Solid-State and Solution Photochemistry of a 1-Aza Diene

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The *N*-acyl-2-cyano-1-aza diene **1** is photochemically reactive both in solution and in the solid state. Irradiation of **1** in solution produced a 98% yield of the bicyclo[3.1.0]hexene derivatives **2a** and **2b**. Irradiation of **1** in the solid state also produced the intramolecular reaction products **2a** and **2b** in 30% yield along with 65% of the intermolecular 2 + 2 cycloadduct **4**. Inspection of the X-ray determined crystal structure of aza diene **1** suggests that the formation of the 2 + 2 cycloadduct in the solid state is primarily the result of topochemical control. The unusual occurrence of both unimolecular and bimolecular photoreactions provides the opportunity to obtain insight into the nature of the solid-state reaction. The ratios of the photoproducts (**4** to **2a** + **2b** and **2a** to **2b**) under the various photochemical conditions are discussed in terms of the changing molecular environment of the solid-state photoreaction as a function of the reaction time.

Dienes and dienones have historically played a very important role in preparative and mechanistic organic photochemistry.[1] Although the photochemistry of 1-aza dienes could also prove to be of considerable mechanistic and synthetic interest, there is little information in the literature regarding their photochemical behavior. The lack of information in the literature on 1-aza dienes[2] is partly because, by analogy to the simple imines, they are not as photochemically active as either carbon–carbon or carbon–oxygen double bonds.[3]

It has been observed that acyl substitution enhances the photochemical reactivity of imines.[2] It would be anticipated that 1-aza dienes would also become more photochemically active by *N*-acyl substitution. However, inspection of the literature reveals that few *N*-acyl-1-aza dienes have been reported and their photochemistry has not been studied.

One of the difficulties of studying any properties of *N*-acyl-1-aza dienes is their instability. In connection with our studies on the pericyclic reactions of carbon–nitrogen double bonds[4] we have developed methods for the preparation of *N*-acyl-1-aza dienes.[4,5] In contrast to simple *N*-acyl-1-aza dienes, which generally cannot be isolated, we have observed that *N*-acyl-2-cyano-1-aza dienes are considerably more stable. They can be isolated and, with care, stored for long periods of time. This situation allowed for a study on the photochemical behavior of the *N*-acyl-1-aza diene **1**.

Solution Photochemistry

Direct ultraviolet irradiation of a 2% solution of **1** in $CDCl_3$ using a medium-pressure mercury lamp resulted in its rapid disappearance with the formation of two photoproducts **2a** and **2b** in a ratio of 6:1. The photochemistry was exceptionally clean. No other photoproducts could be detected by ^1H NMR spectroscopy. These two products, **2a** and **2b**, were readily separated by flash chromatography. Both the ^1H NMR and the mass spectra were consistent with these two photoproducts being isomeric with each other and the 1-aza diene **1**.

A crystal structure of the major isomer **2a** clearly demonstrated that it possessed the molecular structure shown in Scheme I. It was concluded from the spectral data that the minor isomer **2b** was epimeric with the major isomer **2a** at C-5.

Because few *N*-acyl-1-aza dienes have been isolated there is little precedent for the solution-phase photochemical behavior of **1**. The photochemical behavior of the analogous all-carbon diene, 6-phenyl-3,5-hexadien-2-one, has been studied,[6] and it behaves similar to other acyclic dienones. The primary photochemical process is cis–trans isomerization about the two carbon–carbon double bonds. No analogous bicyclo[3.1.0]hex-2-ene ring formation was observed. There appears to be no precedent in the photochemistry of acyclic dienones for the reactivity observed for **1**. However, the formation of the bicyclo[3.1.0]hex-2-ene ring system is a well-established reaction for the photochemistry of acyclic trienes.[7] Because of the stereospecificity displayed by these photochemical cycloadditions, their mechanisms have been frequently interpreted in terms of concerted orbital symmetry controlled processes.[7,8]

In contrast to the photochemical behavior of all-carbon trienes, the irradiation of **1** produces a mixture of stereoisomers **2a** and **2b**. Among the mechanistic pathways that could produce these two stereoisomers we prefer an initial photochemically induced cyclization to produce the five-membered diradical intermediate **3**. The stereoisomers **2a** and **2b** would then be produced by either of two modes of cyclization. Diradical intermediate **3** would be predicted to be particularly stable. One of the radical centers is stabilized by an adjacent phenyl substituent and the other is stabilized by both the electron-withdrawing cyano substituent and the electron-donating vinylogous oxygen substituent.[9]

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[1] For example see *Photochemistry, A Specialist Periodical Report*; Bryce-Smith, D., Ed.; The Royal Society of Chemistry, Burlington House: London; 1991; Chapter 2, Vol. 22, and previous volumes in this series.

[2] (a) Mariano, P. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1987; Vol. 9, p 1. (b) Padwa, A. *Chem. Rev.* **1977**, *77*, 37. (c) Pratt, A. C. *Chem. Soc. Rev.* **1977**, *6*, 63. (d) Koch, T. H.; Anderson, D. R.; Burns, J. M.; Crockett, G. C.; Howard, K. A.; Keute, J. S.; Rodehorst, R. M.; Sluski, R. J. *Top. Curr. Chem.* **1978**, *75*, 64.

[3] (a) Margaretha, P. *Helv. Chem. Acta* **1978**, *61*, 1025; **1982**, *65*, 290.

[4] The Diels–Alder reaction of 1-aza dienes: (a) Cheng, Y. S.; Fowler, F. W.; Lupo, A. T., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 2090. (b) Hwang, Y. C.; Fowler, F. W. *J. Org. Chem.* **1985**, *50*, 2119. The Aza Cope rearrangement: (c) Wu, P.-L.; Fowler, F. W. *J. Org. Chem.* **1988**, *53*, 5998. (d) Wu, P.-L.; Fowler, F. W. *J. Org. Chem.* **1988**, *53*, 963. Electrocyclic reactions: (e) Wyle, M. J.; Fowler, F. W. *J. Org. Chem.* **1984**, *49*, 4025. The ene reaction: (f) Lin, J. M.; Koch, K.; Fowler, F. W. *J. Org. Chem.* **1986**, *51*, 167.

[5] (a) Teng, M.; Fowler, F. W. *J. Org. Chem.* **1990**, *55*, 5646. (b) Teng, M.; Fowler, F. W. *Tetrahedron Lett.* **1989**, *30*, 2481.

[6] Kluge, A. F.; Lillya, C. P. *J. Org. Chem.* **1971**, *36*, 1988.

[7] Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 9, Chapter 2.

[8] (a) Padwa, A.; Brodsky, L.; Clough, S. *J. Am. Chem. Soc.* **1972**, *94*, 6767. (b) Courtot, P.; Rumin, R.; Salaun, J. Y. *Rec. Trav. Chim. Pays Bas* **1979**, *98*, 192. (c) Tanaka, K.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2209.

[9] The apparent synergistic effect on the stability of radical centers produced by electron-donating and electron-withdrawing groups has been extensively studied and called the captodative effect (Viehe, H. G.; Merényi, R.; Janousek, Z. *Pure Appl. Chem.* **1988**, *60*, 1635).

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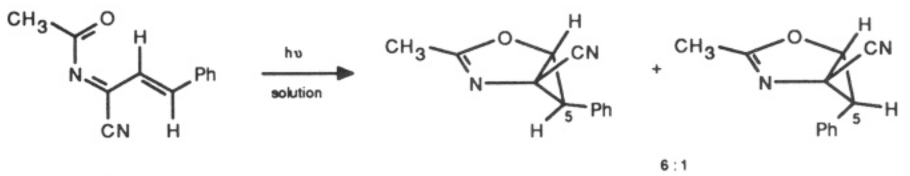
Scheme I. Solution Photochemistry of Aza Diene 1



1 2a 2b

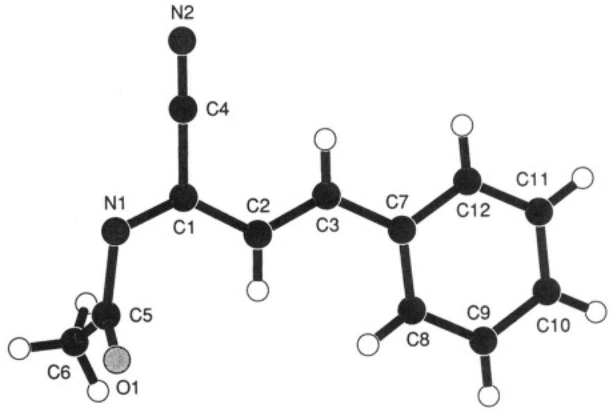


Figure 1. Molecular structure of compound 1.

The two stereoisomers **2a** to **2b** are a result of different modes of rotation about the exocyclic bond connecting the benzyl radical in **3**. The 6:1 ratio of **2a** to **2b** produced by the irradiation of **1** in solution is most reasonably a result of the two transition states reflecting the differences in nonbonding interactions present in these two compounds. The endo phenyl substituent in **2b** experiences more nonbonded interactions than does the corresponding exo phenyl substituent in **2a**. The phenyl ring in **2b** is cis to two substituents on the three-membered ring whereas the phenyl group in **2a** is cis only to the cyano substituent.

Solid-State Photochemistry

An attempt to determine the structure of the 1-aza diene **1** using single-crystal X-ray diffractometry techniques was initially unsuccessful. The standard reflections decayed significantly over the 12 h required for the initial data collection. Subsequently, new data were collected over a 4-h period using a fast scan rate (16.5°/min). Using this new data, the molecular and crystal structures of **1** were successfully determined (see Figure 1). The 1-aza diene crystallizes in the monoclinic space group $P2_1/c$ with a short a axis of 4.697 Å. The crystal structure consists of linear stacks of planar molecules along the short a axis,

Scheme II. Proposed Mechanism for the Conversion of 1 into 2a and 2b

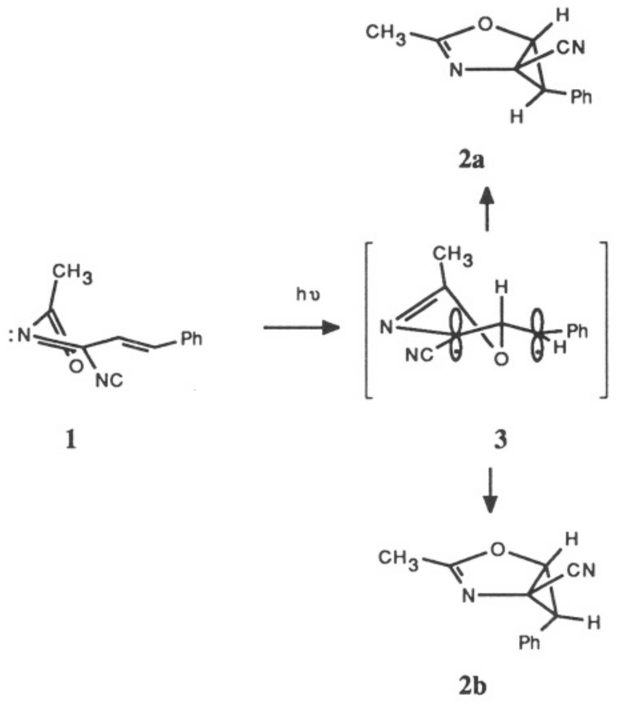


Table I. Intermolecular Distances (Å) for Non-Hydrogen Atoms of Compound 1[a]

O1···O6	3.48 (1)	$1 + x, {}^1/_2 - y, {}^1/_2 + z$
O1···C8	3.510 (9)	$1 + x, y, z$
N1···C2	3.507 (9)	$1 + x, y, z$
N1···C10	3.569 (9)	$1 + x, y, -1 + z$
C1···C7	3.496 (9)	$1 + x, y, z$
C1···C8	3.60 (1)	$1 + x, y, z$
C2···C8	3.427 (9)	$1 + x, y, z$
C3···C4	3.46 (1)	$-1 + x, y, z$
C4···C7	3.60 (1)	$1 + x, y, z$
C7···C10	3.52 (1)	$1 + x, y, z$

[a] The symmetry operation specifies the position of the second atom of the pair.

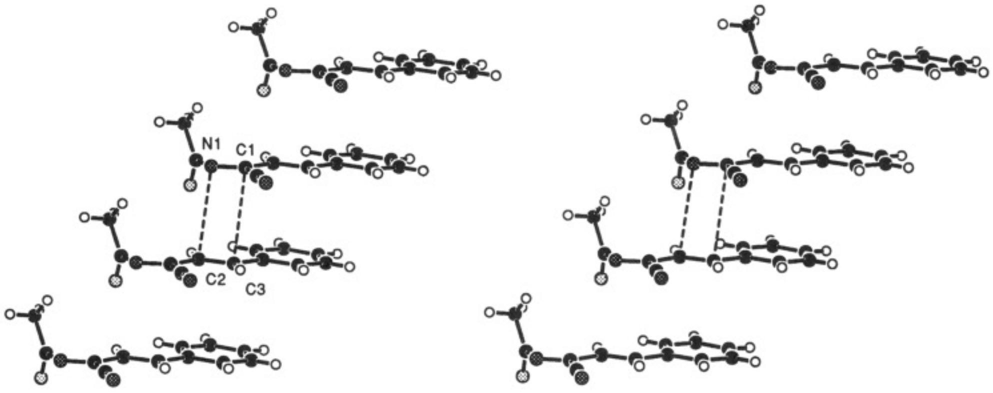


Figure 2. A stereodiagram showing the packing the N-acyl-1-aza diene. The molecules stack along the short, 4.697 (2) Å, a axis. The intermolecular 2 + 2 reaction results in the formation of two new chemical bonds as indicated by the dotted lines. The intermolecular distances are 3.613 (9) Å for C1–C3 and 3.507 (9) Å for N1–C2.

Table II. Intramolecular Distances (Å) and Angles (Deg) for Compound 1

O1–C5	1.212 (8)	C5–C6	1.46 (1)
N1–C1	1.280 (7)	C7–C8	1.392 (8)
N1–C5	1.402 (8)	C7–C12	1.391 (8)
N2–C4	1.129 (7)	C8–C9	1.368 (9)
C1–C2	1.433 (8)	C9–C10	1.375 (9)
C1–C4	1.476 (9)	C10–C11	1.372 (9)
C2–C3	1.332 (8)	C11–C12	1.373 (9)
C3–C7	1.456 (8)		
C1–N1–C5	121.7 (5)	N1–C5–C6	114.6 (7)
N1–C1–C2	128.3 (6)	C3–C7–C8	122.7 (6)
N1–C1–C4	114.2 (6)	C3–C7–C12	119.6 (6)
C2–C1–C4	117.4 (6)	C8–C7–C12	117.7 (6)
C1–C2–C3	124.6 (6)	C7–C8–C9	121.4 (6)
C2–C3–C7	126.8 (6)	C8–C9–C10	119.7 (6)
N2–C4–C1	179.2 (7)	C9–C10–C11	120.3 (7)
O1–C5–N1	120.7 (7)	C10–C11–C12	119.9 (6)
O1–C5–C6	124.3 (7)	C7–C12–C11	121.0 (6)

Table III. Crystal Data for Compound 1

empirical formula	$C_{12}H_{10}N_2O$
formula weight (g/mol)	198.2
crystal system	monoclinic
crystal dimensions (mm)	0.60 × 0.20 × 0.20
a (Å)	4.697 (2)
b (Å)	28.072 (6)
c (Å)	8.537 (3)
β (deg)	104.02 (8)
space group	$P2_1/c$ (#14)
Z value	4
F_{000}	416
2θ maximum (deg)	40
reflections measured	1150
unique obs ($I > 3.0s$)	634
no. variables	136
R	0.056
R_w	0.071
goodness of fit	2.52
maximum peak if final diff. map (e)	0.14

Table IV. Positional Parameters and *B*(eq) for Compound 1

atom	x	y	z	B(eq)
O(1)	0.731 (1)	0.2220 (2)	0.4642 (7)	6.8 (3)
N(1)	0.573 (1)	0.1536 (2)	0.3285 (6)	4.6 (3)
N(2)	0.571 (2)	0.0347 (2)	0.3312 (8)	7.9 (4)
C(1)	0.465 (1)	0.1219 (2)	0.4050 (9)	4.3 (3)
C(2)	0.304 (1)	0.1287 (2)	0.5261 (8)	4.0 (3)
C(3)	0.214 (1)	0.0936 (2)	0.6076 (8)	4.1 (3)
C(4)	0.523 (2)	0.0724 (3)	0.3634 (8)	5.3 (4)
C(5)	0.550 (2)	0.2023 (3)	0.359 (1)	4.7 (4)
C(6)	0.320 (2)	0.2270 (3)	0.242 (1)	7.8 (5)
C(7)	0.055 (1)	0.0986 (2)	0.7336 (8)	3.9 (3)
C(8)	−0.020 (1)	0.1427 (2)	0.7862 (8)	4.7 (4)
C(9)	−0.159 (2)	0.1464 (3)	0.909 (1)	5.5 (4)
C(10)	−0.229 (2)	0.1058 (3)	0.982 (1)	6.2 (4)
C(11)	−0.162 (2)	0.0617 (3)	0.931 (1)	6.6 (5)
C(12)	−0.023 (2)	0.0582 (2)	0.807 (1)	5.4 (4)
H(1)	0.2590	0.1605	0.5504	4.8
H(2)	0.2577	0.0621	0.5804	4.9
H(3)	0.0253	0.1708	0.7353	5.7
H(4)	−0.2076	0.1768	0.9444	6.6
H(5)	−0.3225	0.1080	1.0690	7.5
H(6)	−0.2120	0.0337	0.9807	8.0
H(7)	0.0499	0.0275	0.7713	6.5
H(8)	0.1735	0.2048	0.1930	9.3
H(9)	0.2376	0.2508	0.2961	9.3
H(10)	0.4023	0.2412	0.1622	9.3

Figure 2. All molecules of a given stack are related by a simple crystallographic translation operator requiring that any single molecule of a stack has a conformation and orientation identical to all other molecules within the stack. The carbon–carbon double bonds of adjacent molecules within a stack are related by this translational operator and are thus 4.697 Å apart; intermolecular distances are shown in Table I. However, the respective intermolecular atom–atom distances of the carbon–carbon double bond of one molecule and the carbon–nitrogen double bond of the neighboring molecule within the stack are 3.613 (9) and 3.507 (8) Å, suggesting that it was a 2 + 2 cycloaddition of these two double bonds that was responsible for the changes in the crystal that led to the decay of standard reflections during the X-ray experiment.

The molecular structure of the 1-aza diene 1 is also of interest,[10] Table II. Except for the acyl group the molecules are planar with all atoms within 0.1 Å of a least-squares plane, Figure 1. The acyl group is turned nearly perpendicular to the plane with a dihedral angle of 82°. With this geometry the acyl group will be in conjugation with the nitrogen lone pair and not the diene. As expected the diene portion of the molecule has short N1–C1, 1.280 (7) Å, and C2–C3, 1.332 (8) Å, double bonds and a longer C1–C2, 1.433 (8) Å, single bond. The acyl group has a configuration about the carbon–nitrogen double bond that is cis to the carbon–carbon double bond. This configuration facilitates the intramolecular reaction discussed below.

The solid-state ultraviolet irradiation of the 1-aza diene 1 resulted in the crystals first becoming cloudy followed by clearing. During the irradiation the crystals maintained their original shape and showed no evidence of macroscopic restructuring. After irradiation an examination of the product on the X-ray diffractometer indicated that they had become amorphous. The ^{1}H NMR spectrum of the irradiated crystals demonstrated that they consisted of a mixture of the solution photoproducts, **2a** and **2b** (30%), in a ratio of 1:1 along with a new photoproduct 4 (65%) and a small amount of unreacted 1-aza diene 1 (5%). The ^{1}H NMR and infrared spectra of the new photoproduct were consistent with its structure being the anticipated 2 + 2 cycloadduct, azetidine 4. Thus, a photochemically induced 2 + 2 cycloaddition was occurring with a carbon–carbon and a carbon–nitrogen double bond rather than with two carbon–carbon double bonds. This primary photoproduct proved to be extremely unstable, undergoing rapid hydrolysis to the imide **5** during the chromatographic separation. Confirmation of the azetidine structure for the photoproduct was obtained by single-crystal X-ray diffractometry of the imide **5**.

Because of the low melting point of 1 (45 °C) and its slow rate of crystallization, it was possible to perform the irradiation directly on a melted sample at room temperature. Under these conditions a small amount of the 2 + 2 cycloadduct 4 was formed along with the bicyclo[3.2.0]hexenes, **2a** and **2b**. The ratio of 4 to **2a** plus **2b** was 1:17 and the ratio of **2a** and **2b** was 2:1.

Among the known solid-state photochemical reactions, it is the 2 + 2 cycloaddition reactions of carbon–carbon double bonds that have played a very important role delineating the topochemical principles necessary for photochemical reactivity in the solid state.[11] Most of these studies have involved cinnamic acid derivatives which undergo 2 + 2 cycloaddition reactions of the carbon–carbon double bonds to produce a cyclobutane ring. Compound

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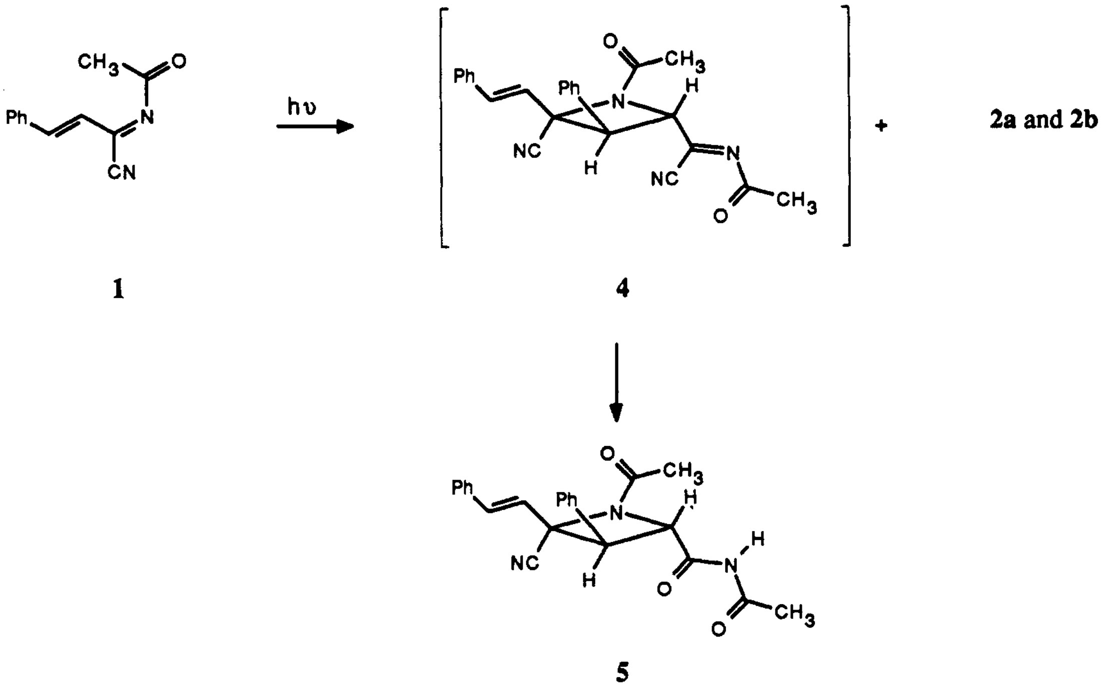
(10) For previous structural studies on *N*-acylimines, see: (a) Allmann, R.; Kupfer, R.; Nagel, M.; Würthwein, E. U. *Chem. Ber.* **1984**, *117*, 1597. (b) Allmann, R.; Krestel, M.; Kupfer, R.; Würthwein, E. U. *Ibid.* **1986**, *119*, 3237. (c) Allman, R.; Krupfer, R.; Würthwein, E. U. *Ibid.* **1985**, *118*, 3089.

(11) (a) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433. (b) Green, B. S.; Arad-Yellin, R.; Cohen, M. D. *J. Chem. Soc., Chem. Commun.* **1986**, *16*, 131.

Scheme III. Solid-State Photochemistry of 1-Aza Diene 1



1 is also a cinnamic acid derivative but its solid-state reactivity possesses a number of features that make it unique among the known photoactive crystalline compounds.

In contrast to the majority of 2 + 2 photochemical cycloadditions, the dimerization of 1 involves two different double bonds to form a four-membered ring. This reaction represents one of the few examples of a photochemically induced 2 + 2 cycloaddition of an imine derivative under any conditions[2,12] and a rare example of this reaction involving an acyclic imine.[2,13] It is also interesting to note that, in principle, there are two photochemical reactions that can produce the azetidine 4. The excited-state 1-aza diene 1 can react with either the C═N bond of the adjacent molecule above or the C═C bond of the adjacent molecule below, (see Figure 2). These two alternate reactions would lead to equivalent 2 + 2 products, but the presence of a molecule in the excited state breaks the symmetry of the crystal lattice. This means that the reaction coordinates for the two reactions can differ. It seems unlikely that the two alternative reactions would occur with equal probabilities, but it cannot be determined from the present data which of these two processes is preferred.

There is a general interest concerning the molecular environment of a crystal as a photochemical reaction of stacked double bonds proceeds. This problem has recently been addressed by two theoretical studies.[14,15] Although these studies were concerned with the evolution of various species, e.g. the 2 + 2 cycloadduct and isolated monomers, the results of these theoretical studies could only be compared with the final yield of previously reported solid state 2 + 2 cycloadditions. An important feature of the solid-state reaction described in the present study is that there are three photochemical transformations occurring, one intermolecular to give the azetidine 4 and two intramolecular to give the stereoisomeric compounds **2a** and **2b**. The ratios of these compounds with respect to each other under various conditions can provide information about the nature of the molecular environment in the solid state as the reaction proceeds.

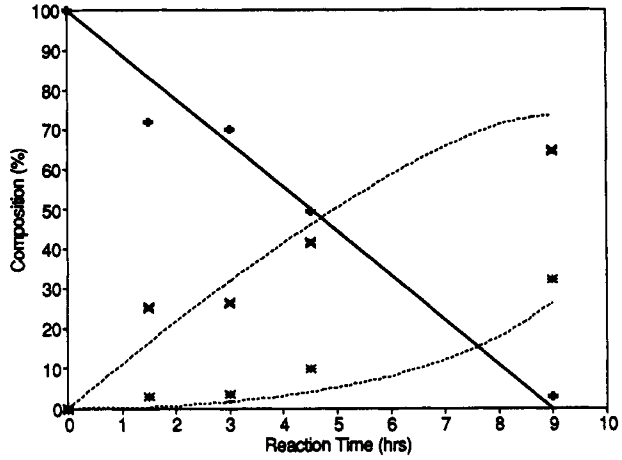


Figure 3. Crystal composition vs reaction time. The solid line represents the linear disappearance of the diene with time; the observed experimental points (+) are shown. The upper dotted line shows the predicted appearance of the azetidine 4 produced by the intermolecular 2 + 2 photochemical cycloaddition reaction; the observed experimental points (×) are also shown. The lower dotted line shows the predicted appearance of the bicyclo[3.1.0]hexenes **2a** and **2b** produced by the intramolecular photochemical reaction; the observed experimental points (*) are also shown. These predicted curves are the result of the computer simulation discussed in the text.

Figure 3 shows the reaction stoichiometry as a function of time. The percent yield of the 1-aza diene decreases linearly with time. This is the expected behavior for a photochemical conversion in which photons are the limiting reagent. The product yields also vary with time. In the initial stages of the reaction the 2 + 2 cycloaddition product predominates with a rate of increase only slightly less than the linear decrease in starting material. As the reaction proceeds this rate falls as the rate of the intra-

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[12] The photodimerization of an imine in the solid state has been observed (Lawrenz, D.; Mohr, S.; Wendländer, B. *J. Chem. Soc., Chem. Commun.* **1984**, 863).

[13] We are only aware of only one other example of an acyclic imine undergoing a 2 + 2 photocycloaddition reaction (see ref 3).

[14] Desiraju, G. R.; Kannan, V. *Proc. Indian Acad. Sci.* (*Chem. Sci.*) **1986**, *96*, 351.

[15] Wernick, D. L.; Schochet, S. *J. Phys. Chem.* **1988**, *92*, 6773.

molecular reaction increases.

There are at least two mechanisms possible for the formation of intramolecular products **2a** and **2b** in the solid state. First, it is possible that the intramolecular reactions can occur within the intact crystal lattice. If this is true, then we would expect the intramolecular and intermolecular reactions to occur simultaneously as the reaction proceeds with relatively fixed product ratios. However, it can be clearly seen from Figure 3 that the product ratio is not constant during the course of the reaction. In the early stages of the reaction there is a much larger percentage of the intermolecular product azetidine **4** than the intramolecular products **2a** and **2b**.

An alternative mechanism, consistent with the data, is that intramolecular reactions can occur in regions of the crystal where the local lattice has been altered by the photochemical reaction and the required neighboring molecule no longer exists or no longer has the required orientation for the intermolecular reaction producing azetidine **4**. In this case one would not expect a constant ratio of products; the degree of lattice alteration would increase as the photoreaction proceeds.

There are two obvious sources of lattice alteration that could suppress the intermolecular 2 + 2 cycloaddition allowing for the intramolecular photoreaction producing **2a** and **2b**. When a 2 + 2 cycloaddition reaction occurs in the solid state there is a considerable dislocation of the atomic nuclei; individual atoms must move by at least 1 Å. This situation would be anticipated to cause a disruption of the crystal lattice in the local environment of the chemical reaction. This disruption could result in the inability of an excited 1-aza diene, in the local environment, to participate in subsequent 2 + 2 reactions.

However, this lattice disruption, due to the nuclear motion of the 2 + 2 cycloaddition, is not necessarily the most important factor. Even if the 2 + 2 cycloaddition reaction did not create a disruption of the crystal, a complete conversion of the 1-aza diene would not be anticipated. If the 2 + 2 cycloaddition reactions take place as random photochemical events, then eventually, as the reaction proceeds, certain isolated 1-aza dienes will be created without the necessary neighbor for a 2 + 2 cycloaddition reaction. A computer simulation of this situation,[16] temporarily ignoring the intramolecular reaction, predicts a maximum yield of 86.5% for the 2 + 2 cycloaddition purely due to this statistical isolation problem compared to an observed yield of 65%.

A more sophisticated model is required if the competition between alternate intermolecular and intramolecular reactions is to be studied. A number of different models were examined, but the following analysis proved to be the most interesting. As discussed earlier there are two alternate photochemical pathways leading to the 2 + 2 azetidine. An excited 1-aza diene can react with either the C=N bond of the adjacent molecule above or the C=C of the adjacent molecule below. We assumed that one of these two nonequivalent reactions was preferred meaning that all 2 + 2 reactions occurred in only one direction in a stack, arbitrarily chosen as the higher direction along the *a* axis, Figure 2. We then simulated photochemical events by choosing random unreacted molecules. If the next higher neighboring molecule in the stack was still available, we assumed that a 2 + 2 intermolecular reaction would take place, if not, the chosen molecule was assumed to give one of the bicyclo[3.1.0]hexene products via an intramolecular reaction. This simulation was continued until all molecules were chosen, the photochemical events were considered to occur at equal time intervals and scaled to a 9-h time period consistent with the experiment. The results of the simulation appear as the theoretical curve shown in Figure 3. The predicted intermolecular 2 + 2 cycloaddition yield of 74% is higher than the observed 65%, but the general shape of the curve is in reasonable agreement with the experimental data.[18]

The question remains as to how much the intermolecular reaction is affected by local environmental effects that disrupt the lattice. Surprisingly, it appears that the reaction is not very sensitive to the state of neighboring molecules. In another simulation we assumed that the 2 + 2 reaction would take place only if both neighbors of a pair of chosen molecules were intact; in other words a single neighboring defect in the stack was deemed sufficient to force the chosen molecule to undergo the intramolecular reaction. The resulting predicted yield drops to only 42%, suggesting that this assumed condition is not valid.[19] The observed 65% yield is much higher and supports the conclusion that the intermolecular reaction can take place even if other adjacent molecules have already undergone reaction.

A comparison of ratios of the two intramolecular photoproducts **2a** to **2b** also gives insight into the molecular environment in the solid state. This ratio changes from 6:1 in solution to 1:1 in the solid state. Inspection of the crystal structure, Figure 2, indicates that the rotation of the exocyclic bond connecting the benzyl radical, Scheme II, will encounter a nonbonded interaction from the molecule above whereas an analogous nonbonded interaction does not exist for a rotation to produce **2b**. Although considerable disruption of the crystal lattice probably occurs to allow for the intramolecular photochemical reaction, it would seem reasonable to expect that the general molecular orientations would remain the same.

Interestingly, the ratio of **2a** to **2b** (2:1), observed from the photochemistry of **1** in the melt, is much closer to the ratio observed in the solid state (1:1). This observation suggests a resemblance between **1** in the melt below its melting point and the solid state. The observation of a small amount of the 2 + 2 cycloadduct in the melt is also

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(16) In our computer simulation we assumed that all 2 + 2 reactions would occur in only one of the two possible directions. A list of the first 100 000 integers was chosen to represent a stack of an equal number of molecules. Photochemical reactions were simulated by eliminating numbers from the list. These eliminations took place as follows: A random number between 1 and 100 000 was chosen. If the selected number n and as well as the number $n + 1$ were both still in the list, then both numbers were eliminated from the list. The procedure was continued until all remaining consecutive pairs of numbers had been eliminated from the list. The results of 500 runs were averaged. The result of this simulation is identical to the analytical solution, $(1 - 1/e^2) \times 100\% = 86.47\%$, obtained by Flory[17] many years ago. If the reaction can take place in either direction then a slightly higher maximum yield of 87.67% is predicted by our simulation. To obtain this result the computer model was changed to allow the number n to pair up with the number $n - 1$ as an alternate to $n + 1$. If both pairs were possible one of the pairs was chosen at random. Wernick and Schochet[15] have obtained similar results for both models although they do not discuss the results in terms of directionality.

(17) Flory, P. J. *J. Am. Chem. Soc.* **1939**, *61*, 1518.

(18) This simulation was a modification of the first procedure discussed in ref 16. As before, if the number n as well as the number $n + 1$ were both still in the list then they were both eliminated and counted as an event modeling the 2 + 2 intermolecular reaction. If the number $n + 1$ was not in the list then the single number n was eliminated representing an intramolecular reaction. The predicted yield of the intermolecular product was 74%.

(19) In this simulation a run of four consecutive numbers was required for the simulation of a 2 + 2 event. If the numbers $n - 1$, n, $n + 1$, and $n + 2$ were all in the list, then the numbers n and $n + 1$ were eliminated, simulating an intermolecular reaction. If any of the four numbers were absent from the list, then only the number n was eliminated, simulating a intramolecular reaction. The predicted yield of the intermolecular product was 42%.

consistent with local ordering of the molecules in the melt, similar to the crystal.

In summary, this study represents the first report on the photochemical behavior of an *N*-acyl-1-aza diene. Compound 1 was particularly interesting because it proved to be photochemically active both in solution and in the solid state. The solution photochemistry produced the novel bicyclo[3.1.0]hexene derivatives **2a** and **2b**, whereas the solid-state photochemistry provided one of the few examples of a 2 + 2 cycloaddition between a carbon–carbon and a carbon–heteroatom double bond.[2] The existence of both unimolecular and topochemically controlled bimolecular photoreactions provided a rare and interesting probe of the molecular environment as a photochemical reaction proceeds.

Experimental Section[20]

3-Methyl-6-phenyl-1-cyano-2-aza-4-oxabicyclo[3.1.0]hex-2-ene (2a and 2b). A solution (2%) of aza diene 1[5] (17.9 mg) in $CDCl_3$ was irradiated using a Hanovia 450-W medium-pressure mercury vapor lamp for total 4 h at room temperature. ^1H NMR analysis of this sample indicated a clean and nearly quantitative transformation of aza diene 1 into two isomeric products, **2a** and **2b**, in a ratio of 6:1. Purification of the reaction mixture by column chromatography (ethyl acetate/hexanes (1:5)) furnished **2a** (15.0 mg, 84%) and **2b** (2.5 mg, 14%). Compound **2a**: mp 112.5–113 °C; ^1H NMR ($CDCl_3$) δ 1.98–1.99 (d, $J = 2.61$, 1 H), 2.11 (s, 3 H), 5.19–5.20 (d, $J = 2.63$, 1 H), 7.24–7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 33.2, 49.3, 67.3, 114.7, 127.5, 128.2, 128.9, 131.5, 168.4; IR (KBr) 3065, 2237, 1639, 1504, 1384, 1280, 1227, 1984, 902, 815, 756 cm^{-1}; MS m/e 198 (M^+), 169, 156, 155 (base peak), 128, 102. Compound **2b**: ^1H NMR δ 1.62 (s, 3 H), 2.79–2.81 (d, $J = 6.0$, 1 H), 5.18–5.20 (d, $J = 5.99$, 1 H), 7.24–7.31 (m, 5 H); IR (neat) 3061, 2925, 2240, 1646, 1498, 1382, 1256, 1098, 985, 889 cm^{-1}; MS m/e 198 (M^+), 183, 169, 156, 155 (base peak), 140, 128, 102; HRMS calcd for $C_{12}H_{10}N_2O$: 198.0794. Found: 198.0797.

The molecular structure of compound **2a** was determined by single-crystal X-ray diffractometry.

***N*-Acetyl-2-styryl-2-cyano-3-phenyl-4-(*N*-acetylcarbamoyl)azetidine (5).** Single crystals of aza diene 1[5] (24.2 mg) were subjected to photoirradiation for 9 h in an ice bath. The brown crystals were dissolved in $CDCl_3$ and were analyzed by ^1H NMR which showed that the reaction mixture contained compounds 4, **2a** and **2b**, and a small amount of unreacted aza diene 1. The reaction mixture was purified by column chromatography (ethyl acetate/hexanes (1:5) followed by (1:1)) to afford **2a** and **2b** (7.19 mg, 30%) and **5** (15.8 mg, 65.3%) as colorless crystals. Azetidine **5**: mp 174–185 °C dec; ^1H NMR δ 2.07 (s, 3 H), 2.43 (s, 3 H), 4.84–4.86 (d, $J = 7.13$, 1 H), 5.42–5.44 (d, $J = 7.20$, 1 H), 5.71–5.76 (d, $J = 15.89$, 1 H), 6.95–7.01 (d, $J = 15.94$, 1 H), 7.09–7.42 (m, 10 H), 9.97 (b, 1 H); IR (KBr) 3263, 3194, 2235, 1706, 1675, 1499, 1374, 1263, 1031, 971, 745 cm^{-1}; MS m/e 387 (M^+), 345, 328, 286, 259, 189, 155, 149, 146, 131, 100 (base peak), 99.

The molecular structure of compound **5** was determined by single-crystal X-ray diffractometry.

A Study of the Photochemistry of 1 as a Function of Time. Four 5-mm NMR tubes, each containing single crystals of 1, were attached to a medium-pressure Hanovia mercury lamp and irradiated at room temperature. Analysis of the photoreaction after 1.5, 3.0, 4.5, and 9 h was performed by dissolving the crystals of one of these tubes in $CDCl_3$ and recording the ^1H NMR spectrum. The relative ratios of the compounds present were estimated from the integrals of the appropriate absorptions and the calculated percentages are shown in Figure 3.

The Photochemistry of 1 in the Pure Liquid State. Single crystals of 1 were dissolved in a small amount of CH_2Cl_2. The solvent was evaporated and the yellow liquid was irradiated for 11 h. Crystallization of the sample was not observed during the irradiation. Analysis of the reaction mixture by ^1H NMR demonstrated that the ratio of **2a** to **2b** was 2:1 and the ratio of **2a** plus **2b** to 4 was 17:1.

X-ray Diffraction Studies. All X-ray data were measured at room temperature using a Enraf Nonius CAD4 diffractometer using a Cu X-ray source and a graphite monochromator. During data collection standard reflections were measured every hour. For compounds **2a** and 7 no significant changes in standard intensities were observed over the course of the data collection. However the standards for compound 1 decayed as much as 95% over a period of 12 h. Subsequently a fast data collection at maximum scan rate (16.5 deg/min) of the CAD4 was employed. The data collection was completed in a 4-h period with standard intensities falling about 10%. Corrections for this limited decay were included in the subsequent data analysis.

The structures were solved using the programs of the TEXAN Structure Analysis Software package. Full-matrix least-square refinements were carried out for all three compounds with anisotropic thermal parameters for the non hydrogen atoms. The hydrogen atoms of compounds **2a** were refined with isotropic temperature factors; they were added as fixed contributions to the other two structures. Full crystallographic details as well as tables of bond distances and angles and coordinate and thermal parameters are included as supplemental material.

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Registry No. 1, 136445-09-5; (±)-2, 136445-10-8; (±)-3, 136521-66-9; (±)-4, 136445-11-9; (±)-5, 136445-12-0.

Supplementary Material Available: Table of the thermal parameters for compound 1; figures of the molecular structures; and tables of crystal and data collection parameters, refined atom coordinates, thermal parameters, and bond distances and angles for compounds 2a and 5 (14 pages). Ordering information is given on any current masthead page.

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[20] The photochemistry was performed using a 450-W Hanovia medium-pressure lamp cooled with a quartz water jacket. Melting points were recorded using a Fisher–Johns apparatus and are uncorrected. NMR spectra were recorded with a QE-300 instrument using tetramethylsilane as an internal standard, and all chemical shifts are reported in ppm units from the internal standard. NMR absorptions are described as being a singlet (s), doublet (d), triplet (t), quartet (q), quintet (q′), broad (b) or multiplet (m). *J* values are given in hertz. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. Mass spectra were recorded on a Hewlett-Packard 5980 (low resolution) and a AEI-MS-80 spectrometer (high resolution). Elemental analyses were performed by MHW laboratories, Phoenix, AZ. Column chromatography analyses were performed using silica gel 60, 200–400 mesh, and thin-layer chromatography analyses were performed using Analtech thin-layer silica gel GF plates.