

# Photochemical generation of acetonitrile oxide *via* the C–N bond cleavage of 3-methyl-2-(4-nitrophenyl)-2*H*-azirine

Hiroshi Inui and Shigeru Murata\*

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Meguro, Tokyo 153-8902, Japan. E-mail: cmura@mail.ecc.u-tokyo.ac.jp

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Acetonitrile oxide (**2**) is produced by the irradiation of the title azirine **1** in the presence of O<sub>2</sub> in fluid solutions and in low-temperature matrices through the capture of the biradical **7** with O<sub>2</sub>, which is generated by the photochemical C–N bond cleavage of the azirine ring.

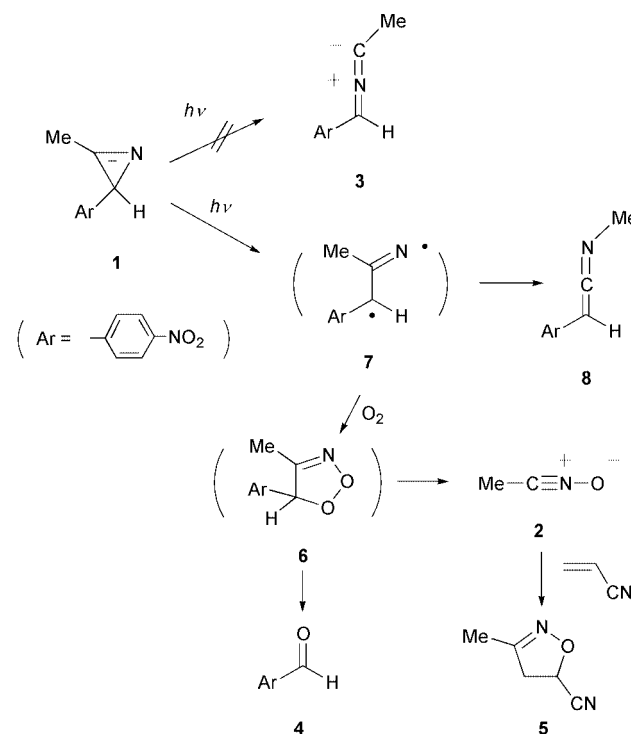
The photochemistry of 2*H*-azirines has aroused wide interest from the mechanistic and synthetic points of view. It has been established that the photolysis of 2*H*-azirines causes the C–C bond cleavage to yield 1,3-dipolar nitrile ylides, the [3 + 2] cycloaddition reactions of which provide a useful method for constructing a variety of five-membered heterocyclic systems.<sup>1</sup> However, in the course of our studies of the reactivities of photolytically-generated intermediates having an electron-withdrawing group,<sup>2</sup> we found that the photodecomposition of the title azirine **1** proceeded by a mechanism drastically different from that reported for 2*H*-azirines so far. In this paper, we report the photochemistry of the azirine **1** in fluid solutions and in low-temperature matrices, where the first example of the selective C–N bond cleavage in the 2*H*-azirine photochemistry, as well as of the photochemical generation of acetonitrile oxide (**2**) through trapping of the intermediate with O<sub>2</sub>, is demonstrated.

The new azirine, 3-methyl-2-(4-nitrophenyl)-2*H*-azirine (**1**),<sup>3</sup> was obtained by the reaction of 1-(4-nitrophenyl)propan-2-one trimethylhydrazonium iodide with sodium hydride in dimethyl sulfoxide,<sup>1b,c</sup> and purified by silica gel column chromatography with hexane–chloroform (1 : 1). When a degassed solution of **1** containing 5% (v/v) acrylonitrile in acetonitrile was irradiated with the Pyrex-filtered light of a high-pressure mercury lamp, **1** was recovered nearly quantitatively. In the <sup>1</sup>H NMR spectrum of the photoreaction mixture, no signals assigned to the pyrroline, which could be formed by the cycloaddition of the expected nitrile ylide **3** with acrylonitrile, were observed. On the other hand, under conditions identical to those described above, except for the saturation of the solution with O<sub>2</sub>, irradiation of **1** afforded 4-nitrobenzaldehyde (**4**, 46%) and 4-nitrobenzoic acid (14%), together with the adduct identified as the isoxazoline **5** (45%). The formation of **5** could be interpreted in terms of the capture of acetonitrile oxide (**2**) generated in the course of the photoreaction of **1** with acrylonitrile. The structure of **5** was confirmed by comparison of spectroscopic data with those of an authentic sample, which was obtained by a chemical generation of **2** by the base-induced reaction of phenylisocyanate with nitroethane in the presence of acrylonitrile.<sup>4,5</sup>

There are no precedents of the photochemical generation of **2** in solution, though it has been reported that photolysis of ozone matrix-isolated in Ar containing acetonitrile at 15 K gave **2** together with hydroxyacetonitrile.<sup>6</sup> We propose that **2** is produced by a fragmentation of the dioxazoline **6**, which is generated by the capture of the biradical **7** with O<sub>2</sub> (Scheme 1). The formation of 4-nitrobenzaldehyde (**4**) in amounts equimolar with the isoxazoline **5** is also explained by this scheme, assuming that the cycloaddition reaction of **2** with acrylonitrile proceeds quantitatively. Thus, the generation of **2**, as well as the failure to obtain the product derived from the nitrile ylide **3**,

strongly suggests that the photolysis of **1** causes not the C–C bond but the C–N bond cleavage to produce the biradical **7** as a reactive intermediate.

To gain further evidence of the C–N bond cleavage in the irradiation of **1**, we examined the photochemistry of **1** in an Ar matrix at 10 K. Irradiation (> 300 nm) of **1** matrix-isolated in Ar resulted in a slow decrease in intensities of the IR peaks due to **1** (1537, 1351, and 858 cm<sup>−1</sup>). Simultaneously, IR peaks appeared at 2046, 1597, and 1340 cm<sup>−1</sup>, indicating the formation of product having a cumulenenic double bond (designated as **A**). In the UV-vis spectrum, upon photolysis of **1** a broad band with a maximum at 341 nm appeared with isosbestic points at 266 and 317 nm. To identify the structure of **A**, we carried out the calculations of vibrational frequencies for the nitrile ylide **3**, which would be a possible candidate for **A**, with the DFT method (B3LYP/6-31G(d)).<sup>7,8</sup> Unfortunately, as shown in Table 1, the vibrational frequencies calculated for **3** are not consistent with those observed for **A** in the following two points: (i) a large deviation of the wavenumber predicted for the C=N<sup>+</sup>=C<sup>−</sup> stretching of **3** from that of the observed cumulenenic double bond, and (ii) a lack of the peak predicted to have a relatively large intensity at 1027 cm<sup>−1</sup> for **3**. However, we have found that the vibrational frequencies calculated for the ketene imine **8** are in excellent agreement with those observed for **A** (Table 1). Therefore, we conclude that the photoproduct of **1** in an Ar matrix at 10 K is not the nitrile ylide **3**, but the



Scheme 1

**Table 1** IR spectroscopic data of the photoproduct **A** generated in Ar at 10 K and of **3** and **8** calculated with the DFT Method

Experimental <sup>a</sup> ν/cm <sup>-1</sup>	Calculated <sup>b</sup> ν/cm <sup>-1</sup>		
<b>A</b>	<b>3</b>	<b>8</b>	Assignment
	2780 (7)	2795 (6)	Me str
2046 s		2024 (100)	C=C=N str
	1946 (81)		C=N <sup>+</sup> =C <sup>-</sup> str
	1585 (11)	1590 (9)	Ar ip, NO <sub>2</sub> unsym
1597 m	1583 (32)	1585 (21)	Ar ip
1539 m	1534 (11)	1539 (10)	Ar ip, NO <sub>2</sub> unsym
	1490 (4)		Ar ip
	1440 (6)	1412 (4)	Me deform
1340 s	1338 (100)	1342 (68)	NO <sub>2</sub> sym
	1329 (8)		Ar ip
1197 w		1180 (5)	CH ip
1111 m	1108 (13)	1106 (12)	ArCH ip
	1027 (47)		Me rock
	856 (7)		ArCH ip
851 w	851 (5)	858 (4)	ArCH op

<sup>a</sup> Measured in Ar at 10 K; s = strong; m = medium; w = weak.

<sup>b</sup> Calculated frequencies are scaled by the use of a linear scaling function; See ref. 7. Relative intensities are designated in parentheses. Frequencies with relative intensities greater than 5% were given in the table.

ketene imine **8**. The direct observation of **8** provides a strong piece of evidence in support of the C–N bond cleavage in the photolysis of **1**, because the formation of **8** is rationalized in terms of the Curtius-like rearrangement of the methyl group in the biradical **7** having a vinyl nitrene character.<sup>9</sup>

When **1** was photolyzed (>300 nm, 10 K) in the Ar matrix doped with a large amount of O<sub>2</sub> (20%), we could observe no IR peaks assigned to **8**. Instead, the irradiation afforded 4-nitrobenzaldehyde (**4**), the structure of which was readily confirmed by comparison of the IR spectrum with that of the authentic sample matrix-isolated in Ar at 10 K, together with a species having IR bands at 2334 and 1315 cm<sup>-1</sup> (designated as **B**) as primary photoproducts. The species **B** could be identified as acetonitrile oxide (**2**) on the basis of the agreement of the vibrational frequencies with those reported for **2**.<sup>6,10</sup> Isotopic labeling supports this identification of **B**. With use of <sup>18</sup>O<sub>2</sub> (97% doubly labeled), the intense band at 2334 cm<sup>-1</sup> was slightly shifted (1 cm<sup>-1</sup>), while a large isotopic shift of 28 cm<sup>-1</sup> was observed in the band at 1315 cm<sup>-1</sup>, which is assigned to the N–O stretch. These values are in fair agreement with those reported for the isotopic shifts of the bands assigned to **2**.<sup>6,11</sup> Consequently, the generation of **2** in the photolysis of **1** in the presence of O<sub>2</sub>, which is presumed on the basis of the characterization of reaction products in solutions, is unambiguously confirmed by the direct observation using a low-temperature matrix-isolation technique.

It is generally accepted that the photochemical C–C bond cleavage of 2*H*-azirines to produce nitrile ylides proceeds from the excited singlet state having an n–π\* character.<sup>1</sup> However, the theoretical calculation using the INDO/S method<sup>12</sup> predicted that the lowest excited singlet state of **1**, S<sub>1</sub>, could be roughly described as a local π–π\* excitation of its 4-nitrophenyl group. Moreover, it is reasonable to think that a large spin-orbit interaction in the nitro group can accelerate the intersystem-crossing from the S<sub>1</sub> state to the excited triplet state, T<sub>1</sub>. Thus, we propose that the selective C–N bond cleavage observed in the photolysis of **1** results from the participation of its T<sub>1</sub> state. This assumption is supported by the DFT calculations on the

triplet biradicals which are expected to be formed by the bond cleavage. It was found that the biradical **7** formed by the C–N bond cleavage was more stable by 7.6 kcal mol<sup>-1</sup> than the triplet biradical formed by the C–C bond cleavage. The triplet biradical **7** can be readily captured by O<sub>2</sub> to afford **6**, while in the absence of O<sub>2</sub>, the biradical undergoes the Curtius-like rearrangement to yield **8** from its singlet state which would be accessible from the triplet state.

In conclusion, it is established that on the irradiation of the azirine **1**, the C–N bond is selectively cleaved, in contrast to the C–C bond cleavage of the normal 2*H*-azirines reported so far. On the basis of the calculations, we propose that the selective C–N bond cleavage is due to the participation of the excited triplet state of **1** in the bond cleavage. Moreover, we have demonstrated that acetonitrile oxide (**2**) is produced through the capture of **7** with O<sub>2</sub> followed by the fragmentation, which would provide a convenient method of photochemical generation of **2**.

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## Notes and references

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- The INDO/S calculations were carried out by the WinMOPAC program package.