

Charge-Transfer-Induced Photoreduction of Azoalkanes by Amines

Waldemar Adam,^{*,†} Jarugu N. Moorthy,[†] Werner M. Nau,^{‡,§} and J. C. Scaiano^{*,†}

Contribution from the Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, and the Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada

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Abstract: The unique DBH-type azoalkanes **1**, which exhibit high intersystem crossing quantum yields, have made possible the exploration of the bimolecular photoreduction of the n,π^* triplet-excited azo chromophore. In the laser-flash photolysis, amines were found to quench the triplet azoalkane **1a** with high rate constants (k_q ca. $10^8 \text{ M}^{-1} \text{ s}^{-1}$). Steady-state photolysis of the azoalkanes **1a** and **1b** (ϕ_{ISC} ca. 0.5) in the presence of primary, secondary, and tertiary aliphatic amines gave high chemical yields of the corresponding hydrazines **4a** and **4b** in competition with the unimolecular products, namely the housanes **2** and the aziranes **3**. In contrast, the azoalkane **1c** undergoes appreciable photoreduction only in neat amines, while the azoalkane **1d** (ϕ_{ISC} ca. 0.10) is not reduced even under such conditions. Except for *N,N*-dimethylbenzylamine, the amine oxidation products of the azoalkane photoreduction are analogous to those obtained from the reactions of amines with triplet benzophenone. In marked contrast, the absolute quantum yields of photoreduction for azoalkanes **1** are substantially lower (0.01–0.06) than for benzophenone (0.3–1.0). Efficient deactivation of the triplet-excited states by charge-transfer (k_q^{CT}), which competes with hydrogen atom abstraction (k_{H}^{CT}), is postulated to account for the low quantum yields. The efficiencies of photoreduction follow the trend primary \approx tertiary \gg secondary amines observed with benzophenone, for which secondary amines also display the poorest efficiency. Electron transfer to triplet-excited azoalkanes, analogous to benzophenone, is observed for amines with low oxidation potentials. Thus, when triphenylamine ($E_{\text{ox}} = 0.85 \text{ V}$ versus SCE) is used, the formation of its radical cation can be readily detected by laser-flash photolysis.

Introduction

Bicyclic azoalkanes are useful sources of biradicals and even polyradicals.¹ Their photoreactivity is markedly influenced by the geometrical constraints imposed on the azo chromophore through the bicyclic ring skeleton in which the N=N linkage is incorporated. This is dramatically revealed by the two representative homologous bicyclic azoalkanes, namely 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO). In general, whereas the DBH derivatives extrude molecular nitrogen with a very high efficiency (ϕ_{N_2} ca. 1 for the parent DBH),^{1a,2} the DBO derivatives display significantly lower reactivity (ϕ_{N_2} ca. 0.01 for the parent DBO). The latter dissipate their excitation energy predominantly by fluorescence or radiationless deactivation.³ Thus, deazotation, fluorescence, and radiationless deactivation compete efficiently with intersystem crossing (ISC) from the singlet-excited state to the triplet manifold. As a result, the demonstration of bimolecular reactivity of the n,π^* triplet-excited azo chromophore, as has been extensively documented for n,π^* carbonyl triplets, has remained heretofore a formidable task. To date only one bimolecular reaction of triplet-excited azoalkanes, generated by sensitization, has been reported.⁴

The DBH-type azoalkanes **1** (Scheme 1) are unique in that the geometric features intrinsic to the bicyclic skeleton promote efficient ISC and, thus, represent the first examples for which the elusive triplet states have been recently spectroscopically characterized.⁵ For example, the cyclic azoalkane **1a** undergoes efficient intersystem crossing to the triplet state with ϕ_{ISC} ca. 0.5, whose lifetime has been determined from laser-flash spectroscopic studies to be 0.63 μs . Therefore, the azoalkanes **1** offer at last the opportunity to explore the bimolecular reactivity of the n,π^* triplet-excited azo chromophore. Comparison with the established n,π^* triplet photochemistry of the carbonyl chromophore would enhance our knowledge of the triplet-state reactivity.

The photoreduction of ketones by amines has attracted considerable mechanistic interest.⁶ Subsequent to the seminal investigations by Cohen and co-workers, a comprehensive picture on the dynamics of ketone photoreduction was provided by Peters et al. through laser-flash photolysis studies.⁷ Accordingly, electron transfer from the amine to the benzophenone

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[†] Universität Würzburg.

[‡] University of Ottawa.

[§] Present address: Institute of Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

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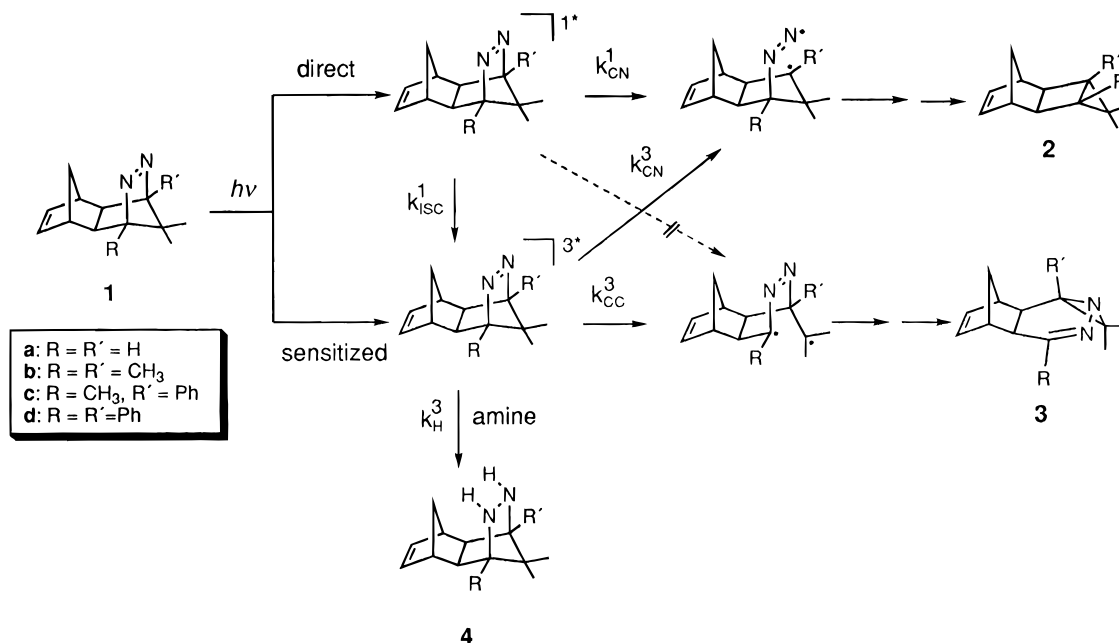
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Scheme 1



triplet forms the radical anion and amine radical cation as a triplet contact ion pair (CIP). The latter may subsequently undergo solvation to the solvent-separated ion radical pair (SSIP) and proton transfer to form the neutral radicals or ISC followed by electron back-transfer to regenerate the starting materials.

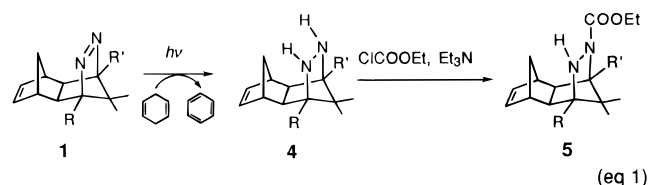
Fluorescence quenching of DBO and of a DBH derivative by amines is precedented.⁸ In a preliminary study⁹ we have found that the triplet absorption of the azoalkane **1a**, in analogy to that of ketones, is quenched by a variety of amines with relatively high rate constants. In view of the high rate constants with which amines quench the triplet state of the azoalkane **1a**, we were motivated to examine if these triplet states undergo, in analogy to the ketones, bimolecular photoreduction in the presence of amines.⁹ We herein demonstrate that amine quenching of the azoalkanes **1** affords efficiently the corresponding hydrazines, in competition to deazation. The mechanism of photoreduction and the relative efficiencies for primary, secondary, and tertiary amines are contrasted with those of the extensively investigated prototypal carbonyl chromophore, namely benzophenone.

Results

Photoreduction by Amines. The photochemistry of the azoalkanes **1** has been reported previously.^{5a,b} Whereas the direct photoexcitation of these azoalkanes gave a mixture of housanes **2** and aziranes **3** (CN and CC bond cleavage products, Scheme 1), the housanes **2** were exclusively formed in the photolysis of the azoalkanes **1c** and **1d**. The sensitized photolysis has been reported to afford exclusively the aziranes **3**.^{5a,b}

Photoexcitation of the nitrogen-purged solutions of the azoalkanes **1a–c** (ca. 0.1 M) and amines (0.5–1.0 M) led to hydrazines **4** together with the unimolecular products **2** and **3**, as monitored by ¹H NMR spectroscopy (Scheme 1). The identity of the hydrazoalkanes **4** was established by comparison

of the characteristic ¹H NMR signals with those observed upon photolysis of azoalkanes **1a–c** in the presence of an efficient hydrogen donor such as 1,4-cyclohexadiene. The photolysis of azoalkanes **1** in 1,4-cyclohexadiene afforded quantitatively the hydrazoalkanes **4**, which for isolation and characterization were trapped as the derivatives **5** (eq 1) by treatment with ethyl



chloroformate and triethylamine. Furthermore, exposure of the photolysates to air over a period of 2–3 days regenerated the azoalkanes **1** by oxidation of the hydrazines **4**, as monitored by ¹H NMR analysis.¹⁰ The product distributions for the photolysis of the azoalkanes **1** in the presence of a variety of amines are summarized in Table 1.

The azoalkanes **1a** and **1b** afforded the hydrazines **4a** and **4b** in moderate to high yields when photolyzed in the presence of primary, secondary, and tertiary amines (Table 1). In contrast, at similar amine concentrations (up to 1.0 M), the azoalkane **1c** produced the hydrazine **4c** only in low yields (<10%, data not shown); however, photolysis in neat amines resulted in much higher yields of the hydrazine (entries 26–28). Similarly, a substantial enhancement in the hydrazine yields was found when azoalkane **1b** was photolyzed in neat amines (entries 13, 17, and 23). The azoalkane **1d** gave the housane **2d** exclusively even at high concentrations of the amines (entries 29–31). The poor solubility of azoalkane **1d** precluded its photolysis in neat amines. Most significantly, *tert*-butylamine and diphenylamine were found to be ineffective in the photoreduction of azoalkanes **1a** and **1b** (entries 3, 6, 15, and 19). It is noteworthy that no coupling products between the azoalkanes and amines were observed.

Oxidation Products of the Amines. ¹H NMR analysis of the photolysates derived from the azoalkanes **1a** and **1b** with

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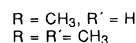
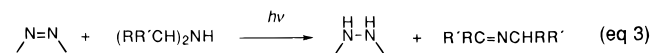
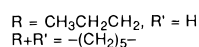
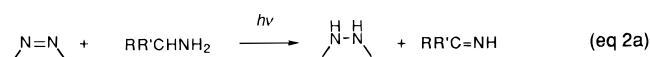
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Table 1. Product Studies^a for the Photolysis of Azoalkanes **1** in the Presence of Amines

entry	azo	amine	concn (M)	solvent	conversion (%)	mass balance (%)	product distribution ^b		
							2 + 3	4	
1	1a	<i>n</i> -butylamine	1.0	C ₆ D ₆	71	90	29	71	
2		cyclohexylamine	0.9	C ₆ D ₆	72	95	37	63	
3		<i>tert</i> -butylamine	1.0	C ₆ D ₆	100	90	100		
4		diethylamine	1.0	C ₆ D ₆	76	94	20	80	
5		diisopropylamine	0.7	C ₆ D ₆	66	90	38	62	
6		diphenylamine	0.3	CD ₃ CN	25	95	100		
7		triethylamine	0.6	C ₆ D ₆	76	60	40	60	
8			0.6	CD ₃ CN	73	80	33	67	
9			0.6	CD ₃ OD	97	75	34	66	
10			Me ₂ NCH ₂ Ph	0.6	C ₆ D ₆	89	90	18	82
11				0.6	CD ₃ CN	100	90	11	89
12	1b	<i>n</i> -butylamine	1.0	C ₆ D ₆	88	93	62	38	
13			10.1	neat	84	90	10	90	
14		cyclohexylamine	0.9	C ₆ D ₆	95	90	55	45	
15		<i>tert</i> -butylamine	1.0	C ₆ D ₆	100	90	100		
16		diethylamine	1.0	C ₆ D ₆	94	95	28	72	
17			9.6	neat	76	90	10	90	
18		diisopropylamine	0.7	C ₆ D ₆	82	90	45	55	
19		diphenylamine	0.3	CD ₃ CN	40	95	100		
20		triethylamine	0.6	C ₆ D ₆	95	75	61	39	
21			0.6	CD ₃ CN	87	90	41	59	
22			0.6	CD ₃ OD	99	89	39	61	
23			7.2	neat	84	90	10	90	
24			Me ₂ NCH ₂ Ph	0.6	C ₆ D ₆	83	90	30	70
25				0.6	CD ₃ CN	80	90	28	72
26	1c	<i>n</i> -butylamine	10.1	neat	100	>90	50	50	
27		diethylamine	9.7	neat	100	>90	25	75	
28		triethylamine	7.2	neat	100	>90	31	69	
29	1d	<i>n</i> -butylamine	7.0	C ₆ H ₆	100	90	100		
30		diethylamine	7.0	C ₆ H ₆	100	90	100		
31		triethylamine	5.0	C ₆ H ₆	100	>90	100		

^a A ca. 0.1 M solution of the azoalkane **1** was irradiated ($\lambda = 350$ nm) in the Rayonet photoreactor at 8 °C for 15 h, except for entries 4 and 15 (ca. 40–44 h). ^b Analysis by ¹H NMR spectroscopy; relative yields are normalized to 100%, error limit $\pm 6\%$ of the stated values.

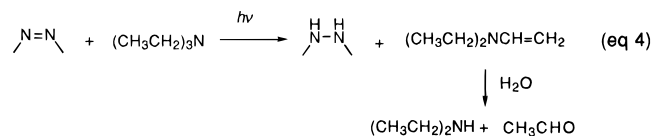
primary and secondary amines revealed that the oxidation products were similar to those formed in the photoreduction of benzophenone by amines,^{6a,11} as confirmed by comparison with the authentic materials. The stoichiometry of the photoreductions (eqs 2 and 3) were deduced from the relative areas of the



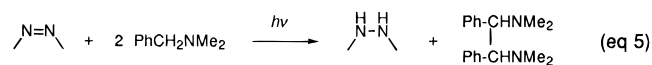
characteristic NMR signals of the hydrazoalkanes **4** and the oxidation products of the primary and secondary amines. Accordingly, two molecules of the primary amine are consumed to produce one molecule of the hydrazine and one molecule of the imine, while for secondary amines, only one molecule of the amine leads to one molecule of the hydrazine and the imine.

The oxidation products derived from the photolysis of azoalkanes **1a** and **1b** in the presence of triethylamine were more complex than for the primary and secondary amines. GC analysis of the photolysates indicated diethylamine (60% relative to the yield of the hydrazine), which presumably is formed from

the hydrolysis of the enamine (eq 4) by adventitious water.



Because of the volatile nature of diethylamine, the measured yields constitute a lower limit. The photolysis in the presence of *N,N*-dimethylbenzylamine (Table 1) yielded the dimers as the sole products according to the stoichiometry in eq 5, as de-



duced from ¹H NMR analysis. Thus, the pathway for the formation of hydrazine appears to be the disproportionation of the intermediate hydrazinyl radicals, while the corresponding (*N,N*-dimethylamino)benzyl radicals undergo dimerization (cf. Discussion). It is noteworthy in this context that aminobenzyl radicals undergo such dimerization in the photoreduction of aryl imines.¹²

Quantum Yields and Relative Efficiencies. The determination of quantum yields was accomplished by isolating the 333-nm line of the argon-ion laser and by employing 2,3-diazabicyclo[2.2.1]heptane (DBH) as an actinometer, whose decomposition quantum yield has been reported to be unity.¹³ The products were quantified by GC analysis with diphenyl ether as an internal standard. The GC response factors for the hydrazines were determined by combined ¹H NMR and GC analyses. To assess the relative order in the efficiency with which the amines (primary, secondary, and tertiary) reduce the

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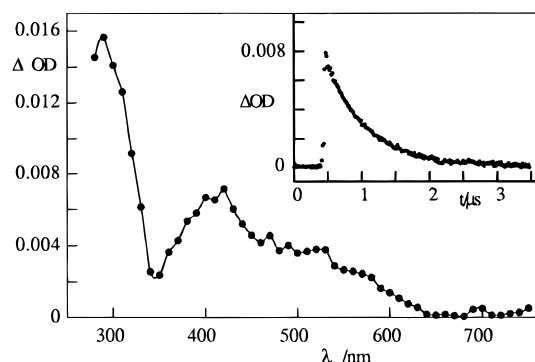
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Table 2. Quantum Yields^a for the Photolysis of Azoalkane **1b** (0.05 M) in the Presence of Various Hydrogen Donors^b

hydrogen donor	ϕ_r^c	$\phi(2b)^d$	$\phi(4b)^e$
none	0.550	0.039	
<i>n</i> -butylamine	0.070	0.031	0.037
cyclohexylamine	0.090	0.034	0.049
diethylamine	0.020	0.008	0.011
diisopropylamine	0.037	0.018	0.026
triethylamine	0.070	0.023	0.040 (0.46) ^f
Me ₂ NCH ₂ Ph	0.089	0.029	0.063

^a At 333 nm in benzene; GC analysis, error $\pm 10\%$, conversion 5–20%. ^b The concentration was 1.0 M. ^c Quantum yields for azoalkane disappearance. ^d Quantum yield for **2b** formation. ^e Quantum yield for hydrazine **4b** formation. ^f Value in parentheses refers to acetonitrile.

**Figure 1.** Transient absorption spectrum of the triplet-excited azoalkane **1a** obtained upon laser-flash photolysis in benzene and a representative decay trace recorded at 450 nm (inset).**Table 3.** Quenching Rate Constants (k_q)^a for Triplet Azoalkane **1a**

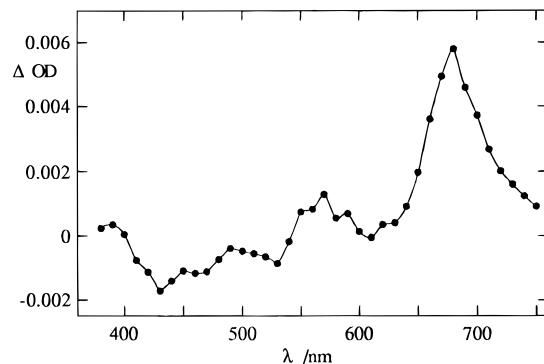
amine	$E_{1/2}$ (ox) (versus SCE) ^b	k_q ($10^8 \text{ M}^{-1} \text{ s}^{-1}$)
triethylamine	0.96	1.5
diphenylamine	0.84	13
triphenylamine	0.85	6.6
1,1-dimethylhydrazine		14

^a Determined by laser-flash photolysis ($\lambda_{exc} = 355 \text{ nm}$) by using the triplet absorption of the azoalkane **1a** in benzene, error $\pm 15\%$. ^b In acetonitrile from ref 22.

azoalkanes, quantum yields for the hydrazine **4b** formation from the azoalkane **1b** were determined at 1 M amine concentration. At this amine concentration, >95% of the azoalkane triplets are quenched since the triplet lifetime of azoalkane **1b** is 440 ns^{5c} and a quenching rate constant of the order of $10^8 \text{ M}^{-1} \text{ s}^{-1}$ applies. In Table 2 are summarized the results for the quantum yields of azoalkane decomposition (ϕ_r), housane **2b** formation [$\phi(2b)$], and the hydrazine **4b** formation [$\phi(4b)$]. The relative efficiencies of the amines to photoreduce the triplet azoalkanes follows the order primary \approx tertiary \gg secondary. Thus, the poorest efficiency is displayed by secondary amines (Table 2).

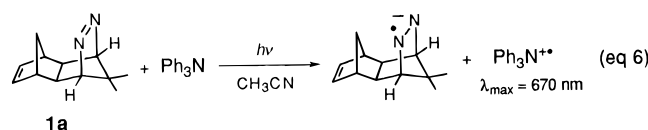
Rate Constants for Amine Quenching. The T–T absorption of azoalkane **1a** in benzene shows one maximum in the UV region at ca. 300 nm and a second one in the visible region at ca. 420 nm (Figure 1). The slight shift of the absorption maxima as compared to the previously reported data^{5c} is supposedly due to different spectral recording techniques. The transient triplet lifetimes were obtained by single-exponential fitting to the decay traces, typically recorded at 450 nm (Figure 1).

The triplet lifetimes of azoalkane **1a** or its C=C hydrogenated derivative were plotted ($\tau_0/\tau = 1 + k_q\tau_0[\text{amine}]$) versus the amine concentration (typically five data points) to obtain the bimolecular quenching constants (Table 3). The quenching rate constant for 1,1-dimethylhydrazine, a model for the hydrazine photoproducts **4**, was also determined for comparison. The large

**Figure 2.** Difference transient absorption spectrum of azoalkane **1a** in the presence of triphenylamine (ca. 1.5 mM) in benzene obtained by subtraction of the transient absorption spectra at 1.0- and 0.2- μs time delay.

error (15–30%) in the rate data is due to a number of limitations, which comprise low signal intensity of the visible absorption ($\Delta OD^{450} \approx 0.01$), absorption of the additives in the monitored spectral region (at ca. 300 nm), photochemistry of the aromatic amines upon 355-nm irradiation, and the formation of additional (transient) photoproducts. Hence, the rate data could only be obtained from changes of the weak absorption in the visible region, since photoproducts interfered in the relevant UV region (supposedly aminoalkyl and hydrazinyl radicals). The experimental problems encountered during the determination of the quenching rate constants of the amines discouraged the examination of a more comprehensive set of amines, because the variations in the rate constants for different amines were likely to be smaller than the experimental error. In some cases, the influence of the solvent was examined, e.g., in benzene, carbon tetrachloride, methylene chloride, and acetonitrile, but the differences were within the rather large experimental error.

Laser-flash photolysis of a solution of azoalkane **1a** in benzene or acetonitrile in the presence of triphenylamine (ca. 1.5 mM) produced a time-resolved growth at ca. 670 nm, assigned to the triphenylamine radical cation,¹⁴ which was accompanied by a concomitant decay in the absorption of **31a**. In such case, the spectra of the growing and decaying transient can be readily extracted by recording the transient absorption spectra at two different delay times (e.g., at 0.2 and 1.0 μs) and subsequent spectral subtraction. This procedure afforded the difference spectrum in Figure 2, in which negative ΔOD values belong to the decaying transient and positive ones indicate a transient growth (note that the spectral region below 550 nm represents virtually the mirror image of the **31a** absorption in the absence of amine, cf. Figure 1). The assignment of the growth to the amine radical cation was based on the comparison with its formation in the photolysis of benzophenone in the presence of triphenylamine.¹⁴ This provides evidence that at least a fraction of **31a** undergoes electron transfer (eq 6).



Discussion

The azoalkanes **1** represent a unique category of azo compounds in which intersystem crossing from the n, π^* singlet-excited state competes efficiently with α C–N bond cleavage (k_{CN}^1 , Scheme 1). Some of the relevant photophysical para-

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Table 4. Photophysical Parameters for Azoalkanes **1**^a

azoalkane	ϕ_{ISC}^b	${}^3\tau$ (ns) ^c	ϕ_f^d	E_T^e (kcal/mol)
1a	0.5	630 ± 20	0.59	62.2
1b	0.5	440 ± 20	0.60	61.5
1c		≤440 ± 40 ^f		
1d	0.1	200 ± 10	0.88	61.6

^a Reference 5c. ^b Quantum yield for intersystem crossing in benzene. ^c Triplet lifetimes. ^d Quantum yield for azoalkane disappearance, error ±10%, except for **1a** (5%). ^e Triplet energy, ±0.1 kcal mol⁻¹. ^f This work in benzene ($\lambda_{exc} = 351$ nm); the value constitutes an upper limit since it cannot be decided whether the observed transient ($\lambda_{mon} = 315$ nm) is the triplet azoalkane or the triplet biradical derived therefrom (cf. ref 5c).

eters of the azoalkanes **1** are given in Table 4. The direct photolysis of azoalkanes **1a** and **1b** affords not only the expected housanes **2a** and **2b** but also the aziranes **3a** and **3b** derived from β C–C bond cleavage (k_{CC}^3).^{5a,b} From triplet-quenching experiments with piperylene, the intersystem-crossing quantum yields for the azoalkanes **1a** and **1b** have been estimated to be as high as 0.5.^{5a,c} Furthermore, from the temperature dependence of the photoproduct distribution, the activation energies for α C–N bond cleavage from the singlet state (k_{CN}^1) and α C–N (k_{CN}^3) and β C–C (k_{CC}^3) bond cleavages from the triplet state have been estimated^{5b} for the parent azoalkane **1a** as ${}^1E_\alpha > 3.2$, ${}^3E_\alpha > 10.5$ and ${}^3E_\beta > 7.8$ kcal mol⁻¹. Particularly noteworthy is the influence of incipient radical stabilization: the better the carbon radical site in the intermediate diazenyl biradical is stabilized, i.e., Ph (**1c** and **1d**) \gg Me (**1b**) $>$ H (**1a**), the more α C–N cleavage to the housane occurs. Thus, the phenyl substitution in **1c** and **1d** is so effective that denitrogenation from the singlet-excited state dominates with marginal ISC to the triplet manifold (ϕ_{ISC} ca. 0.10).^{5c} Furthermore, the influence of the radical-stabilizing ability of the substituents is also reflected in the triplet lifetimes (Table 4), which follow the order **1a** (630 ns) $>$ **1b** (440 ns) \geq **1c** (≤ 440 ns) $>$ **1d** (200 ns). A manifestation of these two factors, namely shortened triplet lifetimes and lower ISC quantum yields, is clearly revealed in the results of photoreduction by the amines collected in Table 1. Whereas the photolysis of azoalkanes **1a** and **1b** at moderate concentrations of amines affords high yields of the hydrazines **4a** and **4b** (Table 1), that of **1c** leads to major amounts of the hydrazine **4c** only in neat amines (entries 26–28). The azoalkane **1d** undergoes no photoreduction at all, even at high concentrations of amines (entries 29–31).

Strong evidence has been brought forward in our preliminary study⁹ that the triplet states of azoalkanes **1** are responsible for the observed photoreduction. For example, the fact that only azoalkanes with high quantum yields of intersystem crossing (ϕ_{ISC} ca. 0.5, Table 4) undergo photoreduction implies that the observed bimolecular photochemistry results from relatively long-lived (${}^3\tau$ ca. 0.5 μ s) triplet states. Early fluorescence measurements^{8c} by Ramamurthy and Turro have shown that the singlet-excited azoalkanes (also of DBH-type) are also quenched by aliphatic amines with rate constants as high as 10⁸ M⁻¹ s⁻¹, and since the singlet lifetimes of azoalkanes **1a** and **1b** are relatively long (${}^1\tau$ ca. 2–3 ns),^{5c} bimolecular quenching of the azoalkane singlet states is expected (<20%) at the typically employed preparative concentrations of the amines (0.5–1.0 M). Hence, contributions due to singlet quenching cannot be entirely ruled out in the preparative experiments, in particular in neat amines as solvents. The efficiency for singlet photoreduction must be low, however, since the previous fluorescence quenching studies did not lead to bimolecular photoproducts with the amines.^{8c} Regardless of the possible involvement of singlet quenching, it should be noted that our data can be satisfactorily rationalized by triplet photoreduction and that the

basic aspects of our mechanistic interpretation are independent of spin multiplicity.

The photoreduction of azoalkanes **1a–c** may, in principle, occur by a mechanism which involves direct hydrogen atom abstraction from the α carbon atoms of the amines. This mechanism, however, cannot be reconciled for the following two reasons: Firstly, despite rather comparable bond dissociation energies for the α C–H bonds of amines (e.g., 94, 87 and 84 kcal mol⁻¹ for H₂NCH₂–H, MeNHCH₂–H, and Me₂NCH₂–H)^{16a} and a typical hydrogen donor such as 2-propanol (88 kcal mol⁻¹),^{16b} the rate constants for quenching of triplet azoalkane **1a** by amines, e.g., triethylamine ($k_q = 1.5 \times 10^8$ M⁻¹ s⁻¹, Table 3), are 2 orders of magnitude higher than for 2-propanol ($k_q = 6.4 \times 10^5$ M⁻¹ s⁻¹).¹⁵ This is in contrast to what would be expected from the dependence of the rate of hydrogen abstraction based on bond dissociation energies.¹⁷ Secondly, the quantum yield for decomposition of azoalkane **1b** in pure benzene is 0.55 (Table 2), while that in the presence of 1.0 M amines decreases to typically ca. 0.08, which points to substantial deactivation of the excited states.

A perusal of the results of laser-flash photolysis experiments in Table 3 shows that the quenching rate constants determined for the triplet azoalkane **1a**, a representative case, are relatively high. Furthermore, the dependence of quenching rate constants on the oxidation potentials of the amines, e.g., the rate constant for diphenylamine is 1 order of magnitude higher than for triethylamine, clearly suggests the importance of charge-transfer interactions. It should be noted that the fluorescence quenching of DBO^{8a,b} by olefins and of a DBH derivative by olefins and amines^{8c} has also been interpreted in terms of charge transfer.

To rationalize the results of the bimolecular photochemistry in Table 1, let us consider the various mechanistic pathways in Scheme 2 to produce the primary hydrazinyl radical, for which on the basis of the aforementioned we propose that n, π^* triplet-excited states serve as the precursors. The initial interaction of the triplet azoalkanes **1** with the ground state amines may lead either (i) to a *partial charge transfer* (k_q^3) complex (or exciplex) or (ii) to *electron transfer* (k_{ET}^3) to produce the radical ion pair; in polar solvents, the latter may also be formed by ionic dissociation of the *polar charge transfer* (k_{CT}^3) complex.¹⁸ Hydrogen atom transfer within the *charge-transfer* complex would generate the hydrazinyl radical (k_H^{CT}); alternatively, the latter may be produced by proton transfer from the amine radical cation to the radical anion of the azoalkane (k_H^{ET}). Which of these two pathways prevails should be governed by the redox properties of the donor/acceptor pair and the polarity of the medium.

From the known excitation energies and redox potentials of the donor/acceptor pair, the thermodynamic feasibility of electron transfer may be predicted by the Rehm–Weller equation,¹⁹ $\Delta G_{el} = 23.06[E_{ox} - E_{red} - e_0^2/a\epsilon] - E_T$. Although the triplet energies of azoalkanes **1a** and **1b** are fortunately available from a previous study,^{5c} the irreversible electrochemical reduction of the azoalkanes **1a–d** (estimated in the range –2.4 to –2.7 V *versus* SCE in acetonitrile)²⁰ makes a prediction

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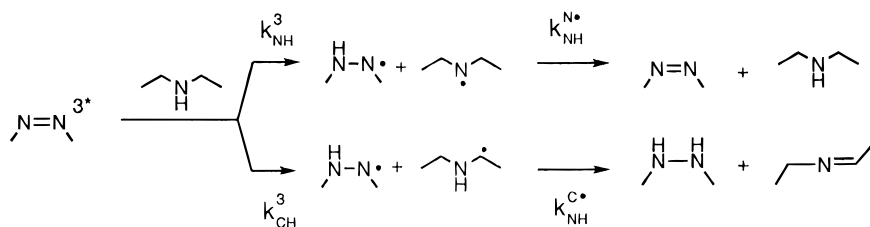
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Scheme 3



(k_q^3) and provides evidence against the electron-transfer-mediated processes (k_{ET}^3) in Scheme 2. Thus, for azoalkanes **1a** and **1b**, a change from benzene (Table 1, entries 7, 10, 20, and 24) to acetonitrile (entries 8, 11, 21, and 25) or methanol (entries 9 and 22) causes only a marginal enhancement of the yields of hydrazines. Also, the quenching rate constants in the polar acetonitrile (data not shown), assessed through laser-flash photolysis, were found to be comparable within an experimental error of 15% to the values determined for the nonpolar benzene (Table 3). In regard to the solvent effects, the high yields of hydrazines from the photolysis in neat amines are a puzzle (Table 1, entries 13, 17, and 23). The amine medium may promote more efficient hydrogen atom transfer in the charge-transfer complex, but the reasons for this are not evident as yet.

The unfavorable energetics for electron transfer (k_{ET}^3 , Scheme 2) from the aliphatic amines to the azoalkanes **1a-c** is remedied by triphenylamine as a better donor, as evidenced by the fact that the corresponding radical cation is readily detected in the laser-flash photolysis of azoalkane **1a** (eq 6). Hence, an oxidation potential corresponding to that of triphenylamine (0.85 V *versus* SCE in acetonitrile)²² constitutes a higher limit, equal to or below which the free energy change is negative and the electron transfer is favored. For such amines the charge-transfer complex (or triplet exciplex) may undergo dissociation (k_{ET}^{CT}) to the radical ion pair, which may also be formed directly (k_{ET}^3) as in the case of the benzophenone/amine system.

Let us now consider the relative reactivity with which the charge-transfer complex (k_q^3) for primary, secondary, and tertiary aliphatic amines undergoes hydrogen atom transfer. With the quenching rate constants of the order of $10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Table 3), one calculates that >95% of the triplets are quenched by the aliphatic amines at 1.0 M concentration. Thus, from the quantum yields of photoreduction in Table 3 for the azoalkane **1b**, a representative case, in the presence of a variety of amines (1.0 M), we note that the photoreduction efficiencies [$\phi(\mathbf{4b})$ ca. 0.01–0.06, Table 2] are substantially lower as compared to those for benzophenone (ϕ ca. 0.30–1.00).^{6b} Furthermore, a definite trend in the efficiencies of hydrazine formation [$\phi(\mathbf{4b})$] for primary, secondary, and tertiary amines is evident in Table 2. Thus, the primary and tertiary amines display comparable efficiencies of photoreduction, while those for secondary amines are definitely lower.

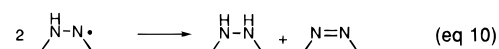
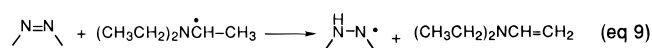
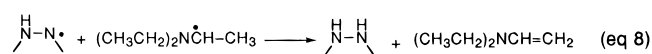
A similar trend in the photoreduction has been reported for benzoylbenzoic acid by amines in water as the medium.^{11a} It has been found from laser-flash photolysis studies that the photoreduction of benzophenone by secondary amines leads to hydroxydiphenylmethyl radicals with unit efficiency;^{6b} however, the overall steady-state quantum yields of photoreduction are significantly lower when compared to those for primary and tertiary amines. The lower efficiency of photoreduction of benzophenone for secondary amines has been rationalized in terms of the possibility of competitive hydrogen atom transfer from both α C–H and N–H bonds. In view of the difference

in N–H bond dissociation energies of secondary and primary amines (96 *versus* 103 kcal mol⁻¹),^{6b} a larger proportion of transfer of the hydrogen atom from the N–H bond to produce aminyl radicals has been proposed to take place in secondary *versus* primary amines.²⁸ Subsequent disproportionation of the ketone-derived hydroxydiphenylmethyl and secondary aminyl radicals to regenerate the ketone and the secondary amine by hydrogen back-transfer has been advanced as the reason for the observed lower efficiency of photoreduction.

Similar mechanistic considerations as those above for benzophenone may explain the lower efficiency of reduction of the triplet azoalkane **1b** by secondary amines, except that the mechanism involves a partial charge (k_q^3) rather than electron transfer (k_{ET}^3) in Scheme 2. Thus, the reaction of triplet azoalkanes with secondary amines may result in hydrazinyl and alkylaminyl radicals (k_{NH}^3 , Scheme 3) as well as α -aminoalkyl radicals (k_{CH}^3), the latter formed by the transfer of a hydrogen atom from the α carbon atom of the secondary amine. Whereas the α -aminoalkyl radicals react further to the hydrazine and imine ($k_{NH}^{C\bullet}$), hydrogen back-transfer from the hydrazinyl radical ($k_{NH}^{N\bullet}$) to the aminyl radical regenerates the azoalkane and amine, which lowers the efficiency of photoreduction. Besides this relative order of efficiencies for the photoreduction of the triplet azoalkanes by amines, i.e., tertiary \approx primary > secondary, one recognizes from Table 2 that the efficiency of photoreduction is higher for diisopropylamine as compared to that for diethylamine. Presumably, this results from a lower bond dissociation energy of the α C–H bond in the isopropyl *versus* ethyl substituents.

As mentioned previously, the N–H bond dissociation energy of the primary amines is substantially higher as compared to that of the secondary amines. In view of this, the transfer of a hydrogen atom from N–H bond of the primary amines to the triplet-excited azoalkanes does not seem feasible. This is underscored by the lack of photoreduction in the presence of amines that do not contain α C–H bonds, namely *tert*-butylamine and diphenylamine (Table 1).

Finally, the formation of the hydrazine product from the hydrazinyl radical in Scheme 2 may occur by the pathways depicted in eqs 8–10. The first pathway (eq 8) involves



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(28) The higher kinetic acidity for N–H versus α C–H deprotonation has been borne out also in the photoreactions between cyanoarenes and secondary amines; cf. ref 26.

hydrogen transfer from the α -aminoalkyl radical, e.g., derived from trialkylamines such as triethylamine, to the hydrazinyl radical to produce the hydrazine and the enamine (eq 4). The reduction by primary and secondary amines presumably follows the same pathway (eq 8), except that the second hydrogen atom is transferred from the N–H bond of the α -aminoalkyl radical to produce imines (eqs 2 and 3). Alternatively, the α -aminoalkyl radical may reduce the ground-state azoalkane to produce the hydrazinyl radical and the enamine (eq 9). The latter reaction pathway must contribute to photoreduction, since it is well established that hydroxydiphenylmethyl radicals, which in fact are less potent reducing agents ($E_{\text{ox}} = -0.7$ V versus SCE)³⁰ than α -aminoalkyl radicals (E_{ox} ca. -1.0 V versus SCE),^{16a,29} are known to reduce azoalkanes efficiently.^{30b}

In the second pathway (eq 10), the disproportionation of two hydrazinyl radicals affords one molecule of the azoalkane and one molecule of the hydrazine. Indeed, such a disproportionation of hydrazinyl radicals has been well established in the literature.³¹ This case applies for the photoreduction of azoalkanes **1a** and **1b** by *N,N*-dimethylbenzylamine (eq 5), because the intermediary α -(dimethylamino)benzyl radical has no α hydrogen atoms available and, thus, couples to form the dehydro dimers of the amine.

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In summary, similar to benzophenone, the n,π^* excited azoalkanes are efficiently quenched by amines to afford hydrazines as photoreduction products. Electron transfer to azoalkanes by amines with low oxidation potentials, e.g., triphenylamine (E_{ox} ca. 0.85 V versus SCE), to produce radical ion pairs is analogous to the photoreduction of benzophenone by amines. In marked contrast to benzophenone, however, the quantum yields of photoreduction of azoalkanes are significantly lower for amines with higher oxidation potential, for which efficient deactivation by charge transfer is postulated. Besides deactivation of the triplet-excited azoalkanes, charge transfer also promotes hydrogen atom abstraction and the efficiencies follow the trend observed for benzophenone, e.g., secondary amines display the poorest efficiency despite efficient quenching. These new results encourage further exploration of the bimolecular photochemistry of azoalkanes.

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Supporting Information Available: Experimental data (6 pages). See any current masthead page for ordering and Internet access instructions.

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