

Viscosity Dependence of the Denitrogenation Quantum Yield in Azoalkane Photolysis: Experimental Evidence for Reversible Formation of the Diazenyl Diradical[†]

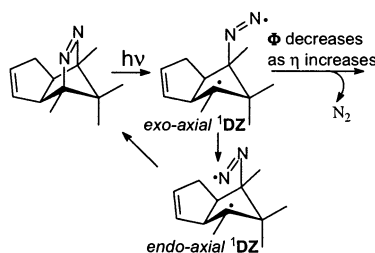
Waldemar Adam,[‡] David A. Corley,[§] Alexei V. Trofimov,^{‡,||} and Rick C. White^{*,§}

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany, Department of Chemistry, Sam Houston State University, Huntsville, Texas 77341, and Institute of Biochemical Physics, Russian Academy of Sciences, 117977 Moscow, Russia

adam@chemie.uni-wuerzburg.de

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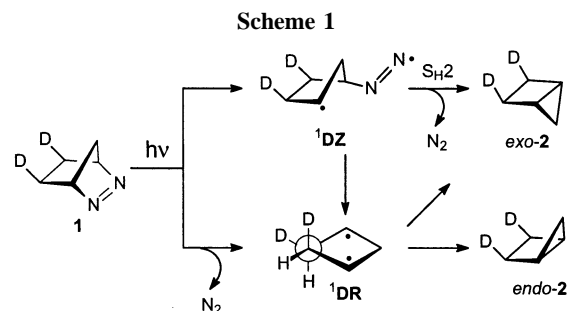
ABSTRACT



Experimental evidence is reported for the reversible formation of the singlet diazenyl diradical (¹DZ), photolytically generated from the structurally elaborate DBH-type azoalkane. Reversibility of the ¹DZ formation manifests itself through the decrease of the photodenitrogenation quantum yield over a ca. 40-fold viscosity variation (from 0.5 to 19.3 cP). This viscosity behavior is interpreted in terms of frictional effects on the competitive reaction modes of the diazenyl diradical.

The mechanism of the unusual double inversion in the photochemical denitrogenation of the bicyclic azoalkane *exo-d*₂-2,3-diazabicyclo[2.2.1]heptene (DBH-*d*₂, **1**) to afford mainly (*exo/endo* ratio 75:25) *exo-d*₂-bicyclo[2.1.0]pentane, the *exo-d*₂-**2** housane (Scheme 1), has attracted much attention since its discovery about 35 years ago.¹ The originally suggested stepwise mechanism through the singlet diazenyl diradical ¹DZ accounts for the double inversion in terms of the S_H2 process (second-order homolytic substitution), whereas the C₂-symmetric, nitrogen-free 1,3-cyclo-

pentanediy l singlet diradical ¹DR would lead to a 1:1 mixture of the *exo-2* and *endo-2* housanes (Scheme 1). Subsequently it was reasoned that the n,π* excitation, usually employed



[†] This work is dedicated to Professor Jakob Wirz on the occasion of his 60th birthday.

[‡] University of Würzburg.

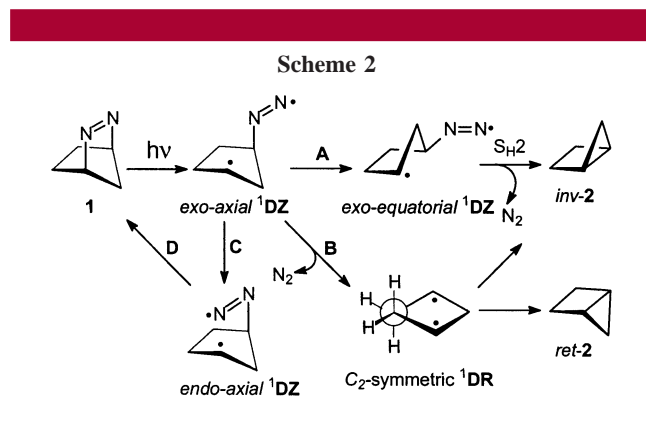
[§] Sam Houston State University.

^{||} Russian Academy of Sciences.

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in the photodenitrogenation of azoalkanes, should on symmetry grounds (Salem–Dauben–Turro theory)² generate the ¹DZ diradical, in support of the stepwise extrusion of molecular nitrogen.³ Recent viscosity studies have confirmed experimentally the intervention of the ¹DZ diradical as a bona fide intermediate.⁴

Extensive computational work on the parent DBH (**1**) provided a detailed mechanistic scenario for the photochemical evolution of the ¹DZ diradical and its subsequent chemical transformation to the inverted housane **2**; the salient features are displayed in Scheme 2.⁵

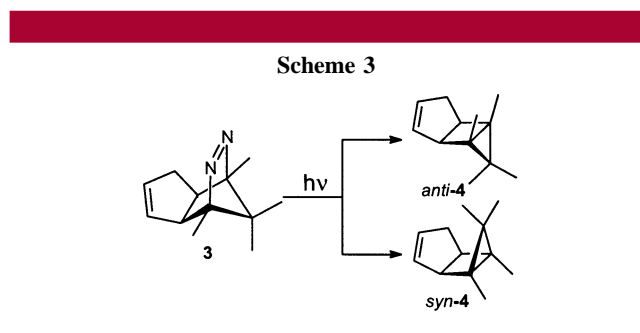


On n,π^* excitation, the DBH (**1**) generates initially the *exo-axial* ¹DZ intermediate by passage through a conical intersection. Thereafter, along pathway **A** (major route), the ¹DZ species carries sufficient momentum to convert the *exo-axial* to the *exo-equatorial* conformer; the latter is predestined for N₂ loss to afford the inverted housane *inv-2* along the S_{H2} trajectory. Alternatively, pathway **B** competes to generate the C₂-symmetric ¹DR diradical on denitrogenation, which cyclizes in equal amounts to the *inv-2* and *ret-2* housanes. The third pathway **C** entails the rotational change of *exo-axial* to the *endo-axial* ¹DZ diradical, with subsequent reclosure to the azoalkane **1**. For the parent DBH (**1**), pathway **C** may be neglected, since the quantum yield of DBH consumption is unity.⁶

The above reaction scheme is consistent with viscosity studies,⁴ in that frictional forces oppose the conformational motion necessary for pathway **A** and diminish the population of the *exo-equatorial* ¹DZ species so that other pathways may compete. Thus, if denitrogenation of the *exo-axial* ¹DZ

is enhanced along pathway **B** versus pathway **A** to generate the C₂-symmetric ¹DR, diminution of the diastereoselectivity is expected, as observed experimentally for DBH-*d*₂ (**1**) in more viscous solvents. Should pathway **C** be more enhanced, the consequences would be reclosure of the *endo-axial* ¹DZ to the azoalkane along pathway **D**, which should manifest itself in a lower quantum yield for the photodenitrogenation in more viscous solvents. Such a study of the dependence of the quantum yield of azoalkane disappearance on solvent viscosity has not yet been conducted but should provide valuable insight into the photodenitrogenation mechanism; in particular, it would allow assessment of the feasibility of reversible ring closure of the ¹DZ diradical along the pathways **C** and **D**. Reversible formation of a diazenyl-radical species has been documented for both the photolysis⁷ and thermolysis⁸ of acyclic azoalkanes through traditional cage-effect studies for the intermolecular process but has yet to be demonstrated for the *intramolecular* case of bicyclic azoalkanes such as the parent DBH and derivatives.

In this work, we report the photodenitrogenation efficiency as a function of viscosity (η) in nujol–isooctane mixtures for the parent DBH (**1**) and the structurally more elaborate azoalkane **3**. The photolysis of the latter DBH derivative leads to the *anti-4* (retention) and *syn-4* (inversion) housanes (Scheme 3). Our results imply that the lifetimes of the



intermediary ¹DZ diradicals determine whether a viscosity effect is experimentally observable.

In preliminary experiments, we examined the photodenitrogenation quantum yields of azoalkane **3** in solvents of similar low viscosity, i.e., isooctane ($\Phi = 0.61 \pm 0.03$), acetonitrile ($\Phi = 0.68 \pm 0.03$), and methanol ($\Phi = 0.12 \pm 0.01$). These data reveal that whereas solvent polarity (isooctane versus acetonitrile) has only a nominal effect on the photodenitrogenation efficiency of azoalkane **3**, hydrogen bonding (methanol) dramatically diminishes the Φ value. Such hydrogen-bonding effects are well-documented in azoalkane photolysis;⁹ consequently, protic polar solvents such as alcohols had to be avoided for the viscosity variation in our quantum-yield studies. For this reason, we employed nujol–isooctane mixtures, an aprotic solvent system of low

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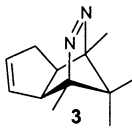
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polarity that permits a sufficiently broad change in the viscosity of the medium. The quantum-yield data for the photolysis of the azoalkanes **1** and **3** are given in Table 1.

Table 1. Photodenitrogenation Quantum Yields of the Azoalkanes **1** and **3** as a Function of Viscosity in Nujol/ Isooctane Mixtures^a

azoalkane	nujol/isooctane	viscosity (η) (cP)	Φ^b
 1	0/100	0.50	0.98
	70/30	19.3	0.97
 3	0/100	0.50	0.61
	20/80	1.06	0.57
	40/60	2.41	0.55
	50/50	5.10	0.52
	65/35	11.2	0.50
	70/30	19.3	0.48

^a Photodenitrogenation at $\lambda = 350$ nm and 20 °C. ^b Error $\pm 5\%$ of the stated values.

Whereas the quantum yield for the parent DBH is constant (first two entries) over the ca. 40-fold change in viscosity (higher amounts of nujol could not be used because of limited solubility of the azoalkanes), a definite decrease in Φ is observed for the azoalkane **3** over the employed viscosity range (last six entries). This viscosity dependence is clearly evident in the Φ versus η plot in Figure 1.

The quantum yield for the photoprocess is given by

$$\Phi = \frac{k_r}{k_r + k_f + k_{IC}} \quad (1)$$

in which k_r is the reaction photodenitrogenation rate constant, k_f is the rate constant of fluorescence, and k_{IC} is the rate constant for internal conversion.¹⁰ As for the viscosity influence on the fluorescence rate constant (k_f), this intrinsic photophysical property of the excited molecule should be relatively independent of the medium. Moreover, comparison of the quantum yields of photodenitrogenation [$\Phi = 0.61$ (third entry in Table 1)] and fluorescence ($\Phi_f < 0.05$ ^{5b}) of

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(10) As for possible singlet-to-triplet intersystem crossing (k_{ISC}) in azoalkane **3**, recent studies (cf. ref 5b) have disclosed that at room temperature this deactivation pathway does not compete with the photodenitrogenation and, therefore, need not be considered in eq 1.

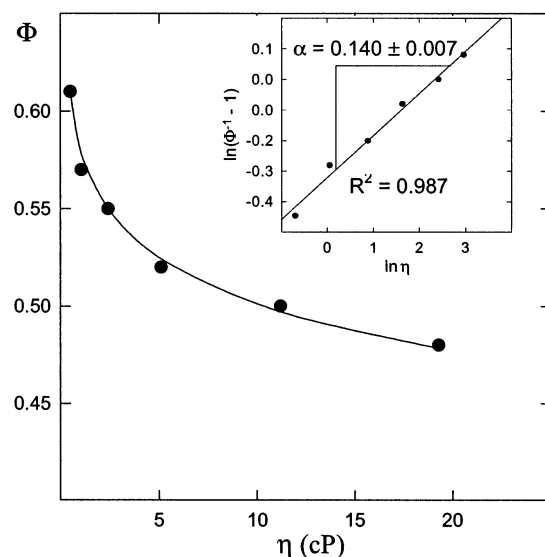


Figure 1. Viscosity dependence of the denitrogenation quantum yield in the photolysis (350 nm) of azoalkane **3** (6 mM); the insert displays the linearity of the experimental data according to eq 4.

the azoalkane **3** under similar experimental conditions (isooctane at room temperature) reveals that k_f is more than an order of magnitude lower than k_r ($\Phi/\Phi_f = k_r/k_f > 0.61/0.05 > 10$) and may be neglected in eq 1. In regard to the rate constant for the internal conversion (k_{IC}), it is expected that a more viscous medium (less mobility), should decrease this radiationless deactivation (k_{IC}).¹¹ As becomes apparent from eq 1, a decrease of k_{IC} should increase the quantum yield, contrary to what has been obtained experimentally (Figure 1). Thus, the observed viscosity dependence of the photodenitrogenation quantum yield does apparently not derive from changes in the k_{IC} value in eq 1; its origin stems mainly from the changes of the photodenitrogenation rate constant k_r .

For liquid-phase photodenitrogenations of azoalkanes, k_r decreases with viscosity (η); this decrease obeys the fractional-power dependence, as expressed by eq 2.⁴ The latter equation

$$k_r \sim \eta^{-\alpha} \quad (2)$$

is based on the *free-volume model*, in which the α parameter constitutes the characteristic fraction of the molecular volume that is involved in the rearrangement process. With the neglect of k_f , eq 1 allows k_r to relate to the experimental Φ

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data in the rearranged form shown in eq 3. Substitution of

$$\Phi^{-1} - 1 = \frac{k_{IC}}{k_r} \quad (3)$$

the viscosity relation of eq 2 into eq 3 and taking the logarithm leads to eq 4, in which $k_{IC} = const$, as explained

$$\ln(\Phi^{-1} - 1) = const - \alpha \ln \eta \quad (4)$$

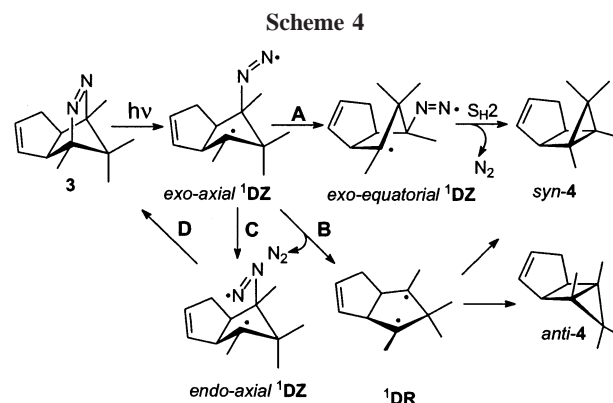
above. The double-logarithmic plot of the function $\Phi^{-1} - 1$ versus viscosity gives a straight line ($R^2 = 0.987$), whose slope takes the value $\alpha = 0.140 \pm 0.007$ (cf. insert in Figure 1). This α value is similar to that recently reported for the formation of the inverted product *syn-4* ($\alpha = 0.20 \pm 0.01$) in the photolysis of azoalkane **3** and the thermal *syn-anti* isomerization of housane *syn-4* ($\alpha = 0.16 \pm 0.03$).⁴ The similarity of these α values implies that the viscosity effect results from similar frictional impositions on the skeletal inversion process, namely, the flap motion of the methylene bridge in the photodenitrogenation of the azoalkane **3** and the thermal isomerization of housane *syn-4*.

The choice of the structurally more elaborate azoalkane **3** for this study has been most fortunate^{5b} in that a definite viscosity dependence of the quantum yield of its photodenitrogenation is observable (Figure 1). Therewith it has been experimentally demonstrated that the intermediary *exo-axial* ¹DZ diradical may revert to the starting azoalkane (an energy-dissipating process) provided the appropriate azoalkane is selected, as was the choice of the DBH-type derivative **3**. For this substrate, we have previously shown that the extent of double inversion depends on viscosity, namely, that less *syn-4* housane is observed in more viscous solvents.^{4e} This has been rationalized in terms of diminution of pathway **A** (Scheme 4) through frictional impediments exerted by the medium, and therefore, denitrogenation along pathway **B** is preferred to afford increased amounts of *anti-4* (retention).

Additionally, we disclose now for the first time that the more viscous medium sufficiently enhances the lifetime of the *exo-axial* ¹DZ species, initially generated on photochemical activation, to enable the conformational change to the *endo-axial* ¹DZ (pathway **C**) and subsequent reclosure to the starting azoalkane **3** (pathway **D**).

Not only do the present results establish reversibility in the photodenitrogenation of DBH-type azoalkanes, but they identify the *exo-axial* ¹DZ as the pivotal intermediate in the competitive transformations of the diazenyl diradical.

A point of concern is why the parent DBH does not display a viscosity dependence in the photodenitrogenation efficiency



(Table 1), although the extent of double inversion clearly depends on viscosity.⁴ It should be noted in Table 1 that the Φ values for the parent DBH are nearly unity within the experimental error, while those for azoalkane **3** are about half as large. Presumably, the denitrogenation steps for the parent DBH are so facile that the lifetime of its *exo-axial* ¹DZ species is too small for the viscosity dependence of the quantum yield to be experimentally accessible. This implies an appreciably longer lifetime for the *exo-axial* ¹DZ intermediate derived from the structurally more elaborate DBH derivative **3**, such that the viscosity of the medium may act more effectively on the various transformations in Scheme 4.

In summary, our study has disclosed the hitherto unprecedented reversible formation of the singlet diazenyl diradical ¹DZ in the photodenitrogenation of a DBH-type azoalkane. Reversibility in the ¹DZ formation is manifested by the decrease of the photodenitrogenation quantum yield at increasing solvent viscosity. Thus, the present study furnishes a demonstrative example that viscosity serves as a convenient tool to elucidate complex reaction mechanisms.

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

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