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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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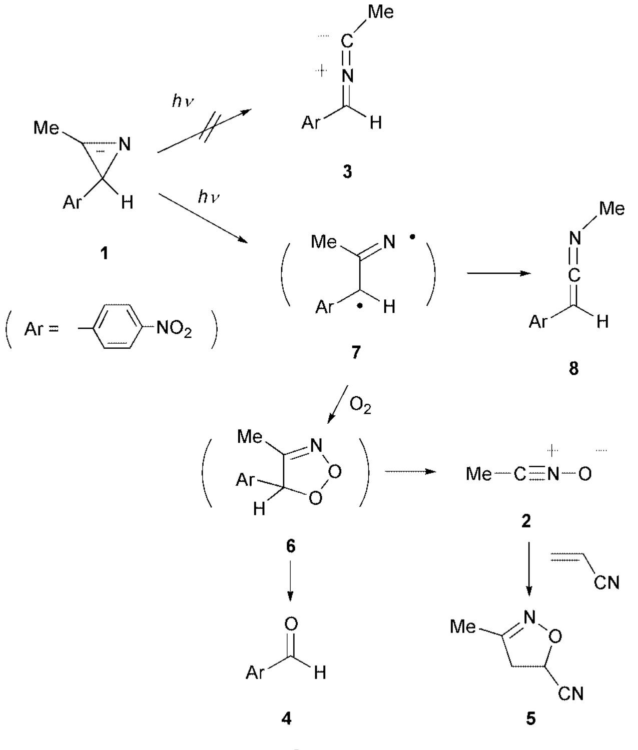
Acetonitrile oxide (2) is produced by the irradiation of the title azirine 1 in the presence of O_2 in fluid solutions and in low-temperature matrices through the capture of the biradical 7 with O_2, which is generated by the photochemical C–N bond cleavage of the azirine ring.

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.[1] However, in the course of our studies of the reactivities of photolytically-generated intermediates having an electron-withdrawing group,[2] 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_2, is demonstrated.

The new azirine, 3-methyl-2-(4-nitrophenyl)-2*H*-azirine (**1**),[3] was obtained by the reaction of 1-(4-nitrophenyl)propan-2-one trimethylhydrazonium iodide with sodium hydride in dimethyl sulfoxide,[1b,c] 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 ^{1}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_2, 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.[4,5]

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.[6] 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_2 (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^{-1}). Simultaneously, IR peaks appeared at 2046, 1597, and 1340 cm^{-1}, indicating the formation of product having a cumulenic 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)).[7,8] 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 $C{=}N^{+}{=}C^{-}$ stretching of **3** from that of the observed cumulenic double bond, and (ii) a lack of the peak predicted to have a relatively large intensity at 1027 cm^{-1} 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[a] ν/cm^{-1}	Calculated[b] ν/cm^{-1}		
A	**3**	**8**	Assignment
	2780 (7)	2795 (6)	Me str
2046 s		2024 (100)	C=C=N str
	1946 (81)		C=N$^+$=C$^-$ str
	1585 (11)	1590 (9)	Ar ip, NO_2 unsym
1597 m	1583 (32)	1585 (21)	Ar ip
1539 m	1534 (11)	1539 (10)	Ar ip, NO_2 unsym
	1490 (4)		Ar ip
	1440 (6)	1412 (4)	Me deform
1340 s	1338 (100)	1342 (68)	NO_2 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

[a] Measured in Ar at 10 K; s = strong; m = medium; w = weak. [b] 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.[9]

When **1** was photolyzed (> 300 nm, 10 K) in the Ar matrix doped with a large amount of O_2 (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^{-1} (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**.[6,10] Isotopic labeling supports this identification of **B**. With use of $^{18}O_2$ (97% doubly labeled), the intense band at 2334 cm^{-1} was slightly shifted (1 cm^{-1}), while a large isotopic shift of 28 cm^{-1} was observed in the band at 1315 cm^{-1}, 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**.[6,11] Consequently, the generation of **2** in the photolysis of **1** in the presence of O_2, 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.[1] However, the theoretical calculation using the INDO/S method[12] predicted that the lowest excited singlet state of **1**, S_1, 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_1 state to the excited triplet state, T_1. Thus, we propose that the selective C–N bond cleavage observed in the photolysis of **1** results from the participation of its T_1 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^{-1} than the triplet biradical formed by the C–C bond cleavage. The triplet biradical **7** can be readily captured by O_2 to afford **6**, while in the absence of O_2, 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_2 followed by the fragmentation, which would provide a convenient method of photochemical generation of **2**.

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Notes and references

1 The photochemistry of 2*H*-azirines has been reviewed: (*a*) A. Padwa, *Acc. Chem. Res.*, 1976, **9**, 371. For recent developments in this field; see, for example: (*b*) A. Padwa, R. J. Rosenthal, W. Dent, P. Filho, N. J. Turro, D. A. Hrovat and I. R. Gould, *J. Org. Chem.*, 1984, **49**, 3174; (*c*) R. L. Barcus, L. M. Hadel, L. J. Johnston, M. S. Platz, T. G. Aavino and J. C. Scaiano, *J. Am. Chem. Soc.*, 1986, **108**, 3928.

2 (*a*) S. Murata, Y. Mori, Y. Satoh, R. Yoshidome and H. Tomioka, *Chem. Lett.*, 1999, 597; (*b*) T. Mizushima, S. Ikeda, S. Murata, K. Ishii and H. Hamaguchi, *Chem. Lett.*, 2000, 1282; see also, (*c*) H. Tomioka, K. Tabayashi and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, 1985, 906; (*d*) T.-Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, 1987, **109**, 7803.

3 Light yellow granules: mp 100–102 °C; ^{1}H NMR ($CDCl_3$) δ 2.56 (3H, s), 2.96 (1H, s), 7.19 (2H, d, J = 9.0 Hz), 8.15 (2H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 12.6, 32.9, 123.5, 126.0, 146.6, 149.1, 163.3; IR (KBr) 1770, 1594, 1516, 1345, 1104, 853, 697 cm^{-1}; UV (MeCN) λ_{max} (log ε) 301 (4.10) nm.

4 (*a*) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, 1960, **82**, 5339; (*b*) H. Krawczyk and A. Gryff-Keller, *J. Chem. Res. S*, 1996, 452.

5 A number of experimental and theoretical studies on regiochemistry of 1,3-dipolar cycloaddition of nitrile oxides with dipolarophiles have been reported: A. Rastelli, R. Gandolfi and M. S. Amade, *J. Org. Chem.*, 1998, **63**, 7425, and references therein.

6 Z. Mielke, M. Hawkins and L. Andrews, *J. Phys. Chem.*, 1989, **93**, 558.

7 Calculated vibrational frequencies are scaled by the use of a linear scaling function of $1.009446 - 0.0000306\nu$, which is determined experimentally by comparison of frequencies calculated by B3LYP/6-31G(d) with those observed for the authentic sample of **1**, **4**, and (4-nitrophenyl)diazomethane matrix-isolated in Ar at 10 K. Using this scaling function, the agreement between calculated and observed frequencies of these three compounds is within ±14 cm^{-1} in the range of 2100 to 750 cm^{-1}.

8 The DFT calculations were carried out by the Gaussian 98 program package.

9 G. Smolinsky and A. P. Pryde, *J. Org. Chem.*, 1968, **33**, 2411.

10 W. G. Isner and G. L. Humphrey, *J. Am. Chem. Soc.*, 1967, **89**, 6442.

11 The vibrational frequencies for **2** (^{16}O), which are calculated with the DFT method (B3LYP/6-31G(d)) and scaled by the use of the function described in ref. 7, are 2319 and 1368 cm^{-1}. The ^{18}O isotopic shifts in these bands are calculated to be 3 and 27 cm^{-1}, respectively, which are in agreement with the experimental values.

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