products (e.g., due to hydrogen abstraction, see below),[4,21] and (iv) the possible reduction of ground-state azoalkanes by the primary radicals, which is known to be important for the hydroxymethyl radical.[34]

An indirect analysis of the efficiency of photoreduction of the azoalkane triplet state, which bypasses the complications due to singlet deactivation, uses the unimolecular singlet reactivity (housane formation) as internal actinometry and is based on the competition kinetics of the azo triplet state, i.e., photoreduction versus unimolecular reactions (eq 4).[11,12] In our preliminary report,[16] we have derived eq 5 from the kinetic scheme in eq 4, in



(4)

$$[\%\mathbf{4}]/([\ \%\mathbf{2}+\%\mathbf{3}] - {}^{S}[\mathbf{2}]) = k_r\,\Phi\,{}^3\tau\,[\mathrm{HD}] \qquad {}^{S}[\mathbf{2}] \equiv 9\% \quad (5)$$

which %**2**, %**3** and %**4** are the relative experimental yields of the housane **2**, azirane **3**, and hydrazine **4**. ${}^{S}[\mathbf{2}]$ is the fraction of singlet-derived housane and was kept fixed as 9%, the previously determined value.[2,11,12] The term $k_r\Phi{}^3\tau[\mathrm{HD}]$ is the product of the quenching rate constant (k_r), the efficiency of triplet photoreduction (Φ), the triplet lifetime (${}^3\tau$), and the hydrogen-donor concentration ([HD]). Two assumptions are made in eq 5: (a) the interaction between the singlet-excited azoalkane and the hydrogen donor is not chemically productive within the error limit (see section above); (b) stoichiometric photoreduction applies, in which 1 equiv of the hydrogen donor produces one equivalent hydrazine. The latter assumption is justified for benzhydrol and 1,4-cyclohexadiene since both may donate two hydrogen atoms.[16]

To determine the efficiency for triplet photoreduction (Φ) according to eq 5, the preparative yields in the photoreduction of azoalkane **1a** were determined at different hydrogen donor concentrations (up to 0.65 M). Plots of the yield ratios of the photoreduction *versus* the benzhydrol or 1,4-cyclohexadiene concentrantions according to eq 5 yielded linear correlations with slopes ($k_r\Phi{}^3\tau$) of 9 ± 2 M^{-1} (four data points, $r = 0.97$) and 14 ± 3 M^{-1} (six data points, $r = 0.97$). Since the values for k_r (Table 1) and ${}^3\tau$ (630 ± 30 ns)[2,11] are known for azoalkane **1a**, the quantum efficiencies (Φ) for triplet photoreduction may be estimated by division of the slopes by the product $k_r \times {}^3\tau$ and affords values of 0.6−1.0 for benzhydrol and 0.7−1.2 for 1,4-cyclohexadiene.[52] These estimates suggest that the efficiency for the photoreduction of triplet-excited azoalkanes is appreciable and may, in fact, approach unity. Correlation diagrams predict that the initial hydrogen abstraction from n,π*-excited triplet states to form the radical pair should occur with 100% efficiency.[14,23,53−57] Indeed, quantum efficiencies very close to unity have been established in several photoreductions of triplet ketones, e.g., of acetone by tributylstannane[58] and of benzophenone by benzhydrol[30] and 1,4-cyclohexadiene.[59]

The high efficiency estimated for the photoreduction of the triplet azoalkane **1a** by benzhydrol from product studies (0.7−1.2) contrasts the spectroscopically (nanosecond time scale) determined efficiency for the formation of the hydroxymethyl radicals (0.12), which are the primary intermediates in the photoreduction. To rationalize the low radical yield, we propose an associative effect through hydrogen bonding in the incipient radical pair;[60] this association may favor the rapid transfer of the second hydrogen (after intersystem crossing) over diffusion (Scheme 3). This mechanism would account for both the low yields of radicals observed in the time-resolved experiments and the high yields determined from the preparative runs. The postulated association might be assisted by preferential solvation (hydrogen bonding between the ground-state azoalkanes and benzhydrol in solution), which could also account for the higher quenching rate constant of the azoalkane **1a** relative to benzophenone (Table 1). A similar associative effect has been previously postulated to explain the difference in the reactivity between ketones *versus cis*-configured diketones.[61] Note that in simple ketones, the carbonyl carbon atom cannot promote the postulated associative effect.

Mechanism of Hydrogen Abstraction. Both the singlet and triplet states of azoalkanes undergo photoreduction with variable efficiencies, which range from a few

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[52] In the preliminary report,[16] a quantum efficiency of unity ($\Phi = 1$) was assumed in eq 5 to obtain independent estimates of the triplet lifetime (τ); this procedure is mutually consistent with the present analysis, except that different variables (Φ or τ) are kept constant to allow the determination of the other.

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[60] A reviewer has suggested that an alternative explanation for the observed discrepancy of the preparative quantum efficiency for photoreduction and the spectroscopic radical yield could derive from efficient singlet quenching and photoreduction by benzhydrol. This possibility cannot be ruled out because the concentration range of benzhydrol is too limited to acquire accurate data.

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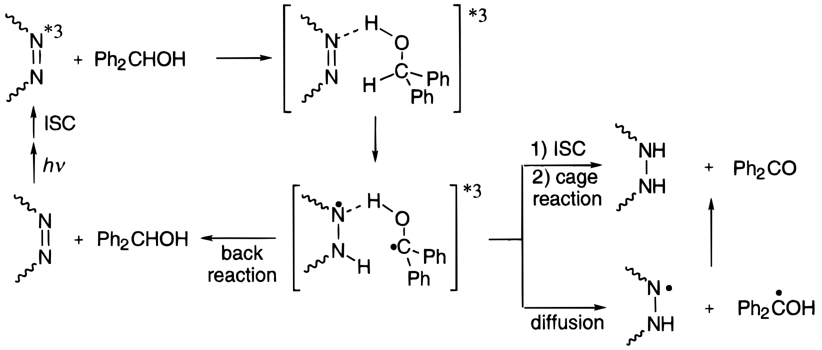
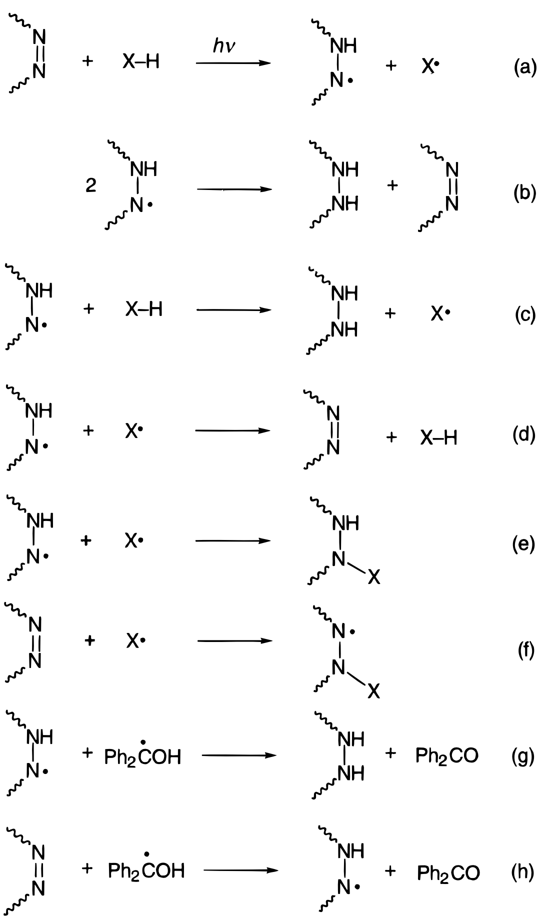
Scheme 3



Scheme 4



percent for the singlet states[21] to unit efficiency for the triplet states (this work). As could be convincingly demonstrated by transient absorption spectroscopy, a technique which has been thoroughly applied to the photoreduction of ketones,[23,25,29,30,59,61−63] the primary step of the reaction of an excited azoalkane leads to a radical pair (Scheme 4, step a). The initial radical pair may undergo cage reactions (after intersystem crossing) or diffusion and subsequent follow-up reactions (Scheme 4, steps b−h). Of course, the relative importance of these follow-up reactions and the fraction of cage reaction are expected to differ between the photoreduction of azoalkanes and ketones since the reactivity pattern of hydroxymethyl radicals should be distinct from that of hydrazinyl radicals.

The back reaction to regenerate the starting material (step d in Scheme 4 and Scheme 3), which represents an energy-wasting process, is spin-allowed only for the singlet radical pair. Hence, step d may be significant for the reaction of singlet-excited azoalkanes, where the quantum yields for product formation are indeed very small (see above), but appears to be of minor importance for the triplet reaction, since the reaction quantum yields approach unity (for 1,4-cyclohexadiene and benzhydrol).

The majority of questions which have remained unanswered pertain to the formation of the final photoproducts (hydrazines) from the radical pairs, and these will require future attention. For example, the disproportionation of two hydrazinyl radicals is a viable pathway to produce the hydrazines (Scheme 4, step b),[34,64,65] since a fast reaction rate ($2k_t$ ca. 2.5×10^9 M^{-1} s^{-1}) has been reported for the reaction between two hydrazinyl radicals.[46] In addition, the disproportionation between different radicals (step g, cf. also Scheme 3) may also contribute for some hydrogen donors (1,4-cyclohexadiene, benzhydrol). The formation of hydrazines by an additional hydrogen abstraction from a hydrogen donor molecule by the hydrazinyl radical (step c)[66] appears unlikely in view of the relatively low (ca. 80 kcal/mol) N−H bond dissociation energy in alkylhydrazines.[44] Not surprisingly, hydrazines may act themselves as powerful hydrogen donors, e.g., the rate constants for reaction with the hydroxy radical (k ca. 1.5×10^{10} M^{-1} s^{-1} in water),[46] an approximate model for n,π^*-excited ketones, and with excited azoalkanes ($k = 1.0{-}3.4 \times 10^9$ M^{-1} s^{-1}) are close to the diffusion-controlled limit.[4,21] Even for the reactive tributylstannane, for which hydrogen abstraction by another radical appears most likely,[67] it is difficult to predict whether the reaction rate with hydrazinyl radicals resembles more that for the *tert*-butoxy radical (2×10^8 M^{-1} s^{-1})[25,26] or that for alkyl radicals ($10^6{-}10^7$ M^{-1} s^{-1}),[68] since only few absolute rate constants for the hydrazinyl radicals are known.[46,69]

The fate of the radicals derived from the hydrogen donors is not entirely resolved either.[70] Radical coupling, e.g., to produce hexabutyldistannane[38,67] from two tributylstannyl radicals, or cross-coupling with the hydrazinyl

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radicals to produce the formal addition product (step e in Scheme 4 and eq 2), are reasonable alternatives. The radicals might also serve as efficient reducing agents of the ground-state azoalkane (step h),[70] at least in the case of alcohols and 1,4-cyclohexadiene, since such hydrogen-transfer reactions are well-established for both ketones[71] and azoalkanes.[13,34] Finally, addition to the ground-state azoalkane, e.g., in the case of tributylstannyl radicals,[67] may occur (step f). The last two reactions, in combination with the (unlikely) step c, could serve to maintain a chain reaction for photoreduction,[67] for which we have as yet no evidence. For example, the estimated efficiencies for triplet photoreduction do not exceed unity within the error (see above and ref 16). Evidence for a chain mechanism, however, has been documented in the literature for the photoreduction of ketones by tributylstannane as the hydrogen donor.[67]

To what extent the photoreduction of azoalkanes by the examined hydrogen donors is mediated by charge-transfer (CT) interactions is not entirely resolved. For amines as photoreducing agents of azoalkanes **1**, the participation of CT appears to be established.[13,21] In contrast, for the presently examined photoreduction of azoalkanes **1** by alcohols, 1,4-cyclohexadiene, stannanes, and silanes, a dependence on the oxidation potentials of the donors is not readily apparent. Instead, the rate constants vary with the BDEs, which favors a direct (covalent) hydrogen abstraction mechanism. Further, analogies to benzophenone are recognized (Table 1), which suggest the absence of significant CT interactions as well. Since the rate constants for the quenching of the *singlet state* of DBO by the various hydrogen donors follow the same trend as for the *triplet state* of azoalkane **1a** (Table 1), no major variation of the CT contributions to the photoreduction appears to apply. However, CT may become more important for the singlet-excited DBO due to its higher singlet energy, and, indeed, has been postulated in the DBO photoreduction on the basis of solvent effects.[21]

In conclusion, the direct hydrogen abstraction by n,π* triplet-excited azoalkanes occurs efficiently with a variety of hydrogen donors. The hydrazine yields depend on the triplet quantum yields and lifetimes of the azoalkanes, i.e., as expected, the higher the triplet yield and the longer-lived the triplet azoalkanes, the more efficient the photoreduction. A dependence of the rate for hydrogen abstraction on the bond dissociation energies is revealed from both the photochemical products studies and the quenching rate constants. The photoreductive behavior of the n,π* triplet azo chromophore in azoalkanes **1** parallels in general that of benzophenone, except that the observed efficiency of hydroxydiphenylmethyl radical generation from benzhydrol as hydrogen donor is significantly lower than for benzophenone, which is attributed to an associative effect.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer infrared ratio-recording spectrometer 1420. NMR spectra were run on a Bruker AC 200 instrument in deuterated solvents as the internal standards. Mass spectra were recorded on Finnigan MAT 8200 and Finnigan MAT 90 mass spectrometers. GC analyses were performed on a Carlo Erba 4100 (FID); as electronic integrator the Shimadzu C−R1B chromatopac was used. Solvents were purified by standard procedures, and the commercial chemicals were used as received. Column chromatography was conducted on silica gel (0.032−0.063 mm, Woelm). The photochemical reactions were carried out in a Rayonet photoreactor equipped with 350-nm lamps.

The azoalkanes **1** were synthesized according to the reported procedures.[72] The photoproducts **2** and **3**[12] as well as the hydrazines **4a**−**c** and their trapping products **5a**−**c** have been previously characterized.[13]

General Procedure for the Photolysis of the Azoalkanes 1 in the Presence of Hydrogen Donors and Product Analysis. A sample of ca. 0.06 mmol of the azoalkanes **1** was dissolved in 0.5 mL of benzene which contained the appropriate concentration of the hydrogen donor. The solution was degassed by two freeze−pump−thaw cycles and irradiated at 350 nm and ca. 8 °C under a nitrogen gas atmosphere directly in an NMR tube. For quantitative analysis, the photolyses were run in the presence of diphenyl ether or hexamethyldisiloxane as internal standards and the product compositions, were determined from the relative peak areas of the characteristic ^{1}H NMR signals of the norbornenyl olefinic protons and/or the methyl protons.

Photoreduction of Azoalkane 1d to Hydrazine 4d. A sample of 0.06 mmol of the azoalkane **1d** was dissolved in 0.5 mL of a mixture (1:1.5) of 1,4-cyclohexadiene and benzene, degassed by two freeze−pump−thaw cycles, and irradiated at 350 nm in a Rayonet photoreactor under a nitrogen gas atmosphere for 8 to 10 h. ^{1}H and ^{13}C NMR analyses after removal of the solvent and diene (20 °C/ 15 Torr) revealed new signals analogous to those of the hydrazines **4a**−**c** in addition to those of the major product **2d**. Upon exposure this solution to air for 2−3 days, the new signals disappeared with concomitant appearance of those characteristic of the precursor azoalkane **1d**. Thus, the identity of the hydrazine **4d** was established. Due to the air sensitivity of the hydrazine **4d** and the lability of the trapping product **5d** on silica gel for isolation, no full characterization was possible. Nevertheless, the characteristic ^{1}H and ^{13}C NMR spectral data (some resonances could not be specified due to severe overlap of the peaks) resembled those of the previously characterized hydrazines **4a**−**c**.[13]

4d: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.75 (s, 3H), 1.15 (s, 3H), 6.33 (m, 2H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 16.5 (q), 19.1 (q), 68.6 (s), 141.6 (d).

Photolysis of Azoalkane 1a in the Presence of Tris(trimethylsilyl)silane. ^{1}H NMR and GC analyses of the photolyzate of the azoalkane **1a** and the silane (Me$_3$Si)$_3$SiH revealed the formation of a new product, which is assigned to the silyl derivative **6a**. This assignment is based on the ^{1}H and ^{13}C NMR signals, which are analogous to those of the carbamate **5a** and on the trapping experiment with ethyl chloroformate, which afforded the carbamate **5a** on workup and isolation by silica gel chromatography (cf. eq 2). The ^{1}H and ^{13}C signals of the silyl derivative **6a** are as follows: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 0.96 (s, 3H), 1.20 (s, 3H), 6.34 (br s, 2H); ^{13}C NMR (C$_6$D$_6$, 50 MHz) δ 20.5 (q), 25.1 (q), 43.7 (t), 54.0 (s), 64.7 (s), 65.0 (s), 141.3 (d), 141.8 (d); the remaining signals could not be specified due to severe peak overlap.

Preparative Photolysis of Azoalkanes 1-H$_2$ in the Presence of Tributylstannane. A sample of the azoalkanes **1a-H$_2$** or **1b-H$_2$** (0.40 mmol) was dissolved in 2.0 mL of benzene, which contained 440.0 mg (1.51 mmol) of tributylstannane, degassed by two freeze−pump−thaw cycles, and

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[70] In the case of benzhydrol, a search for the oxidation products was made and benzophenone was identified as the exclusive product by NMR and GC analyses; this experiment was carried out at low conversion (<20%) to exclude contributions due to the photoreduction of the developing benzophenone, which absorbs as well at the irradiation wavelength of 350 nm. The exclusive formation of benzophenone in the azoalkane−benzhydrol photoreduction excludes the coupling of two hydroxydiphenylmethyl radicals to form benzpinacol and favors either the reaction promoted by an associative effect (Scheme 3), or the follow-up reaction with the azoalkane (Scheme 4, step h).

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irradiated in a Rayonet photoreactor ($\lambda = 350$ nm) under a nitrogen gas atmosphere at ca. 8 °C. After irradiation for 10 h, 0.2 mL of ethyl chloroformate, followed by 0.2 mL of triethylamine, was added to the photolyzate. The resulting reaction mixture was treated with 20 mL of distilled water, and the organic materials were extracted with methyl *tert*-butyl ether (3 × 15 mL). The combined ether extracts were dried over $MgSO_4$, filtered, and concentrated (20 °C/15 Torr). The product was isolated by silica gel chromatography (25% ethyl acetate in petroleum ether). ^1H and ^{13}C NMR spectroscopy revealed some signals as a set of two for the geometrical rotamers of the C−N carbamate bond. Such hydrogen and carbon resonances, which appear as a set of two, have been marked with an asterisk.

5a-H$_2$: Colorless viscous oil; 70.0 mg (66%); IR (neat, cm^{-1}) 3210, 2930, 2850, 1680 (br), 1460, 1420, 1370, 1340; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.03, 1.05 (s, 3H)*, 0.96−1.16 (m, 3H), 1.12, 1.23 (s, 3H)*, 1.20−1.30 (m, 3H), 1.46−1.52 (m, 2H), 1.90−2.16 (m, 3H), 2.16−2.36 (m, 2H), 2.94 (d, $J = 3.2$ Hz, 1H), 3.71, 3.85 (2 × d, $J = 3.0$ Hz, 1H)*, 4.04−4.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.81, 14.83 (q)*, 18.7 (q), 19.6, 19.7 (q)*, 30.4, 30.6 (t)*, 30.5 (t), 35.3 (t), 35.8 (d), 35.8, 35.9 (d)*, 49.0, 49.1 (d)*, 49.5, 49.9 (s)*, 50.1, 50.2 (d)*, 61.0, 61.2 (t)*, 65.3, 65.8 (d)*, 66.6, 67.3 (d)*, 154.7, 154.90 (s)*; HRMS *m/z* calcd for $C_{15}H_{24}N_2O_2$ 264.1838, found 264.1837.

5b-H$_2$: viscous oil; 62.0 mg (53%); IR (neat, cm^{-1}) 3200 (br), 1675 (br), 1500, 1410, 1370, 1340; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.73, 0.76 (s, 3H)*, 0.92, 0.93 (s, 3H)*, 0.94−1.02 (m, 2H), 1.03, 1.04 (s, 3H)*, 1.24 (t, $J = 7.8$ Hz, 3H), 1.35, 1.49 (s, 3H)*, 1.46−1.56 (m, 2H), 1.67 (s, 1H), 1.69 (s, 1H), 1.86−1.97 (m, 2H), 2.24 (br s, 1H), 2.38 (br s, 1H), 4.00−4.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.2 (q), 14.6, 14.8 (q)*, 15.0, 15.4 (q)*, 15.6 (q), 17.3, 17.5 (q)*, 30.3, 30.3 (t), 30.88, 30.91 (t)*, 34.93 (d), 35.06, 35.13 (t)*, 35.2 (d), 53.57, 53.63 (d)*, 53.8, 54.4 (d), 54.25, 54.33 (s)*, 60.5, 60.8 (t)*, 66.7, 67.8 (s)*, 72.0, 72.1 (s)*, 154.23, 155.16 (s)*; HRMS *m/z* calcd for $C_{17}H_{28}N_2O_2$ 292.2147, found 292.2151.

Laser Flash Photolysis. The spectroscopic solvents benzene, acetonitrile, tetrahydrofuran, 1,4-dioxane, toluene, and 2-propanol were Omnisolv grade for UV spectroscopy (BDH). Tributylstannane (Aldrich) was employed as purchased (99%). 1,4-Cyclohexadiene (Aldrich) was fractionally distilled before use. Benzhydrol (99%, Aldrich) was further purified by two recrystallizations from ethanol and subsequent sublimation.

The nanosecond time-resolved laser-flash photolysis technique was employed to monitor the transient absorptions and emissions. The original setup[73] was modified through a Tektronix 2440 digitizer for signal capturing. A PowerMacintosh computer customized with LabVIEW 3.1 software (National Instruments) was used for the data acquisition. Optical absorption spectra were obtained with an HP-8451A diode array spectrophotometer.

The time-resolved studies were done in Suprasil quartz cells with 7-mm optical path. All samples were thoroughly deaerated by bubbling oxygen-free nitrogen through the solution for ca. 15−20 min. The transient lifetimes were determined at 21 ± 2 °C by laser flash photolysis using a Continuum-Surelite Nd:YAG laser with the third harmonic at 355 nm (ca. 30 mJ per 6-ns pulse). The transient emission of DBO was detected at $\lambda_{\mathrm{mon}} = 450{-}550$ nm in solutions with absorbances of ca. 0.20. The transient absorption of azoalkane **1a** was monitored in ca. 2 mM solutions with absorbances of ca. 0.3−0.4 at 355 nm; the monitoring wavelength was generally 450 nm and also 310 nm for additives which did not absorb at this wavelength.

The quenching rate constants were determined from kinetic plots for the transient lifetimes ($\tau_0/\tau_q = 1 + k_q\tau_0[Q]$), which comprised ≥18 data points at ≥6 quencher concentrations; the maximum concentration of quencher was typically chosen to achieve a transient lifetime below 200 ns. The error limit was estimated from the absolute deviation in the values of two independent plots or from the linear regression analysis of only one plot. For some inefficient quenchers, the rate constant was calculated from the transient lifetimes in neat quencher solution (correction for the molarity of the solvent) relative to carbon tetrachloride as solvent for azoalkane **1a** or **1a-H$_2$** or relative to acetonitrile for DBO.

The top-OD produced upon laser-flash photolysis of azoalkane **1a** in the presence 0.3 M benzhydrol in benzene was compared with the top-OD of an optically matched (OD = 0.30) solution of benzophenone in benzene. Using the known ratio of the extinction coefficients of triplet benzophenone ($\epsilon_{525} = 7800\ M^{-1}\ cm^{-1}$) and the hydroxydiphenylmethyl radical ($\epsilon_{550} = 3300\ M^{-1}\ cm^{-1}$),[29,74] and correcting for the fraction of intercepted azoalkane triplets (80%, by using the rate constant from Table 1), provided a radical yield of 12 ± 0.04%. A significant dependence of the ratio of the top-ODs on the laser dose was not observed.

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