Denitrogenation of Bicyclic Azoalkanes through Photosensitized Electron Transfer: Generation and Intramolecular Trapping of Radical Cations

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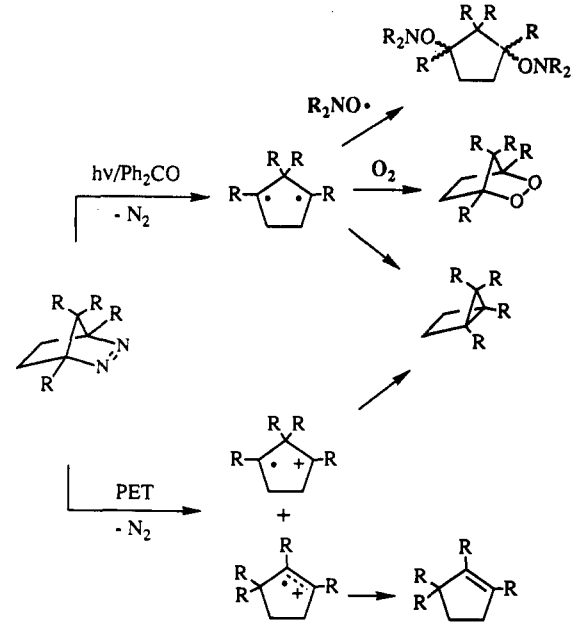
To elucidate the intermediates that intervene in the denitrogenation of bicyclic azoalkanes by photosensitized electron transfer (PET), the 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) derivative **1b** was synthesized, and its PET reactions were examined. With triphenylpyrylium tetrafluoroborate (TPT) or 9,10-dicyanoanthracene (DCA) as sensitizers and biphenyl as cosensitizer, the azoalkane **1b** gave through intramolecular cyclization the spiro ethers **5** and **6** as trapping products, in addition to the bicyclopentane **2b** and the cyclopentenes **3b,b'**, the latter as rearrangement products. Comparison with 1,4-dimethyl-DBH (**1c**) revealed that trapping of a 1,3-diyl radical cation as the major pathway is unlikely. PET experiments with the regioisomeric cyclopentenes **3b,b'**, which both led to the spiro ether **5**, imply the involvement of the allyl cation **3b(-H)**$^+$ as the decisive intermediate in the nucleophilic trapping reactions. Comparison of the PET chemistry of the azoalkane **1b** and the corresponding bicyclopentane **2b** gave further insight into the mechanism of denitrogenation of azoalkanes through single electron transfer. The latter results lend additional support for the involvement of the diazenyl radical cation **1**$^{\bullet+}$, which to date has escaped direct detection.

Introduction

Cyclic azoalkanes are well-known for their propensity to form biradicals upon photolytically or thermally induced denitrogenation.[1] Especially 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and its derivatives have been the focus of numerous mechanistic studies which were concerned with the generation and transformation of localized 1,3-biradicals[2] (Scheme I). More recent work established that cyclic azoalkanes and particularly DBH derivatives extrude nitrogen also upon photosensitized electron transfer (PET)[3,4]— a photochemical process that has become of considerable significance during the last years.[5]

The 1,3-cyclopentanediyl radical cations derived from DBH derivatives or housanes exhibit a high tendency for rearrangement by 1,2-hydrogen or 1,2-alkyl shift as confirmed by liquid-phase PET studies and ESR determinations on γ-irradiated material under matrix isolation.[3c,6] Such rearrangements do not occur in significant amounts, if at all, in the corresponding 1,3 biradicals. While

Scheme I



for the 1,3-biradicals trapping experiments with dioxygen[2a] or nitroxides[7] as radical scavengers were applied as mechanistic tools, no such trapping was reported for the corresponding 1,3-radical cation intermediates. However, for other radical cation systems there do exist numerous studies on reactions with nucleophiles. Besides trapping of 1,2-radical cations through intermolecular reactions with alcohols, amines, and nitriles[5c,8] or through intramolecular reactions,[9,10] the scavenging of distonic radical cations is also known.[11] It was reported recently that radical cations

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(1) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Adam, W.; De Lucchi, O. *Angew. Chem.* **1980**, *92*, 815.

(2) (a) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (b) Engel, P. S.; Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686.

(3) (a) Adam, W.; Dörr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1570. (b) Adam, W.; Miranda, M. A. *J. Org. Chem.* **1987**, *52*, 5498. (c) Adam, W.; Chen, G.-F.; Walter, H.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007. (d) Adam, W.; Denninger, U.; Finzel, R.; Kita, F.; Platsch, H.; Walter, H.; Zang, G. *J. Am. Chem. Soc.* **1992**, *114*, 5027.

(4) (a) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964. (b) Engel, P. S.; Hoque, A. K. M. M.; Scholz, J. N.; Shine, H. J.; Whitmire, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 7880. (c) Karatsu, T.; Hotta, H.; Kitamura, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1451. (d) Goodman, J. L.; Zona, T. A. *Tetrahedron Lett.* **1992**, *33*, 6093. (e) Engel, P. S.; Robertson, D. M.; Scholz, J. N.; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178.

(5) (a) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (b) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988. (c) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Pawda, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (d) For exhaustive reviews of the utilization of PET in various areas, see: *Top. Curr. Chem.* **1990**, *156*; **1990**, *158*; **1991**, *159*; **1992**, *163*.

(6) Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835.

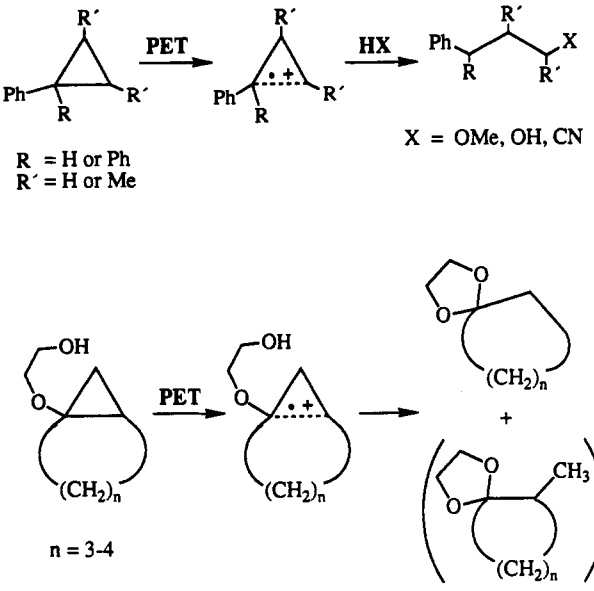
(7) Adam, W.; Bottle, S. E. *Tetrahedron Lett.* **1991**, *32*, 1405. Adam, W.; Bottle, S. E.; Finzel, R.; Kammel, T.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Walz, L. *J. Org. Chem.* **1992**, *57*, 982.

(8) Kropp, P. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, p 124.

(9) (a) Gassman, P. G.; Bottorff, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 7547. (b) Gassman, P. G.; De Silva, S. A. *J. Am. Chem. Soc.* **1991**, *113*, 9870.

0022-3263/93/1958-5316$04.00/0

Scheme II



generated through SET from monocyclic and bicyclic azoalkanes were efficiently trapped by methanol or acetonitrile;[4d,e] however, attempts to scavenge radical cations derived from DBH derivatives with these nucleophiles were futile.[3a]

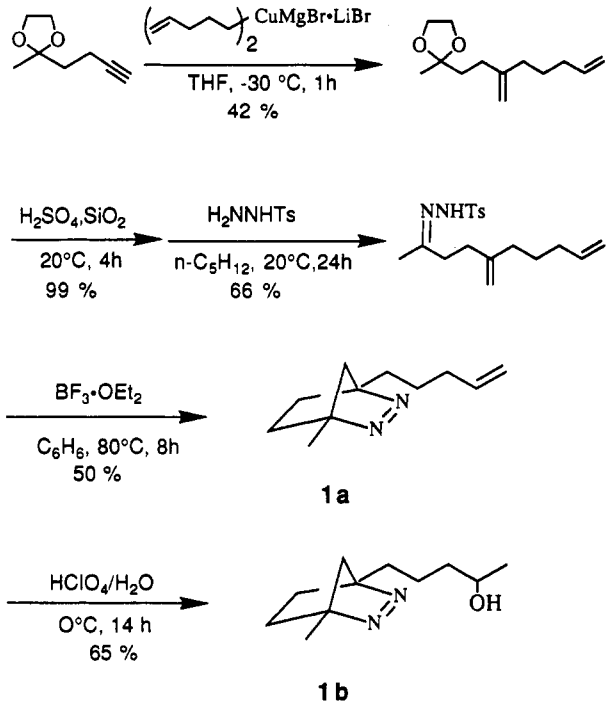
Also relevant for this work, since it is closely related to 1,3-cyclopentanediyl radical cations, are the trapping experiments with cyclopropane-derived radical cations. These intermediates, when stabilized by aryl[13] or alkoxy[14] substituents (Scheme II), underwent reaction with nucleophiles.[12] Not only did such experiments provide detailed mechanistic insights into orbital interactions and reaction rates,[13a] but they also revealed some synthetic potential.[14,15]

The aim of this work was to examine whether the PET chemistry of azoalkane **1b** gives rise to 1,3-radical cations which are subsequently trapped by intramolecular nucleophilic cyclization. The 1,4-dialkyl substitution was chosen because PET experiments on 1,4-dimethyl-DBH (**1c**) showed that alkyl substitution on both bridgeheads generates significantly more stable radical cations.[16] Undoubtedly, the more persistent these transients, the better the chances for nucleophilic trapping.

Results

Synthesis of Starting Materials. Azoalkane **1b** was

Scheme III



prepared according to the synthetic pathway outlined in Scheme III. Addition of a pent-4-ene cuprate to 1-(2-methyl-1,3-dioxolan-2-yl)but-3-yne at low temperature[17] afforded the appropriate ketal, which was hydrolyzed quantitatively to the ketone by stirring with a H_2SO_4/SiO_2 slurry.[18] Conversion to the tosyl hydrazone and cyclization by Wilson's method[19] with BF_3•Et_2O yielded azoalkane **1a**. Hydration of the latter to azoalkane **1b** was achieved in satisfactory yields by treatment with aqueous 70% $HClO_4$ at 0 °C. Azoalkane **1b** was made available by following the published procedure.[19] Direct photolysis of azoalkanes **1b,c** yielded quantitatively the corresponding bicyclopentanes **2b,c**.[20]

PET Reactions. The photosensitized electron transfer (PET) reactions were carried out either in CH_2Cl_2 or in CH_3CN and with two sensitizers, namely 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium tetrafluoroborate (TPT). DCA serves in its excited singlet state as an electron acceptor with a reduction potential of ca. +2.0 V/SCE. TPT exhibits in its excited singlet state a reduction potential of ca. +2.5 V/SCE, but intersystem crossing to its triplet state with a reduction potential of +2.0 V/SCE is feasible.[21a] The latter spin state, however, plays a minor role if diffusion-controlled quenching is supposed.[21b] To avoid direct photolysis of the azoalkanes, the solutions were irradiated by employing a glass filter which absorbed all light below 400 nm.[20] The present results and for comparison those of the PET reactions for azoalkane **1c**[16] are listed in Table I.

(10) (a) Foote, C. S.; Jiang, Z. Q. *Tetrahedron Lett.* **1983**, *24*, 461. (b) Dai, S.; Wang, J. T.; Williams, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1063.

(11) (a) Gassman, P. G.; Carroll, G. T. *Tetrahedron* **1986**, *42*, 6201. (b) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 4227. (c) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (d) Gollnick, K.; Paulmann, U. *Tetrahedron Lett.* **1989**, *30*, 4481.

(12) For trapping of cyclopropyl radical cations with O_2 and NO, which does not necessarily constitute a nucleophilic addition, see: (a) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207. Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780. Gollnick, K.; Xiao, X. L.; Paulmann, U. *J. Org. Chem.* **1990**, *55*, 5945. Gollnick, K.; Paulmann, U. *J. Org. Chem.* **1990**, *55*, 5954. (b) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 4669.

(13) (a) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462. Dinnocenzo, J. P.; Shaik, S. S. *J. Org. Chem.* **1990**, *55*, 3434. (b) Hixon, S. S.; Rao, V. R. *J. Am. Chem. Soc.* **1979**, *101*, 6458.

(14) Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5576.

(15) Mattay, J.; Müller, F. *Angew. Chem.* **1992**, *104*, 207.

(16) Some of the PET chemistry of **1c** was already published in ref 3d.

(17) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.

(18) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.

(19) Wilson, R. M.; Rekers, J. W.; Packard, A. B.; Elder, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 1633.

(20) The bicyclic azoalkanes have their longest wavelength absorption at *ca.* 350 to 360 nm ($n \rightarrow \pi^*$ excitation).

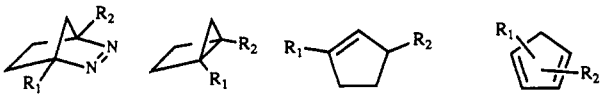
(21) (a) The ground-state reduction potential E^{red} and singlet excitation energy E_s are −0.89 V/SCE and 2.86 eV for DCA and −0.29 V/SCE and 2.82 eV for TPT; the triplet excitation energy E_T for TPT is 2.30 eV.[5a] The excited-state reduction potential E^{red*} is approximated by the following: $E^{red*} = E^{red} + E_{S(T)}$. (b) Akaba, R.; Sakuragi, H.; Tokumaru, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 291.

Table I. Product Studies of the Photosensitized Electron Transfer (PET) Reactions of the Azoalkanes 1, Bicyclopentanes 2, and Cyclopentenes 3[a]

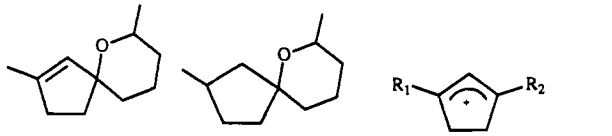
entry	substrate	sensitizer	solvent	convn[a-c] (%)	mb[b,c] (%)	production distribution[b,d] (%) 2	3[e]	4	5[f]	6
				Azoalkanes						
1	1b	DCA	CH_3CN	30	75	52	48			
2	1c	↓	↓	75	100	46	54			
3	1b	DCA	CH_2Cl_2	57	90	70	30			
4	1c	↓	↓	46	97	62	38			
5	1b	TPT	CH_3CN	50	85	21	65		14	
6	1c	↓	↓	66	75	18	74	8		
7	1b	TPT	CH_2Cl_2	40	87	37	26		37	
8	1c	↓	↓	54	70	40	54	6		
9	1b	DCA/Ph_2	CH_3CN	40	95	25	62		7	6
10	1c	↓	↓	22	60	19	78	3		
11	1b	TPT/Ph_2	CH_3CN	21	75	<1	10		89	<1
12	1b	TPT/Ph_2	CH_2Cl_2	23	80	<1	52		45	2
				Hydrocarbons						
13	2b	TPT	CH_3CN	13	15	g			>99	<1
14	2c	↓	↓	55	36	g	100			
15	2b	DCA/Ph_2	CH_3CN	50	15	g			30	70
16	2c	↓	↓	10	50	g	93	7		
17	2b	TPT	CH_2Cl_2	15	37	g			99	1
18	3b	TPT	CH_3CN	16	55		g		100	
19	3b′	↓	↓	20	58		g		100	
20	3b	DCA/Ph_2	CH_3CN	20	35		g		59	41
21	3b′	↓	↓	13	40		g		100	

[a] See Experimental Section for reaction conditions, usual irradiation time about 5–15 min. [b] Mass balance determined by quantitative capillary GC, see Experimental Section for definition. [c] Error 5–10% of stated value. [d] Relative yields normalized to 100%, error ca. 2%. [e] The two regioisomers 3b,b′ were formed in a 1:1 ratio in all cases. [f] Separated into the two diastereomeres by GC, which were formed in a ratio of ca. 1:1. [g] Starting material.

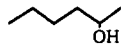
With DCA as electron acceptor, both azoalkanes **1b,c** yielded the bicyclopentanes **2b,c** and the cyclopentenes **3b(′),c**. The ratio of housanes **2** *versus* rearranged products

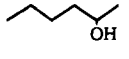


1 **2** **3** **4**



5 **6** **3(-H)$^+$**

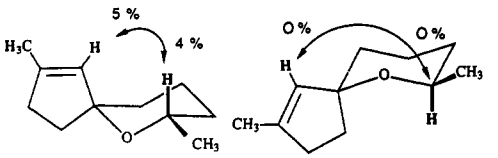
b: $R^1 = CH_3$, R^2= 

b′: R^1 =  , $R^2 = CH_3$

c: $R^1 = R^2 = CH_3$

3 were very similar for the 1,4-dialkyl-substituted azoalkanes **1b,c** (Table I, entries 1–8). The two cyclopentenes **3b,b′** could be distinguished by GC analysis and were in all cases formed in a 1:1 ratio.

Photolysis of azoalkane **1b** in the presence of TPT gave rise to two additional products (Table I, entries 5, 7), which were isolated by preparative GC. Spectral analysis, which also included NOE experiments, proved that the diastereomeric spiro ethers (*R**,*R**)- and (*R**,*S**)-**5** were obtained in a 1:1 ratio.



R*, R* - 5 R*, S* - 5

Addition of biphenyl (Ph_2) as cosensitizer[22] in 10 molar excess caused a substantial change in the product distribution for both azoalkanes **1b,c** (Table I, entries 9–12). In the case of DCA, addition of Ph_2 led to a significant decrease in housane formation (Table I, cf. entries 9, 10 *versus* 1, 2) and the appearance of new products. Azoalkane **1b** afforded not only the unsaturated spiro ether **5**, but also its saturated derivative **6**. ^1H and ^{13}C NMR spectra show that the new product **6** was formed as a mixture of four diastereomers in the ratio 2:2:1:1, which could not be separated even by capillary GC. Its constitution was unambiguously established on the basis of MS, IR, and NMR data, but the exact stereochemistry of the individual isomers could not be elucidated. Interestingly, under the photolysis conditions at which azoalkane **1b** afforded the intramolecular trapping products **5** and **6**, azoalkane **1c** gave minor amounts of dimethylcyclopentadiene **4a**. An analogous product **4b** was not observed in the PET photolysis of azoalkane **1b**.

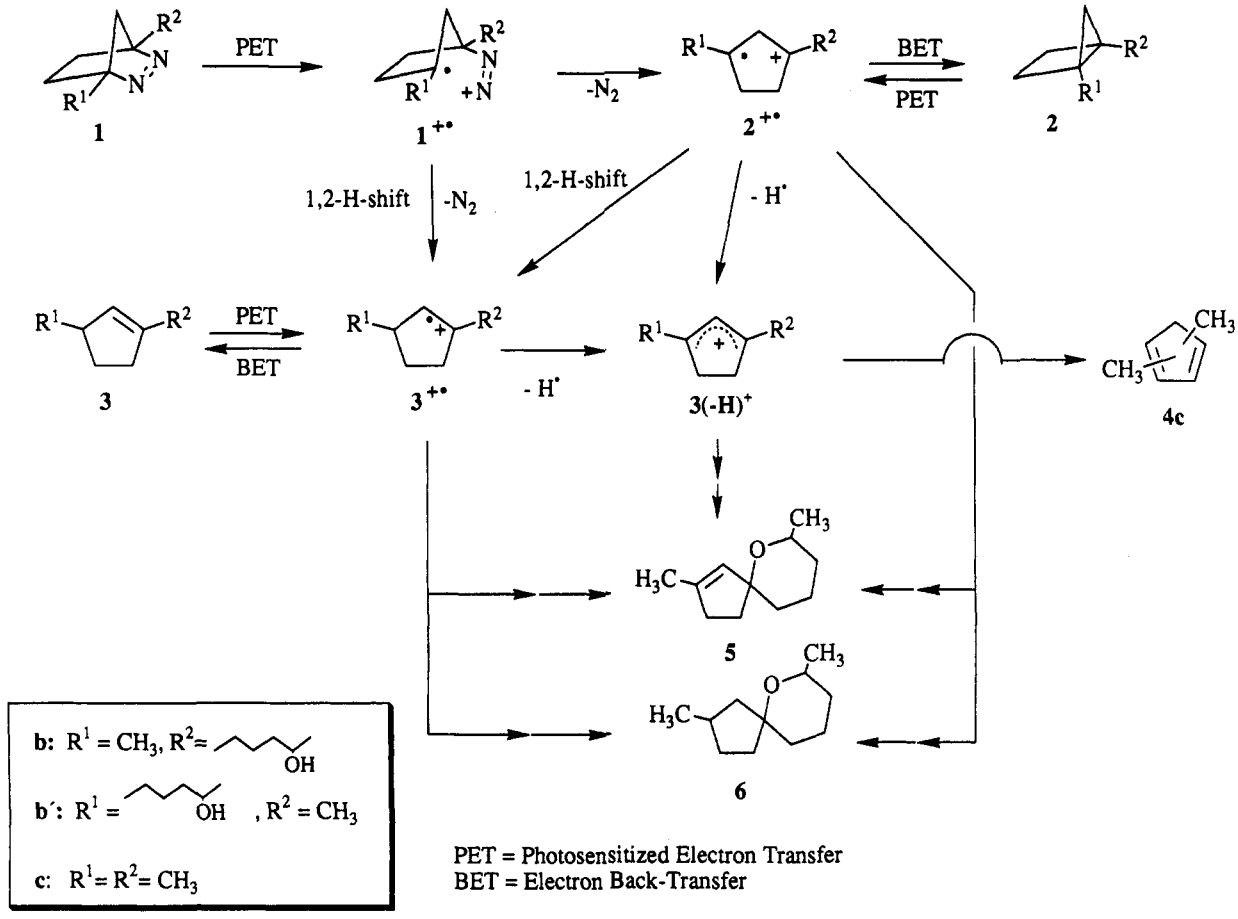
The PET reaction of azoalkane **1c** with DCA/Ph_2 in acetonitrile was also carried out in the presence of methanol (60% v/v). Besides housane **2c** and cyclopentene **3c**, only traces (<2%) of a volatile nitrogen-free product were detected whose mass spectrum (GC–MS) gave evidence for incorporation of a methoxy group in a C_7 hydrocarbon (molecular ion peak with m/z = 126 and a principle fragment with m/z = 95). The nonvolatile residue (80%) consisted of a mixture of intractable higher-molecular-weight material. Thus, for DBH derivatives intramolecular trapping gave much cleaner reactions than intermolecular scavenging.

Also, the strained bicyclo[2.1.0]pentanes **2b,c** were oxidized by PET to generate radical cation intermediates (Table I, entries 13–17). While bicyclopentane **2c** gave the cyclopentene **3c** and the cyclopentadiene **4c** (in some cases), the hydroxy-substituted derivative **2b** afforded only cyclization products **5** and **6**. Cyclopentenes **3b,b′** could not be detected; however, the yield of volatile products in the PET reactions of housanes **2b,c** was low, especially in the case of **2b**. Low mass balances were observed for most PET reactions of bicyclopentanes before.[3c] A very complex mixture of higher-molecular-weight products was formed, which could not be chromatographically separated. Nevertheless, ^1H NMR spectral evidence in the case of housane **2b** suggests that some of these products have incorporated sensitizer molecules (aromatic besides aliphatic protons), while some of the other nonvolatile products must have arisen from oligomerization of bicyclopentane **2b** (only aliphatic protons).

A control experiment showed that cyclopentenes **3b,b′** cyclized also under the PET conditions employed for the azoalkane **1b** and housane **2b**. Thus, cyclopentenes **3b,b′** afforded with TPT as sensitizer the spiro ether **5** (Table I, entries 18, 19). With DCA/Ph_2 cyclopentene **3b** gave

(22) (a) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (b) Julliard, M. In *Photoinduced Electron Transfer Part B*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 216.

Scheme IV



the saturated spiro ether **6** as the major and **5** as the minor product. Isomer **3b'** yielded only the latter under these conditions (Table I, entries 20, 21).

Discussion

The formation of spiro ethers **5** and **6** in the PET reaction of azoalkane **1b** constitutes unambiguous evidence for intramolecular cyclization of electron-deficient intermediates, e.g., radical cations. Nevertheless, careful consideration of the data in Table I reveals quite generally that trapping of the distonic 1,3-diyl radical cation or the proximate 1,2-radical cation, produced after 1,2-H shift of the former, is not the only reaction pathway to the spiro ethers **5** and **6**. For this purpose, important mechanistic implications are drawn from the relative yields of bicyclopentanes **2b,c** which are observed in this PET reaction. Presumably, the bicyclopentanes **2** arise from electron back-transfer (BET) to the 1,3-diyl radical cation prior to any rearrangement or nucleophilic attack. Thus, factors which influence the rate of electron back-transfer (k_{BET}) should become evident in the relative yields of the bicyclopentanes. Indeed, in CH_2Cl_2 the bicyclopentanes **2** were formed in higher amounts than in CH_3CN (Table I, cf. entries 1, 2 and 3, 4). This is consistent with the fact that in the nonpolar CH_2Cl_2 electron back-transfer is more efficient than in the polar CH_3CN, since in the former fast-collapsing contact radical ion pairs (CRIP) intervene while in the latter longer-lived solvent-separated radical ion pairs (SSRIP) are involved and chemical transformations can compete more effectively with BET.[5a,23,24]

The influence of sensitizer on the bicyclopentane yield implies *normal* Marcus region behavior and is in accordance with earlier results.[3c] In the *normal* Marcus region, k_{BET} is proportional to the exothermicity of the BET process,[22a,23] which is greater for DCA than for TPT.[25] Furthermore, the cationic sensitizer TPT gives rise to a geminate pair of a radical cation and a neutral radical, in which diffusive separation to free-radical cations is not encumbered by Coulombic attraction. The results in Table I are consistent with the above arguments. For example, conclusive is the fact that azoalkane **1b**, for which a similar oxidiation potential and thus a similar k_{BET} as for **1c** is expected, yields the same bicyclopentane ratios as azoalkane **1c**, even in runs which afford cyclization (Table I, cf. entries 5, 6 and 7, 8). This implies that trapping of the direct precursor of bicyclopentane **2b**, the 1,3-diyl radical cation **2b**$^{\bullet+}$ (Scheme IV), is not significant. If trapping were to take place at the stage of the 1,2-radical cation **3b**,$^{\bullet+}$ which is formed either by a 1,2-hydrogen shift in the 1,3-diyl radical cation **2b**$^{\bullet+}$ or directly at the stage of the diazenyl radical cation **1**$^{\bullet+}$,[3c] only the 1,2-radical cation **3b**$^{\bullet+}$ and *not* its isomer **3b'**$^{\bullet+}$ should afford the spiro ether **5** (Scheme IV). However, although no isomerization of cyclopentene **3b'** into its regioisomer **3b** and *vice versa* was observed, *both* cyclopentenes give rise to spiro ether **5** (Table I, entries 18, 19). To account for the formation of spiro ether **5** from **3b'** the allyl cation **3b(-H)**$^+$ is proposed as a plausible intermediate. The allyl cation **3(-H)**$^+$ is generated from **2**$^{\bullet+}$ or **3**$^{\bullet+}$ either by H abstraction (for

(23) Farid, S.; Gould, I. R.; Young, R. H.; Moody, R. E. *J. Phys. Chem.* **1991**, *95*, 2068.
(24) Mattay, J.; Vondenhof, M. *Top. Curr. Chem.* **1991**, *159*, 219.
(25) Distinctly different correlations of k_{BET} with the energy gap apply for charge recombination (DCA-derived geminate pair) and charge shift (TPT-derived geminate ion pair).[22a]

TPT•) or by deprotonation (for DCA•⁻) and subsequent oxidation of the allyl radical **3(-H)•**. Both processes are most likely performed by the reduced sensitizer and were explicitly established for similar cases.[9a,11a,26] Indeed, both sensitizers were consumed during photolysis as seen by fading fluorescence and decreasing absorption above 400 nm. Up to the conversions run (cf. Table I) the amount of added sensitizer was enough for the formation of the unsaturated trapping product **5**, even if a stoichiometric reaction between sensitizer and substrate had taken place.

The existence of the allyl cation **3(-H)⁺** or the corresponding allyl radical **3(-H)•** as intermediates would also explain the formation of cyclopentadiene **4c** from azoalkane **1c**, which is observed only under PET conditions (Table I, entries 6, 7, 10) for which **1b** yields spiro ethers **5** and **6**. The allyl radical **3c(-H)•** could subsequently be converted to cyclopentadiene **4c** or cyclopentene **3c**, while proton abstraction from the allyl cation **3c(-H)⁺** would yield cyclopentadiene **4c** directly. Again, the sensitizer radical anion may function as H abstractor; alternatively, a disproportionation mechanism is at play.[11a]

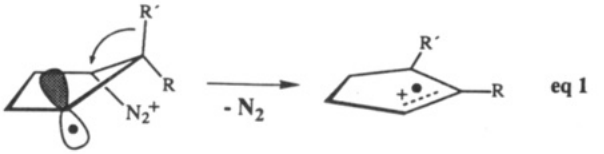
The PET reactions of azoalkanes **1** constitute illustrative examples of the impact a cosensitizer[22] can have on the product distribution. It is well-known that biphenyl (Ph_2) is an efficient cosensitizer, and quantitative laser flash spectroscopic experiments with aromatic donor systems established that DCA gives in the presence of Ph_2 high quantum yields of free radical ions.[22a] Indeed, addition of Ph_2 in the DCA-sensitized photolyses of the azoalkanes **1b,c** gave rise to more cyclopentenes **3** as rearranged products (Table I, entries 9, 10); for **1b** also spiro ether **5** and its saturated derivative **6** were detected, which were not observed in previous photolyses (Table I, entries 5, 7). Even more drastic was the change in the product distribution when TPT was used (Table I, entries 11, 12), for which cosensitization suppressed almost completely the formation of bicyclopentane **2**; this points toward the intervention of long-lived, presumably free-radical ions.

Spiro ether **6** arises either from trapping of the 1,3-diyl radical cation **2b•⁺** or from intramolecular attack on the 1,2-radical cation **3b•⁺** but not **3b′•⁺**, as shown in control experiments (Table I, entries 20, 21). In the TPT-sensitized ET reactions it was said that the significant amounts of spiro ether **5** (Table I, entries 5, 7) were unlikely to arise from trapping of **2b•⁺**, since azoalkane **1b** and its parent compound **1c** always gave similar yields of bicyclopentanes **2b,c**. Nevertheless, it cannot be excluded that the minor amounts of spiro ether **6** (6%) in the DCA/Ph_2-sensitized reaction are formed directly from **2b•⁺**.

If intramolecular trapping of the 1,3 diyl radical cation **2b•⁺**, derived from the PET denitrogenation of azoalkane **1b**, were to take place, the PET reaction of bicyclopentane **2b** should give under the same conditions also the saturated spiro ether **6**. This follows from the fact that the strained hydrocarbon affords directly the 1,3-diyl radical cation **2b•⁺** in the primary oxidation step and no rearrangement at the stage of the diazenyl radical cation **1b•⁺** has to be taken into account (Scheme IV). Indeed, bicyclopentane **2b** yielded in the photolysis with DCA/Ph_2 (Table I, entry 15) mostly the saturated spiro ether **6**, some unsaturated derivative **5**, and more surprisingly, *none* of the cyclopentenes **3b,b′**. In contrast, 1,3-dimethylhousane (**2c**) afforded cyclopentene **3c** as rearrangement product (Table I, entries 14, 16).

(26) Arnold, D. R.; Wayner, D. D. M. *Can. J. Chem.* **1985**, *63*, 871.

The absence of cyclopentenes **3b,b′** could mean that the corresponding 1,2 radical cations **3•⁺** lead exclusively to **3b(-H)⁺**, which is then quantitatively trapped intramolecularly. Alternatively, under these conditions rearrangement cannot compete with trapping; however, comparative studies in the liquid phase and under matrix isolation (ESR) showed that DBH derivatives are more prone to rearrangement upon oxidation than the corresponding bicyclopentanes.[3c] This was attributed to the involvement of diazenyl radical cations **1•⁺**, which undergo facile denitrogenation with concomitant migration of the antiperiplanar substituent (eq 1). Thus, for bicyclopentane **2b**, for which such alternative access to the isomeric cyclopentenes **3b,b′** does not exist, cyclization through intramolecular trapping to spiroether **6** dominates over formation of cyclopentenes **3b,b′** through rearrangement.



eq 1

$1^{+\bullet}$

It is noteworthy that bicyclopentane **2b** yielded with TPT as sensitizer almost exclusively unsaturated spiro ether **5** (Table I, entry 13). This may be due to the higher propensity of reduced TPT (the neutral triphenylpyrylium radical) for hydrogen abstraction. Consistent with this finding are also the results of TPT-sensitized photolyses of azoalkane **1b** in CH_2Cl_2 and CH_3CN (Table I, entries 5, 7). In spite of the generally lower lifetime of radical cations in CRIP (see above), more spiro ether **5** than cyclopentenes **3b,b′** is formed in CH_2Cl_2, while it is *vice versa* in CH_3CN. Therefore, we suggest that the proximity of the triphenylpyrylium radical in the CRIP does not only enhance BET but also the H abstraction from the 1,2-radical cation **3•⁺**, which leads then to a geminate pair of a neutral molecule and the allyl-stabilized cation **3b(-H)⁺**. Addition of the cosensitizer Ph_2 (Table I, entries 11, 12) perturbs this competitive situation at the expense of BET, so that H abstraction is significantly increased, as reflected in the higher yield of spiro ether **5** as trapping product.

In conclusion, the intramolecular trapping experiments helped to establish a rather detailed mechanism of the PET-induced chemistry of azoalkanes **1b** and the bicyclopentane **2b**, which should also apply to other azoalkanes and bicyclopentanes. Thus, the allyl cation **3(-H)⁺** is a likely key intermediate, which explains the formation of products such as cyclopentadienes; their mechanistic origin was until now speculation. The results provide further evidence for the involvement of diazenyl radical cations **1•⁺**, which to date have escaped direct detection. In general, although upon PET the DBH derivatives give rise to interesting radical cation chemistry, to use these azoalkanes as precursors for to 1,3-diyl radical cations **2•⁺** is complicated by competing rearrangement directly into 1,2-radical cations **3•⁺**, as depicted in Scheme IV.

Experimental Section

General Aspects. Gas chromatographic analyses were conducted on capillary GC instruments, equipped with a flame ionization detector (FID). Carbowax and OV-1 30-m fused silica

columns with an internal diameter of 0.25 mm and a film thickness of 0.25 mm were used. IR data are given in cm^{-1}. The PET reactions were carried out by irradiation with a 150-W high-pressure mercury lamp and a Schott GG 400 glass filter to block all light below λ = 400 nm. An argon ion laser, fitted with a selected UV tube (λ = 333–364 nm), was used as irradiation source for the direct photolysis of the azoalkanes.

Conversions, relative yields, and mass balances were determined by GC and corrected for the response factors of the starting material and the products. As quantitative measure were used the integrated peak areas of the chromatograms. The mass balances (mb) were determined according to eq 2, where A_t =

$$\% \text{ mb} = [\sum A_t(\text{P})/A_t(\text{IS})]/[A_o(\text{S})/A_o(\text{IS}) - A_t(\text{S})/A_t(\text{IS})]100 \quad (2)$$

peak area after reaction time t, A_o = peak area before the reaction, S = substrate, IS = internal standard, and P = product. Thus, the amount of unreacted starting material is *not* included in the mass balance. The entries in Table I refer to conversions up to which no secondary photolysis, i.e., change in product distribution, was observed.

Preparation of the Azoalkanes. Solvents and commercially available chemicals were purified by standard procedures. Column chromatography was carried out on silica gel (0.032–0.063 μm).

1,4-Dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1c) was prepared according to the known procedure.[19]

1-(2-Methyl-1,3-dioxolan-2-yl)-3-methyleneoct-2-ene. Under an argon gas atmosphere 1-bromopent-4-ene[27] (48.8 g, 329 mmol) was added by means of a dropping funnel to magnesium shavings (7.99 g, 329 mmol) in 300 mL of THF at such a rate that a gentle reflux was maintained. After the addition was completed the reaction mixture was refluxed for an additional 1 h until all magnesium had disappeared. Upon cooling to −78 °C lithium bromide (13.0 g, 150 mmol) and copper(I) bromide (23.55 g, 104 mmol) were added carefully. The brownish-gray suspension was stirred for 1 h at −78 °C before 1-(2-methyl-1,3-dioxolan-2-yl)but-3-yne[28] (20.0 g, 143 mmol) was administered and the mixture allowed to warm to −30 °C. After being stirred for 1 h at that temperature, the reaction was quenched with 100 mL of aqueous NH_4Cl, which contained 10% potassium cyanide. The colorless aqueous layer was extracted with diethyl ether (3 × 100 mL), and the combined organic layers were washed with aqueous NH_4Cl (1 × 100 mL) and water (2 × 70 mL). After drying over Na_2SO_4 and removal of the solvent at 25 °C/20 Torr, the liquid residue was distilled *in vacuo*. The fraction with a boiling point of 84–90 °C/0.01 Torr was collected (12.5 g, 42%): IR (neat) 3080, 2985, 2930, 2880, 1685, 1450, 1380, 1230, 1065, 895; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.34 (s, 3H), 1.42–1.44 (m, 10H), 3.92 (s, 4H), 4.72 (br s, 2H), 5.02 (m, 2H), 5.73 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 23.7 (q), 26.9 (t), 30.1 (t), 33.3 (t), 35.6 (t), 37.3 (t), 64.5 (2 × t), 108.6 (t), 109.8 (s), 114.4 (t), 138.6 (d), 149.2 (s). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.38; H, 10.28.

5-Methylenedec-9-en-2-one. The above ketal (12.5 g, 59.5 mmol) was added to a suspension of 10 g of silica gel in 4 mL of 20% aqueous sulfuric acid and 15 mL of CH_2Cl_2[18] and stirred for 4 h at room temperature. After filtration and removal of the solvent at 25 °C/20 Torr, the distillation of the residue yielded a colorless liquid (10.1 g, 96%), bp 87–88 °C/5 Torr: IR (neat) 3095, 2995, 2950, 2870, 1725, 1650, 1625, 1445, 1420, 1365; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42–1.62 (m, 2H), 1.94–2.10 (m, 4H), 2.08 (s, 3H), 2.25 (m_c, 2H), 2.55 (m_c, 2H), 4.66 (br s, 1H), 4.72 (br s, 1H), 4.88–5.05 (m, 2H), 5.78 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.9 (t), 29.7 (t), 29.9 (q), 33.3 (t), 35.7 (t), 41.9 (t), 109.2 (t), 114.6 (t), 138.6 (d), 148.1 (s), 208.5 (s); MS (70 eV) m/z 166 (0.1) [M$^+$], 125 (2), 108 (19), 93 (8), 81 (17), 69 (13), 67 (12), 55 (14), 43 (100), 41 (18). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.67; H, 11.22.

5-Methylenedec-9-en-2-one Tosylhydrazone. To a suspension of tosyl hydrazide (15.3 g, 82.2 mmol) in 200 mL of *n*-pentane were added 5-methylenedec-9-en-2-one (12.4 g, 74.4 mmol) and 0.15 mL of glacial acid. After mechanical stirring for 24 h at room temperature, the precipitate was collected and washed with 75 mL of cold *n*-pentane. Recrystallization from 20 mL of ethanol at −20 °C yielded colorless needles (14.9 g, 61%), mp 67–69 °C. The product consisted of a 83:17 mixture of the *anti* and *syn* isomers: IR (KBr) 3220, 3070, 2980, 2960, 2925, 2850, 1635, 1595, 1490, 1450; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33–1.48 (m, 2H), 1.75–2.15 (m, 9H), 2.22–2.33 (m, 2H), 2.39 (s, 3H), 4.51–4.73 (m, 2H), 4.87–5.03 (m, 2H), 5.64–5.85 (m, 1H), 7.26 (br d, J = 8.1 Hz, 2H), 7.82 (br d, J = 8.1 Hz, 2H), 7.96 (br s, 1H); (*anti*-isomer) ^{13}C NMR (63 MHz, $CDCl_3$) δ 15.7 (q), 21.5 (q), 26.7 (t), 31.9 (t), 33.2 (t), 35.2 (t), 36.9 (t), 109.4 (t), 114.5 (t), 127.9 (d), 129.3 (2 × d), 135.4 (s), 138.5 (2 × d), 143.7 (s), 148.0 (s), 157.8 (s); (*syn*-isomer) ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.5 (q), 23.0 (q), 28.8 (t), 30.7 (t), 33.1 (t), 35.3 (t), 36.8 (t), 110.0 (t), 114.6 (t), 127.9 (d), 129.4 (2 × d), 135.3 (s), 138.4 (2 × d), 143.8 (s), 147.5 (s), 159.1 (s); MS (70 eV) m/z 335 (0.2) [M$^+$], 179 (100), 149 (15), 135 (15), 107 (23), 95 (30), 93 (22), 91 (54), 81 (38), 41 (84). Anal. Calcd for $C_{18}H_{26}N_2O_2S$: C, 64.64; H, 7.84; N, 8.38. Found: C, 64.66; H, 7.92; N, 8.26.

1-(Pent-4-enyl)-4-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1a). To a refluxed solution of BF_3·Et_2O (3.20 g, 25.4 mmol) in 440 mL of dry benzene was added over a 7-h period the above tosylhydrazone (6.0 g, 17.9 mmol) in 500 mL of benzene. The reaction mixture was further refluxed for 1.5 h before it was quenched by addition of 120 mL of 2 M K_2CO_3. The benzene solution was washed with saturated, aqueous NaCl (3 × 150 mL), dried over Na_2SO_4, and concentrated by removal of the solvent at 30 °C/20 Torr. Column chromatography on silica gel with petroleum ether/CH_2Cl_2/methyl acetate (10/10/1) as eluent yielded 1.58 g (50%) of a yellow oil. An analytical sample was obtained by Kugelrohr distillation (90 °C/0.3 Torr): IR (CCl_4) 3090, 2970, 2940, 2860, 1640, 1500, 1450, 1435, 1380, 1320; UV (CH_3CN) λ (ϵ) 348 nm (158); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93–1.08 (m, 4H), 1.43–1.71 (m, 4H), 1.78 (s, 3H), 1.96–2.34 (m, 4H), 4.90–5.08 (m, 2H), 5.82 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.0 (q), 25.1 (t), 27.4 (t), 28.8 (t), 30.9 (t), 34.2 (t), 48.3 (t), 84.3 (s), 88.6 (s), 114.8 (t), 138.4 (d); MS (70 eV) m/z 179 (0.1) [M$^+$], 135 (3), 107 (19), 96 (3), 95 (5), 94 (11), 93 (13), 81 (100), 79 (19), 76 (15). Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.91; H, 10.22; N, 15.64.

1-(4-Hydroxypentyl)-4-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1b). A mixture of azoalkane **1a** (640 mg, 3.6 mmol) and 0.2 mL of 70% $HClO_4$ was stirred for 8 h at 0 °C. After neutralization with aqueous NaOH and extraction with CH_2Cl_2 (5 × 10 mL), the combined organic layers were washed with aqueous NH_4Cl (1 × mL) and water (2 × 5 mL) and dried over Na_2SO_4. The solvent was removed at 25 °C/20 Torr and the residue purified by column chromatography on silica gel with ethyl acetate/methanol as eluent. The azoalkane **1b** was obtained as a colorless oil (462 mg, 66%): IR (neat) 3405 (br), 2975, 2940, 2875, 1500, 1450, 1385, 1320, 1245, 1130; UV (CH_3CN) λ (ϵ) 348 nm (245); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95–1.05 (m, 4H), 1.18 (d, J = 6.2 Hz, 3H), 1.46–1.64 (m, 6H), 1.82 (s, 3H), 2.01–2.30 (m, 2H), 2.95 (br s, 1H), 3.82 (m, 1H); ^{13}C NMR (53 MHz, $CDCl_3$) δ 17.0 (q), 22.0 (t), 23.5 (q), 27.5 (t), 28.7 (t), 31.3 (t), 39.6 (t), 48.2 (t), 67.7 (d), 84.2 (s), 88.7 (s). Anal. Calcd for $C_{11}H_{20}N_2O$: C, 67.31; H, 10.27; N, 14.27. Found: C, 67.10; H, 10.24; N, 14.24.

1-(4-Hydroxypentyl)-4-methylbicyclo[2.1.0]pentane (2b). A solution of azoalkane **1b** (400 mg, 2.04 mmol) in 10 mL of CH_2Cl_2 was irradiated for 20 min with all UV-lines of the argon ion laser (UV output 1.9–2.0 W). The solvent was removed at 0 °C/20 Torr, and the residue was purified by preparative gas chromatography to yield a colorless oil (326 mg, 95%): FT-IR (gas phase) 3645, 3041, 2931, 2867, 1452, 1381, 1290, 1245, 1102, 999; ^{1}H NMR (250 MHz, C_6D_6) δ 0.20 (m, 1H), 0.72 (d, J = 3.7 Hz, 1H), 1.06 (d, J = 6.2 Hz, 3H), 1.16 (s, 3H), 1.21–1.55 (m, 9H), 1.66–1.90 (m, 2H), 3.58 (tq, J = 6.0, 6.2 Hz, 1H); ^{13}C NMR (63 MHz, C_6D_6) δ 16.9 (q), 23.8 (q), 24.1 (t), 25.3 (s), 25.9 (t), 26.2 (t), 27.3 (t), 28.1 (s), 31.4 (t), 39.8 (t), 67.8 (d); MS (70 eV) m/z 167 (5) [M$^+$], 107 (15), 91 (12), 94 (29), 93 (35), 81 (100), 79 (46), 67 (22), 55 (27), 53 (25). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.44; H, 12.22.

(27) Antczak, K.; Kingston, J. F.; Alward, S. J.; Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 829.
(28) Flahaut, J.; Migniac, P. *Helv. Chim. Acta* **1978**, *61*, 2275. Abidi, S. L. *J. Org. Chem.* **1986**, *51*, 2687.

General Procedure for PET Reactions. All photolyses were carried out on 5-mL samples in a closed system, which was provided with a gas inlet, a sampling inlet, and a cold finger. The solutions were *ca.* 0.015 M in substrate and contained *n*-dodecane for **1b**, **2b** and *n*-nonane for **1c**, **2c** as internal GC standard. The sensitizers 9,10-dicyanoanthracene (DCA) or 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) were added (10 mol %) and the solutions purged with argon gas for 15 min prior to photolysis. In the case of DCA, which is only partially soluble (*ca.* 10^{-5} M), saturated solutions were employed and the photolyses were run in the presence of undissolved material. The cosensitizer biphenyl was used in 10 molar excess (0.15 M).

The irradiations were performed at −5 °C with $\lambda > 400$ nm while stirring magnetically. The progress of the photolyses was monitored at appropriate intervals by capillary GC. For **1b**, **2b** an OV-1 column was operated at 100 °C for 1 min and then raised within 10 min to 150 °C for 20 min at injector/detector temperatures of 175/175 °C and a carrier gas (He) pressure of 0.8 bar. The carbowax column was operated at 80 °C for 2 min and then raised within 4 min to 120 °C for 20 min under otherwise identical conditions. To elucidate the structure of the products **3b,b′**, **5**, and **6**, a preparative run was conducted in which 460 mg (2.34 mmol) of azoalkane **1b** in 50 mL of CH_3CN was irradiated ($\lambda > 400$ nm) for 8 h in the presence of DCA (200 mg, 0.74 mmol; added in portions of 50 mg each 2 h) and biphenyl (3.45 g, 22.4 mmol). The reaction mixture was concentrated by removing the solvent by distillation on a 30-cm Vigreux column. The products were separated through preparative gas chromatography on a 1.5-m glass column, which was packed with 10% SE 30 on Volaspher A2. The column was operated at 120 °C with the injector/detector temperatures at 160 °C/160 °C and carrier gas (N_2) pressure of 1.8 bar.

2,7-Dimethyl-6-oxaspiro[4.5]dec-1-ene (5). The unsaturated spiro ether **5** was obtained as a mixture of two diastereomers (1:1), which were separated by preparative GC with the above conditions. (*R**,*R**)-**5**: FT-IR (gas phase) 2985, 2938, 2865, 1654, 1451, 1379, 1230, 1225, 1081, 1018; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.04 (d, J = 4.6 Hz, 3H), 1.25–1.65 (m, 6H), 1.69 (br s, 3H), 1.78–2.43 (m, 4H), 3.55 (m_c, 1H), 6.02 (ps q, J = 1.6 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.2 (q), 21.3 (t), 22.7 (q), 33.4 (t), 34.2 (t), 35.7 (t), 40.1 (t), 68.3 (d), 87.6 (s), 125.5 (d), 144.7 (s); MS (70 eV) *m*/*z* 166 (23) [M^+], 151 (9), 107 (12), 98 (11), 97 (100), 96 (74), 94 (25), 91 (30), 81 (22), 79 (35), 53 (31), $C_{11}H_{18}O$ calcd 166.136, found 166.136 (MS). (*R**,*S**)-**5**: FT-IR (gas phase) 2995, 2957, 2868, 1655, 1451, 1380, 1338, 1208, 1083, 1020; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.12 (d, J = 6.2 Hz, 3H), 1.35–1.69 (m, 6H), 1.72 (d, J = 1.5 Hz, 3H), 1.97 (ps t, J = 7.6 Hz, 2H), 2.11–2.42 (m, 2H), 3.57 (m_c, 1H), 5.22 (ps q, J = 1.6 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.6 (q), 22.7 (t), 24.3 (q), 34.0 (t), 34.5 (t), 35.5 (t), 36.7 (t), 68.3 (d), 87.7 (s), 129.9 (d), 140.8 (s); MS (70 eV) *m*/*z* 166 (7) [M^+], 149 (9), 97 (100), 96 (68), 94 (18), 91 (25), 81 (73), 79 (48), 77 (24), 55 (31), 53 (28); $C_{11}H_{18}O$ calcd 166.136, found 166.135 (MS).

2,7-Dimethyl-6-oxaspiro[4.5]decane (6). The saturated spiro ether **6** was obtained as a mixture of four diastereomers (2:2:1:1), which could not be separated by GC: FT-IR (gas phase) 2933, 2871, 1453, 1377, 1305, 1269, 1218, 1122, 1084, 1023; ^{1}H NMR (400 MHz, CD_2Cl_2) of the two major isomers δ 0.94 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H′), 1.03 (d, J = 6.1 Hz, 3H), 1.05 (d, J = 6.1 Hz, 3H′), 1.08–2.26 (m, 13 H + 13 H′), 3.45–3.56 (m, 1H + 1H′); ^{1}H NMR (400 MHz, CD_2Cl_2) of the two minor isomers δ 1.00 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H′), 1.04 (d, J = 6.1 Hz, 3H), 1.05 (d, J = 6.1 Hz, 3H′), 1.08–2.26 (m, 13 H + 13 H′), 3.45–3.56 (m, 1H + 1H′); ^{13}C NMR (63 MHz, CD_2Cl_2) of all four isomers δ 20.0 (2 × q), 20.2 (q), 20.3 (q), 21.1 (t), 21.3 (t), 22.2 (2 × t), 22.3 (q), 22.4 (2 × q), 22.5 (q), 32.0 (d), 32.1 (t), 32.3 (t), 32.8 (t), 32.9 (d), 33.0 (t), 33.3 (d), 33.4 (t), 33.5 (t), 33.7 (2 × t), 33.8 (d), 35.5 (t), 35.7 (t), 36.0 (2 × t), 41.2 (t), 41.5 (t), 41.9 (t), 42.4 (t), 50.4 (t), 50.5 (t), 50.7 (2 × t), 66.8 (d), 67.3 (d), 67.4 (d), 67.8 (d), 83.4 (s), 83.5 (s), 83.7 (s), 83.9 (s); MS (70 eV) *m*/*z* 168 (11) [M^+], 139 (20), 125 (36), 112 (100), 98 (14), 97 (16), 83 (22), 81 (44), 71 (14), 69 (22), 55 (37); $C_{11}H_{20}O$ calcd 168.151, found 168.152 (MS).

1-(4-Hydroxypentyl)-3-methylcyclopent-1-ene (3b). FT-IR (gas phase) 3655, 3039, 2957, 2876, 1649, 1457, 1379, 1246, 1101, 942; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.91 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.1 Hz, 3H), 1.19–1.55 (m, 6H), 1.92–2.20 (m, 5H), 2.63 (br s, 1H), 3.74 (m_c, 1H), 5.16 (ps quin, J = 1.7 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.4 (q), 23.5 (q), 23.9 (t), 31.1 (t), 32.5 (t), 34.7 (t), 39.1 (t), 39.8 (d), 68.1 (d), 129.9 (d), 143.6 (s); MS (70 eV) *m*/*z* 168 (4) [M^+], 150 (14), 135 (32), 108 (60), 106 (33), 95 (28), 94 (33), 93 (100), 81 (72), 79 (87), 67 (47); $C_{11}H_{20}O$ calcd 168.151, found 168.152 (MS).

1-(4-Hydroxypentyl)-3-methylcyclopent-2-ene (3b′). FT-IR (gas phase) 3655, 3039, 2931, 2869, 1654, 1453, 1381, 1246, 1107, 941; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.11 (d, J = 6.1 Hz, 3H), 1.14–1.41 (m, 8H), 1.62 (br s, 3H), 1.92–2.18 (m, 3H), 2.60 (br s, 1H), 3.70 (m_c, 1H), 5.18 (ps sept, J = 2.2 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.6 (q), 23.5 (q), 24.1 (t), 30.8 (t), 36.3 (t), 36.4 (t), 39.6 (t), 45.8 (d), 68.2 (d), 128.9 (d), 140.1 (s); MS (70 eV) *m*/*z* 168 (5) [M^+], 108 (10), 107 (29), 94 (25), 93 (20), 81 (100), 79 (28), 77 (11), 66 (6), 53 (13); $C_{11}H_{20}O$ calcd 168.151, found 168.151 (MS).

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