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Photolysis of 2,3-Diazabicyclo[2.2.2]oct-2-ene: Electronic Spin Determines the Distribution of Products

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Abstract: The distribution of products from the photolysis of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) is determined primarily by the electronic spin state of the cyclohexane-1,4-diyl intermediate. DBO undergoes photolysis by direct irradiation of the N=N chromophore and singlet-sensitization to produce 1,5-hexadiene and bicyclo[2.2.0]hexane with a product ratio of 51:49 in *n*-octane. Triplet-sensitized photolysis in *n*-octane produces a product ratio of 70:30 1,5-hexadiene−bicyclo[2.2.0]hexane. The ^{14}N/^{15}N kinetic isotope effect on deazatization is 1.025 for DBO and 1.004 for the more-strained analogue, 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH). The large kinetic isotope effect on DBO photolysis is consistent with rate-limiting C−N bond scission in excited DBO. The amount of hexadiene can be increased by heavy atom solvents that contain bromine and iodine, or by an increase in photolysis intensity, to a maximum of 70:30 hexadiene:bicyclohexane. The product distribution and ^{15}N kinetic isotope effect is insensitive to solvent viscosity, temperature, and magnetic field (up to 7.05 T). The ratio of products can be quantitatively accounted for by fast intersystem crossing (ISC) due to spin−orbit coupling as the boat conformer of the cyclohexane-1,4-diyl is forming. A statistical distribution of 25:75 singlet-triplet cyclohexane-1,4-diyl in the boat geometry is produced by direct and singlet-sensitized photolysis. The singlet cyclohexane-1,4-diyl boat collapses to form bicyclohexane with unit efficiency, whereas the triplet boat is long-lived such that relaxation to the twist-boat occurs. The triplet cyclohexane-1,4-diyl twist-boat is unreactive toward ring closure or bond scission and can only undergo further reaction after ISC to the singlet spin state. In the twist-boat, the singlet cyclohexane-1,4-diyl undergoes ring-opening to 1,5-hexadiene at a rate that is 7/3 faster than it undergoes ring closure to [2.2.0] bicyclohexane. Triplet-sensitized photolysis also produces cyclohexane-1,4-diyl in the boat geometry, but the singlet spin state is not populated because it is 22 kcal/mol higher in energy.

Introduction

Over the past 30 years, the mechanism of dinitrogen extrusion from bicyclic diazenes has been studied to learn of the interplay and the priority of factors that dominate reactivity in reactions with biradical intermediates:[1−5] *Intrinsic* properties of the reaction, such as the biradical electron spin, the biradical conformation, the thermal energy distribution, and the mixing of free-energy surfaces, compete with *extrinsic* properties of the reaction, such as solvent viscosity and electron spin relaxation, to control the reaction rate and the distribution of products. Reactions with only a single product will tend to have well-defined free-energy surfaces that constrain reactivity to narrow limits that are enforced by severe energy penalties. Reactions with a product manifold that arises from a common intermediate are more complex and must have junctures or energetically "shallow" surfaces that allow a complex distribution of products.[5,6] In reactions that involve the homolytic cleavage of bonds or the condensation of two open valence shell atoms, the spin state of the radical pair or biradical will have a significant impact on the product distribution of the reaction.

2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) is the paradigm for a class of bicyclic diazenes that undergoes thermal and photochemical extrusion of N_2 to generate a reactive 1,4-biradical intermediate[1] (Scheme 1). Absorption of a photon produces the excited singlet state.[2,4] Fluorescence from the lowest excited singlet state of DBO is favorable ($\Phi_F = 0.39$ and $\tau_F = 434$ ns).[2,4] Intersystem crossing (ISC) in bicyclic diazenes is unfavorable, since there is no evidence of phosphorescence or formation of triplet DBO from direct irradiation of the N=N chromophore.[2,4] If deazatization begins with homolysis of one C−N bond to produce the diazenyl biradical, **1**, spin conservation requires that biradical **1** be formed in the singlet spin state.[7] In theory, non-productive recombination of the C−N bond may compete with homolysis of the second C−N bond.[3d] The cyclohexane-1,4-diyl biradical, **2**, is formed in the boat geometry, but this species probably does not lie at an energy minimum and the molecule quickly relaxes to a twist-boat.[8] DBO and its derivatives are termed "reluctant azoalkanes" because of their characteristically low photochemical quantum yields (direct photolysis, $\Phi_D = 0.02$; triplet-sensitized photolysis, $\Phi_T = 0.014$)[2] and unusual thermal stability,[3] as compared to

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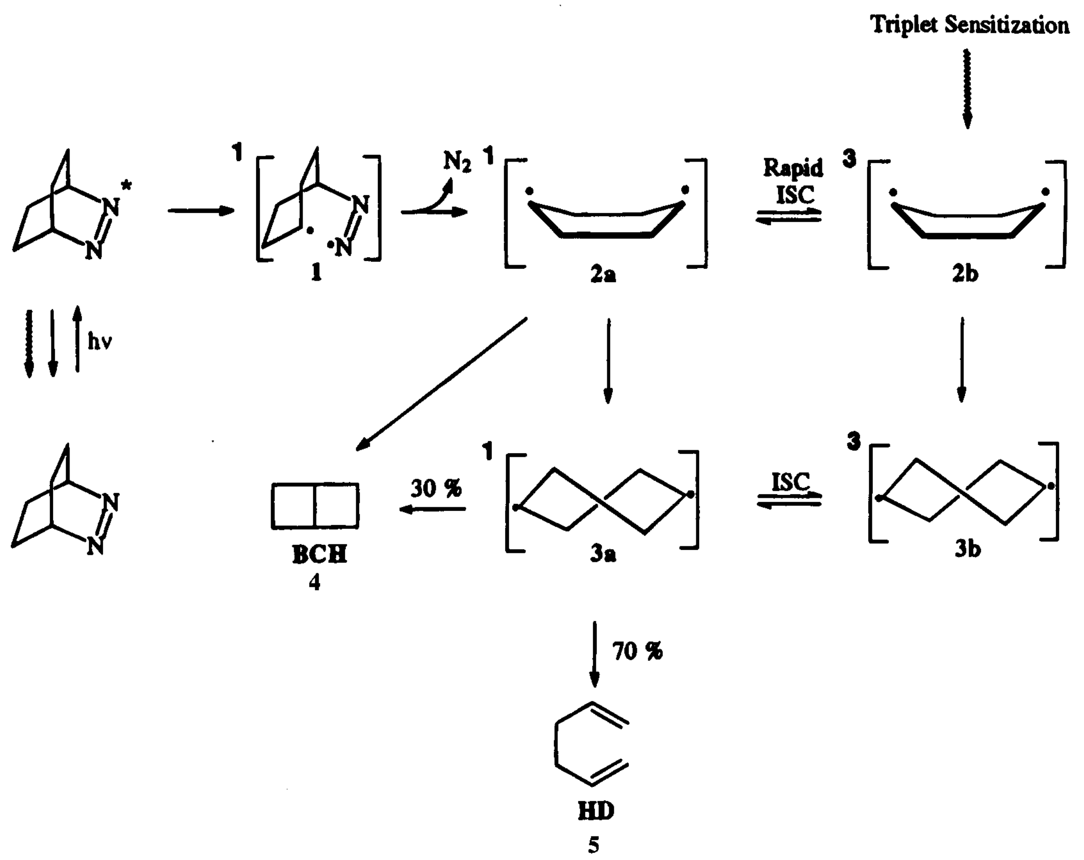
Scheme 1



the homologous 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) system ($\Phi_{D,T} \approx 1$).[2] Two major products are generated by the photolysis and thermolysis of DBO (Scheme 1): bicyclo[2.2.0]hexane (**4**, BCH) and 1,5-hexadiene (**5**, HD). Direct irradiation of the R−N=N−R chromophore at 366 nm produces a 51:49 ratio of HD:BCH, whereas triplet-sensitized photolysis employing benzophenone produces a 70:30 ratio of HD:BCH.[2c,e] Only 1,5-hexadiene is detectable in the thermolysis of DBO because the high temperature required to initiate thermolysis also opens the bicyclo[2.2.0]hexane product.[3c,9]

A *prima facia* examination of these data suggests a role for electron spin correlation in the biradical, such that direct photolysis produces only the singlet biradical, **2a**, and leads to BCH, whereas triplet-sensitized photolysis leads to the triplet biradical, **2b**, that is sufficiently long-lived to give rise to HD.[2c,10] This scheme requires fast intersystem crossing (ISC) in excess of 10^{10} s^{-1} to mix the singlet and triplet spin states prior to relaxation of the boat biradicals, **2a** and **2b**.[2c,10] In the boat conformation, the open-shell atoms are oriented for maximum orbital overlap.[10c,11] Intersystem crossing through spin−orbit coupling (SOC) is maximal when the angle between the two open-shell molecular orbitals approaches 90°.[10c,11] In the rigid cyclohexane-1,4-diyl boat, the singlet spin state of the biradical is 22 kcal/mol higher than the corresponding triplet. The singlet boat conformation of cyclohexane-1,4-diyl, **2a**, can collapse to form a covalent bond when the electron spins are antiparallel, whereas the triplet boat biradical, **2b**, lives long enough to relax to the twist-boat, **3b**, thereby minimizing ISC.[2c,10c] Unless the hydrocarbon biradical exists in the boat geometry, ISC is unlikely to proceed at a significant rate, as only 1% of the molecules contain either ^{13}C or ^{15}N to mix the spin states via nuclear hyperfine interactions. Molecules that start on a high-energy surface are more likely to have sufficient energy to undergo ISC than molecules at lower energy excited states.

Although ISC in the excited singlet (intact) DBO is known to be insignificant because of the long fluorescent lifetime, the question of ISC (and even electron spin-dependent recombination) in the diazenyl biradical is still an open question. Herein, we have examined the ^{15}N kinetic isotope effect on N_2 extrusion to show that recombination in the diazenyl biradical **1** is not significant, and we show that direct photolysis of DBO leads to C−N bond cleavage in the excited singlet state of DBO, whereas C−N bond cleavage in the more strained diazene, DBH, occurs in a much earlier transition state. The difficulty in overcoming the homolysis energy barrier in excited DBO is responsible for the low photochemical quantum yield.[2e]

Perhaps of greater significance, the product ratios that result from the direct and the triplet-sensitized photolysis of DBO can be explained *quantitatively* by a model that proposes fast ISC in a thermally-excited and short-lived boat cyclohexane-1,4-diyl such that equilibration of the singlet and triplet spin states occurs (see Discussion Section).[12] Thus, direct photolysis produces a statistical distribution of 25% singlet and 75% triplet spin states. In the boat cyclohexane-1,4-diyl, only the 25% singlet diyl can close to BCH, whereas the 75% triplet biradical will relax to the twist-boat where slower ISC will populate the singlet spin state and allow for a ≈70:30 mixture of HD:BCH formation, where the product ratio is determined by the energy barriers to ring fluxion.

Dynamic Control in DBH. Carpenter has shown that the distribution of products in the thermal deazatization of 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo-exo*-5,6-d_2 is under dynamic

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control.[5] The stereoisomers arise from a common intermediate that occurs after the rate-limiting step and small changes in product distribution are due to a variation in the amount of excess energy that the cyclopentane-1,3-diyl carries forward from bond homolysis.[5] He states that "...the reaction coordinate for nitrogen expulsion imprint[s] on the hydrocarbon fragment a set of atomic motions that carr[y] it to a part of the potential energy hypersurface where the arrangement of atoms [is] closer to the structure [of the 4-*exo-exo* product, rather than the *endo-endo* product]".[5b] An enthalpy surface for the reaction was constructed using a combination of experimental heats of formation, Benson group additivity calculations, and AM1 semiempirical MO calculations.[5] The most notable feature of Carpenter's enthalpy surface is a plateau after the transition state. This flat portion of the surface leads to the two diastereomeric products observed. Independent *ab initio* calculations on DBH confirm this result.[8] Interactions of the biradical with solvent change the product ratio in a predictable fashion.

In the thermolysis or triplet-sensitized photolysis of DBH, the spin state of the 1,3-biradical will be exclusively singlet or triplet, and there is poor electronic overlap of the radical centers, so no physical mechanism exists to interconvert the two spin states. In the photolysis of DBO both singlet and triplet cyclohexane-1,4-diyl can be produced by photolysis and the two electronic spin states can interconvert while on the way to the boat cyclohexane-1,4-diyl. In this case, the spin state of the biradical becomes the major determinant of the product distribution with dynamic factors being only a minor determinant of the product distribution. It is this interplay between electronic spin control and dynamic control that influences the distribution of products resulting from the photolysis of DBO.[12]

Results and Discussion

Product Analysis. Direct photolysis of DBO or its homologue, 1-Me-DBO, was accomplished by 366-nm irradiation of 0.030 M diazene in *n*-octane or the specified solvent. Triplet-sensitized photolysis was accomplished by 313-nm irradiation of 1% benzophenone (or the indicated triplet sensitizer) in 0.030 M diazene in *n*-octane. 1,5-Hexadiene is the major product of direct and triplet-sensitized photolysis, with an HD:BCH product ratio of 51:49 and 70:30, respectively, as determined by analytical GC and preparative GC/^{1}H NMR analysis (see Experimental Section for product characterization). These product ratios are consistent with the values observed in previous studies.[2]

Heavy Atom Solvent Dependence. DBO homologues with bridgehead chlorine and bromine atoms quench the excited singlet DBO by internal conversion and thereby decrease Φ_F and the fluorescence lifetime, τ_F, by nearly an order of magnitude.[2e] However, the possibility of a SOC-induced heavy atom effect on the product distribution was not addressed in that study.

To address the possibility of solvent increased ISC in biradical **2**, the relative amount of hexadiene produced by the photolysis of DBO and 1-Me-DBO was examined as a function of heavy atom solvent concentration. Figure 1 shows the percent of HD product at increasing concentrations of 1-bromooctane and 1-iodooctane in *n*-octane. An increase in heavy-atom solvent concentration leads to an increase in the production of diene. The largest amount of diene is seen in solutions with the highest proportion of iodooctane. The photochemical quantum yield decreases inversely to the increase in HD:BCH product ratio, presumably due to selective quenching of the excited singlet. Since bromooctane and iodooctane have similar dielectric constants (bromooctane, $\epsilon = 4.78$; iodooctane, $\epsilon = 4.54$),[13] a change in solvent polarity is not responsible for the change in HD:BCH product ratio.

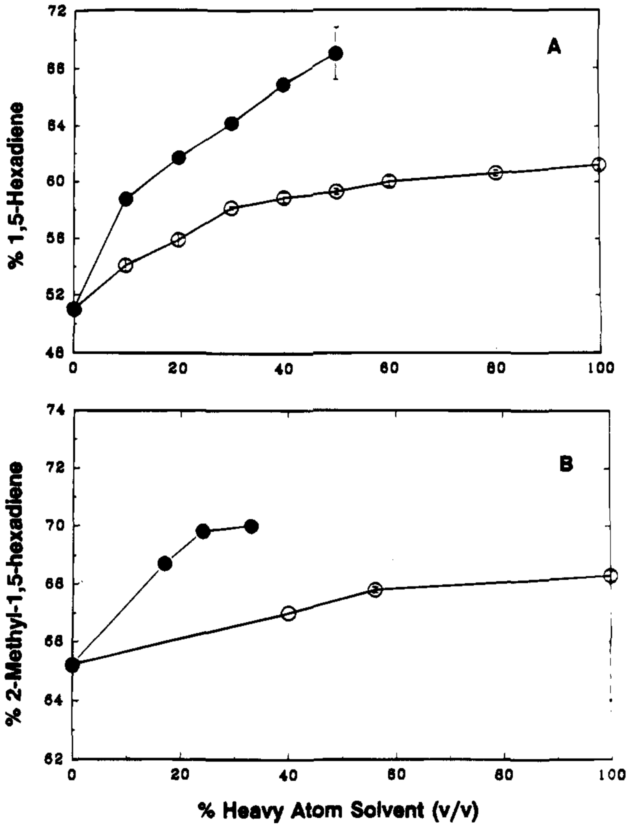

Figure 1. Direct photolysis (366 nm) at 25 °C as a function of heavy-atom solvent concentration: (A) 0.030 M DBO in 1-bromooctane/*n*-octane (○) and 0.030 M DBO in 1-iodooctane/*n*-octane (●); (B) 0.030 M 1-Me-DBO in 1-bromooctane/*n*-octane (○) and 0.030 M 1-Me-DBO in 1-iodooctane/*n*-octane (●). Standard error bars may be smaller than the plotted symbol.

There is a slight difference in viscosity between bromooctane and iodooctane.[14] Although not likely, a mechanism could be proposed in which the first C—N bond breaks and the nitrogen-centered radical remains close to the bridgehead radical.[3d] Solvents of higher viscosity would then favor recombination to regenerate DBO. For deazatization to occur, the diazenyl biradical probably must twist away, thereby increasing the distance between the open-shell atoms and disfavoring recombination. Once this happens, the second C—N bond will homolyze and N_2 will be released. In this scenario, it is clear that N_2 will not recombine with the carbon biradical. Therefore, increasingly viscous solutions that would slow diffusional escape should have no effect on the production of diene. If the carbon skeleton relaxes to the twist-boat conformation, no recombination can occur. The major reaction pathway is now B-scission to form the diene. Adam showed that any intermolecular reaction of the boat biradical **2** is unlikely.[10a] In the triplet-sensitized photolysis of DBO in 10 atm of O_2, the endoperoxide is formed in less than 10% yield.[10a]

To help understand whether heavy-atom content or solvent viscosity is responsible for the increase in diene production, DBO was photolyzed in alkanes of increasing viscosity. The

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(12) A preliminary report of this result was presented at the national meeting of the American Chemical Society, Washington, DC, August 24, 1994.

(13) *Landolt—Börnstein Numerical Data Funct. Relationships Sci. Tech.* **1991**, *6*, 157.

(14) At 25 °C, the viscosity of bromooctane was 1.42 Cp and the viscosity of iodooctane was 1.71 Cp, by measurement with an Ostwald viscosimeter.

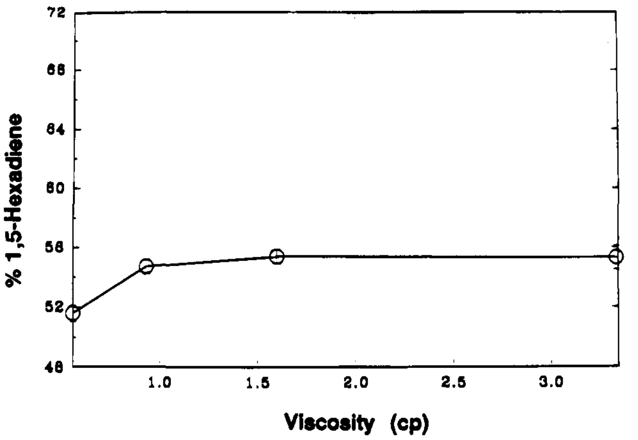

Figure 2. Percent of 1,5-hexadiene (HD) resulting from the direct photolysis (366 nm) of 0.030 M DBO at 25 °C as a function of solvent viscosity. Alkane solvents (lowest to highest viscosity): *n*-octane, *n*-decane, *n*-tridecane, *n*-hexadecane. Standard error bars may be smaller than the plotted symbol.

viscosity of 100% bromooctane is 1.42 at 25 °C.[14] If an increase in viscosity causes the increase in diene production, a higher viscosity solvent should produce the same effect as 1-bromooctane. The results are shown in Figure 2. An increase of only 3.7% diene is observed over a 3-fold increase in viscosity. This small increase in diene falls well short of the 10.2% increase observed in the photolysis of DBO in 100% bromooctane. This result suggests that an increase in solution viscosity is not responsible for the increase in diene yield.

Since the increase in diene production does not correlate with the increase in solvent viscosity, this leaves only the difference in SOC between bromine ($\xi = 2460\ \mathrm{cm}^{-1}$)[15a] and iodine ($\xi = 5060\ \mathrm{cm}^{-1}$)[15a] as being responsible for the observed difference in the HD:BCH product ratio. The heavy-atom induced change in fluorescence quenching that was observed previously can be explained by enhanced internal conversion of the excited singlet state.[2e] Similarly, a heavy-atom induced decrease in the photochemical quantum yield is consistent with any depletion of the excited DBO singlet prior to ISC to a dissociative triplet surface. The heavy-atom induced change in the product ratio is more difficult to explain without suggesting that the product ratio is determined by rate-limiting ISC in biradical **1** or **2**.

Can the Biradical Undergo Magnetic Field Dependent ISC? If the spin state of biradical **2** controls the ratio of products and SOC is not the dominant mechanism for ISC, it might be possible to perturb the rate of ISC with an external magnetic field.[16] In order to induce ISC, the difference in singlet and triplet energy levels, ΔE_{ST}, must be small. In many biradicals with a rigid structure and a small distance between the electrons, ΔE_{ST} is large and ISC does not occur. In intact DBO,[2] $E_{\mathrm{S\text{-}DBO}} = 76$ kcal/mol, $E_{\mathrm{T\text{-}DBO}} = 54$ kcal/mol, and $\Delta E_{\mathrm{ST\text{-}DBO}} = 22$ kcal/mol, but this does not reflect ΔE_{ST} in either **1**, **2**, or **3**. Even with a favorable ΔE_{ST}, a physical mechanism must exist to mix the singlet and triplet spin states. Equation 1 describes the rate of ISC as a function of nuclear hyperfine coupling and applied magnetic field, B_0.[16]

$$k_{\mathrm{ISC}} = \Delta g B_0 \beta + \Delta \sum a_i m_i \qquad (1)$$

In eq 1, Δg is the difference in Lande *g*-factor (typically 0.000–0.0001 for organic radicals) for the two unpaired electrons, B_0 is the applied magnetic field, β is the Bohr magneton, a_i is the nuclear-electronic hyperfine coupling constant, and m_i is the magnetic quantum number. Although nuclear-electronic hyperfine coupling is a valid mechanism for ISC, only 1.4% of the molecules contain either ^{13}C or ^{15}N at the open-shell centers. This simplifies eq 1 to eq 2

$$k_{\mathrm{ISC}} = \Delta g B_0 \beta \approx \Delta\omega \qquad (2)$$

where $\Delta\omega$ is the difference in Larmor precession rates for the two electrons. Magnetic field dependent ISC will now be determined solely by the strength of the applied magnetic field and the difference in *g*-values.[16]

In a symmetrical biradical where the open-shell carbon centers are identical, $\Delta g = 0$ and no magnetic field dependent increase in ISC will be observed. The 1,4-biradical **2** has a C_{2v} axis of symmetry that equates the two radical centers, such that $\Delta g = 0$. In 1-Me-DBO, there is a σ-plane of symmetry through the radical centers, but the environment at the radical centers is different and $\Delta g \neq 0$.

The HD:BCH product ratio for the photolysis of DBO and 1-Me-DBO was examined as a function of magnetic field. No magnetic field induced change in the product ratio is observed in the range 0–0.2 T (see Supplementary Material). If $\Delta g = 0.0001$, then $k_{\mathrm{isc}} \approx 6 \times 10^7\ \mathrm{s}^{-1}$ at 6.6 T. Even at the higher field, ISC will not be able to compete with the other dynamic processes available to the molecule. To test this, photolysis of DBO and 1-Me-DBO was carried out in an NMR magnet at 7.05 T. No change in product ratio was observed (data not shown). This precludes ISC as occurring by any mechanism other than geometry-dependent overlap at the open-shell centers in the cyclohexane-1,4-diyl boat, or in a conformation derived from the twist-boat.

The replacement of a bridgehead hydrogen by a methyl group has little effect on electron density or stabilization of the biradical. Other bridgehead substituents, such as phenyl groups, would introduce a larger Δg, but they also stabilize the radical and increase the triplet lifetime such that the system will always reach the chair conformation.[10a] Once this chair conformation is attained, the lifetime of the triplet is extended to 280 ns and only the diene is formed.[10a] This is observed experimentally in the photolysis of 1-phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene where the biradical produces only 2-phenyl-1,5-hexadiene because reactivity is limited to β-scission in the chair conformer.[10a] Presumably, the bridgehead methyl substituent increases the amount of 1,5-hexadiene by incompletely displacing the conformational equilibrium toward the chair and away from the boat conformer. A derivative of DBO whose 1,4-diyl possesses a long lifetime due to electronic stabilization of the radical and has a manifold product distribution has not been found.

^{15}N Kinetic Isotope Effect. The ^{15}N kinetic isotope effect (KIE) on the elimination of N_2 was used as a further probe of the spin dependence in biradicals **1** and **2**. If the first C–N bond cleavage is rate-limiting, a normal ^{15}N KIE is expected. The ^{15}N KIE was calculated according to eq 3 where *f* is the fraction of reaction, R_0 is the isotopic ratio of DBO starting material, and R_f is the isotopic ratio of product N_2.[17]

$$^{14}k/^{15}k = [\log(1-f)]/[\log(1-fR_p/R_0)] \qquad (3)$$

Table 1 shows the ^{15}N KIE for DBO photolysis in *n*-octane as a function of magnetic field; Table 2 shows the ^{15}N KIE for

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Table 1. DBO Nitrogen Kinetic Isotope Effect[a]

magnetic flux density, mT	% conversion	atom fraction of ^{15}N[b]	isotope effect[c]
0	5.7	0.003 576	1.025 ± 0.001
5	5.0	0.003 575	1.025
10	6.6	0.003 576	1.025 ± 0.001
25	5.3	0.003 578	1.025
50	6.5	0.003 573	1.026
75	6.6	0.003 578	1.025
100	4.6	0.003 563	1.029
860	3.9	0.003 578	1.024 ± 0.001

[a] Conditions: 0.030 M DBO in *n*-octane at 22 °C. [b] Isotopic composition of DBO (determined by the complete combustion of DBO to N_2 and hydrocarbon) = 0.003665 ± 0.000001 atom fraction of ^{15}N. [c] If no standard error is specified, the measurement was carried out with only one sample. If a standard error is specified, duplicate measurements were carried out and the isotope effect is an average. The absence of additional replicates is justified by the nearly-constant isotopic ratio throughout the samples.

Table 2. DBO Solvent Dependence of the Nitrogen Kinetic Isotope Effect[a]

solvent	% conversion	atom fraction of ^{15}N[b]	isotope effect[c]
chlorobenzene	13.1	0.003 556	1.032
tert-butylbenzene	10.2	0.003 567	1.0283 ± 0.0001
20% bromooctane[d]	9.8	0.003 580	1.024
40% bromooctane[d]	9.0	0.003 581	1.024
60% bromooctane[d]	13.6	0.003 588	1.022

[a] Conditions: 0.030 M DBO in the indicated solvent at 22 °C. [b] Isotopic composition of DBO (determined by the complete combustion of DBO to N_2 and hydrocarbon) = 0.003665 ± 0.000001 atom fraction of ^{15}N. [c] If no standard error is specified, the measurement was carried out with only one sample. If a standard error is specified, duplicate measurements were carried out and the isotopic ratio and isotope effect are averages. The absence of additional replicates is justified by the constant isotopic ratio throughout the samples. [d] Balance is *n*-octane.

Table 3. DBH Solvent Dependence of the Nitrogen Kinetic Isotope Effect[a]

solvent	% conversion	atom fraction of ^{15}N[b]	isotope effect[c]
n-octane	13.5	0.003 634	1.002 ± 0.002
chlorobenzene	10.5	0.003 623	1.006 ± 0.001
tert-butylbenzene	5.0	0.003 627	1.004
20% 1-bromooctane[d]	9.4	0.003 625	1.005
40% 1-bromooctane[d]	6.1	0.003 625	1.004

[a] Conditions: 0.030 M DBH in the indicated solvent at 22 °C. [b] Isotopic composition of DBH (determined by the complete combustion of DBH to N_2 and hydrocarbon) = 0.003640 atom fraction of ^{15}N. [c] If no standard error is specified, the measurement was carried out with only one sample. If a standard error is specified, duplicate measurements were carried out and the isotopic ratio and isotope effect are averages. The absence of additional replicates is justified by the constant isotopic ratio throughout the samples. [d] Balance is *n*-octane.

DBO photolysis as a function of solvent; and Table 3 shows the ^{15}N KIE for DBH photolysis as a function of solvent. DBO exhibits a normal ^{15}N KIE of 1.025 in *n*-octane. This value is consistent with a fully-expressed ^{15}N isotope effect on cleavage of the C−N bond in a rate-limiting process. In contrast, DBH exhibits a much smaller ^{15}N isotope effect of only 1.004 since homolysis of the C−N bond occurs without thermal activation. This is consistent with the higher quantum yield of DBH and the release of ring strain by N_2 elimination. These data support the proposed mechanism for DBO, in which cleavage of the first C−N bond is fully rate-limiting. In direct photolysis, cleavage of the first C−N bond in DBO occurs from the excited singlet state in a process that is thermally activated, in spite of the energy input in photolysis. E_a is known to be 8.6 kcal/mol for the direct photolysis of DBO and 9.0 kcal/mol for triplet-sensitized photolysis.[2e] If cleavage occurred without the requirement for thermal activation, then only a small KIE similar to the value seen in DBH should be observed. Since C−N bond cleavage is rate-limiting, there still must be a significant energy barrier to overcome to achieve C−N bond cleavage. This 8.6 kcal/mol barrier must be the barrier to C−N bond cleavage from the excited singlet.

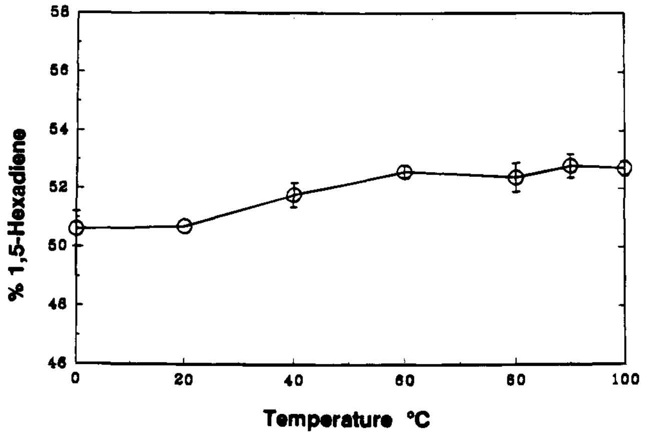

Figure 3. Percent of 1,5-hexadiene (HD) resulting from the direct photolysis (366 nm) of 0.030 M DBO as a function of temperature. The solvent is *n*-octane. Standard error bars may be smaller than the plotted symbol.

The nitrogen KIE also provides a sensitive probe of spin state in biradicals **1** and **2**. Only ≈0.7% (2 × 0.37%) of the molecules will contain ^{15}N with nuclear spin $I = {}^1/_2$. These molecules will exhibit slightly enhanced ISC due to hyperfine coupling from the ^{15}N nucleus to the unpaired electron on nitrogen.[17] Consequently, the spin state of the diazenyl biradical **1** will interconvert faster when ^{15}N is present. If **1** can only form in the singlet state, hyperfine coupling will populate the triplet state of **1**. Recombination of **1** containing ^{15}N will be decreased and a kinetic isotope effect that is smaller than the classical limit of ≈1.025 (based on differences in zero-point energies) will be observed.[17] An external magnetic field will remove the degeneracy of the three triplet spin states and decrease any hyperfine coupling that induces ISC. Table 1 shows the independence of the ^{15}N isotope effect on applied magnetic field. These data show conclusively that the ^{15}N isotope effect is not modulated by electron spin sensitive recombination in the diazenyl biradical **1**.

Thermal Energy. The photochemical quantum yield of DBO is increased substantially at high temperature because of the 8−9 kcal/mol energy barrier to deazatization. Figure 3 shows the temperature dependent increase in diene yield over the range 0−100 °C. Although the quantum yield increases significantly with a 100 °C increase in temperature (E_a = 8.6 kcal/mol), the diene yield increases by a trivial 1%. If the product ratio is determined solely by the rate of thermal relaxation from the triplet boat biradical **2b** to the twist-boat **3b** a substantial increase in diene would be expected for a 100 °C increase in temperature. However, only a trivial increase in diene is observed. This argues against thermal relaxation from the boat **2b** to the twist-boat **3b** as being the step that determines the product ratio.

Photochemical Energy. Table 4 shows the amount of hexa-1,5-diene produced as a function of energy input. Direct irradiation of the n → π^* transition of the N=N chromophore with a low-intensity continuous-wave light source in the range 340−380 nm gives a yield of 50.5−52.7% 1,5-hexadiene. Over this 40 nm range, $E_{h\nu}$ decreases from 84.1 to 75.3 kcal/mol, but the percent hexadiene changes only slightly in a random

Table 4. Diene Production in the Direct and Sensitized Photolysis of DBO as a Function of Energy[a]

direct photolysis	$E_{h\nu}$[i]	% 1,5-hexadiene
Continuous Wave Irradiation		
340-nm Xe lamp[b]	84.1	52.7 ± 0.1
348-nm Xe lamp[b]	82.2	51.6 ± 0.1
351-nm Kr laser[c]	81.5	51.5 ± 0.2
355-nm Xe lamp[b]	80.6	52.3 ± 0.3
356-nm Kr laser[c]	80.4	50.5 ± 0.2
360-nm Xe lamp[b]	79.4	50.9 ± 0.1
365-nm Xe lamp[b]	78.4	51.5 ± 0.1
366-nm Hg lamp[d]	78.2	51.5 ± 0.3
375-nm Xe lamp[b]	76.3	50.5 ± 0.2
380-nm Xe lamp[b]	75.3	50.8 ± 0.4
Pulsed Irradiation		
337-nm N_2 laser[e]	84.9	59.8 ± 0.4
351-nm XeCl laser[f]	81.5	65.6 ± 0.2

sensitized photolysis[g]	$E_{\text{T-SENS}}$[i]	$E_{\text{S-SENS}}$[i]	% 1,5-hexadiene
Singlet Sensitizer[h]			
pyrene	49	83	53.4 ± 0.3
naphthalene	61	89	56.2 ± 1.6
phenanthrene	62	83	54.9 ± 0.3
Triplet Sensitizer[h]			
benzil	54	59	70.1 ± 0.4
benzophenone	69	74	70.2 ± 0.3
acetophenone	74	80	68.7 ± 0.8

[a] Photolysis at 25 °C in *n*-octane. [b] High-pressure Xe lamp (150 W) and monochromator to give a half-height bandwidth of ±2 nm with an intensity of <1 mW. [c] Continuous Kr^+ laser at the indicated frequency. Intensity <1 mW per line. [d] High-pressure Hg lamp (450 W) and bandpass solution filter (described in the Experimental Section). [e] N_2 laser (70 μJ, 300 ps pulse). [f] XeCl laser (350 mJ, 25 ns pulse). [g] Irradiation at 313 nm with a filtered high-pressure Hg lamp. [h] Reference 18. [i] In units of kcal/mol.

fashion. Since the ratio of HD:BCH does not change significantly, the energy in excess of the amount required to cleave the C−N bonds must be dissipated through internal conversion to yield the lowest energy vibrational state that undergoes bond scission. The resulting cyclohexane-1,4-diyl will carry the same energy to product formation. High-intensity pulsed irradiation with a N_2 or XeCl laser at 337 or 351 nm produces a markedly different product ratio of 59.8% and 65.6% 1,5-hexadiene, respectively. In this case, the higher photon density leads to multiple-photon processes that populate an entirely different reaction surface. The ratio of photohomolysis products derived from multiple-photon excitation will not be considered further in this paper.

Indirect photolysis with a singlet or triplet sensitizer produces excited singlet or triplet DBO, respectively. Pyrene, naphthalene, and phenanthrene are singlet sensitizers by virtue of their slow ISC from the excited singlet to triplet state (typical $k_{\text{ISC}} \approx 10^6-10^7\ \text{s}^{-1}$).[18] These singlet sensitizers produces 53.4−56.2% 1,5-hexadiene. These values are close to the amount of hexadiene observed from direct irradiation of the N=N bond. In contrast, benzil, benzophenone, and acetophenone are triplet sensitizers by virtue of their fast ISC from the excited singlet to triplet state (typical $k_{\text{ISC}} \approx 10^{10}-10^{11}\ \text{s}^{-1}$).[18] These triplet sensitizers produce 68.7−70.2% hexadiene. The lowest singlet and triplet energies for these sensitizers are given in Table 4. Recalling that $E_{\text{S-DBO}}$ is 76 kcal/mol and $E_{\text{T-DBO}}$ is 54 kcal/mol, pyrene, naphthalene, and phenanthrene could *not* be acting as triplet sensitizers. They can only populate the excited singlet state of intact DBO.

Direct photolysis and singlet-sensitized photolysis leads to a product ratio that varies only slightly from 51:49 HD:BCH. In contrast, triplet-sensitized photolysis produces a product ratio that does not vary significantly from 70:30 HD:BCH. Photochemical energy in excess of the amount required to break the first C−N bond is dissipated among vibrational energy levels. This argues against Carpenter's idea of dynamic control being able to alter the product distribution in DBO, even though there is a common high-energy diazenyl biradical intermediate, **1**, that follows cleavage of the first C−N bond.

Triplet-sensitized photolysis will produce the cyclohexane-1,4-diyl in the triplet spin state exclusively. In intact DBO, the lowest-energy triplet surface is 22 kcal/mol below the energy of the singlet surface and all of the triplet sensitizers employed have energies of 74 kcal/mol or less. In the rigid boat cyclohexane-1,4-diyl, the energy surface of the singlet biradical is 22 kcal/mol above the corresponding triplet energy level.[8] Therefore, triplet DBO has insufficient energy to populate the singlet surface and ISC in the cyclohexane-1,4-diyl boat can only occur from the excited singlet state and is effectively an irreversible process.

Quantitative Model for Product Formation. The product ratio cannot be shifted exclusively to BCH or HD under any photolysis conditions even though direct photolysis must produce DBO in the excited singlet state and triplet-sensitized photolysis must yield the excited triplet state. No ISC can occur in intact DBO, but fast ISC following (or concomitant with) C−N bond homolysis can equilibrate the singlet and triplet spin state as the singlet cyclohexane-1,4-diyl reaches the ground state boat conformation. A large ^{15}N kinetic isotope effect shows that initial C−N bond homolysis must occur through a thermally-activated late transition state that approximates the boat biradical geometry.

If fast ISC is possible at the moment the cyclohexane-1,4-diyl forms from the excited DBO singlet precursor, a statistical distribution of 25% singlet and 75% triplet cyclohexane-1,4-diyl will be produced in the boat geometry, **2a** and **2b**. Overlap of the unfilled electron orbitals, although good for ISC, makes this an unstable conformation with a short lifetime. Twenty-five percent of the biradical will react within the time of a bond vibration to produce BCH with unit efficiency. The remaining 75% boat biradical that is in the triplet state will relax to the twist-boat geometry, **3b**. The triplet twist-boat cannot form either product directly. Instead, **3b** must undergo ISC to the singlet twist-boat, **3a**, in order to close to BCH or open to HD. The limiting ratio of ≈70:30 HD:BCH derives from product formed in the singlet twist-boat, **3a**. The 7/3 preference for HD formation translates into a ≈0.5 kcal/mol discrimination against BCH formation at 25 °C. This could reasonably be a conformational barrier to the geometry that allows ring closure to BCH. This 70:30 product ratio is intrinsic to HD:BCH formation in the twist-boat and is not affected by the history of the triplet boat precursor.

The product ratio can be described quantitatively by eq 4.

$$\text{HD:BCH} = \underset{\substack{\text{(ratio of products}\\ \text{formed in the boat}\\ \text{biradical, }\mathbf{2a}\text{ or }\mathbf{2b})}}{S(0{:}100)} + \underset{\substack{\text{(ratio of products}\\ \text{formed in the twist-}\\ \text{boat biradical, }\mathbf{3a}\text{ or }\mathbf{3b})}}{T(70{:}30)} \tag{4}$$

In this equation, *S* is the fraction of boat cyclohexane-1,4-diyl in the singlet spin state and *T* is the fraction of boat cyclohexane-1,4-diyl in the triplet spin state. Direct irradiation of the N=N chromophore and singlet sensitized photolysis always yields $S = 0.25$ and $T = 0.75$ due to efficient ISC from the higher energy singlet state that lies on an energy surface where $\Delta E_{\text{ST}} \approx 0$. Once the rigid ground state cyclohexane-1,4-diyl boat geometry is reached, $\Delta E_{\text{ST}} \approx 22$ kcal/mol and no ISC occurs.[8] Triplet-

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(18) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; pp 290−292.

sensitized photolysis produces the cyclohexane-1,4-diyl exclusively in the lower-energy triplet spin state to give $S = 0$ and $T = 1$. The singlet spin state of the boat cyclohexane-1,4-diyl is significantly higher in energy and no ISC occurs. In this scenario, ISC becomes a unidirectional process that only siphons the singlet state to the triplet manifold and not *vice versa*.

Under conditions of direct irradiation or singlet-sensitized photolysis, $S = 0.25$ and $T = 0.75$ and the product distribution of 51:49 HD:BCH is faithfully reproduced. Under conditions of triplet-sensitized photolysis, $S = 0$ and $T = 1$ and the HD:BCH product ratio of 70:30 that is predicted by eq 4 is observed. Additional ISC induced by an external heavy atom effect produces intermediate values of S and T to give a limiting 70:30 ratio of HD:BCH.

Conclusion

DBO exhibits a large ^{15}N kinetic isotope effect that is consistent with a thermally-activated late transition state and gives rise to the cyclohexane-1,4-diyl in the boat geometry. In contrast, the more-strained DBH exhibits a small ^{15}N kinetic isotope effect that is consistent with an early transition state. Neither of these kinetic isotope effects is magnetic field (spin) dependent. The ratio of HD:BCH products in DBO photolysis is determined by the electronic spin state of the intermediate boat cyclohexane-1,4-diyl. Direct irradiation of the N=N chromophore or singlet-sensitized photolysis produces the boat cyclohexane-1,4-diyl in a statistical distribution of 25% singlet and 75% triplet. The singlet biradical boat, **2a**, closes to BCH, while the triplet biradical boat, **2b**, lives long enough to relax to the triplet twist-boat **3b**. The triplet twist-boat **3b** cannot form closed-shell products directly, but must undergo slow ISC to the singlet twist-boat **3a**. The ratio of HD:BCH product formation in the twist-boat is determined only by the intrinsic energy barriers to ring closure to BCH vs ring opening to HD. Triplet-sensitized photolysis of DBO produces the boat cyclohexane-1,4-diyl exclusively in the triplet spin state and with less energy. In the rigid boat geometry, $\Delta E_{ST} \approx 22$ kcal/mol and insufficient energy exists to populate the higher energy singlet state from the lower energy triplet state. Consequently, no T → S conversion occurs. This makes ISC a one-way process to convert singlet to triplet, but not the reverse.

Experimental Section

General Methods. DBO,[3a,19] 1-Me-DBO,[1b] and DBH[20] were synthesized according to literature methods. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ at 300 MHz and referenced to $CDCl_3$, at 7.24 and 77.0 ppm respectively, or to tetramethylsilane.

Magnetic fields from 0–0.25 T were produced with an electromagnet and constant current power supply. A magnetic field of 6.6 T was achieved in the sample compartment of a 300 MHz Varian NMR spectrometer.

Photolysis of compounds inside the NMR magnet was carried out using a C. Technologies UV fiber optics bundle, 2.0 m × 1 mm, equipped with aluminum collars and Kevlar coating. The light source was a filtered Ushio high-pressure Hg arc Lamp.

Gas Chromatography Studies. Product ratio analysis was carried out by GLC analysis with a 0.56 mm × 30.0 m J & W Scientific capillary column (DB1). Conditions: injector 130 °C, detector (FID) 250 °C, column 40 °C for 1 min, 8 °C/min to 130 °C, 130 °C for 1 min, 40 °C/min to 225 °C, and 225 °C for 2 min.

Photolysis products were isolated by preparative GLC. The column was 20.3 m × 6.25 mm aluminum tubing. The aluminum was pretreated with dichlorodimethylsilane and packed with 13% SE30 and Chromosorb W, non-acid washed (100/120 mesh). Conditions: flow rate 30 mL/min, injector 130 °C, detector (TCD) 150 °C, and column 80 °C.

Filter Systems. The 366 nm band pass filter system consisted of a water-ported Pyrex cylinder, 5.0 cm × 2.0 cm, sealed with two Pyrex windows, 2.0 cm × 2.0 cm × 0.3 cm. The front window was covered with a Roscolux theatrical filter (lime green, No. 96) and an Oriel 200–400 nm broadband pass filter (No. 59800). The relative transmittance was 3.3% at 408 nm, 100% at 360 nm, and 3.5% at 300 nm.

The 313 nm solution filter was constructed according to the design described by Calvert and Pitts.[21] An aluminum pipe, 2.5 cm × 15.0 cm, was separated into four compartments by polished quartz windows, 2.5 cm i.d. × 0.15 cm. The lengths of the individual compartments were 3, 5, 5, and 1 cm. The solutions in each compartment were H_2O, 0.178 M aqueous $NiSO_4$, 5×10^{-4} M aqueous K_2CrO_4, and 0.0245 M aqueous monobasic potassium phthalate, respectively. The relative transmittances were 1.3% at 334 nm, 100% at 313 nm, and 1.0% at 303 nm.

Photolysis. Unless otherwise stated, all photolysis was carried out at 25 °C. Direct photolysis was carried out at 366 nm while triplet-sensitized photolysis was carried out at 313 nm using benzophenone as the sensitizer, unless otherwise stated. All samples for photolysis were prepared as 15 μL aliquots of 0.030 M DBO or 0.030 M 1-Me-DBO solutions in Pyrex melting point capillary tubes. The solutions were degassed by a series of 5 freeze–pump–thaw cycles and flame sealed in the capillary tube. Photolysis was carried out with a 500 W high-pressure compact mercury Ushio arc lamp or a high-pressure Xe lamp. Where indicated, the output of the Xe lamp was focused on the entrance slit of a Beckman DB monochromator to give an approximate bandwidth of ±2 nm in the range of 340–380 nm photolyses. The samples were irradiated at a distance of 14.0 cm for direct and 11.5 cm for triplet sensitized. All photolysis was carried out between the poles of an electromagnet. For non-magnetic field studies the magnet was adjusted to 0 T.

Characterization of Photolysis Products. The products were characterized by ^{1}H NMR, EI MS, and co-injection of authentic samples on a capillary GLC. ^{1}H NMR δ for the products of DBO photolysis: 1,5-hexadiene, 2.10–2.15 (m, 4H), 4.90–5.05 (m, 4H), 5.70–5.87 (m, 2H); bicyclo(2.2.0)hexane, 1.95–2.06 (m, 4H), 2.33–2.44 (m, 4H), 2.68–2.77 (m, 2H). ^{1}H NMR δ for the products of 1-Me-DBO photolysis: 2-methyl-1,5-hexadiene, 1.55 (s), 4.70 (d), 4.90–5.08 (m), 5.73–5.89 (m);[22] 1-methylbicyclo[2.2.0]hexane, 1.10 (s), 1.75–2.4 (m).[23]

Nitrogen Isotope Effects. Ampules for the photolysis of DBO or DBH were prepared from Pyrex tubing that was 7.5 × 1.5 cm (i.d.) and sealed at one end, with a transition to 20 × 0.6 cm tubing ending in a 14/20 ground-glass joint. Constrictions were placed at the transition and at a point 15 cm from the ground glass joint. Each tube was flame-dried under vacuum.

Each ampule was filled with 7 mL of 0.03 M DBO or DBH dissolved in the indicated solvent. The solutions were degassed by 5 freeze–pump–thaw cycles using a mercury diffusion pump that achieved an ultimate vacuum of less than 1 mTorr. The ampules were flame-sealed at the uppermost constriction. The samples were photolyzed as a function of magnetic field. Samples for the solvent study were photolyzed at 0 T. Photolysis was carried out with the liquid occupying the larger diameter portion of the ampule. Photolysis was terminated after 40 min for DBO and 45–75 s for DBH to give 5–15% conversion. The liquid was frozen at −196 °C and the lower constriction was flame-sealed to separate the N_2 gas sample from the remaining solvent. The ^{14}N/^{15}N ratio of the gas was determined by isotope ratio mass spectrometry on a Finnegan MAT Delta S mass spectrometer. The amount of diene product and residual DBO or DBH starting material in solution was analyzed by GC to determine the fraction of conversion.

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The isotopic composition of the DBO or DBH starting material was determined by complete combustion of the diazene to N_2 according to the modified Dumas method.[24] Solid samples (5−10 mg) of DBO or DBH were placed in a Pyrex tube (9 mm × 15 cm). A mixture of 1 g of CuO, 100 mg of Cu^0, and 1 g of CaO (freshly heated to 1000 °C) was added to each tube. The solid mixture was cooled to −196 °C, evacuated for 15 min, and flame-sealed. The contents of the solid sample were mixed by shaking, and each tube was placed in a muffle furnace that was preheated to 580 °C. Combustion was complete after 4 h. The N_2 gas was passed through cold-finger traps at −196 °C to remove condensable gases, and the N_2 was collected on silica gel at −196 °C. The isotopic ratio of the N_2 gas was analyzed on a Finnigan MAT Delta S isotope ratio mass spectrometer. The completeness of conversion and the accuracy of this method were determined by sending duplicate samples of DBO to the University of Nebraska for independent analysis, with a reference to the absolute ^{15}N content of the biosphere. The isotopic ratio of DBO determined by combustion at the University of Utah and the University of Nebraska agreed to within 0.0002% ^{15}N.

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Supplementary Material Available: Magnetic field dependence of product ratio for direct and triplet-sensitized photolysis of DBO and 1-Me-DBO (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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