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Photochemical Denitrogenation of Norbornene-Annelated 2,3-Diazabicyclo[2.1.1]hept-2-ene-Type Azoalkanes: Crystal-Lattice versus Zeolite-Interior Effects

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An unprecedented product control in the spin-multiplicity-dependent denitrogenation of 2,3-diazabicyclo[2.1.1]hept-2-ene-(DBH)-type azoalkanes **1** is reported herein, when the photolysis is conducted in the crystalline state or in zeolites compared to in solution. Although such medium effects are well documented in photoreactions, particularly in organized assemblies,[1,2] the photochemical deazetation of azoalkanes appears to have been so far only little investigated.[3] Spatial restrictions inhibit molecular motion in the electronically excited molecule, such that the photophysical and photochemical behavior may be dramatically changed. For example, impressive cases have been reported in the crystalline state, in which molecular motion may be so severely restricted that well-established photochemical transformations are either suppressed or proceed highly selectively.[1] Also the channels and cavities of zeolites may restrict molecular flexibility, the extent of which depends on the relative dimensions of the guest with respect to the zeolite pore size; consequently, in this way significant effects have been observed in the product selectivity of photochemical transformations.[2]

Previously it was shown that the solution photochemistry of azoalkanes **1** depends on the spin multiplicity (Scheme 1).[4] Thus, product studies have demonstrated that the singlet excited state leads exclusively to housane **2**, and the triplet one predominantly to the azirane **3**. Since these two photochemical modes require fundamentally different conformational changes in the singlet (α-CN-bond cleavage) and triplet (*β*-CC-bond cleavage) pathways, it was of mechanistic import to assess whether this remarkable spin-selective photoreaction is subject to the external spatial restrictions imposed by the crystal lattice and zeolite interior. Indeed, the presently observed novel spin-multiplicity-dependent medium effects confirm our anticipations: In the crystalline state, the housane **2** (singlet-state product) is selectively formed, and the azirane **3** (triplet-state product) is completely suppressed, while in zeolites the azirane **3** is enhanced compared to the solution photochemistry in benzene.

Scheme 1

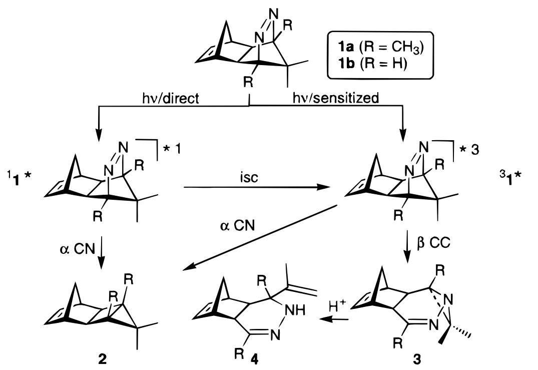

Table 1. Product Studies of the Photolysis[a] of Azoalkane **1a** in Solution, in the Crystalline State, and in Zeolites

	medium	photolysis	time (h)	convn[b] (%)	product distribution[b]	
					2	3
1	C_6D_6[c]	direct	-	>95	60	40
2	CD_3OD[c]	direct	-	>95	19	81
3	crystals[d]	direct	10	48	100	0
4	powder	direct	15	75	100	0
5	crystals[e]	sens[f]	135	5	100	0
6	NaY	direct	70	>95	32	68[g]
7	CsY[h]	direct	70	>95	42	58[g]

[a] Carried out at 10 °C. [b] By ^{1}H NMR analysis; error limits ±3%; mass balance (mb) >95%, except entry 7 (50%) and entry 8 (85%). [c] Reference 3. [d] From isooctane. [e] Cocrystallization of azoalkane and benzophenone from isooctane. [f] Benzophenone (λ < 330 nm, cf. experimental details in Supporting Information). [g] Products **3** and **4**. [h] Reference 2a.

The azoalkanes **1** were synthesized according to the Hünig route[5] and crystallized from isooctane.[6] The photolysis in the crystalline state was conducted in NMR tubes, that in zeolites as a hexane slurry in test tubes (for details, cf. Supporting Information). The photolysis (Table 1) of azoalkane **1a** crystals yielded only the housane **2a** product (entries 3 and 4). This absolute product selectivity was observed even at high conversions, although the housane **2a** is a liquid. Moreover, the same selectivity was found for whole crystals (entry 3) and finely ground samples (entry 4). When the irradiated samples were dissolved in $CDCl_3$, vigorous gas evolution ensued, which indicates that nitrogen gas had been entrapped in the crystal lattice. This observation implies that the photoreaction proceeds mainly in the crystal interior and not at the surface.[7]

To promote deliberately the formation of azirane **3a** by triplet sensitization, the benzophenone-sensitized photolysis was carried out in the solid state. For this purpose, the sample was prepared by co-crystallization of the azolkane **1a** and the benzophenone sensitizer from isooctane. Again, the photolysis gave only housane **2a** (entry 5), while no conversion was observed for a sample without benzophenone, irradiated at the same conditions.[8]

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(1) (a) Scheffer, J. R.; García-Garibay, M. A.; Nalamasu, O. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 8, pp 249−345. (b) Ramamurthy V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V.; VCH: New York, 1991. (c) Yoshikatsy, I. *Synthesis* **1998**, 1−32.

(2) (a) Ramamurthy, V.; Eaton, D. F.; Caspar, J. V. *Acc. Chem. Res.* **1992**, *25*, 299−307. (b) García, H.; Scaiano, J. C. *Acc. Chem. Res.* **1999**, *32*, 783−793.

(3) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766−6775.

(4) (a) Adam, W.; Nau, W. M.; Sendelbach, J.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 12571−12572. (b) Adam, W.; Nau, W. M.; Sendelbach, J. *J. Am. Chem. Soc.* **1994**, *116*, 7049−7054. (c) Adam, W.; Fragale, G.; Klapstein, D.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1995**, *117*, 12578−12592. (d) Adam, W.; Moorthy, J. N.; Nau, W. M.; Scaiano, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 5550−5555.

(5) Beck, K.; Höhn, A.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 517−533.

(6) Full crystallographic data will be published elsewhere; Peters K.; Peters, E.-M.; Adam, W.; Martí, V. *Z. Kristallogr.*, in press.

(7) Choi, T.; Cizmeciyan, D.; Khan, S. I.; García-Garibay, M. A. *J. Am. Chem. Soc.* **1995**, *117*, 12893−12894.

(8) García-Garibay, M. A.; Scheffer, J. R.; Trotter, J.; Wireko, F. *Tetrahedron Lett.* **1987**, *28*, 1741−1744. The very low conversion (long irradiation times) is due to the trace amounts of benzophenone sensitizer in the crystalline sample (cf. Supporting Information).

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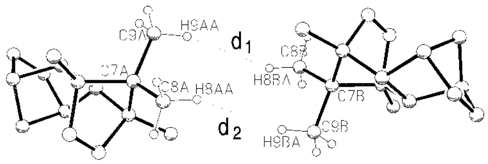
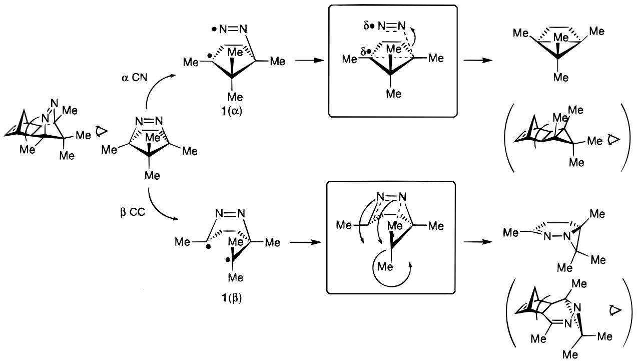


Figure 1. Selected view of two neighboring molecules in the crystal lattice of azoalkane **1a**.

Scheme 2



What is the reason for this high housane selectivity in the direct singlet and also, more significantly, triplet-sensitized photolysis in the solid state? Inspection of the crystal-lattice structure of azoalkane **1a** presented in Figure 1 provides an answer: The selected view of two neighboring azoalkane **1a** molecules reveals the expected dense packing, with the distances d_1 (H9AA−H8BA) and d_2 (H8AA−H9BA) between the hydrogen atoms of the *gem*-dimethyl groups for neighboring azoalkane molecules of about 307 pm. More informative, however, is the fact that the geminal methyl groups between the neighboring azoalkane molecules point toward each other, such that these structural data imply restricted mobility of the *gem*-dimethyl groups in the crystal lattice, at least for larger translations and rotations. While the formation of housane **2a** requires only small *gem*-dimethyl displacements from their initial position,that is, merely a slight downward motion to generate the bicyclo[2.1.0]pentane ring, for the azirane **3a** the *gem*-dimethyl group must move quite a bit downward and simultaneously rotate by ∼90° to the right to afford the annelated three-membered ring (Scheme 2). Such extensive molecular displacements are possible in the solid state,[9] as long as the nonbonding distances are not significantly shorter than d_1 and d_2 (Figure 1). Consequently, the housane pathway with comparatively little conformational adjustment prevails. Although the triplet-excited azoalkane **1a** is produced in the direct and certainly in the benzophenone-sensitized photolyses and the cleavage of the β-CC bond expected to generate the **1**(β) diradical, prevention of the necessary conformational changes due to crystal-lattice effects obliges the diradical to cyclize back to the azoalkane **1** rather than reorganize to the azirane **3**.

That these conformational impediments of the *gem*-dimethyl group are caused by intermolecular steric interactions between azoalkane molecules in the crystal lattice and not by the bridgehead methyl groups (R = Me in **1a**), is demonstrated by conducting the photolysis of azoalkane **1b** (R = H) in the crystalline state. Again, only the housane **2b** is formed with 100% selectivity at 40% conversion. Presumably, a similar dense packing of the azoalkane **1b** restricts the rotational motion necessary for the formation of the azirane **3b**.

Zeolites also provide a medium to confine the molecular motion of enclosed guests in the reaction cavity. Given the dimensions of zeolite Y supercages (∼1400-pm diameter), much less severe geometrical constraints are expected than in the crystal lattice.[1b,2] In contrast to the crystal lattice, zeolites provide a polar environment which may influence a reaction, especially in the present photodenitrogenation of azoalkane **1a**, whose product selectivity is subject to polarity effects.[4d] Moreover, substantial heavy-atom effects may be induced by charge-balancing cations present in the same guest cavity and thereby promote the triplet channel.[2] In fact, in regard to azoalkanes, in the photochemistry of diazabicyclooctane (DBO) a heavy-atom effect was reported in Cs^+-exchanged Y zeolite.[10] It was, therefore, of interest to assess the influence of the spatially less restricting NaY and CsY zeolites on the product selectivity in the photochemistry of azoalkane **1a**. Mechanistically significant, the photolysis of azoalkane **1a** in these zeolites (entries 6 and 7) afforded both the housane **2a** and the azirane **3a** products. Compared to the benzene photolysis (entry 1), the azirane **3a** product is favored in the zeolite photolysis; indeed, the **2a**:**3a** product ratio in the zeolites resembles more closely the results in the polar methanol solvent (entry 2). Furthermore, the photolysis of azoalkane **1a** is not subject to a significant heavy-atom effect since NaY and CsY give a similar product distribution. Thus, the enhancement of the triplet pathway (azirane **3a** formation) in zeolites derives from polarity effects. The polarity of the supercages in the NaX and LiX zeolites has been estimated to be similar to that of a methanol-water (1:1) mixture, while that of CsX is close to that of propanol.[2a] In view of these facts, the polarity of the Y zeolites modifies the photophysical and photochemical behavior of azoalkane **1**, presumably by enhancing the singlet-triplet intersystem crossing.[4d] Indeed, it was previously established in the solution photolysis of azoalkanes **1** that polar solvents favor azirane **3** formation through stabilization of the more polar triplet excited state ^{3}**1*** and diradical **1**(β).[4d] The prevalence of azirane formation in the photolysis in the Y zeolites indicates that the *gem*-dimethyl group does not experience any rotational restriction in the supercages due to steric hindrance, which is in good agreement with the larger dimension of this reaction cavity compared with the dense packing in the crystal.

In summary, photochemical denitrogenation of azoalkanes **1** in the crystalline state is a highly product-selective process, controlled by the close packing in the crystal lattice, which even overrides spin effects. The formation of the triplet product, that is, aziranes **3**, is completely suppressed by preventing the required conformational motion of the *gem*-dimethyl group in the azoalkane-azirane rearrangement. By contrast, the photolysis in zeolites promotes the triplet channel through polarity effects.

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

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(9) Kaupp, G.; Haak, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2774−2777.

(10) Anderson, M. A.; Grissom, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 9552−9556.