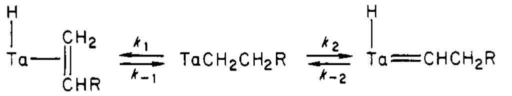
we feel that the second alternative is more plausible.

One of the most interesting aspects of the mechanism shown in eq 2 is the last step, an α-elimination reaction to give the new alkylidene hydride complex.[17] We want to point out that our results do not *necessarily* imply that β elimination to give an olefin hydride intermediate is relatively slow. It is possible that although $K_2 > K_1$ (where $K_2 = k_2/k_{-2}$ and $K_1 = k_1/k_{-1}$), k_1 is still greater than k_2 (eq 3), i.e., β elimination is still faster. If this is true, it



$$\begin{array}{c}\mathrm{H}\\|\\\mathrm{Ta}\end{array}\!-\!\begin{array}{c}\mathrm{CH_2}\\\|\\\mathrm{CHR}\end{array} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TaCH_2CH_2R} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \begin{array}{c}\mathrm{H}\\|\\\mathrm{Ta}\end{array}\!=\!\mathrm{CHCH_2R} \qquad (3)$$

must also be true that the olefin hydride complex is *relatively* stable toward displacement of $CH_2{=}CHR$ by ethylene under the reaction conditions that we employed here. Chain transfer is most likely a result of an occasional displacement of $CH_2{=}CHR$ from the olefin hydride complex.

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[14] An example of a complex that reacts slowly with ethylene in a manner consistent with ethylene "insertion" into the metal–alkyl bond is $Co(\eta^5\text{-}C_5H_5)(PPh_3)Me_2$.[15] There are some less well-studied examples.[1] A recent report[16] of the stepwise reaction of a metal–alkyl complex $(Lu(\eta^5\text{-}C_5Me_5)_2R)$ with an olefin (propylene) is the only other example of observed polymer growth at a well-characterized metal center. It is an especially important observation since it can be argued that propylene inserts into a metal–alkyl bond (the Cossee mechanism), not a metal–alkylidene bond.

[15] Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3973.

[16] Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337–339.

[17] The recently observed equilibrium between $Ta(CHCMe_3)(C_2H_5)L_2Cl_2$ and $Ta(CH_2CMe_3)(C_2H_4)L_2Cl_2$ ($L = PMe_3$)[18] is an example of α elimination competing successfully with β elimination.

[18] Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481.

Photochemistry of 2,3-Diazabicyclo[2.1.1]hex-2-ene. β C–C Cleavage to a Stereorandom Triplet Biradical

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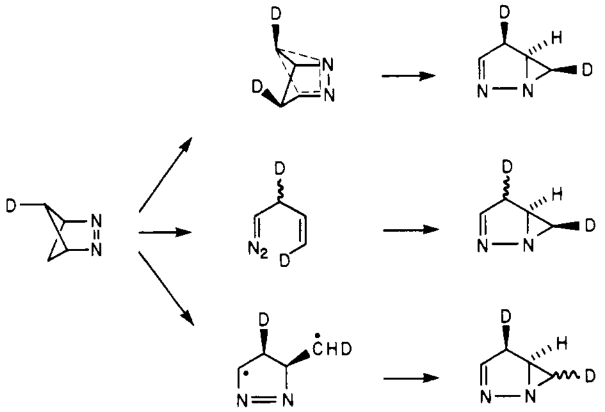
The photochemistry of 1,2-diazenes (azo compounds) has been intensively studied because of its potential synthetic utility,[1] the unique dependencies on structural variations,[2] and the theoretical interest in this simple chromophore.[3,4] We describe herein the photochemistry of 2,3-diazabicyclo[2.1.1]hex-2-ene (**1**),[5] the smallest and most strained member of the series of homologous bicyclic azoalkanes. This simple compound displays a rich and varied photochemistry that is quite different from that of related compounds.

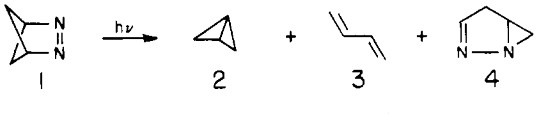
Photolysis of **1** in benzene or cyclohexane produces bicyclo[1.1.0]butane (**2**), butadiene (**3**), and 1,2-diazabicyclo[3.1.0]hex-2-ene (**4**) in overall quantitative yield.[6] Table I shows that the relative yields are dependent on temperature and spin multiplicity. We have determined the quantum yield[7] for overall decomposition of **1** upon direct photolysis at 25 °C to be 0.45 ± 0.05, and thus **1** is not a "reluctant" azoalkane.[8] The next higher homologue **5** also loses N_2 efficiently, but the next symmetrical homologue **6** is quite photoinert.[8] Fluorescence is observed for **1** with $\lambda_{max} = 337$ nm (hexane), and a near mirror image relationship with the absorption spectrum, as expected for such a rigid structure.[3]

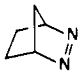
Table I. Product Yields from Photolysis of 1

conditions	2	3	4
direct, 25 °C	55	17	28
direct, −100 °C	23	13	64
sensitized, 25 °C	6	10	84

Scheme I







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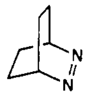

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The most surprising feature of the photochemistry of **1** is the formation of the nitrogen-retained product **4**. It is the parent of a ring system that has recently been the subject of several studies,[9] and its structure was assigned on the basis of spectral data.[10] One can envision three different routes to **4**. It is formally related to **1** by a [1,3]-sigmatropic shift, and such a photochemically allowed, concerted reaction seems plausible, at least upon direct excitation.

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[1] Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762–779.

[2] Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150.

[3] Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122–5129.

[4] Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639–2642.

[5] Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4090–4092.

[6] Photolyses were carried out in Pyrex vessels using either a 450-W Hanovia medium-pressure mercury lamp or a 1000-W Oriel Xe arc. Products were analyzed by a combination of NMR spectroscopy, GC, and HPLC, and control experiments demonstrate that all products are stable to the various reaction conditions.

[7] Quantum yields were determined by using **5** as an actinometer ($\Phi = 1.0^2$) in photolyses to low conversion. Identical results were obtained whether monochromatic or broad-band irradiation was used.

[8] See, for example, ref 2 and Engel et al. (Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W.-K. *J. Am. Chem. Soc.* **1979**, *101*, 6435–6437).

[9] (a) Nishizawa, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1980**, *102*, 1776–1777. (b) Padwa, A.; Ku, H. *Tetrahedron Lett.* **1980**, *21*, 1009–1012. (c) Miyashi, T.; Fujii, Y.; Nishizawa, Y.; Mukai, T. *J. Am. Chem. Soc.* **1981**, *103*, 725–727. (d) Padwa, A.; Rodriquez, A. *Tetrahedron Lett.* **1981**, *22*, 187–190.

[10] ^{1}H NMR (500 MHz; coupling constants from extensive decoupling and complete spectral simulation; *n* = *endo*; *x* = *exo*; $CDCl_3$): δ 7.29 (H3), 3.06 (H4*x*), 3.03 (H4*n*), 2.71 (H5), 2.29 (H6*x*), 1.11 (H6*n*); J (in Hz) H4*n*–H4*x* = 18, H4*x*–H5 = 7, H4*n*–H5 = 3, H6*n*–H6*x* = 1.5, H5–H6*x* = 7, H5–H6*n* = 5, H3–H4*n* = H3–H4*x* = H3–H6*n* = 1.2, H3–H6*x* = 1.5, H4*x*–H6*n* = H4*n*–H6*n* = 0.6. ^{13}C NMR ($CDCl_3$) δ 36.78 (CH), 39.05 (CH_2), 39.76 (CH_2), 158.88 (C=N). IR (CCl_4) 3050, 3000, 2930, 2840, 1595, 1435, 1295, 1260 cm^{-1}. UV (hexane) 210 (ϵ 1295), 243 nm (ϵ 645). Mass spectrum: calcd for $C_4H_6N_2$, 82.0531; found, 82.0529, 82 (17), 55 (100), 54 (86), 53 (77), 41 (15), 40 (11).

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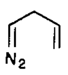
Hydrazone **4** can also be formed by a thermal, nitrene-like, internal 1,1 cycloaddition of diazoalkene **7**, a process that has recently been



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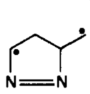

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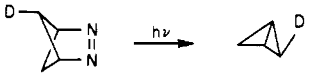
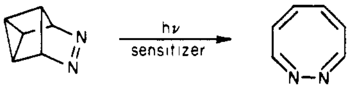
demonstrated in several substituted derivatives of **7**.[9] As shown below, **7** is a primary photoproduct from **1** and is responsible for the formation of **3**. Finally, β C–C cleavage in **1** would produce biradical **8**, which could subsequently close to **4**. As shown in Scheme I, photolysis of *exo*-5-^{2}H-**1** (**1-D**)[11] unambiguously differentiates the three mechanisms. The [1.3]-sigmatropic shift pathway should be stereospecific with respect to both C4 and C6 of the product, while the diazoalkene route should scramble C4 but not C6.[9c,d] The biradical path should be stereospecific at C4 but would scramble C6 if C–C rotation is faster than ring closure.



1-D 2-D

In practice, either direct or sensitized photolysis of **1-D** produces **4** with completely stereospecific labeling at C4 but complete scrambling at C6. Thus, upon direct or sensitized photolysis, **4** is formed by β C–C cleavage to a stereorandom biradical. The labeling result also demands that this cleavage be irreversible, since closure to **1** would scramble the ^{2}H label in **1** and therefore also at C4 in **4**.

Turro and Katz have previously reported that sensitized photolysis of the highly strained diazene **9** leads to C–C cleavage.[12] More recently, Adam has observed a formal [1,3]-sigmatropic shift upon sensitized photolysis of **10**.[13] Both results are consistent



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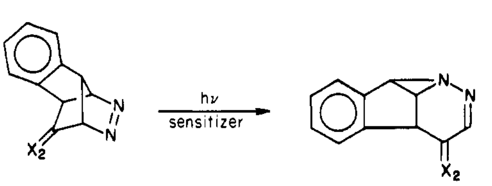

10 $X_2 = H_2$; $-CH_2CH_2-$

with our finding for the sensitized photolysis of **1**, and taken in combination the three results suggest some generality for β C–C cleavage to triplet biradicals from triplet azoalkanes. There is presumably a stereoelectronic requirement, analogous to that proposed for β C–C cleavage in cyclopropyl ketones,[14] that requires some overlap between the N–N π bond and the C–C bond that will undergo cleavage. Apparently, the C–C cleavage must also relieve a substantial amount of strain, since **5** and **6** do not show such a reaction. The ratio of deuteria at C4 and C6 in **4** from either direct or sensitized photolysis of **1-D** is 1.14 ± 0.08. This is consistent with a secondary kinetic isotope effect for the β cleavage reaction[15] and would seem to indicate that there must be a finite barrier to the cleavage.

Several lines of evidence suggest that formation of **4** upon direct irradiation also proceeds from the triplet azoalkane. That is, intersystem crossing (ISC) to the triplet state of diazene **1** is fairly efficient, an unusual result for azoalkanes.[12] The deuterium labeling results are identical in the direct and sensitized photolyses. We cannot rule out the possibility that structural constraints force the molecule to reject the continuous overlap afforded by the allowed, concerted process and that S_1 produces a stereorandom singlet biradical. However, the fact that at lower temperatures the yield of **4** increases substantially (Table I) provides strong support for the ISC mechanism. The singlet α-cleavage reaction presumably must overcome an energy barrier,[8] and its rate is expected to decrease at lower temperatures. However, ISC rates are generally independent of temperature,[12] and thus at lower temperatures ISC should become more competitive with the singlet photochemistry. Of course, the fact that **4** is the dominant product from sensitized photolysis is also consistent with the ISC mechanism. This interpretation is analogous to a previous analysis of the photochemistry of **9**, which is the only other system for which ISC has been implicated.[12]

Concerning the other products, bicyclobutane was expected based on the results for **5**, which gives a 10:1 mixture of bicyclo[2.1.0]pentane and cyclopentene.[16] Photolysis of **1-D** gives a 47% excess of the double-inversion product, *exo*-2-^{2}H-**2** (**2-D**). This is consistent with the photolysis of **5**, which proceeds with a 20% excess of inversion.[17] However, it is in sharp contrast to the solution phase thermolysis of **1-D**, which produces stereorandomized **2-D**.[11]

Butadiene (**3**) is a secondary photoproduct, arising from photolysis of **7**. That **7** is produced from **1** was shown by the observation of a red color and an intense IR signal at 2063 cm^{-1} when the photolysis was carried out with monochromatic light (325 ± 10 nm). As expected, photolysis of **1** in methanol-d_4 led to no detectable butadiene formation. Neither bicyclobutane nor butadiene can be detected when methanol-d_4 is the solvent for sensitized photolysis. This implies that **7** is the precursor to both **2** and **3** in the triplet manifold. The conversion $\mathbf{1} \rightarrow \mathbf{7}$ is formally a retro-[3 + 2] cycloaddition. However, we cannot at present distinguish between a concerted route and a sequence of individual C–N and C–C cleavages.

In summary, the photochemistry of **1** is much more complex than that of its higher homologues **5** and **6**. Competitive with α C–N cleavage leading to N_2 loss is β C–C cleavage to give a stereorandom biradical, with spin multiplicity a major factor in determining the relative efficiencies of the two processes. Formal retro-[3 + 2] cycloaddition to a diazoalkene is also observed, although the exact mechanism of this reaction is not known. Several lines of evidence suggest that ISC is unusually efficient in this simple, bicyclic azoalkane. The small size and high symmetry of **1** coupled with its surprisingly complex photochemistry suggest that it would be an interesting structure for theoretical studies of excited-state reactivity, and such studies are planned.[18]

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Registry No. 1, 72192-13-3; **2**, 157-33-5; **3**, 106-99-0; **4**, 81194-34-5; **8**, 81205-67-6.

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[15] For another example of a secondary kinetic isotope effect in a photochemical reaction, see: Kwart, H.; Benko, D. A.; Streith, J.; Harris, D. J.; Shuppiser, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 6501–6502.

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[18] Photolysis of **1** at 8 K in various solvents in the cavity of an ESR spectrometer does not produce a triplet signal, even though 1,3-cyclobutanediyl is calculated to have a triplet ground state.[19] This contrast to the classic result of Closs[20] on **5** is presumably a consequence of the fact that the triplet state of **1** does not lose N_2, but instead gives **4** and **7**.

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