

Solvent Effect on Product Distribution in Photochemical Pathways of α C–N versus β C–C Cleavage of n,π^* Triplet-Excited Azoalkanes

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Abstract: The product distribution in the photolysis of the triplet-excited azoalkanes **1a,b** depends markedly on the type of solvent used; in contrast, the azoalkanes **1c,d**, which undergo efficient deazation from the singlet-excited state, display solvent-independent photobehavior. Thus, the aziranes **3** are produced essentially exclusively in polar protic solvents, while the housanes **2** predominate in nonpolar ones. The excellent correlation ($r^2 = 0.963$, seven solvents) of the azirane **3b** yield with Gutmann's AN solvent parameter reveals that a combination of solvent properties such as the polarity and polarizability of the medium and the hydrogen-bonding ability is decisive for the photoproduct distribution. That the observed solvent dependence derives from bulk medium effects is borne out by the similar product distribution for the hydroxy-substituted derivative **1f** to that for the azoalkane **1b** in benzene, i.e., the intramolecular hydroxy functionality in the azoalkane **1f** is ineffective in influencing the photochemistry of the triplet azo chromophore. Selective formation of the aziranes **3** from the triplet-excited azoalkanes **1** in the polar protic solvents is rationalized in terms of solvent stabilization of the more polar transition state for β cleavage (azirane **3**) over that for the α scission (housane **2**). In marked contrast to the appreciable deuterium isotope effect for quenching of the singlet-excited azoalkanes by protic solvents, the lifetimes (laser-flash photolysis) and reactivity (product analysis) of the triplet azoalkanes are not affected by deuterium substitution.

Introduction

Solvents play an important role in determining the fate of the electronically excited molecules. In addition to chemical interactions, the solvent can promote radiationless deactivation of singlet-excited states,¹ it can accelerate intersystem crossing,² and it can cause the so-called state switching,³ i.e., the reversal of the n,π^* and π,π^* excited-state configurations.

The investigation of the photophysical properties of cyclic azoalkanes has demonstrated that the fluorescence of cyclic azoalkanes is efficiently quenched by certain solvents like methanol and chloroform.^{4,5} Reversible proton transfer⁴ or, more recently, covalent hydrogen-bonding interactions⁵ have been held responsible for this efficient quenching of singlet-excited azoalkanes. Despite these detailed investigations of solvent effects on the fluorescent properties of azoalkanes, surprisingly little has been reported on the solvent influence of the photochemical product distribution.⁶ In contrast, the solvent-dependent thermal decomposition and isomerization of azoalkanes is well documented.⁷

Azoalkanes **1** are unique in that not only do they constitute the first examples in which the triplet states have been directly characterized⁸ but they also lead to the housanes **2** (k_{CN}^3) as well as the aziranes **3** (k_{CC}^3) upon direct photoexcitation; quenching experiments have established that the latter derive exclusively from the triplet manifold (Scheme 1).⁸ Herein, we report significant solvent effects on the triplet lifetimes and photochemistry of the azoalkanes **1** (Scheme 1), from which we conclude that a combination of medium effects (polarity, polarizability, and hydrogen-bonding ability) may be decisive in controlling photochemical product formation. Indeed, the respective photoproducts **2** and **3** may be selectively formed by appropriate selection of the solvent.

Most striking, an enhancement of azirane **3** formation was observed in polar protic solvents, which suggests that part of this photoproduct might be formed through the acid–base photoreaction (proton abstraction) in Scheme 2. However, the product distribution of the azoalkane **1f**, which contains a hydroxy functionality capable of interacting intramolecularly with the n,π^* -excited azo chromophore, was virtually the same as for the derivative **1b** without the hydroxy group in nonpolar solvents. Thus, proton transfer is no common denominator for the observed solvent effects.

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(1) (a) Herbich, J.; Hung, C.-Y.; Thummel, R. P.; Waluk, J. *J. Am. Chem. Soc.* **1996**, *118*, 3508. (b) Houten, J. V.; Watts, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 3843.

(2) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978; p 125.

(3) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.

(4) (a) Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122. (b) Ramamurthy, V.; Turro, N. J. *Ind. J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1978**, *18*, 72.

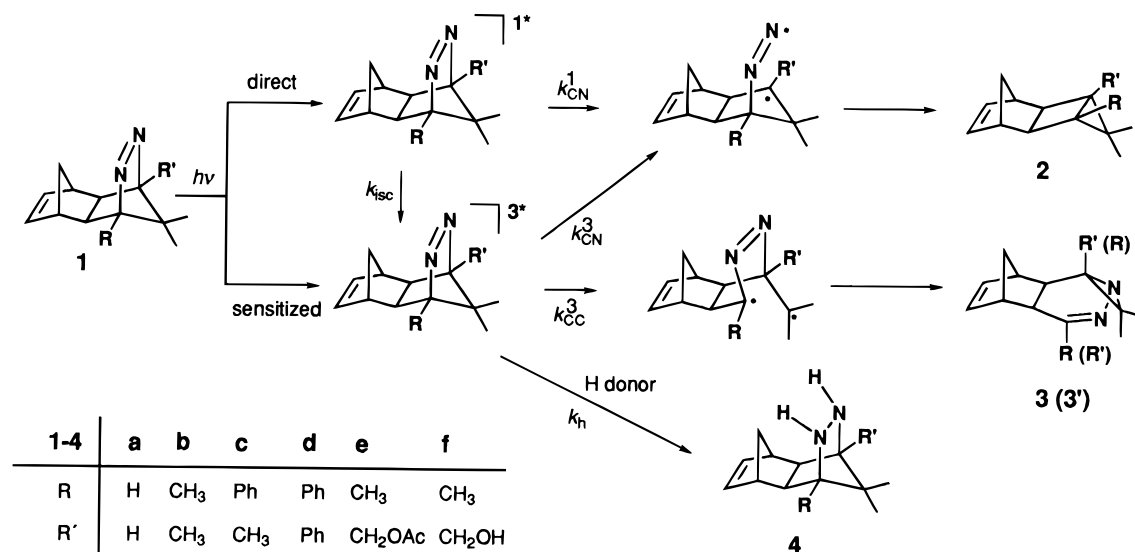
(5) Adam, W.; Nau, W. M.; Scaiano, J. C. *Chem. Phys. Lett.* **1996**, *253*, 92.

(6) (a) Turro, N. J.; Liu, J.-M.; Martin, H.-D.; Kunze, M. *Tetrahedron Lett.* **1980**, *21*, 1299. (b) Lyons, B. A.; Pfeifer, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1991**, *113*, 9006. (c) Anderson, M. A.; Grissom, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 5041.

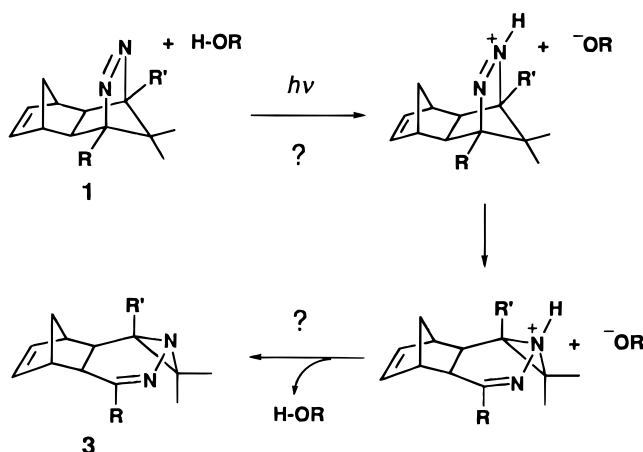
(7) (a) Schulz, A.; Rüdhardt, C. *Tetrahedron Lett.* **1976**, *3883*. (b) Neuman, R. C., Jr.; Grow, R. H.; Binegar, G. A.; Gunderson, H. J. *J. Org. Chem.* **1990**, *55*, 2682. (c) Neuman, R. C., Jr.; Gunderson, H. J. *J. Org. Chem.* **1992**, *57*, 1641. (d) Schmittel, M.; Rüdhardt, C. *J. Am. Chem. Soc.* **1987**, *109*, 2750.

(8) (a) Adam, W.; Nau, W. M.; Sendelbach, J.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 12571. (b) Adam, W.; Nau, W. M.; Sendelbach, J. *J. Am. Chem. Soc.* **1994**, *116*, 7049. (c) Adam, W.; Fragale, G.; Klapstein, D.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1995**, *117*, 12578.

Scheme 1



Scheme 2

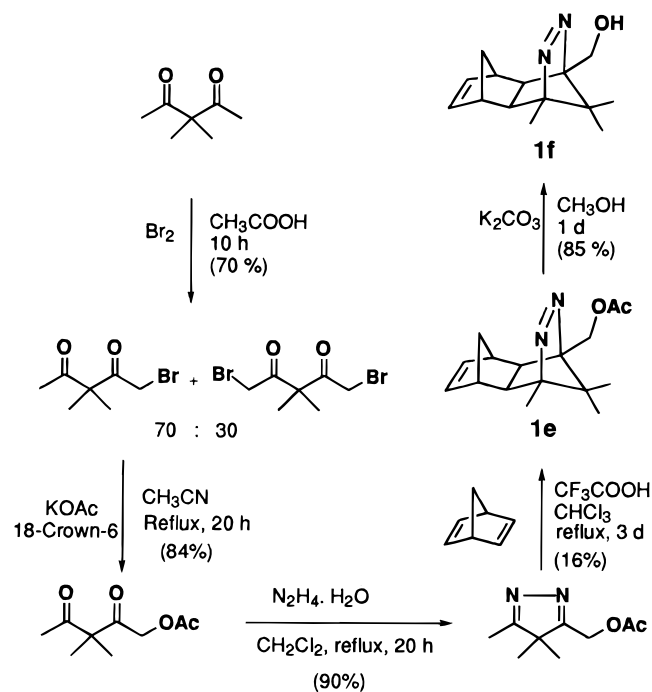


Results

Synthesis of the Azoalkanes. The azoalkanes **1a–d** were synthesized according to the Hünig route.⁹ The synthesis of the azoalkanes **1e,f** was accomplished according to the reaction sequence in Scheme 3. Addition of a molar equivalent of bromine to the solution of 3,3-dimethylpentane-2,4-dione in acetic acid furnished a mixture (70:30) of monobromo and dibromo diketones. Acetoxy substitution of the 1-bromo-3,3-dimethylpentane-2,4-dione under phase-transfer conditions with 18-crown-6 ether as catalyst afforded 1-acetoxy-3,3-dimethylpentane-2,4-dione in a good yield (84%). Subsequent treatment of the acetoxy dione with hydrazine hydrate led quantitatively to the isopyrazole. Acid-catalyzed Diels–Alder cycloaddition with 2,5-norbornadiene afforded the azoalkane **1e** in a poor yield (16%). Hydrolysis of the azoalkane **1e** to **1f** was accomplished under mild conditions with potassium carbonate in methanol.

Photolysis Products of the Azoalkanes. Direct irradiation of the solutions of azoalkanes **1** (0.1 M) under a nitrogen gas atmosphere was conducted in a Rayonet photoreactor ($\lambda = 350$ nm). The respective photoproducts **2a,b,d** and **3a,b,d** of the azoalkanes **1a,b,d** have previously been characterized.^{8,9} The photoproducts **2c,e,f** and **3e,f** from the azoalkanes **1c,e,f** were identified by comparison of the characteristic spectral data. The product distribution was determined in each case by ¹H NMR

Scheme 3



analysis of the characteristic and well-resolved methyl and olefinic signals. GC analysis was also attempted, but the aziranes **3** decomposed at elevated temperatures. In Table 1 are summarized the results of the product studies for the photolysis of the azoalkanes **1** in the various solvents.

A quite similar trend was displayed in the product distribution for the photolysis of the azoalkanes **1a,b** in a variety of solvents. Whereas the irradiation in nonpolar solvents yielded the housanes **2** (Scheme 1) selectively (Table 1, entries 1, 6, and 7), the aziranes **3** were formed predominantly in polar protic solvents (entries 3, 10–12, and 16). It is noteworthy that the photolysis in trifluoroethanol led to the formation of aziranes **3a,b** essentially exclusively (entries 5 and 15). Efficient photoreduction was found to occur in the presence of hydrogen donors to produce the hydrazines **4a,b** in significant yields (entries 1, 13, and 14). The identity of the hydrazines **4** was established by comparison of the characteristic ¹H and ¹³C NMR signals of authentic signals produced upon photolysis of **1a,b** in the presence of the excellent hydrogen donor 1,4-cyclohexa-

(9) (a) Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 477. (b) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis* **1995**, 1163.

Table 1. Product Composition^a and Disappearance Quantum Yields^b for the Photolysis of Azoalkanes **1**

	azo	solvent	product distribution ^c			ϕ_p^d	AN ^e
			2	3	4		
1	1a	<i>n</i> -hexane	75	18	7		
2		benzene- <i>d</i> ₆	51	49		0.59 (0.04) ^{f,g}	
3		methanol- <i>d</i> ₄	11	89			
4		acetonitrile- <i>d</i> ₃	50	50			
5		trifluoroethanol	<5	>95			
6	1b	<i>n</i> -hexane	88	12		0.67	0.0
7		benzene- <i>d</i> ₆	60	40 ^h		0.55 (0.06) ^g	8.2
8		acetone- <i>d</i> ₆	57	43		0.66	12.5
9		acetonitrile- <i>d</i> ₃	51	49		0.65	18.9
10		methanol	20	80		0.13 (<0.01) ^g	41.3
11		methanol- <i>d</i> ₄	19	81 ^h		0.31	
12		methanol- <i>d</i>	24	76		0.32	
13		2-propanol	17	18	65	0.11	
14		2-propanol- <i>d</i> ₈	21	31	48	0.27	
15		trifluoroethanol	<5	>95		0.12	52.9
16		<i>tert</i> -butyl alcohol	41	59		0.26	
17		acetic acid- <i>d</i> ₄	12	88 ⁱ			52.9
18	1c	benzene- <i>d</i> ₆	100				
19		methanol- <i>d</i> ₄	100				
20		trifluoroethanol	95	<5			
21		acetic acid- <i>d</i> ₄	95	<5			
22	1d	benzene- <i>d</i> ₆	100				
23		methanol/benzene (3:1)	100				
24		acetic acid/benzene (3:1)	100				
25	1e	benzene- <i>d</i> ₆	74	26			
26		methanol- <i>d</i> ₄	28	72			
27	1f	benzene- <i>d</i> ₆	72	28 ^j		0.60 (0.09) ^g	
28		acetonitrile- <i>d</i> ₃	52	48 ^j			
29		methanol- <i>d</i> ₄	21	79 ^j			
30		trifluoroethanol	8	92 ^j			

^a Photolyses were conducted in a Rayonet photoreactor (350 nm) at 8 °C, except for entries 16 and 24 (ca. 25 °C). ^b Determined by isolating the 333 nm line of the argon ion laser; 2,3-diazabicyclo[2.2.1]heptene (DBH) was employed as actinometer; analysis by GC. ^c Conversions and mass balances were >90%; relative yields (normalized to 100%) determined by ¹H NMR analysis of the appropriate methyl and olefinic signals of the norbornene moiety; error ±3%. ^d Quantum yields for azoalkane disappearance; error ±10%. ^e Solvent acceptor numbers (AN) from ref 16 used for the correlation in Figure 1. ^f In benzene from ref 8c. ^g Value in parentheses refers to 1.0 M piperylene as additive. ^h A similar product distribution was observed for laser photolysis at 333 and 364 nm; note that azoalkanes **1** have their λ_{\max} at ca. 360 nm (ref 8). ⁱ Represents the sum of the yields of the hydrazones **5b** and **6b** (see text). ^j The yield of the isomeric azirane **3f** was <6%, except ca. 15% for entry 29.

diene; the hydrazines have been trapped and characterized spectroscopically.¹⁰

The photolysis of azoalkane **1b** in acetic acid (entry 17) led to the hydrazones **5b** and **6b** (Scheme 4) together with the housane **2b**. The hydrazones **5b** and **6b** were isolated from a preparative photolysis and fully characterized. In a control experiment, the azirane **3b** was found to undergo ring-opening upon treatment with acetic acid to afford quantitatively the hydrazones **5b** and **6b** (Scheme 4). Thus, the combined yield of the hydrazones from the photolysis in acetic acid refers to the primary photoproduct, namely the azirane **3b** (entry 17).

The yield of azirane **3b** from the photolysis of azoalkane **1b** in various solvents (Table 1) was found to correlate well (Figure 1) with the Gutmann's acceptor number (AN) solvent parameters ($r^2 = 0.963$).

In this correlation, the case of *tert*-butyl alcohol was excluded since the photolysis was conducted at a higher temperature (ca. 25 °C), which is known to reduce azirane formation.^{8b} Similarly, the data for 2-propanol were omitted since photoreduction

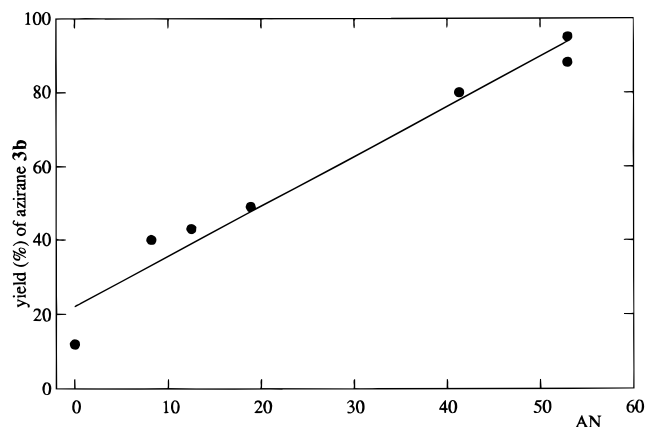


Figure 1. Plot of the yields of azirane **3b** from the photolysis of azoalkane **1b** in different solvents versus the "solvent acceptor numbers" (AN) taken from Table 1. The data points for *tert*-butyl alcohol and 2-propanol were excluded from the correlation, see the text for details.

competes (hydrazine **4d**) and lowers the azirane yield.^{10,12b} As the azirane yields are essentially the same in deuterated or protiated solvents, the correlation is not affected.

The influence of the azo triplet quencher,^{8a} namely piperylene (1.0 M), on the product distribution was probed for the photolysis of azoalkane **1b** in methanol, trifluoroethanol, and acetic acid (data not shown). From ¹H NMR monitoring, the absence of the azirane **3b** was established for the photoreaction in methanol conducted to >50% conversion of the azoalkane **1b**. Unfortunately, the complex nature of the ¹H NMR spectra of the crude photolysates for the azoalkane **1b** with piperylene (1.0 M) in trifluoroethanol and acetic acid made even a reliable qualitative analysis of the products difficult; nevertheless, the characteristic ¹H NMR resonances of the aziranes **3b** were not observed.

The dependence of the product distribution on the wavelength was examined for the azoalkane **1b**. Essentially identical product distributions (entries 7 and 11) were revealed by ¹H NMR spectroscopy for the photolysis of benzene and methanol solutions of the azoalkane **1b** at two distinct wavelengths (333 and 364 nm lines of the argon ion laser). Hence, solvent effects on the product distribution do not arise from the hypsochromic shifts of the n,π^* absorptions caused by the polar protic solvents.

In contrast to the photoproduct profile displayed by the azoalkanes **1a,b**, the azoalkanes **1c** (entries 18–21) and **1d** (entries 22–24) exhibited solvent-independent photobehavior (Table 1). Even in acetic acid, the photolysis of azoalkane **1c** led essentially exclusively to the housane **2c** (entry 21). The poor solubility of the azoalkane **1d** precluded photolysis in neat methanol and acetic acid, so that benzene was used as a cosolvent and only the housane **2d** was observed in these media (entries 23 and 24).

The azoalkanes **1e,f** exhibited a rather similar photochemistry to that of the derivatives **1a,b**. Thus, the housanes **2e,f** were selectively produced in the nonpolar benzene (entries 25 and 27) and the aziranes **3e,f** in polar protic solvents (entries 26, 29, and 30). In acetonitrile, the photolysis of azoalkane **1f** (entry 28) yielded a product distribution identical to that observed for the azoalkane **1b** (entry 9).

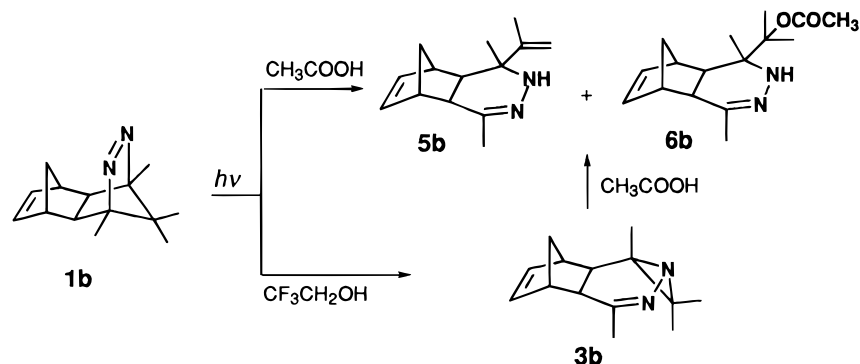
Disappearance Quantum Yields. The disappearance quantum yields for the azoalkane **1b** at 333 nm (argon ion laser) were determined by employing 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) as actinometer, whose decomposition quantum yield

(10) Adam, W.; Moorthy, J. N.; Nau, W. M. Unpublished results.

(11) Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* **1971**, *93*, 6347.

(12) (a) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015. (b) Adam, W.; Moorthy, J. N.; Nau, W. M.; Scaiano, J. C. *J. Org. Chem.* **1996**, *61*, 8722.

Scheme 4

Table 2. Triplet Lifetimes of Azoalkane **1a-H₂** in Various Solvents

solvent	$^3\tau/\text{ns}^a$	solvent	$^3\tau/\text{ns}^a$
Nonpolar		Polar Nonprotic	
<i>n</i> -pentane	445	acetonitrile	485
<i>n</i> -hexane	455	acetonitrile- <i>d</i> ₃ (>99.5%)	500
<i>n</i> -heptane	470	methyl <i>tert</i> -butyl ether	500
isooctane	545	tetrahydrofuran	130
cyclohexane	500	1,4-dioxane	400
cyclohexane- <i>d</i> ₁₂ (>99.5%)	545	ethyl vinyl ether	no signal
benzene	600	acetone	500 ^b
benzene- <i>d</i> ₆ (>99.5%)	540	ethyl acetate	515
toluene	495	<i>N,N</i> -dimethylformamide	200
		dimethyl sulfoxide	285
Halogenated		Polar Protic	
methylene chloride	465	CH ₃ -OH	240
methylene chloride- <i>d</i> ₂ (>99.6%)	500	CD ₃ -OD (>99.0%)	220
chloroform	505	ethanol	100
chloroform- <i>d</i> (>99.8%)	480	2,2,2-trifluoroethanol	no signal
carbon tetrachloride	630	2-propanol	100
Freon-113	630	hexafluoro-2-propanol	no signal
tetrachloroethylene	no signal	<i>tert</i> -butyl alcohol	no signal
1,2-dibromoethane	530	water	115 ^c
		deuterium oxide (>99.9%)	120 ^c

^a Determined by transient absorption spectroscopy on laser excitation ($\lambda_{\text{exc}} = 355$ nm, ca. 6 ns pulse, $\lambda_{\text{mon}} = 310$ and 450 nm); error from five measurements was ca. 30 ns. ^b Not detected at 310 nm. ^c Acetonitrile (50%) was added to solubilize.

has been reported to be unity.¹¹ The photolysates were analyzed by GC with diphenyl ether as internal standard. The instability of the azirane **3b** under GC condition (see above) presented no complications, since only the disappearance of the azoalkane **1b** was monitored. In Table 1 are recorded the disappearance quantum yields for the azoalkane **1b** (entries 6–16) in the various solvents. The values in parentheses for the entries 7 and 10 refer to the decomposition quantum yields in the presence of 1.0 M piperylene.

Whereas the quantum yields of azoalkane **1b** disappearance in nonpolar aprotic solvents such as hexane (0.67) and benzene (0.55) were found to be quite high (entries 6 and 7), a dramatic reduction was observed for the photolysis in the polar protic media (entries 10, 13, and 15) methanol (0.13), 2-propanol (0.11), and trifluoroethanol (0.12). Moreover, the substantial deuterium isotope effect (ϕ_r^D/ϕ_r^H ca. 2.5) is noteworthy for the photolysis in CD₃OD and CH₃OD versus CH₃OH (entries 10–12). The quantum yield for disappearance of the azoalkane **1b** in the presence of 1.0 M piperylene in methanol (entry 10) was found to be essentially negligible (<0.01), and for the azoalkane **1b** in benzene (entry 27) with and without added piperylene, the ϕ_r values were found to parallel those observed for the azoalkane **1b** (entry 7).

Triplet Lifetimes of the Azoalkane 1a-H₂. The triplet lifetimes in selected solvents were measured for the azoalkane **1a-H₂**, a derivative of the azoalkane **1a** for which the C=C double bond was hydrogenated, as a prototypal case. This

azoalkane displayed the strongest transient triplet absorption of all the azoalkanes of this class and was, therefore, preferred for the laser flash studies. Since its photophysics and photochemistry closely resemble those for the azoalkanes **1a,b**, the saturated derivative **1a-H₂** serves as a suitable model.

Whereas the triplet lifetime was found to be quite similar in the various solvents, a significant shortening was observed in polar protic solvents (Table 2). The absence of a signal in some solvents is presumably due to efficient quenching of the singlet-excited states,⁵ which results in a reduced triplet yield and, hence, a low signal intensity or even no measurable signal. Note that the low triplet lifetimes in 2-propanol and tetrahydrofuran may also be due to chemical reactions with the solvent (hydrogen abstraction).¹²

Discussion

The direct photolysis of azoalkanes **1a,b** not only affords the expected housanes **2a,b** by the α C–N bond cleavage (k_{CN}^3), but also the aziranes **3a,b** from β scission of the C–C bond (k_{CC}^3) (cf. Scheme 1).⁸ From the triplet quenching experiments with piperylene, the intersystem-crossing (ISC) quantum yields for the azoalkanes **1a,b** have been estimated⁸ to be as high as 0.5. Particularly noteworthy is the incipient radical stabilization: the better the carbon radical site in the intermediate diazenyl diradical is stabilized, i.e., Ph (**1c,d**) \gg Me (**1b**) \gg H (**1a**), the more α C–N bond cleavage to the housanes occurs. Thus, the phenyl substitution in **1c,d** is so effective in stabilizing

the incipient carbon radical site that deazation from the singlet-excited state predominates with marginal ISC to the triplet manifold [ϕ_{ISC} (**1d**) ca. 0.1].^{8c}

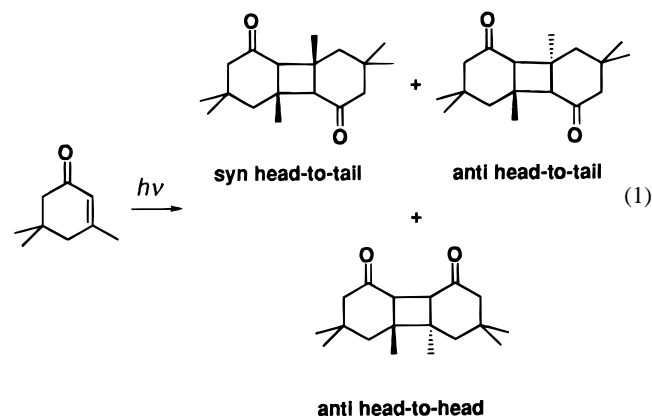
As mentioned at the outset, certain solvents are capable of promoting efficient radiationless deactivation of singlet-excited azoalkanes, and the rate constants for this deactivation process are strongly subject to deuterium isotope substitution of the solvents.^{4,5} Since this physical quenching of the singlet-excited states does not alter the photoproduct distribution, it should merely show up as a reduction in the quantum yield for azoalkane decomposition. Indeed, our data (Table 1) exhibit a dramatic (ca. 5-fold) reduction in the quantum yields for the disappearance of the azoalkane **1b** in the polar methanol (entry 10) versus the nonpolar *n*-hexane (entry 6). Indicative is the appreciable isotope effect ϕ_r^D/ϕ_r^H (k_D/k_H) of ca. 2.5 for both pairs CH₃OH versus CD₃OD (entries 10 and 11) and CH₃OH versus CH₃OD (entries 10 and 12). Clearly, it is the deuterium substitution of OH rather than CH in methanol which exhibits a more pronounced effect on the azoalkane photoreactivity. These results, taken together with the cited literature evidence,⁴ signify efficient deactivation of the singlet-excited states for the azoalkane **1b** by the hydroxyl group of the alcohol solvent.

Apart from the solvent effects on the disappearance quantum yields, a perusal of the results in Table 1 shows that pronounced solvent effects operate on the product profiles for the photolysis of the azoalkanes **1a** (entries 1–5), **1b** (entries 6–17), **1e** (entries 25 and 26), and **1f** (entries 27–30). Let us consider the photobehavior of the azoalkane **1b** as a representative case. Whereas the azirane **3b** is the main product in the polar protic solvents methanol (entries 10–12), trifluoroethanol (entry 15), and acetic acid (entry 17), the housane **2b** predominates in *n*-hexane (entry 6) and benzene (entry 7). Furthermore, photolysis in benzene as well as methanol with the triplet quencher piperylene (1.0 M) leads exclusively to the housane **2b**. In contrast, the azoalkanes **1c,d**, which undergo efficient deazation from the singlet-excited state,⁸ display solvent-independent photobehavior and produce essentially exclusively (>95%) the housanes **2c** (entries 18–21) and **2d** (entries 22–24). Thus, the pronounced shift of the product distribution for the azoalkane **1b** as a function of solvent (Table 1), i.e., from housane **2b** as main product in the *n*-hexane and benzene (entries 6 and 7) to mainly azirane **3b** in the polar and protic CH₃OH, *i*PrOH, CF₃CH₂OH, and CH₃COOH (entries 10–17), must be sought in the triplet-state photoreactivity of the azoalkane **1b**.

Since the photolysis of azoalkane **1b** in the presence of the triplet quencher (1.0 M) leads exclusively to the housanes **2b**, the azirane **3b** is unambiguously identified as a characteristic triplet-state product. Thus, the observed increase or decrease of azirane in the various solvents is best reconciled as a manifestation of the solvent effects on the triplet-state reactivity. The previous studies have established that the triplet-excited azoalkanes **1a,b** produce the respective housanes **2** as well as the aziranes **3** from α and β cleavages (k_{CN}^3 and k_{CC}^3 , Scheme 1).⁸ Furthermore, it has been shown that the rate constants for α and β cleavages are strongly temperature dependent due to the marked difference in the relative activation energies.^{8b} Therefore, it is perhaps not surprising that the solvent properties also have an effect on the relative rates of α and β cleavages. Since the azirane **3b** is favored in polar protic solvents, presumably such solvents stabilize the transition state for β cleavage or destabilize the one for α scission. In support of the enhanced β cleavage in polar protic solvents, we find that the triplet lifetimes, which reflect the propensity of the triplet-excited states to undergo chemical transformations, are indeed significantly shorter in protic solvents for which azirane

formation is promoted (Tables 1 and 2). It is noteworthy in this context that the triplet lifetimes (Table 2), unlike those of the singlet lifetimes, are not affected by deuterium substitution in the solvent, which is analogous to the lack of an isotope effect on the product distribution (Table 1, entries 10–12). Note also that the triplet lifetime is not significantly shortened in 1,2-dibromoethane (Table 2), which provides additional evidence for the absence of measurable heavy atom effects on the lifetimes of n,π^* -excited azoalkanes.^{8c}

On the basis of the computational results obtained for the parent 2,3-diazabicyclo[2.2.1]hept-2-ene at the UHF/6-31G* *ab initio* level of theory,¹³ which included a full geometry optimization at the same level, the transition state for β scission of the triplet state displays a larger dipole moment (3.45 D) than that for the α cleavage (3.24 D), while that of the azoalkane triplet state falls between these values (3.34 D). This calculated increase or decrease in dipole moments becomes significantly more pronounced if the primary triplet diradicals derived from β C–C scission (3.84 D) or α C–N cleavage (2.76 D) are used as reference (Scheme 1). Hence, β C–C cleavage affords a diradical with a significantly higher dipole moment, and the increased polarity is reflected in the transition state, while the opposite is true for α cleavage. This clear-cut trend in dipole moments suggests that a polar protic solvent should lower the energy of the β versus α rupture through better stabilization, and thus, azirane formation should be promoted, as is experimentally observed. In support of this dipole moment argument, we cite the solvent-dependent photodimerization of isophorone (eq 1).^{14a} It was observed that the ratio of the head-to-head



and head-to-tail dimers increased from 1:4 to 4:1 when the solvent was changed from cyclohexane to methanol. As expected, the higher dipole moment of the head-to-head dimer is better stabilized in methanol and, hence, preferentially produced.

(13) *Gaussian 94*, Revision A.1; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian Inc.: Pittsburgh, PA, 1995.

(14) (a) Chapman, O. L.; Nelson, P. J.; King, R. W.; Trecker, D. J.; Griswold, A. *Recl. Chem. Prog.* **1967**, 28, 167. (b) Hrnjez, B. J.; Mehta, A. J.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1989**, 111, 2662. (c) Challand, B. D.; de Mayo, P. *Chem. Commun.* **1968**, 982. (d) Pappas, S. P.; Pappas, B. C.; Blackwell, J. E., Jr. *J. Org. Chem.* **1967**, 32, 3066. (e) Lee, K.-H.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1979**, 493. (f) Wagner, P. J.; Stout, C. A.; Sarless, S.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, 88, 1242. (g) Ninomiya, I.; Naito, T. *Photochemical Synthesis*; Academic Press: Tokyo, 1989; p 75. (h) Shiloff, J. D.; Hunter, N. R. *Can. J. Chem.* **1979**, 57, 3301.

Scattered reports of solvents effects on various photochemical transformations are documented in the literature.¹⁴ The photoproduct control by solvents has in some cases been rationalized in terms of physical properties of the solvents such as the polarity^{14a,b} and the dielectric constant.^{14c,e} Interestingly, the thermal decomposition of azoalkanes has been reported to be strongly solvent dependent and a remarkable correlation of the decomposition rates of *cis*-azoisobutane with the Reichardt's $E_T(30)$ solvent polarity parameters has been documented.^{6a} Nevertheless, the presently observed solvent-dependent product distribution for the photolysis of azoalkane **1b** in the solvents examined does not correlate with solvent parameters such as viscosity, dielectric constant, α (a measure of hydrogen-bond-donating ability),^{15a} and π^* (solvent polarity and polarizability).^{15b} However, the azirane **3b** yield correlates excellently with Gutmann's AN solvent parameter (Figure 1, $r^2 = 0.963$ for seven solvents, see also Results),¹⁶ while a relatively poor correlation is found for the $E_T(30)$ values¹⁷ ($r^2 = 0.897$). The AN numbers, derived from P³¹ NMR chemical shifts produced through solvent effects on Et₃PO, display a linear relationship with the $E_T(30)$ parameters¹⁷ and measure the ability of solvents to interact with electron pairs from suitable electron donors. The advantage of this solvent parameter is that the donor-acceptor interactions such as hydrogen bonding, ion-dipole interactions, and charge transfer are collectively taken into account. Taft *et al.*¹⁸ have shown that the AN parameter for a nonpolar solvent is equivalent to π^* , while for the polar solvents AN measures the composite effects of π^* and α . Thus, the dependence of the formation of azirane **3b** on the polarity and polarizability of the medium expressed by π^* , in addition to the hydrogen-bonding ability (α), is evident from the correlation with the AN numbers.

That the observed solvent effect on the product distribution is caused by the "macroscopic" solvent property of the medium is borne out by the photobehavior of the hydroxymethyl-substituted azoalkane **1f** (Table 1). If the enhancement of azirane **3** formation in polar protic solvents was due to the acid-base photoreaction (proton abstraction) in Scheme 2, the product distribution for the azoalkane **1f** should parallel that for the azoalkane **1b** in protic solvents (entries 10–17). In azoalkane **1f**, the bridgehead hydroxyl group is sufficiently well disposed for *intramolecular* proton abstraction by the azo group as suggested by the force-field calculations.¹⁹ In fact, in the lowest energy conformation, the O...N nonbonding distance and the

angle O–H...N are 2.62 Å and 127.6°, which fall within the range observed for significant hydrogen-bonding interaction, especially if one considers the limiting values for much weaker and *intermolecular* C–H...O hydrogen bonds.²⁰ Consequently, analogous to the *intermolecular* interactions of the azoalkane **1b** with the hydroxy groups of protic solvents, the hydroxy-substituted derivative **1f** should promote azirane formation *intramolecularly*, if proton abstraction were to play a major role. However, the azoalkane **1f** (entries 27–30) portrays quite similar product profiles as the methyl-substituted **1b** (entries 7, 9, 11, and 15) and as the acetoxymethyl-substituted derivative **1e** (entries 25 and 26) in a variety of solvents, which range from the nonpolar benzene to the polar alcohols. Thus, the lack of a significant influence by the intramolecularly tethered hydroxyl functionality in the azoalkane **1f** compared to **1b** in benzene is convincingly evident both from the product distribution and disappearance quantum yields with and without the triplet quencher piperylene (Table 1). Thus, proton abstraction (Scheme 2) is not responsible for promoting the azirane formation. In fact, the absence of deuterium isotope effects on the product distribution (see above) speaks also against such a proton-mediated process. Clearly, the importance of the properties intrinsic to the solvent as medium is decisive in affecting the photobehavior of the azoalkane n,π^* triplets.

In conclusion, the present results demonstrate that the triplet state reactivity of azoalkanes is profoundly influenced by solvents in that the polar azirane photoproduct is favored by polar protic solvents. In contrast to the quenching of singlet-excited azoalkanes, the triplet-state reactivity and the triplet lifetimes remain unaffected by deuterium substitution of the solvent. The excellent correlation of the azirane yield with the AN solvent parameter reveals that a combination of solvent properties like polarity, polarizability, and hydrogen-bonding properties govern the product distribution in the azoalkane photolysis.

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Supporting Information Available: Experimental data (5 pages). See any current masthead page for ordering and Internet access instructions.

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(19) Sybyl 6.0, Tripos Associates, 1699 S. Hanley Road, Suite 303, St. Louis, MO 63144.

(20) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Allen, F. H.; Goud, S.; Hoy, V. J.; Howard, J. A. K.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2729.

(15) (a) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 2887. (b) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(16) (a) Gutmann, V.; Schmid, R. *Coord. Chem. Rev.* **1974**, *12*, 263. (b) Gutmann, V. *The Donor Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978. (c) Parker, A. J.; Mayer, U.; Schmid, R.; Gutmann, V. *J. Org. Chem.* **1978**, *43*, 1843.

(17) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98.

(18) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* **1981**, *46*, 661.