

# Photoreduction of Polycyclic DBO-Type Azoalkanes with Amines to Hydrazine Products

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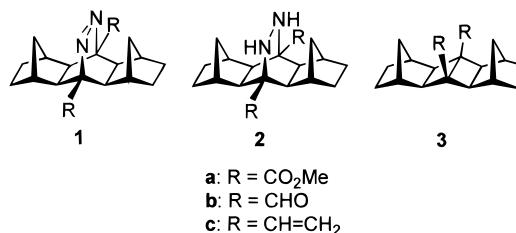
**Abstract:** The  $n,\pi^*$ -singlet-excited polycyclic,  $\alpha$ -substituted DBO-type azoalkanes **1** are reduced by amines to form the corresponding hydrazines **2** as photoreduction products in competition to denitrogenation to the bicyclo[2.2.0]hexane photoproducts **3**. The photophysical, photochemical, and electrochemical properties of the azoalkane determine the product ratio of the hydrazine **2** versus the bicyclo[2.2.0]hexane **3**. The quantum yields of the photoreduction are quite low ( $<0.1$ ), for which efficient deactivation of the singlet excited state through charge transfer is postulated. The charge transfer in the exciplex between the azoalkane and the amine promotes the hydrogen abstraction of the  $\alpha$ -CH bond from the amine by the azoalkane and, thus, facilitates its photoreduction, a general photochemical process applicable to singlet- as well as triplet-excited azoalkanes.

## Introduction

The photochemistry of the azo chromophore has long been the subject of extensive investigation.<sup>1</sup> 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 succinctly the distinct photophysical and photochemical properties of cyclic azoalkanes in general. In contrast to the diazabicyclo[2.2.1]hept-2-ene (**DBH**), which eliminates molecular nitrogen smoothly upon photoexcitation ( $\Phi_r$  ca. 1<sup>1a,2</sup>), the photoreactivity of **DBO** is extraordinarily low ( $\Phi_r = 0.022$  in MeCN<sup>3</sup>) and, therefore, the latter constitutes a *photopersistent* azoalkane. Besides the investigation of the photophysical and photochemical properties of the azo chromophore, some work has been conducted in the past in regard to the photoelectron-transfer (PET) chemistry of azoalkanes. Especially the photoreduction of **DBH**-type azoalkanes by amines has been recently studied in detail;<sup>4</sup> however, only little is known so far on the photoreduction of **DBO** derivatives. A study by Engel has demonstrated the photoreduction of the parent singlet-excited **DBO** azoalkane by 1,3-cyclohexadiene,<sup>5</sup> but the numerous oxidation products of the cyclohexadiene made for a complex reaction. Moreover, in recent work Nau has described an inverted solvent effect on the fluorescence quenching of the parent **DBO** by amines and sulfides, in which he examined in detail the charge-transfer interaction in the excited state.<sup>6</sup>

Our previous studies disclosed that the fluorescence of ester-substituted, polycyclic **DBO**-type azoalkanes may be quenched by olefins and arenes more effectively than the parent **DBO**

through exciplex formation and H-atom abstraction.<sup>7</sup> Consequently, we decided to examine whether photoreduction of such azoalkanes is feasible. Moreover, since a decrease of the electron density on the azo chromophore should be advantageous for the electron-transfer process, a study of the dependence of the efficiency for hydrazine formation on the electronic properties of the azo chromophore would be of considerable mechanistic interest. For this purpose we have investigated the photoreduction of the  $\alpha$ -substituted polycyclic azoalkanes **1a–c** by primary,



secondary, and tertiary amines. Our present results confirm that a long-lived singlet excited state, a low reduction potential, and a low photoreactivity of the azoalkane promote the photoreduction of the azoalkanes **1** to the hydrazines **2**.

## Results

**Photophysical and Electrochemical Data.** The photophysical<sup>8</sup> and the electrochemical data of the azoalkanes **1a–c** are presented in Table 1. The determination of the reaction quantum yields was accomplished by irradiation with the 363.8-nm line of an argon-ion laser and by employing 1-phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (Ph-DBO) as an actinometer, whose decomposition quantum yield has been reported to be unity.<sup>9</sup> The fluorescence quantum yields were measured by steady-state emission spectra versus quinine bisulfate (QBS) as reference.

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**Table 1.** Photophysical and Electrochemical Data for the Azoalkanes

azoalkane	$\Phi_r^{a,b}$	$\Phi_f^{a,c}$	$\tau$ [ns] <sup>a,d</sup>	$E_{Pa}^{Ox}$ [V] <sup>e</sup>	$E_{Pa}^{Red}$ [V] <sup>f</sup>
<b>1a</b>	0.35	0.090	273	+2.04 <sup>g</sup>	-2.23
<b>1b</b>	0.64	0.049	111	+1.98	-2.03
<b>1c</b>	0.67	0.16	268	+1.45	-2.47

<sup>a</sup> In MeCN, 20 °C. <sup>b</sup> Reaction quantum yield, error  $\pm 10\%$  of the stated values. <sup>c</sup> Fluorescence quantum yield, error  $\pm 10\%$  of the stated values. <sup>d</sup> Fluorescence lifetime; error  $\pm 10\%$  of the stated values. <sup>e</sup> Oxidation potential, measured by cyclic voltammetry in  $CH_2Cl_2$  vs SCE with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte, scan rate 100 mV s<sup>-1</sup>. <sup>f</sup> Reduction potential, measured by cyclic voltammetry in DMF vs SCE with 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> as supporting electrolyte, scan rate 200 mV s<sup>-1</sup>. <sup>g</sup> In MeCN + 1.93 V.

The singlet lifetimes were determined by means of single-photon counting by irradiation of the sealed azoalkane solutions at 358 nm and by fitting of the deconvoluted exponential fluorescence decay.<sup>8</sup> The oxidation potentials were determined by CV measurements on a Ag<sup>0</sup>/Ag<sup>+</sup> electrode with ferrocene as internal standard and the reduction potentials on a hanging-mercury-drop electrode (HMDE) with benzophenone as internal standard.

Azoalkane **1a** exhibits a moderate photoreactivity ( $\Phi_r$ ), a comparatively high fluorescence quantum yield ( $\Phi_f$ ), and a long singlet lifetime ( $\tau$ ). In view of the better radical-stabilizing ability of the formyl (**1b**) and vinyl (**1c**) compared to the ester group (**1a**),<sup>10</sup> the photoreactivity of **1b** and **1c** is considerably higher and, consequently, their fluorescence quantum yields lower.<sup>8</sup> Compared to **1a** and **1c**, the azoalkane **1b** exhibits a shorter fluorescence lifetime, which is based on its comparatively high reactivity and the better accessibility of its azo chromophore.<sup>8</sup> Moreover, as the bridgehead carbonyl groups possess a strong electron-withdrawing effect, derivatives **1a** and **1b** are easier to reduce (lower  $E^{red}$  values) than the azoalkane **1c**, but more difficult to oxidize (higher  $E^{ox}$  values).

**Product Studies.** Photoexcitation (Rayonet, 350 nm) of nitrogen-purged solutions of the azoalkanes (ca. 0.06 M) in the presence of amines (ca. 0.6 M) led to the corresponding hydrazines (Table 2), in some cases accompanied by the denitrogenated bicyclo[2.2.0]hexane photoproducts. The cyclic hydrazines **2** are very sensitive toward oxidation and, hence, their characterization is mainly based on NMR spectral data. When the photolyzate is exposed to air for about 3–5 days, the hydrazine <sup>1</sup>H NMR signals disappear with concomitant appearance of the azoalkane signals, which unequivocally establishes the intervention of the hydrazine. The efficiency of hydrazine formation depends on the amine and on the azoalkane that are used, as shown by the ratio of hydrazine **2** versus bicyclo[2.2.0]hexane **3** products in Table 2. The most efficient photoreduction to the corresponding hydrazine was observed in the case of the ester-substituted azoalkane **1a**; for almost all amines exclusive formation of hydrazine was detected (Table 2, entries 1–5). In contrast, the photoreduction of the azoalkanes **1b** and **1c** yielded mixtures of the bicyclo[2.2.0]hexanes **3** and the hydrazines **2**.

A requirement for hydrazine formation is the presence of  $\alpha$ -hydrogen atoms in the amine, as illustrated by diphenylamine and *tert*-butylamine (entries 6 and 7 for **1a**; entry 12 for **1b**; entries 19 and 20 for **1c**), for which exclusively the bicyclo[2.2.0]hexane was observed without any photoreduction. It is interesting to note, however, that with diphenylamine the azoalkane conversion drops dramatically, i.e., 0% (**1a**), 13%

**Table 2.** Product Studies<sup>a</sup> for the Photolysis of Azoalkanes in the Presence of Amines

entry	azo-alkane	amine	convn [%]	prod. balance <sup>b</sup> [%]	prod. distribution <sup>c</sup>		
					<b>2</b>	<b>3</b>	
1	<b>1a</b>	diethylamine	100	>95	100	0	
2		<i>n</i> -butylamine	100	>95	100	0	
3		diisopropylamine	98	>95	100	0	
4		cyclohexylamine	100	>95	100	0	
5		triethylamine	99	>95	92	8	
6	<b>1b</b>	<i>tert</i> -butylamine	20	>95	0	100	
7		diphenylamine	0	>95			
8		diethylamine	84	67	51	49	
9		<i>n</i> -butylamine	<sup>d</sup>				
10		diisopropylamine	79	65	57	43	
11		triethylamine	75	61	59	41	
12		<i>tert</i> -butylamine	95	60	0	100	
13		diphenylamine	13	78	0	100	
14		<b>1c</b>	diethylamine	74	>95	93	7
15			<i>n</i> -butylamine	95	92	44	56
16			diisopropylamine	97	>95	57	43
17			cyclohexylamine	88	>95	47	53
18			triethylamine	96	>95	50	50
19	<i>tert</i> -butylamine		100	94	0	100	
20	diphenylamine		37	>95	0	100	

<sup>a</sup> A degassed solution of ca. 0.06 M azoalkane and ca. 0.6 M amine was irradiated ( $\lambda = 350$  nm) in the Rayonet photoreactor at 8 °C in C<sub>6</sub>D<sub>6</sub> for 15 h. <sup>b</sup> Hexamethyldisiloxane as internal standard for <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Analysis by <sup>1</sup>H NMR spectroscopy; relative yields are normalized to 100%, error limit  $\pm 6\%$  of the stated values. <sup>d</sup> Quantitative formation of the corresponding imine; the formation of the imine with *tert*-butylamine (entry 12) is disfavored due to steric reasons.

(**1b**), and 37% (**1c**). This is most likely due to the efficient quenching of the excited singlet state by this amine (see below).

The product balances have been determined by <sup>1</sup>H NMR spectroscopy against an internal standard (hexamethyldisiloxane). For the azoalkanes **1a** and **1c** the product balance is excellent (>90%), whereas in the case of **1b** only 60–70% were accounted for.

The oxidation products of the amines have been identified by their characteristic <sup>1</sup>H NMR signals and confirmed by comparison with the authentic materials formed by photooxidation of the amines in benzophenone.<sup>4,11</sup> In almost all cases the oxidation products were formed quantitatively (Table 3).

For the primary amines (Table 3, entries 3 and 4) two molecules are consumed to form one molecule of the hydrazine **2** and one molecule of the imine. The latter is formed by condensation of the initial imine with the primary amine under elimination of ammonia. In contrast, for secondary amines (entries 1 and 2) only one molecule of the amine produces one molecule of the hydrazine and one molecule of the initial imine, which persists. For triethylamine, ca. 20% acetaldehyde was detected by <sup>1</sup>H NMR spectroscopy (entry 5). In a previous study with DBH-type azoalkanes, it was established that from triethylamine the enamine is formed, which is hydrolyzed by adventitious water to diethylamine and acetic aldehyde.<sup>4</sup> In the present case, the diethylamine signal was hidden below the triethylamine one in the <sup>1</sup>H NMR spectrum and, hence, could not be detected.

**Quantum Yields and Relative Efficiencies.** The determination of the quantum yields of the photoreduction ( $\Phi_p$ ) was

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**Table 3.** Oxidation Products of the Amines

entry	amine	oxidation product <sup>a</sup>
1		
2		
3		
4		
5 <sup>b</sup>		+

<sup>a</sup> Determined by characteristic <sup>1</sup>H NMR signals and confirmed by comparison with authentic materials formed by photooxidation of the amines with benzophenone; ref 11. <sup>b</sup> Only 15–20% of the expected aldehyde detected; the diethylamine was hidden under the signal of the triethylamine.

**Table 4.** Quantum Yields of the Photoreduction  $\Phi_p$  of the Azoalkanes<sup>a</sup>

amine	$\Phi_p$ ( <b>1a</b> ) <sup>b</sup>	$\Phi_p$ ( <b>1b</b> ) <sup>b</sup>	$\Phi_p$ ( <b>1c</b> ) <sup>b</sup>
<i>n</i> -butylamine	0.080	<i>c</i>	0.058
diethylamine	0.049	0.038	0.026
diisopropylamine	0.038	0.016	0.041
triethylamine	0.050	0.050	0.030

<sup>a</sup> At 350 nm in benzene, determined by means of the ferrioxalate actinometer; conversion 5–10%, <sup>1</sup>H NMR analysis. <sup>b</sup> Quantum yield for the formation of hydrazine **3**. <sup>c</sup> Formation of the corresponding imine, cf. Table 2.

**Table 5.** Quenching Rate Constants  $k_q$ <sup>a</sup> for the Singlet-Excited Azoalkanes

entry	quencher	IP [eV] <sup>b</sup>	log $k_q$		
			<b>1a</b>	<b>1b</b>	<b>1c</b>
1	diethylamine	8.01	9.23	9.12	8.44
2	triethylamine	7.50	8.59 <sup>c</sup>	8.77	7.52
3	diisopropylamine	7.73	8.53	8.60	7.34
4	diphenylamine	7.16	9.27	9.43	9.13

<sup>a</sup> Determined by the Stern–Volmer method ( $\lambda^{\text{Ex}} = 350$  nm;  $\lambda^{\text{Em}} = 370$ –550 nm, [Q] = 0–0.55 M,  $n = 5$ –8,  $r^2 = 0.960$ –0.999) in degassed MeCN, 20 °C, error  $\pm 10\%$  of the stated values. <sup>b</sup> Ionization potential of the amine, ref 11. <sup>c</sup> Time-resolved measurements yield 8.51.

accomplished by employing the ferrioxalate actinometer (Table 4).<sup>13</sup>

The conversion of the azoalkanes was monitored by <sup>1</sup>H NMR spectroscopy up to a conversion of 5–10%. The quantum yields are all quite low ( $\Phi_p < 0.1$ ) and the relative efficiencies of the amines to reduce the singlet-excited azoalkanes **1** follows the general order primary > tertiary > secondary, with the poorest efficiency displayed by secondary amines.

**Fluorescence Quenching.** The fluorescence emission of all azoalkanes was well quenched by the employed amines. The corresponding quenching constants  $k_q$  of the azoalkanes **1a–c** with some of the amines were acquired by steady-state fluorescence spectroscopy applying the Stern–Volmer method (Table 5). Additionally, for one case (azoalkane **1a**, triethylamine) we measured the fluorescence quenching by time-

resolved fluorescence spectroscopy, which yielded almost the same result (cf. footnote *c* in Table 5). The quenching efficiency differs significantly for the azoalkanes in that the fluorescence of **1a** and **1b** was quenched much better than that of **1c**.

## Discussion

The azoalkanes **1** possess extraordinary long lifetimes for the excited singlet state and display moderate photoreactivities. The direct photolysis of these compounds affords exclusively the expected bicyclo[2.2.0]hexane photoproducts **3**. Irradiation in the presence of amines yields additionally the corresponding hydrazines **2**. The product ratio of hydrazines **2** versus bicyclo[2.2.0]hexanes **3** depends on the photophysical, photochemical, and electrochemical properties of the azo compounds. For example, the ester-substituted derivative **1a**, as long as suitable amines and photolysis conditions are employed, generates exclusively hydrazine **2a** without any trace of the bicyclohexane photoproduct **3a**. Its moderate photoreactivity, long singlet lifetime, and low reduction potential (Table 1) provide azoalkane **1a** with the essential photochemical, photophysical, and electrochemical properties for quantitative hydrazine formation. The endergonic energies for electron transfer cause exciplex formation to become competitive (Scheme 2), an important intermediate during the photoreduction.<sup>4</sup> Furthermore, a low reduction potential favors thermodynamically electron transfer, which may be involved in the photoreductive process, as predicted by the Rehm–Weller equation (see below).<sup>14</sup> In contrast, the formyl-substituted **1b** possesses a shorter lifetime and a higher photoreactivity and the vinyl-substituted **1c** a higher reduction potential than **1a**; consequently, hydrazine formation becomes less efficient with these two azoalkanes.

As for the amine partner, the electron donor, some structural requisites must be fulfilled for photoreduction to take place at all. Of these requisites, most important is that the amine carries  $\alpha$ -hydrogen atoms for effective hydrogen transfer to reduce the azoalkane to its hydrazine. This has been established for the photoreduction of benzophenone<sup>11</sup> and of DBH-type azoalkanes<sup>4</sup> by the use of *tert*-butylamine and diphenylamine. Also in the current study, in the presence of these amines, only the bicyclohexanes **3** were observed as photoproducts during irradiation of the azoalkanes. Diphenylamine quenches the excited singlet state of the azoalkanes very efficiently (Table 2, entries 7, 13, and 20) and, thus, the photochemical conversion drops significantly because the quenching constants  $k_q$  (Table 5, entry 5) are quite high for diphenylamine due to its rather low ionization potential and weak N–H bond.

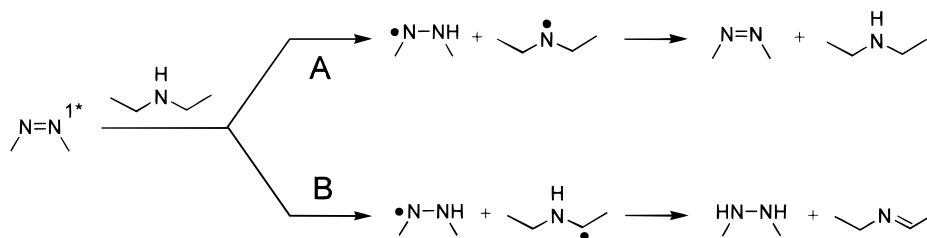
The photoreduction of the azoalkanes **1a–c** is a rather inefficient process, as evidenced by the low quantum yields for hydrazine formation, which are all well below 0.1 (Table 4). These are about 1 order of magnitude lower than for benzophenone,<sup>11</sup> but comparable to those observed during the photoreduction of triplet-excited DBH-type azoalkanes.<sup>4</sup> Efficient quenching of the azoalkane singlet-excited state through the intermediate exciplex is responsible for the ineffective photoreduction. Previous work has established that the low efficiency of the photoreduction of azoalkanes by amines is due to exciplex formation,<sup>4</sup> for which a charge-transfer interaction between the nitrogen lone pair of the amine as the donor and the  $n,\pi^*$ -singlet-excited azoalkane (acceptor) weakens the  $\alpha$ -CH bond of the amine and, thus, facilitates the abstraction of the hydrogen atom.<sup>15</sup> Additional evidence for exciplex formation during the photoreduction is the less efficient fluorescence quenching of

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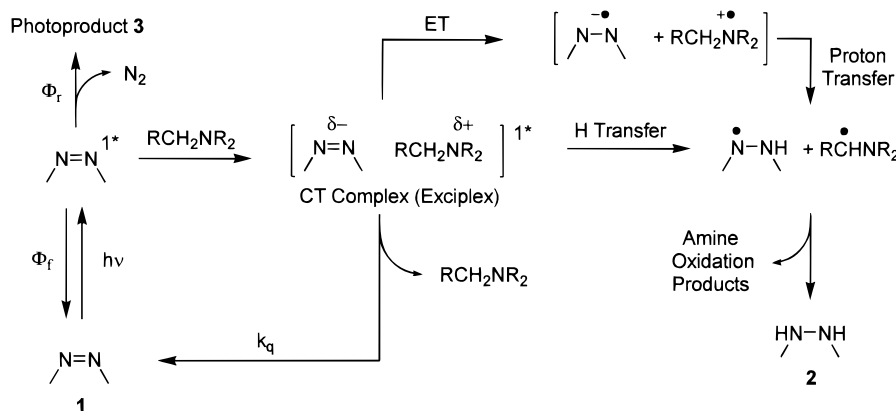
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## Scheme 1



## Scheme 2



azoalkane **1c** compared to **1a** and **1b**. Since the vinyl-substituted **1c** possesses a higher reduction potential (no electron-withdrawing substituents), the charge-transfer interaction between **1c** and the corresponding amine is weaker than that for **1a** and **1b**. However, a quantitative correlation between the quenching constants and the ionization potentials of the amines is not justified, because additionally steric effects come into play.

The efficiency of the hydrazine formation varies significantly with the amine used. The most efficient photoreduction was observed for the primary *n*-butylamine, whereas secondary amines exhibit the lowest efficiencies (Table 4). A similar trend has been observed in the photoreduction of benzoylbenzoic acid by amines in water<sup>11b</sup> and in the photoreduction of the DBH-type azoalkanes.<sup>4</sup> This trend has been rationalized in terms of competitive hydrogen-atom transfer from both  $\alpha$ -CH and NH bonds [the CH-bond dissociation energy of secondary (96 kcal/mol) and tertiary (91 kcal/mol) amines is significantly lower than that of primary amines (103 kcal/mol)],<sup>16,17</sup> which decreases the photoreduction efficiency, as shown for diethylamine in Scheme 1. The hydrogen transfer from the NH bond (Scheme 1, path A) yields an aminyl radical, which undergoes electron back-transfer to the amine, whereas the hydrogen transfer from the  $\alpha$ -CH bond (Scheme 1, path B) forms an  $\alpha$ -amino alkyl radical, which is stabilized by a two-center-three-electron bond with the nitrogen lone pair and, therefore, is oxidized further to the imine.<sup>4</sup> This is analogous to the case of the photoreduction of benzophenone by amines, for which it has been established<sup>16</sup> that the disproportionation of the initially formed ketone-derived hydroxydiphenylmethyl and secondary aminyl radicals to regenerate the ketone and secondary amine by hydrogen back-transfer accounts for the lower efficiency of the photoreduction.

The overall mechanism of the photoreduction is presented in Scheme 2. The question whether the photoreduction operates

**Table 6.** Free Energy  $\Delta G$  of the Electron Transfer Estimated by the Rehm–Weller Equation

entry	quencher	$E_{1/2}^{\text{Ox}}(\text{amine})^a$ [V]	$\Delta G^b$ [eV]		
			<b>1a</b> <sup>c</sup>	<b>1b</b> <sup>d</sup>	<b>1c</b> <sup>e</sup>
1	diethylamine	+1.31	+0.239	+0.0798	+0.580
2	triethylamine	+0.96	-0.110	-0.2670	+0.230
3	diisopropylamine	+1.23	+0.160	0.0	+0.500
4	diphenylamine	+0.84	-0.230	-0.3900	+0.110

<sup>a</sup> Oxidation potential of the amine. <sup>b</sup> Free energy for the electron transfer from the amine to the azoalkane; solvent term (DMF) = -0.06 eV. <sup>c</sup>  $E^{0-0}(\mathbf{1a}) = 3.24$  eV. <sup>d</sup>  $E^{0-0}(\mathbf{1b}) = 3.20$  eV. <sup>e</sup>  $E^{0-0}(\mathbf{1c}) = 3.14$  eV.

through sequential electron and proton transfers or by direct H-atom abstraction from the amine by the excited azoalkane can only be answered speculatively on the basis of the free energies for the electron transfer estimated by the Rehm–Weller equation (Table 6). For all amines, the electron transfer to the excited azoalkane **1c** is endergonic and, thus, it seems likely that direct H-atom transfer dominates in these cases. Nevertheless, the two-step process by sequential electron and proton transfers during the photoreduction of the electron-poor azoalkanes **1a** and **1b** by the electron-rich triethylamine is feasible thermodynamically because the electron transfer is estimated to be sufficiently exergonic (Table 6). For these azoalkanes, electron transfer should definitely occur with the easily oxidized diphenylamine, but for this amine no reduction is observed since it lacks  $\alpha$ -C hydrogen atoms for transfer (Table 2); however, such facile electron transfer would explain the high quenching rate constants ( $k_q$ ) by this amine (Table 5).

In summary, the  $n, \pi^*$ -singlet-excited DBO-type azoalkanes are efficiently reduced by amines to afford hydrazines as photoreduction products. The ratio of hydrazine **2** (reduction) versus bicyclo[2.2.0]hexane **3** (denitrogenation) products may be rationalized in terms of the photophysical, photochemical, and electrochemical properties of the azoalkane. In contrast to benzophenone, the quantum yields of photoreduction are significantly lower, for which efficient deactivation by charge transfer is postulated. The charge transfer promotes hydrogen

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abstraction and the efficiencies generally follow the trend observed for benzophenone. This is similar to the DBH-type azoalkanes, which in contrast to the DBO-type azoalkanes of this study react out of their triplet rather than singlet state. Consequently, the reduction of  $n,\pi^*$ -excited azoalkanes by amines is a general photochemical process for singlet as well triplet states.

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**Supporting Information Available:** Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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