

# Control of C–C and C–N Bond Cleavage of 2*H*-Azirine by Means of the Excitation Wavelength: Studies in Matrices and in Solutions

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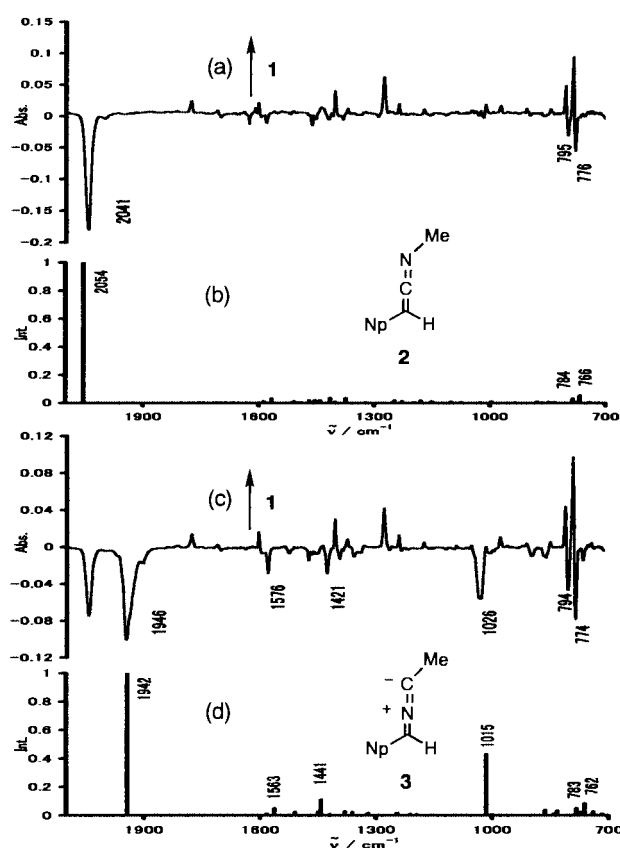
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The remarkable wavelength-dependent photoreactions of 3-methyl-2-(1-naphthyl)-2*H*-azirine (**1**) were observed in matrices at 10 K and in solutions at room temperature. Irradiation of **1** with the long-wavelength light (366 nm) exclusively gave the products formed by the cleavage of the C–N bond of the 2*H*-azirine ring, while the products derived from the C–C bond cleavage were predominantly obtained in the irradiation with the short-wavelength irradiation (>300 nm).

The photocycloaddition of 2*H*-azirines with alkenes provides a useful approach to a variety of five-membered heterocyclic systems.<sup>1</sup> It has been established that the irradiation of 2*H*-azirines gives nitrile ylides as reactive intermediates through the C–C bond cleavage, which have been directly observed by the use of a laser flash photolysis method<sup>2–4</sup> and a matrix-isolation technique.<sup>5</sup> However, we have recently found that irradiation of the 2*H*-azirine having 4-nitrophenyl group at the 2-position causes the selective cleavage of the C–N bond of the 2*H*-azirine ring.<sup>6</sup> This finding has opened a new field in the 2*H*-azirine photochemistry. In this paper, we report the wavelength effect on the photolysis of 3-methyl-2-(1-naphthyl)-2*H*-azirine (**1**)<sup>2</sup> in matrices and in solutions, which provides the first example of the perfect control of the C–C and C–N bond cleavage of 2*H*-azirines by means of the excitation wavelength.

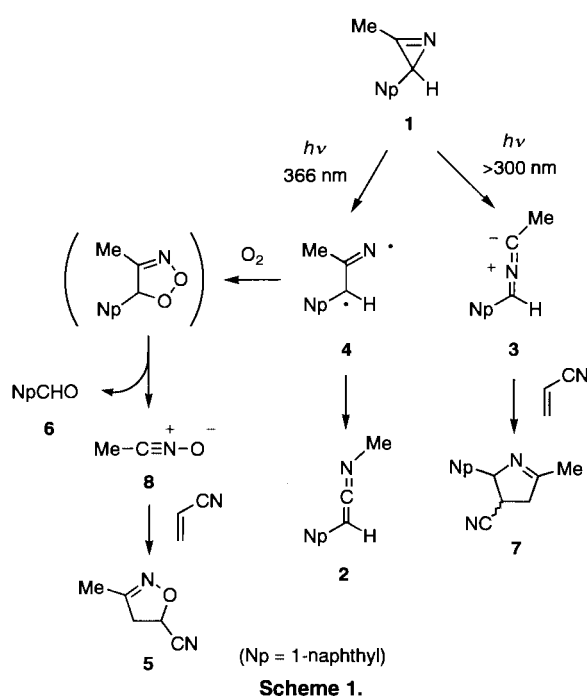
The azirine **1** matrix-isolated in Ar showed an imine stretching band having a medium intensity at 1775 cm<sup>–1</sup> and intense bands at 800 and 781 cm<sup>–1</sup> assigned to the out-of-plane deformation of C–H bonds of the naphthyl ring. Irradiation of **1** in an Ar matrix at 10 K with light of 366 nm of a high-pressure mercury lamp caused a decrease in the intensities of the bands due to **1**.<sup>7</sup> Simultaneously, a very intense peak appeared at 2041 cm<sup>–1</sup>, which revealed the formation of product having a cumulenenic double bond (designated as **A**). On the other hand, irradiation of **1** with the short-wavelength light (>300 nm) gave another product having a cumulenenic double bond at 1946 cm<sup>–1</sup> and IR peaks with medium intensities at 1026, 794, and 774 cm<sup>–1</sup> (designated as **B**), along with the product **A**. To identify the structure of the products, we carried out the calculations of vibrational frequencies for possible compounds having a cumulenenic double bond with the DFT method (B3LYP/6-31G(d)).<sup>8</sup> As shown in Figure 1, we found that the vibrational frequencies and their relative intensities calculated for the ketene imine **2** and the nitrile ylide **3** were in excellent agreement with those observed for the products **A** and **B**, respectively. The formation of **2** is interpreted in terms of the migration of the methyl group in the biradical **4** generated from the cleavage of the C–N bond (Scheme 1). On the other hand, as mentioned in an introductory part, nitrile ylides are well-known reactive intermediates formed by the photolysis of 2*H*-azirines.<sup>1–5</sup> Thus, we conclude



**Figure 1.** (a) Difference IR spectrum recorded after irradiation of **1** in Ar at 10 K with light of 366 nm. (b) IR spectrum calculated for **2**. (c) Difference IR spectrum recorded after irradiation of **1** in Ar at 10 K with light of >300 nm. (d) IR spectrum calculated for **3**.

that the C–C bond cleavage of the azirine ring of **1** to produce the nitrile ylide **3** is caused by the irradiation with the short-wavelength light (>300 nm), while the selective C–N bond cleavage can be achieved by the irradiation with the long-wavelength light (366 nm).

The remarkable wavelength effect was also observed in the photolysis of **1** in solutions at room temperature. Irradiation of an O<sub>2</sub>-saturated solution of **1** containing 6% (v/v) of acrylonitrile in acetonitrile with the long-wavelength light (366 nm) caused a slow consumption of the starting azirine **1**.<sup>9</sup> From the photoreaction mixture, the isoxazoline **5**<sup>10</sup> and 1-naphthalenecarbaldehyde (**6**) were isolated in 57 and 61% yields, respectively. On the other hand, the irradiation of **1** under identical conditions with the short-wavelength light (>300 nm) afforded an *E*–*Z* mixture of the pyrroline **7**<sup>2</sup> in 82% yield (*E*/*Z* = 1.0), along with a small amount of **6** (3%). No trace amounts of



**5** were detected in the photoreaction mixture obtained by the irradiation with the short-wavelength light. We have recently reported that the isoxazoline **5** is produced by a [2 + 3] cycloaddition reaction of acrylonitrile and acetonitrile oxide (**8**), which is generated in situ through the capture of the biradical **4** with  $O_2$  (Scheme 1).<sup>6</sup> On the other hand, it is well-known that pyrrolines are produced by the capture of nitrile ylides with acrylonitrile.<sup>1,2</sup> Thus, the selective C–N bond cleavage of the azirine ring of **1** is observed by the irradiation with light of 366 nm, which is consistent with the wavelength effect observed in matrices. Moreover, the product derived from the C–C bond cleavage, that is, **7** was exclusively obtained by the photolysis with light of >300 nm. Thus, we can practically achieve the perfect control of the C–C and C–N bond cleavage of the 2H-azirine by means of the excitation wavelength in the photolysis of **1** in solutions.

In order to have information about the excited state of **1**, we carried out molecular orbital calculations using the INDO/S method. The calculations predicted that the lowest excited singlet state,  $S_1$ , as well as the second excited singlet state,  $S_2$ , of **1** could be roughly described as a local  $\pi$ – $\pi^*$  excitation of its naphthyl moiety. The transition energies for the  $S_1$  and  $S_2$  states were calculated to be 3.96 and 4.47 eV, respectively. On the other hand, an  $n$ – $\pi^*$  excitation of the azirine moiety contributed largely to the third excited singlet state,  $S_3$ , having the transition energy of 4.90 eV.

Taking into account that the excited state having an  $n$ – $\pi^*$  character participates in the C–C bond cleavage of the azirine ring,<sup>1</sup> the fact that no products derived from the C–C bond cleavage were obtained by the long-wavelength irradiation (366 nm) can be explained in terms of the selective excitation into the  $S_1$  state having no  $n$ – $\pi^*$  character. We propose that the C–N bond cleavage is caused from the excited triplet state,  $T_1$ , which can be produced by the intersystem-crossing from the  $S_1$

state.<sup>11</sup> The experimental and theoretical evidences supporting this assumption are as follows: (i) the addition of benzophenone as a triplet sensitizer to the  $O_2$ -saturated solution of **1** containing acrylonitrile in acetonitrile considerably enhanced the rate of photodecomposition of **1**. Analogously to the direct irradiation, the benzophenone-sensitized photolysis of **1** afforded the equimolar mixture of the isoxazoline **5** and the aldehyde **6**. No trace amounts of the pyrroline **7** were detected. (ii) the DFT calculations (B3LYP/6-31+G(d)//B3LYP/6-31G(d)) predicted that the biradical **4** in the triplet state was more stable by 8.7 kcal mol<sup>–1</sup> than the triplet biradical which was expected to be formed by the C–C bond cleavage.

On the other hand, the higher excited singlet state,  $S_3$ , which can cause the C–C bond cleavage of the azirine ring, participates in the photoreaction initiated by the short-wavelength irradiation (>300 nm). It seems that the high quantum yield for the formation of the product derived from the C–C bond cleavage, as well as the low efficiency of the C–N bond cleavage,<sup>9</sup> is responsible for the selective C–C bond cleavage observed by the irradiation with the short-wavelength light in solutions.

## References and Notes

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- 7 The absorption spectrum of the azirine **1** shows a transition with maximum at 290 nm (log  $\epsilon$  = 3.90 in acetonitrile). Having a weak tailing to ca. 400 nm, **1** can be photolyzed with light of 366 nm.
- 8 The calculated vibrational frequencies are scaled by a factor of 0.96.
- 9 The azirine **1** was recovered quantitatively by the irradiation in the absence of  $O_2$ , which is probably due to an efficient recombination between the radical centers of the biradical **4**.
- 10 Viscous oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.08 (3H, s), 3.28 (1H, dd,  $J$  = 17.3, 6.0 Hz), 3.40 (1H, dd,  $J$  = 17.3, 11.0 Hz), 5.20 (1H, dd,  $J$  = 11.0, 6.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  12.2, 44.3, 65.6, 117.3, 155.3.
- 11 The formation of **2** observed in an Ar matrix is rationalized in terms of the Curtius-like rearrangement of the methyl group in the biradical **4** having a vinyl nitrene character. It appears that this reaction proceeds through the biradical **4** in its singlet state which would be accessible from the vibrationally excited triplet state.