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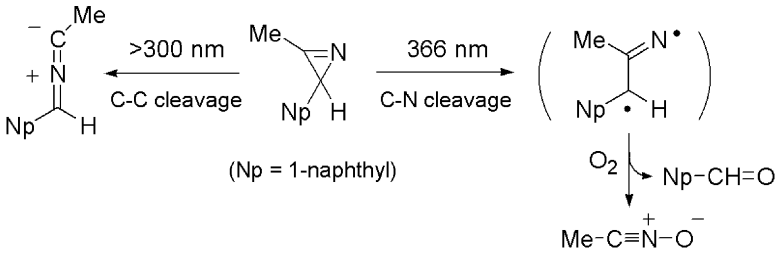

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Photochemistry of 2-(1-Naphthyl)-2*H*-azirines in Matrixes and in Solutions: Wavelength-Dependent C−C and C−N Bond Cleavage of the Azirine Ring

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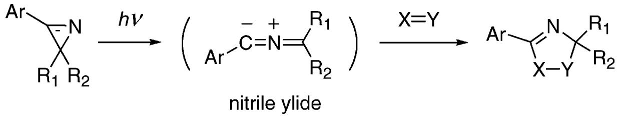
Abstract: The photochemistry of 3-methyl-2-(1-naphthyl)-2*H*-azirine (**1a**) was investigated by the direct observation of reactive intermediates in matrixes at 10 K and by the characterization of reaction products in solutions. As already reported, the photolysis of the azirine **1a** with the short-wavelength light (>300 nm) caused the C−C bond cleavage of the 2*H*-azirine ring to produce the nitrile ylide **2**. However, the products derived from the C−N bond cleavage were exclusively obtained in the irradiation of **1a** with the long-wavelength light (366 nm) both in matrixes and in solutions. When **1a** was irradiated in the presence of O_2 with the long-wavelength light, acetonitrile oxide (**6**) was produced through the capture of the biradical **4** generated by the C−N bond cleavage of **1a** with O_2. An introduction of a nitro group into the naphthyl ring of **1a** resulted in an acceleration of the decomposition in the long-wavelength irradiation and an extension of the wavelength region where the products derived from the C−N bond cleavage were selectively obtained. On the basis of molecular orbital calculations with the INDO/S method, the reason for the wavelength-dependent selective C−C and C−N bond cleavage of the azirine ring of **1a** is discussed.

2*H*-Azirines are unique strained molecules having a C═N double bond incorporated into a three-membered ring, which were first isolated as an intermediate in the reaction of oxime tosylates with base to give α-aminoketones by Neber and co-workers in 1932.[1] Since the structure of 2*H*-azirines was confirmed by Hatch and Cram in 1953,[2] an extensive study of the reactivity of 2*H*-azirines has been made by many research groups. Especially, photochemistry of 2*H*-azirines has aroused wide interest from the mechanistic and synthetic points of view.[3] In 1973, Padwa and Schmid independently reported that upon irradiation aryl-substituted 2*H*-azirines were rearranged with an azirine ring opening to give dipolar species as reactive intermediates and that the products derived from cyclizations with a variety of 1,3-dipolarophiles were obtained (Scheme 1).[4] The first-formed reactive intermediates originate from the photochemical cleavage of the C═C bond of the azirine ring, which are called nitrile ylides. The direct observation of nitrile ylides was achieved by Schmid and co-workers, who observed nitrile ylides generated by the irradiation of 2*H*-azirines in organic rigid matrixes at −185 °C by means of UV spectroscopy.[5] Recently, laser flash photolysis was applied to investigate the photoreactions of 2*H*-azirines in solutions, where the lifetime of nitrile ylides and the bimolecular rate constants for cycloaddition between nitrile ylides and various olefins were estimated.[6,7] Moreover, Pimentel's group investigated the direct observation of the nitrile ylides generated photochemically from 3-phenyl-2*H*-azirine and its isotopic-labeled derivatives in N_2 matrixes at 12 K by the use of IR spectroscopy.[8] Their detailed examination of the IR spectra revealed that the nitrile ylides had not a propargy structure $C{\equiv}N^{+}{-}C^{-}$ but an allene structure with a slightly bent $C^{-}{=}N^{+}{=}C$ moiety.

Scheme 1. General Scheme of 2*H*-Azirine Photochemistry



Thus, it has been established that the photolysis of 2*H*-azirines causes the C−C bond cleavage to afford nitrile ylides, the [3 + 2] cycloadditions of which with dipolarophiles provide a useful method to construct a variety of five-membered heterocyclic systems. However, in the course of our studies of the

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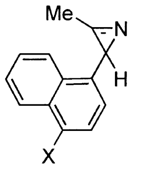
Chart 1



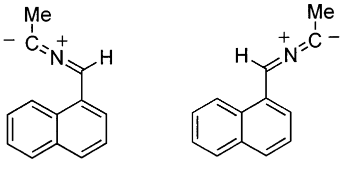
1a; X = H
1b; X = Br
1c; X = NO_2

reactivities of photolytically generated intermediates having an electron-withdrawing group,[9] we found that irradiation of 3-methyl-2-(4-nitrophenyl)-2*H*-azirine caused the cleavage of not the C−C bond but C−N bond of the azirine ring selectively.[10] This is the first observation of the C−N bond cleavage in the photochemistry of 2*H*-azirines, although it was reported that thermolysis of 2-aryl-2*H*-azirines yielded products derived from the C−N bond cleavage.[11] This finding reawakened interest in the photochemistry of 2*H*-azirines, leading us to investigate as to whether the C−N bond cleavage could be observed in the photochemistry of 2*H*-azirines other than the azirine having a 4-nitrophenyl group. Thus, we found that 3-methyl-2-(1-naphthyl)-2*H*-azirine (**1a**), the photolysis of which had been established to generate the corresponding nitrile ylide through the C−C bond cleavage,[7] also gave the products formed through the cleavage of the C−N bond when it was photolyzed with the long-wavelength light.[12] In this paper, we report our detailed studies of the photochemistry of **1a** and its derivatives **1b** and **1c** (Chart 1) in matrixes at cryogenic temperatures and in solutions at room temperature, where the perfect control of the C−C and C−N bond cleavage of the 2*H*-azirene ring by means of the excitation wavelength is demonstrated.

Results and Discussion

Photoreactions of 1a in Matrixes. The azirine **1a** matrix-isolated in Ar showed an imine stretching band having a medium intensity at 1775 cm^{-1} and intense bands at 800 and 781 cm^{-1} assigned to the out-of-plain deformation of C−H bonds of the naphthyl ring. The IR spectrum is in excellent agreement with that based on the vibrational analysis of the most stable conformer of **1a** obtained by the density functional theory (DFT) calculation (B3LYP/6-31G(d)). Irradiation of **1a** in an Ar matrix at 10 K with 366 nm light from an extra-high-pressure mercury lamp resulted in a decrease in the intensities of the bands due to **1a** and a simultaneous appearance of a very intense peak at 2040 cm^{-1}, indicating the formation of a product having a cumulenic double bond (designated as product **A**). On the other hand, irradiation of **1a** with the short-wavelength light (>300 nm) gave another product having a cumulenic double bond at 1946 cm^{-1} and IR peaks with medium intensity at 1026, 794, and 774 cm^{-1} (designated as product **B**), along with the product **A**. After the formation of **B**, a subsequent irradiation of the matrix with 366 nm light caused a decrease in the intensity of the bands due to **B** and reappearance of **1a** accompanied with further formation of **A**, indicating that the photochemical transformation of **1a** to **B** was reversible. These phenomena could be also observed by means of UV−vis spectroscopy. Upon irradiation (>300 nm) of **1a** in Ar at 10 K, the UV band with a maximum at 287 nm due to **1a** decreased, and a new band with a maximum at 378 nm appeared with isosbestic points at 272 and 301 nm. On further irradiation of the matrix with 366 nm light, this new band almost disappeared, and the regeneration of **1a** and the formation of the band with a shoulder at 320 nm were observed. Taking into account the results of IR experiments, the bands characterized by λ_{max} 378 nm and λ_{sh} 320 nm were assigned to the UV bands due to **B** and **A**, respectively.

Chart 2



2$_{syn}$ **2**$_{anti}$

To identify the structure of the products **A** and **B**, the calculations of vibrational frequencies were carried out with the DFT method (B3LYP/6-31G(d)) for possible compounds having a cumulenic double bond. At the beginning, geometry optimization of the nitrile ylide **2**, which was expected to be produced through the C−C bond cleavage of the azirine ring of **1a**, was performed. It was revealed that the two allene-type conformers **2**$_{syn}$ and **2**$_{anti}$ (Chart 2) existed as true energy minimum structures on the energy surface of **2** and that **2**$_{anti}$ was more stable than **2**$_{syn}$ by 1.7 kcal mol^{-1}. In both conformers, the nitrile ylide moiety $CH{=}N^{+}{=}C^{-}$ was slightly twisted from the naphthyl ring (18.7° and 6.3° in **2**$_{syn}$ and **2**$_{anti}$, respectively) to avoid steric repulsion with the hydrogen atom at the peri-position of the naphthyl ring. The vibrational frequencies were calculated for **2**$_{syn}$ and **2**$_{anti}$ and compared with experimental values after scaled by the factor recommended by the literature, 0.9614.[13] As illustrated in Figure 1, the frequencies calculated for **2**$_{anti}$, as well as **2**$_{syn}$, are in excellent agreement with those observed for **B**, although it appears that the spectrum calculated for the more stable isomer **2**$_{anti}$ reproduces the observed spectrum better than that for **2**$_{syn}$ in terms of the relative intensity of the peak assigned to the methyl deformation at 1421 cm^{-1}. As mentioned in an introductory part, the azirine **1a** was known to afford the nitrile ylide **2** photolytically in solutions.[7] The transient UV spectrum of **2** observed by using laser flash photolysis technique in acetonitrile was reported to have a maximum at 386 nm, which is in fair agreement with the UV spectrum of **B** recorded in our experiment. Moreover, it was also reported that nitrile ylides were rearranged photochemically to the starting 2*H*-azirines in rigid matrixes.[5] Thus, it is concluded that the product **B** produced by the photolysis of **1a** with >300 nm light in an Ar matrix at 10 K is the nitrile ylide **2**.

Next, to identify the product **A** yielded by the photolysis of **1a** with 366 nm light, calculation of vibrational frequencies for the ketene imine **3**, another candidate for compounds having a cumulenic double bond was carried out. The ketene imine **3** could also exist in two conformers **3**$_{syn}$ and **3**$_{anti}$ (Chart 3), and the latter isomer was more stable by 0.6 kcal mol^{-1}.

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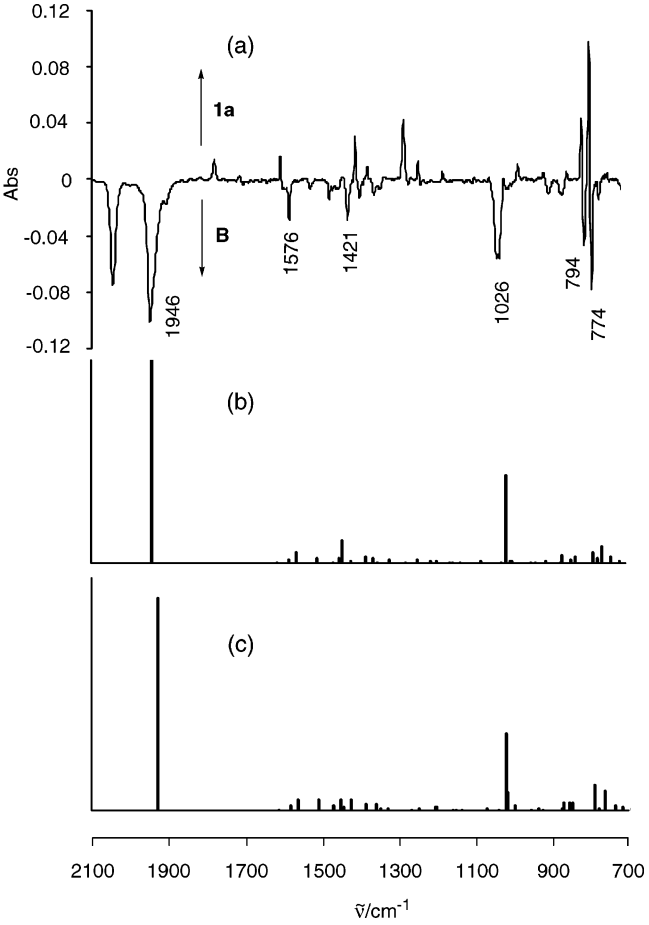
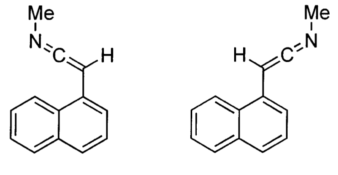


Figure 1. (a) Difference IR spectrum recorded after irradiation of **1a** in Ar at 10 K with >300 nm light; (b) IR spectrum calculated for $\mathbf{2}_{anti}$; (c) IR spectrum calculated for $\mathbf{2}_{syn}$.

Chart 3



$\mathbf{3}_{syn}$ $\mathbf{3}_{anti}$

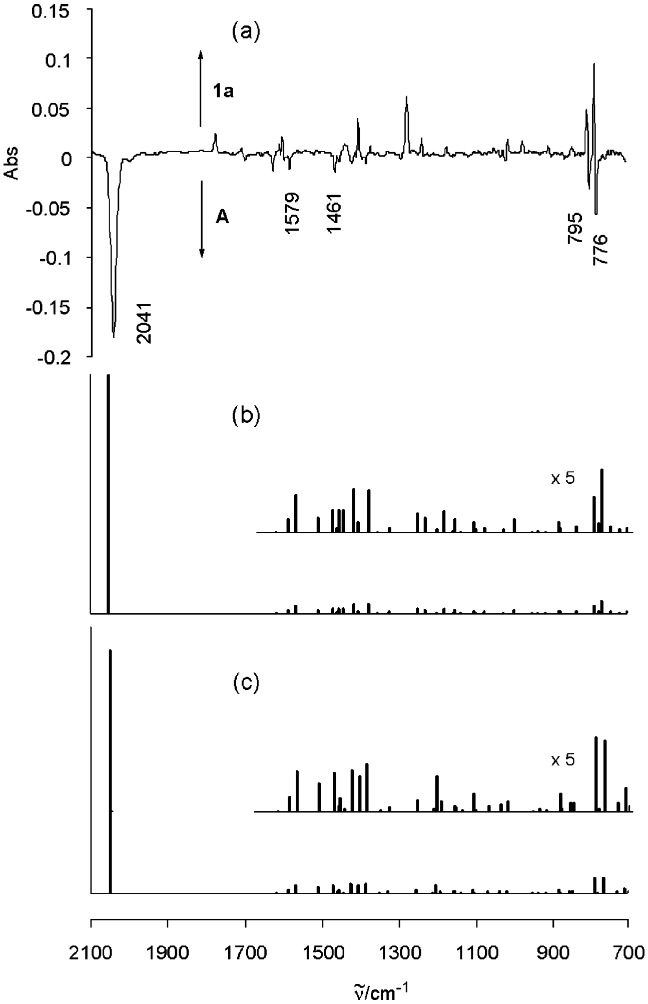
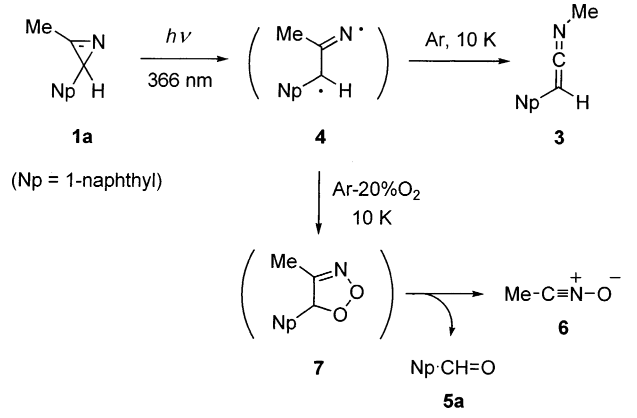


Figure 2. (a) Difference IR spectrum recorded after irradiation of **1a** in Ar at 10 K with 366 nm light; (b) IR spectrum calculated for $\mathbf{3}_{anti}$; (c) IR spectrum calculated for $\mathbf{3}_{syn}$.

Scheme 2. Irradiation of **1a** in Ar at 10 K with 366 nm Light



Similarly to the nitrile ylide **2**, the ketene imine moiety CH═C═N of **3** was slightly twisted from the naphthyl ring (17.0° and 20.5° in $\mathbf{3}_{syn}$ and $\mathbf{3}_{anti}$, respectively). The calculations revealed the following three features of the ketene imine **3** in the vibrational frequencies and their relative intensities compared with the nitrile ylide **2**: (i) the stretching of the cumulenic double bond C═C═N of **3** appears in the higher wavenumber region than that of $C{=}N^{+}{=}C^{-}$ of **2**, (ii) the intensity of the stretching of the cumulenic double bond of **3** is considerably large relative to those of other vibrational modes, and (iii) the vibrations including the rocking of the methyl group are very weak in **3**, while the corresponding vibration of **2** appears at around 1020 cm^{-1} with a moderate intensity. As shown in Figure 2, all these features are completely consistent with the features of the IR spectrum of the product **A**. Thus, we conclude that the product **A** produced by the photolysis of **1a** with 366 nm light in an Ar matrix at 10 K is the ketene imine **3**, although it cannot be determined whether it exists only in the more stable isomer $\mathbf{3}_{anti}$. The structure of the ketene imine **3** clearly exhibits the cleavage of the C─N bond of the azirine ring of **1a**. The formation of **3** is rationalized in terms of the Curtius-like rearrangement of the methyl group in the biradical **4** having a vinyl nitrene character generated from the cleavage of the C─N bond (Scheme 2). This transformation is identical to that reported in the photolysis of 3-methyl-2-(4-nitrophenyl)-2*H*-azirine.[10] It should be noted that

Table 1. IR Spectroscopic Data of the Photoproducts Generated by the Irradiation of **1a** with 366 nm Light in an Ar Matrix Doped with O_2 at 10 K and of **5a** and **6** Calculated with the DFT Method

experimental[a] ν/cm^{-1}		calculated[b] ν/cm^{-1}		
5a	**C**	**5a**	**6**	assignment
	2333 (s, −2)		2389 (100, −3)	C≡N str
1695 (s, −30)		1714 (100, −32)		C=O str
1577 (m, 0)		1563 (20, 0)		Ar ip
1521 (w, 0)		1509 (7, −1)		Ar ip
			1398 (5, −4)	Me deform
	1318 (w, −30)		1361 (42, −27)	N−O str
1345 (w, 0)		1332 (11, −1)		Ar ip, ArCH ip
1229 (m, 0)		1210 (15, 0)		ArCH ip
		1196 (17, 0)		Ar ip, ArCH ip
		842 (6, 0)		Ar ip
809 (m, −1)		790 (18, 0)		ArCH op
			772 (6, −13)	Me−C str
775 (m, −1)		759 (11,0)		ArCH op
		751 (9, −2)		Ar ip

[a] Recorded in an Ar matrix doped with 20% O_2 at 10 K; s = strong; m = medium; w = weak. $^{18}O_2$ isotopic shifts are disignated in parentheses. [b] Calculated frequencies are scaled by 0.9614. Relative intensities and $^{18}O_2$ isotopic shifts are designated in parentheses. Frequencies less than 2500 cm^{-1} having relative intentities greater than 5% were given in the table.

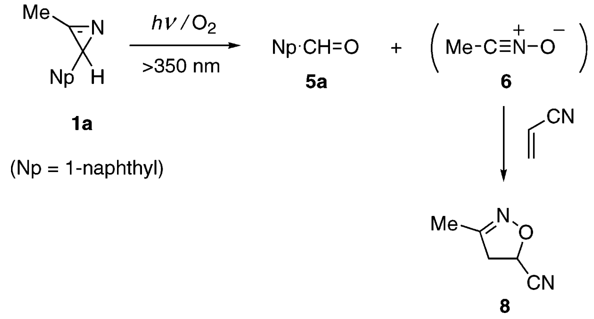
the long-wavelength irradiation causes a selective cleavage of the C−N bond of the azirine **1a**, since no IR peaks due to the nitrile ylide **2** were detected in the photolysis of **1a** with 366 nm light.

Moreover, the photolysis of the azirine **1a** with 366 nm light was carried out in an Ar matrix doped with O_2, which provides further evidence supporting the C−N bond cleavage in the photolysis of **1a**. When **1a** was photolyzed (366 nm, 10 K) in an Ar matrix containing a large amount of O_2 (20%), the formation of the ketene imine **3** was considerably suppressed. Instead, the irradiation afforded 1-naphthaldehyde (**5a**), the structure of which was readily confirmed by comparison of the IR spectrum with that of the commercially available authentic sample isolated in an Ar matrix at 10 K. Furthermore, we found that a species having IR bands at 2333 and 1318 cm^{-1} (designated as product **C**) was also produced as a primary photoproduct. When $^{18}O_2$ (97% doubly labeled) was used, the intense band at 2333 cm^{-1} was slightly shifted (2 cm^{-1}), while a large isotopic shift of 30 cm^{-1} was observed in the band at 1318 cm^{-1}. The product **C** could be identified as acetonitrile oxide (**6**) on the basis of the agreement of the vibrational frequencies and ^{18}O isotopic shifts with those reported,[10,14] as well as calculated, for **6** (Table 1). The simultaneous formation of **5a** and **6** could be interpreted in terms of a fragmentation of the dioxazoline **7** produced by the capture of the biradical **4** with O_2, confirming that the irradiation of **1a** with 366 nm light causes a cleavage of the C−N bond of the azirine ring (Scheme 2).

Consequently, it is concluded that in an Ar matrix at 10 K the C−C bond cleavage of the azirine ring of **1a** to produce the nitrile ylide **2** is caused by the irradiation with the short-wavelength light (>300 nm), while the selective C−N bond cleavage to give the biradical **4** is achieved by the irradiation with the long-wavelength light (366 nm).

Photoreactions of 1a in Solutions. (1) Photoproducts and Wavelength Effect. Next, we examined whether this remarkable dependence of the reactivity of **1a** on the excitation wavelength could be observed in solutions at room temperature. When a degassed solution of **1a** in acetonitrile was irradiated with the long-wavelength light (>350 nm) of a high-pressure mercury lamp in the presence of 6% (v/v) of acrylonitrile for the sake of trapping of reactive intermediates, **1a** was recovered quantitatively. On the other hand, when **1a** was photolyzed in O_2-saturated acetonitrile containing acrylonitrile with >350 nm light, the starting material was slowly consumed to give a mixture of 1-naphthaldehyde (**5a**, 57%) and the adduct identified as 5-cyano-3-methylisoxazoline (**8**, 61%). The formation of **8** is rationalized in terms of a [3 + 2] cycloaddition of acrylonitrile and acetonitrile oxide (**6**) which is produced in situ through the capture of the biradical **4** generated by the C−N bond cleavage with O_2 (Scheme 2, 3). The structure of the adduct **8** was confirmed by comparison of spectroscopic data with those of an authentic sample, which was obtained by a chemical generation of **6** by the base-induced reaction of phenyl isocyanate with nitroethane in the presence of acrylonitrile.[15] When **1a** was irradiated in the presence of benzophenone as a triplet sensitizer in O_2-saturated acetonitrile containing acrylonitrile, the consumption of the starting material was accelerated by a factor of ca. 25 compared with the irradiation in the absence of the sensitizer, but the product distribution was unchanged. This observation suggests that the excited triplet state of **1a** participates in the C−N bond cleavage.

Scheme 3. Irradiation of **1a** in O_2-Saturated Acetonitrile Containing Acrylonitrile with >350 nm Light



On the other hand, the irradiation of an O_2-saturated solution of **1a** in acetonitrile containing acrylonitrile with the short-wavelength light (>300 nm) afforded an *E*/*Z* mixture of the

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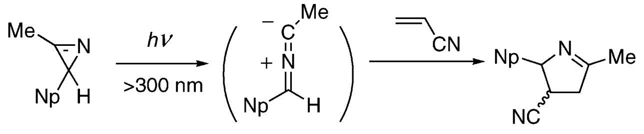
Scheme 4. Irradiation of **1a** in O_2-Saturated Acetonitrile Containing Acrylonitrile with >300 nm Light



1a **2** **9a**

(Np = 1-naphthyl)

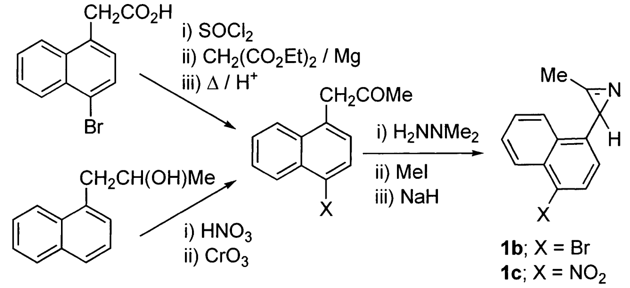
pyrroline **9a** (E/Z = 1.0) in 82% yield, along with a small amount of **5a** (3%). It has been already reported that the pyrrolines **9a** are produced by the capture of the nitrile ylide **2** generated through the C−C bond cleavage of the azirine ring with acrylonitrile (Scheme 4).[7] No trace amounts of the isoxazoline **8** were detected in the photoreaction mixture obtained by the irradiation with the short-wavelength light.

Consequently, the products derived from the C−N bond cleavage of the azirine ring of **1a** are selectively obtained by the irradiation with the long-wavelength light, while the exclusive C−C bond cleavage is observed by the photolysis with the short-wavelength light. It should be emphasized that this wavelength effect is consistent with that observed in an Ar matrix at 10 K. Furthermore, it is established that acetonitrile oxide (**6**), which is an important reactive intermediate in the field of synthetic organic chemistry, can be readily generated not only in matrixes but also in solutions by irradiation of **1a** with the long-wavelength light in the presence of O_2. Although it has been reported that photolysis of O_3 in an Ar matrix containing acetonitrile at 15 K gives **6**,[14] there are no precedents of the photochemical generation of **6** in solutions.

(2) Substituent Effect on the Wavelength-Dependent Photoreaction. As mentioned in the previous section, the cleavage of the C−C and C−N bond of the azirine ring of **1a** is perfectly controlled by means of excitation wavelength in solutions. The C−N bond cleavage of an azirine ring should open a new field in the 2*H*-azirine photochemistry. However, the efficiency of the C−N bond cleavage of **1a** was considerably low, which was probably due to a small absorptivity in a long-wavelength region and/or a low quantum yield for the C−N bond cleavage. Thus, to increase the efficiency of the C−N bond cleavage, the effect of substituent groups on the photochemical reactivity of **1a** was investigated.

We designed two new 2-(1-naphthyl)-2*H*-azirines **1b** and **1c**. An internal heavy-atom perturbation of a bromine atom of **1b** would accelerate the intersystem-crossing process to the excited triplet state which appears to participate in the C−N bond cleavage, while a nitro group on the naphthyl ring of **1c** is expected to cause a large bathochromic shift of its $\pi-\pi^*$ transition increasing the absorptivity in a long-wavelength region. The scheme for the syntheses of these azirines is shown in Scheme 5, and their UV−vis absorption spectra are illustrated in Figure 3, together with that of **1a**. Solutions of **1b** and **1c** in O_2-saturated acetonitrile containing 6% of acrylonitrile were irradiated with light of various wavelengths. The products were essentially identical to those obtained from **1a**, that is, E/Z isomers of pyrrolines **9b** and **9c** derived from the C−C bond cleavage of the azirine ring, and an equimolar mixture of the corresponding aldehydes **5b** and **5c** and the isoxazoline **8** arising from the initial C−N bond cleavage of the azirine ring. The wavelength dependence of the conversion of the starting azirines and the yield of the photoproducts are summarized in Table 2, along with the results of **1a**. As shown in the table, it is revealed that although the selective C−N bond cleavage is observed in the photolysis of **1b** and **1c** with the long-wavelength light analogously to the case of **1a**, the wavelength required for the selective C−N bond cleavage is considerably dependent on the substituent group of the naphthyl ring. Especially, upon irradiation with >300 nm light, **1a** affords the C−C bond cleavage product **9a** exclusively, while a mixture of the products arising from the C−C and C−N bond cleavage is obtained in the photolysis of **1b**, and the selective C−N bond cleavage is observed in the photolysis of **1c**. As expected, a large bathochromic shift of $\pi-\pi^*$ transition induced by a nitro group enables **1c** to be photolyzed with >400 nm light, so that the

Scheme 5. Synthetic Scheme of **1b** and **1c**



1b; X = Br
1c; X = NO_2

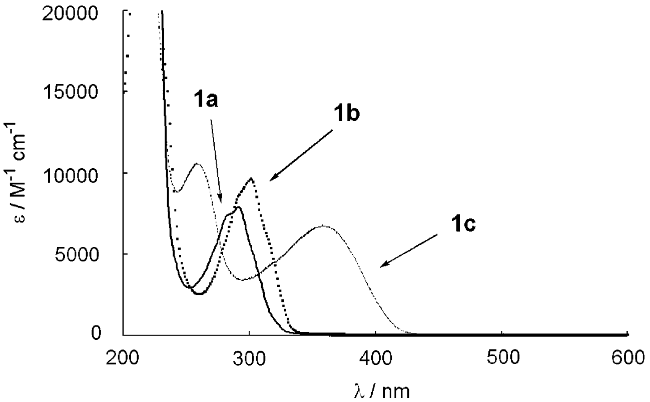


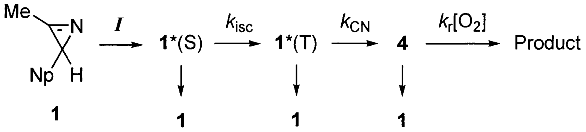
Figure 3. UV−vis spectra of **1a**−**c** in acetonitrile.

Table 2. Wavelength Dependence of the Photoproducts of the Azirines **1a**−**c** in O_2-Saturated Acetonitrile Containing 6% Acrylonitrile

			yield[c,d] (%)		
azirine	conditions[a]	conversion[b,c]	5	8	9[e]
1a	245 nm (10 min)	55	4	6	85
	>300 nm (1 h)	57	3	<1	82
	>350 nm (4 h)	3	57	61	<1
	>400 nm (4 h)	<1			
1b	245 nm (10 min)	61	5	4	42
	>300 nm (1 h)	49	16	19	45
	>350 nm (4 h)	32	62	54	<1
	>400 nm (4 h)	<1			
1c	245 nm (10 min)	12	13	14	86
	>300 nm (1 h)	34	57	53	<1
	>350 nm (4 h)	63	56	57	<1
	>400 nm (4 h)	52	60	57	<1

[a] [**1a**−**c**] = 6.1 mM, [acrylonitrile] = 920 mM. Irradiation time is designated in parentheses. [b] Conversion of the starting azirines. [c] Determined by the integration of ^{1}H NMR spectra. [d] Yields of the photoproducts based on the consumed starting azirines. [e] Total yields of the E/Z isomers. The E/Z ratio obtained by the irradiation of **1a**, **1b**, and **1c** with 254 nm light was 1.1, 1.3, and 2.3, respectively.

Scheme 6. Mechanism Assumed for the Photodecomposition of the Azirines **1a**−**c** in O_2-Saturated Acetonitrile with 366 nm Light



selective cleavage of the C−N bond of the azirine ring is observed in the irradiation of **1c** with light of the wide-wavelength region of 300−420 nm.

The conversion of the starting azirines shown in Table 2 suggests that the introduction of a nitro group considerably accelerates the C−N bond cleavage of the azirine ring in the irradiation with the long-wavelength light. To reveal the effect of substituent groups on the C−N bond cleavage in detail, a semiquantitative kinetic analysis of the photoreaction of **1a**−**c** was carried out. Solutions of **1a**−**c** in O_2-saturated acetonitrile containing 6% of acrylonitrile were irradiated with 366 nm light from an extra-high-pressure mercury lamp, and the consumption of the starting azirines was monitored by the use of high-performance liquid chromatography. On the basis of the first-order analysis of the initial part of the decrease in the concentration of the starting azirines, the relative rates of the photodecomposition of the azirines were evaluated to be **1a:1b:1c** = 1:3.69:596 under our irradiation conditions.

Assuming that the rate of the photodecomposition of the azirines **1a**−**c**, v_{dec}, is proportional to the product of the rate constant for the reaction of the biradical **4** with O_2, $k_r[O_2]$, and its steady-state concentration, [**4**] (Scheme 6), v_{dec} is given by $v_{dec} = k_r[O_2][\mathbf{4}] = I\,\Phi_{dec}$ by using a steady-state approximation. In this equation, I is the number of photons absorbed by the azirine, and Φ_{dec} shows a quantum yield for photodecomposition of the azirine, which is depicted by the product of a quantum yield for intersystem crossing of the excited singlet azirine **1***(S) to its excited triplet state **1***(T), the efficiency for **1***(T) to undergo the C−N bond cleavage to give **4**, and the efficiency for **4** to be captured by O_2 in competition with a recombination to give the starting azirine. By using a photon counting meter, the quantum yield for photodecomposition, Φ_{dec}, of the azirine **1c** could be determined to be 0.014 under the irradiation conditions described above. Moreover, Φ_{dec}'s of **1a** and **1b** relative to that of **1c** can be estimated by the relative rates of the azirine photodecomposition obtained above, because I for each azirine is evaluated by $I = I_0(1-10^{-\epsilon cl})$, in which I_0, ϵ, c, and l represent the number of incident photons, molar extinction coefficient of the azirine at 366 nm, initial concentration of the azirine, and length of the cell used in the irradiation experiment. Thus, the quantum yields for photodecomposition, Φ_{dec}, of the azirines **1a**−**c** can be determined, which are collected in Table 3, together with the data employed for their estimation. As shown in the table, Φ_{dec}'s of the azirines **1a**−**c** coincide within the experimental error. Therefore, it is concluded that the C−N bond cleavage of 2-(1-naphthyl)-2*H*-azirine induced by the irradiation with 366 nm light is remarkably accelerated by the introduction of a substituent group, especially of a nitro group, at the 4-position of its naphthyl ring, and that this acceleration is primarily attributed to an increase not in the quantum yield for photodecomposition but in the absorptivity at 366 nm.

Table 3. Relative Rates and Quantum Yields for the Photodecomposition of the Azirines **1a**−**c** in O_2-Saturated Acetonitrile Containing 6% Acrylonitrile with 366 nm Light

azirine	v(rel)[a]	ϵ[b] (M^{-1} cm^{-1})	I(rel)[c]	Φ_{dec}(rel)[d]	Φ_{dec}
1a	1	5.41	1	1	0.012
1b	3.69	18.9	3.49	1.06	0.013
1c	596	6420	502	1.19	0.014

[a] Relative rates of the decomposition of the azirines **1a**−**c** in the photolysis. [**1a**−**c**] = 0.14 mM, [acrylonitrile] = 840 mM. [b] Molar extinction coefficient of **1a**−**c** at 366 nm. [c] Relative values of the number of photons absorbed by **1a**−**c**. [d] Relative quantum yields for the photodecomposition of **1a**−**c** calculated by v(rel) and I(rel).

Table 4. Excited Singlet States of **1a** Calculated with the INDO/S Method

state	transition energy eV	nm	excited state composition[a]
S_1	3.964	312.8	34 → 36(0.58), 33 → 35(0.39)
S_2	4.468	277.5	34 → 35(0.89)
S_3	4.711	263.2	34 → 37(0.50), 30 → 37(0.21), 31 → 37(0.18)
S_4	5.448	227.6	33 → 38(0.39), 31 → 36(0.22), 34 → 39(0.10)
S_5	5.557	223.1	34 → 38(0.68), 33 → 35(0.15)

[a] Configurations are designated as $n \rightarrow m$, which shows the transition from the n-th molecular orbital to the m-th molecular orbital. Molecular orbitals and their energy levels are illustrated in Figure S6. The number of HOMO and LUMO is 34 and 35, respectively. Contribution of the configuration is designated in parentheses. Only configurations with a contribution greater than 0.10 are included.

Discussion of the Wavelength Effect Based on the Theoretical Studies. The wavelength-dependent photoreactions in solutions have been the subject of great interest over the years.[16] Although most photochemical reactions in solutions are known to occur from the lowest excited state, it is possible that higher excited states are involved in photochemical reactions when the energy gap between a higher excited state and the lowest excited state is large and/or the overlap of the electronic wave functions of these two excited states is poor.[17−20]

To have a clue to understanding the observed wavelength effect, we gained information about the excited states of **1a** by molecular orbital calculations with the INDO/S method, the results of which are summarized in Table 4. The calculation of the molecular orbitals of **1a** shows that not only HOMO (#34) and LUMO (#35) but also NHOMO (#33) and HLUMO (#36) are thoroughly composed of the π orbitals of the naphthyl group. Thus, it is revealed that the lowest excited singlet state, S_1, as well as the second excited singlet state, S_2, of **1a** can be described as a local $\pi \rightarrow \pi^*$ excitation of its naphthyl moiety. On the other hand, an $n \rightarrow \pi^*$ excitation of the azirine moiety, that is, the electronic transitions from the molecular orbitals involving a nonbonding orbital on the nitrogen atom (#30 and #31) to the π^* orbital of the C−N double bond of the azirine

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(16) For a review of wavelength effect on photoreactions in solutions, see: Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

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(19) (a) Murata, S.; Kobayashi, J.; Kongou, C.; Miyata, M.; Matsushita, T.; Tomioka, H. *J. Am. Chem. Soc.* **1998**, *120*, 9088. (b) Murata, S.; Kobayashi, J.; Kongou, C.; Miyata, M.; Matsushita, T.; Tomioka, H. *J. Org. Chem.* **2000**, *65*, 6082.

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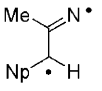
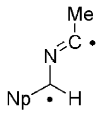
Table 5. Electronic Total Energies of Triplet Biradicals Derived from the C−N and C−C Bond Cleavage of **1a**

Triplet biradical	 **4**	
Total energy[a] (hatree)	-556.7049	-556.6906
$\Delta\Delta H_f$ (kcal mol^{-1})	0	+9.0

[a] Calculated with B3LYP/6-31+G(d) on the geometry optimazed with B3LYP/6-31G(d). Zero-point energies are included.

ring (#37), contributes largely to the third excited singlet state, S_3. Very recently, based on CASSCF and CASPT2 calculations, Klessinger and Bornemann predicted that the S_1 and S_2 state of 3-phenyl-2*H*-azirine was a $\pi-\pi^*$ and $n-\pi^*$ excited state, respectively, and discussed the wavelength dependence of its photochemistry.[21]

Taking into account that the excited state having an $n-\pi^*$ character participates in the C−C bond cleavage of an azirine ring to give a nitrile ylide,[3,21] our observation that no products derived from the C−C bond cleavage were obtained by the irradiation of **1a** with the long-wavelength light can be explained in terms of the selective excitation into the S_1 state having no $n-\pi^*$ character. Moreover, based on the result that the triplet-sensitized photolysis of **1a** afforded the products derived from the C−N bond cleavage, we propose that **1a** excited into the S_1 state undergoes an intersystem crossing to the excited triplet state, T_1, which causes the C−N bond cleavage of the azirine ring. The selective cleavage of the C−N bond rather than the C−C bond from T_1 can be rationalized in terms of the stability of the resulting biradical. This prediction is supported by the DFT calculation (B3LYP/6-31+G(d)//B3LYP/6-31G(d)), which indicates that the biradical **4** in its triplet state is more stable by 9.0 kcal mol^{-1} than the triplet biradical expected to be formed by the C−C bond cleavage (Table 5).

When irradiated with the short-wavelength light (>300 nm), **1a** is excited into the higher singlet state, S_3. This excited state causes the C−C bond cleavage of the azirine ring in preference to a nonradiative internal conversion to S_1, since the electronic wave functions of these two excited states are separately located on the azirine ring and the naphthyl moiety, respectively, leading to a significant decrease in the rate of the internal conversion. The selective formation of the product derived from the C−C bond cleavage observed in the short-wavelength irradiation (>300 nm) of **1a** in solutions is probably due to the quantum yield for the C−C bond cleavage is much higher than that for the C−N bond cleavage.

It is possible that the high vibrationally excited states of the ground state participate in the C−N bond cleavage observed in the irradiation of **1a** with the long-wavelength light. However, it appears that this possibility can be excluded, because the thermolysis of **1a** in *o*-dichlorobenzene at 150 °C afforded 2-methyl-3*H*-benz[*e*]indole (**10**)[22] (Scheme 7). No trace amounts of the products obtained in the long-wavelength irradiation of **1a** were detected in its thermolysis even in the presence of O_2.

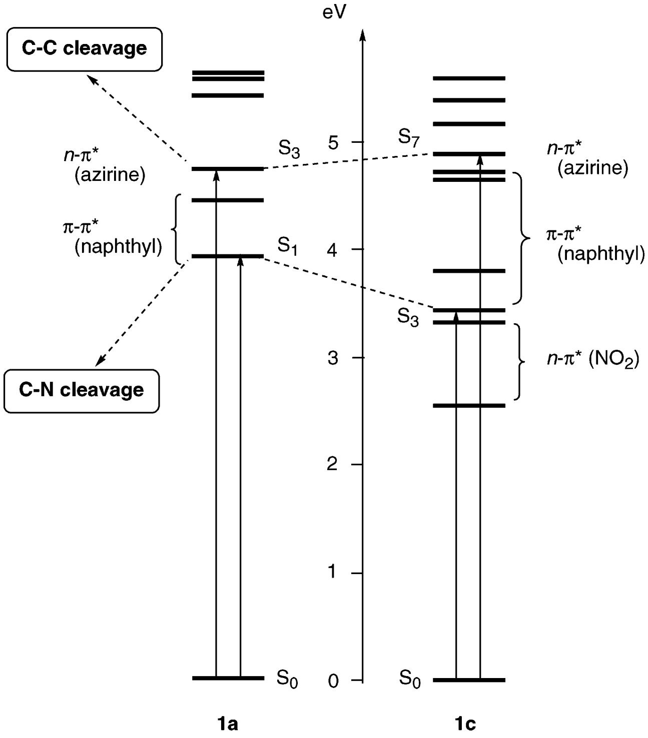
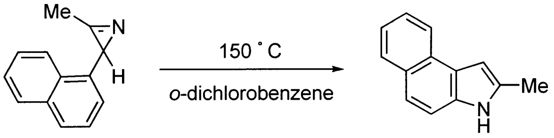


Figure 4. Diagram of excited singlet states calculated for **1a** and **1c** using the INDO/S method. The configuration of each excited state of **1a** and **1c** is shown in Tables 4 and S4, respectively.

Scheme 7. Thermolysis of **1a**



1a **10**

In the previous section, we have demonstrated the remarkable effect of a nitro group introduced into the naphthyl ring on the photoreactivity of **1a**. The INDO/S calculation done on **1c** reveals that the introduction of a nitro group into the 4-position of the naphthyl ring results in not only a decrease in the energy level of the lowest excited state described as a local $\pi\rightarrow\pi^*$ excitation of the naphthyl moiety by 0.57 eV but also an increase in the energy level of the excited state having an $n-\pi^*$ character of the azirine ring by 0.18 eV (Figure 4). On the basis of this calculation, it is expected that the introduction of a nitro group gives rise to an extension of the wavelength region in which the azirine can be excited selectively to its $\pi-\pi^*$ excited state leading to the C−N bond cleavage. It should be noted that the effect of a nitro group observed experimentally in the photolysis of **1c** is in accord with this expectation.

Conclusions

The photochemistry of 3-methyl-2-(1-naphthyl)-2*H*-azirine (**1a**) has been investigated by the direct observation of reactive intermediates in Ar matrixes and by the characterization of reaction products in solutions. It is established that upon irradiation of **1a** with the long-wavelength light the C−N bond is selectively cleaved, while the products derived from the C−C bond cleavage are predominantly obtained in the irradiation with the short-wavelength light. On the basis of the calculations, we propose that the C−N bond of the azirine ring is cleaved through

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the excited triplet state which is produced by the intersystem crossing from the S$_1$ state having an electronic character of a local $\pi-\pi^*$ excitation of the naphthyl moiety. Although wavelength-dependent photoreactions of keto-azirines involved as reactive intermediates in the photochemical oxazole-isoxazole rearrangement were reported,[17] our observation 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. Moreover, we have demonstrated that acetonitrile oxide (**6**) is produced through the capture of the biradical **4** generated by the C−N bond cleavage with O$_2$, which would provide a convenient method of photochemical generation of **6**. We recommend the nitro-substituted naphthylazirine **lc** for the photochemical generator of **6** in solutions, because it is demonstrated that the introduction of a nitro group into the naphthyl ring enhances the efficiency of the C−N bond cleavage of the azirine ring considerably.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively. UV−vis spectra were recorded on a JASCO V-560 spectrometer. IR spectra were recorded on a JASCO FT/IR-420 spectrometer. EI-MS spectra (70 eV) were recorded on a JEOL JMS-600H spectrometer. Gel permeation liquid chromatography (GPLC) was performed on a Nippon Bunseki Kogyo LC-08 equipped with two JAIGEL-H columns. The high-performance liquid chromatography (HPLC) analyses were carried out on a JASCO 880 high-pressure liquid chromatograph system equipped with a Finepak SIL-5 column. Preparative thin-layer chromatography (TLC) was carried out with Merck Silica Gel 60 F$_{254}$, and column chromatography was done with Kanto Chemical Co., Inc. Silica Gel 60. Acetonitrile was purified by distillation from CaH$_2$ under Ar. Acrylonitrile was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without purification. 3-Methyl-2-(1-naphthyl)-2*H*-azirine (**1a**) was synthesized according to the procedure described in the literature.[7]

Irradiation for Preparative Experiments. (1) Irradiation of 1b and 1c with the Short-Wavelength Light. A solution of the azirine (4.5 mM) and acrylonitrile (730 mM) in acetonitrile was placed into a quartz tube, and it was deaerated by bubbling Ar for 20 min. The sample was irradiated with light from a 400 W high-pressure mercury lamp (Riko-Kagaku Sangyo, UVL-400HA) through a Pyrex filter (>300 nm) for 3 h for **1b** and with 254 nm light from a 4 W low-pressure mercury lamp (Irie Seisakusho, LP-11B) for 1 h for **1c**. After irradiation, the solvent was evaporated under reduced pressure. The residue was separated by a preparative TLC with dichloromethane−hexane (4:1) to give a mixture of *E* and *Z* isomers of the pyrroline. (*E*)- and (*Z*)-2-Methyl-4-cyano-5-(4-bromo-1-naphthyl)pyrroline (**9b**): ^{1}H NMR (CDCl$_3$) δ 2.31 (3H, s), 2.97−3.12 (3H, m), 6.20 (1H, br), 7.06 (1H, d, J = 7.5 Hz), 7.61−7.67 (2H, m), 7.73 (1H, d, J = 7.5 Hz), 8.16 (1H, d, J = 8.0 Hz), 8.35 (1H, d, J = 8.0 Hz) for *E*-isomer; 2.32 (3H, s), 3.15−3.18 (2H, m), 3.87−3.91 (1H, m), 6.06 (1H, br), 7.38 (1H, d, J = 7.5 Hz), 7.62−7.67 (2H, m), 7.82 (1H, d, J = 7.5 Hz), 7.88 (1H, d, J = 8.0 Hz), 8.36 (1H, d, J = 8.0 Hz) for *Z*-isomer; MS *m/z* (rel intensity) 314 (M+2, 65), 312 (M$^+$, 66), 261 (M+2−CH$_2$CHCN, 78), 259 (M$^+$−CH$_2$CHCN, 79), 246 (M+2−CH$_2$CHCN− CH$_3$, 77), 244 (M$^+$−CH$_2$CHCN−CH$_3$, 76), 180 (M$^+$−CH$_2$CHCN−Br, 54), 139 (M$^+$−CH$_2$CHCN−CH$_3$CN−Br, 100). (*E*)- and (*Z*)-2-Methyl-4-cyano-5-(4-nitro-1-naphthyl)pyrroline (**9c**): ^{1}H NMR (CDCl$_3$) δ 2.33 (3H, s), 2.96−3.00 (1H, m), 3.11−3.14 (2H, m), 6.28 (1H, br), 7.32 (1H, d, J = 8.0 Hz), 7.71−7.81 (2H, m), 8.12 (1H, d, J = 8.0 Hz), 8.30−8.32 (1H, m), 8.57−8.59 (1H, m) for *E*-isomer; 2.33 (3H, s), 3.18−3.21 (2H, m), 3.91−3.95 (1H, m), 6.09 (1H, br), 7.67 (1H, d, J = 8.0 Hz), 7.71−7.81 (2H, m), 8.00 (1H, d, J = 8.0 Hz), 8.23 (1H, d, J = 8.0 Hz), 8.64 (1H, d, J = 9.0 Hz) for *Z*-isomer; MS *m/z* (rel intensity) 279 (M$^+$, 95), 226 (M$^+$−CH$_2$CHCN, 97), 209 (81), 179 (M$^+$−CH$_2$CHCN−NO$_2$−H, 100), 139 (M$^+$−CH$_2$CHCN−CH$_3$CN−NO$_2$, 80).

(2) Irradiation of 1b and 1c with the Long-Wavelength Light. A solution of the azirine (4.5 mM) in acetonitrile was placed into a Pyrex tube, and O$_2$ was bubbled into the solution for 20 min. The solution was irradiated with the light of a 400 W high-pressure mercury lamp through the filter that cut wavelengths to <350 nm (Toshiba, UV-35) for 20 and 8 h for **1b** and **1c**, respectively. The solvent was evaporated under reduced pressure to afford the corresponding aldehyde as a sole isolable product. 4-Bromo-1-naphthaldehyde (**5b**): ^{1}H NMR (CDCl$_3$) δ 7.68−7.78 (2H, m), 7.81 (1H, d, J = 7.5 Hz), 7.98 (1H, d, J = 7.5 Hz), 8.37 (1H, d, J = 7.5 Hz), 9.28 (1H, d, J = 7.5 Hz), 10.4 (1H, s); MS *m/z* (rel intensity) 236 (M+2, 98), 234 (M$^+$, 100), 208 (M+2−CO, 34), 206 (M$^+$−CO, 36), 155 (M$^+$−Br, 18), 126 (M$^+$−CO−Br, 97). 4-Nitro-1-naphthaldehyde (**5c**): ^{1}H NMR (CDCl$_3$) δ 7.79−7.85 (2H, m), 8.09 (1H, d, J = 7.5 Hz), 8.17 (1H, d, J = 7.5 Hz), 8.37 (1H, dd, J = 8.5, 1.5 Hz), 9.30 (1H, dd, J = 8.5, 1.5 Hz), 10.5 (1H, s); MS *m/z* (rel intensity) 201 (M$^+$, 100), 172 (M$^+$−CHO, 9), 155 (M$^+$−NO$_2$, 12), 127 (M$^+$−CO−NO$_2$, 78) 106 (71).

Irradiation of 1a−c for Analytical Experiment. A solution of **1a**−**c** (6.1 mM) and acrylonitrile (920 mM) in acetonitrile was place into a Pyrex tube, and O$_2$ was bubbled into the solution for 20 min. A quartz tube was used for the irradiation with 254 nm light. In the triplet sensitized irradiation, benzophenone (11 mM) was added into the solution. The solution was irradiated with 254 nm (a 4 W low-pressure mercury lamp), >300 nm (a 400 W high-pressure mercury lamp) and >400 nm (a 500 W xenon arc lamp through Ushio super cold filter 750) light and concentrated after an addition of phthalide as an internal standard. The consumption of the material and the yield of the products were determined by the integration of ^{1}H NMR in the crude reaction mixture. Identifications of the products **5a**−**c**, **8**, and **9a**−**c** were established by the agreement of their ^{1}H NMR spectra with those of authentic samples. In the irradiation of **1a**−**c** for comparison of their photodecomposition rate, as well as of **1c** for determination of the quantum yield, a solution of the azirine (0.14 mM) in O$_2$-saturated acetonitrile containing acrylonitrile (840 mM) was photolyzed in a quartz cell (10 mm × 10 mm) with 366 nm light emitted by a 500 W extra-high-pressure mercury lamp (Ushio, SX-UI D500HAMP) through both a Toshiba optical cutoff filter (UV-35, >350 nm) and a band-path filter (UV-D36B, 360 ± 20 nm) under slow bubbling of O$_2$ with stirring. The consumption of **1a**−**c** was determined by HPLC with an eluent of dichloromethane−hexane (2:3) for **1a** and **1b** and dichloromethane−hexane (3:2) for **1c** on the basis of an internal standard (bibenzyl). In the irradiation of **1c** for determination of the quantum yield, the number of photons was measured by the use of a photon counting meter (Ushio, UIT-150).

Thermolysis of 1a. A solution of **1a** (10 mg, 55 mmol) in 1 mL of *o*-dichlorobenzene was added slowly to 1 mL of *o*-dichlorobenzene heated at 150 °C with stirring under Ar. After stirring for 1 h, the solution was cooled to room temperature. The solution was developed on a column chromatography with a hexane eluent to remove the solvent at first and then purified with a dichloromethane eluent to give 8.0 mg (80%) of 2-methyl-3*H*-benz[*e*]indole (**10**) as light yellow oil. **10**: ^{1}H NMR (CDCl$_3$) δ 2.48 (3H, s), 6.75 (1H, s), 7.36−7.40 (2H, m), 7.49−7.52 (2H, m), 7.87 (1H, d, J = 8.0 Hz), 8.06 (1H, br), 8.15 (1H, d, J = 8.0 Hz); ^{13}C NMR (CDCl$_3$) δ 13.8, 99.8, 112.2, 121.6, 122.9, 123.0, 123.7, 125.4, 127.7, 128.4, 129.1, 132.0, 133.0; IR (KBr) 3407, 3047, 1540, 1372, 799, 767, 745 cm^{-1}; MS *m/z* (rel intensity) 181 (M$^+$, 100). The ^{1}H NMR and IR data of the product were in agreement with those of **10** reported by Gassman and co-workers.[21] Even when the thermolysis of **1a** was carried out under vigorous bubbling of O$_2$, no products other than **10** were detected. Moreover, heating **1a** in *o*-dichloromethane at 80 °C resulted in the recovery of the starting material.

Matrix-Isolation Spectroscopy. The matrix-isolation equipment was similar to that described in the literatures.[23] Cooling was carried out on an Iwatani Cryo Mini D310 refrigeration system equipped with a high vacuum pump (DIAVAC, DS-412R). For the material of a spectroscopic cold window, CsI for IR experiments or sapphire for UV−vis was used. The temperature of the window was regulated by a heater connected to an Iwatani TCU-4 temperature controller and monitored with an Advantest thermometer (Digital multi TR2114/H). The azirine **1a** was sublimed under 10^{-6} Torr at 40 °C and co-deposited with Ar onto a cold window cooled at 20 K. Irradiation was carried out at 10 K with a 500 W extra-high-pressure mercury lamp. The excitation wavelength was regulated by the use of a Pyrex filter (>300 nm) and a Toshiba optical cutoff glass filter (UV-35, >350 nm). The matrix isolation in Ar containing O_2 was achieved by the co-deposition of the sample with Ar mixed with O_2 in advance using the gas-handling system. The purities of Ar (Sumitomo Seiki), $^{16}O_2$ (Suzusho Medical), and $^{18}O_2$ (Isotec Inc.) are 99.99%, 99.5%, and 97%, respectively.

Calculations. The geometry optimizations, as well as the calculation of vibrational frequencies and intensities, were carried out with the DFT method at the restricted or unresticted B3LYP level of theory with the 6-31G(d) basis set. For energy calculations of the biradicals, the 6-31+G(d) basis set was employed. The DFT calculations were carried out by the Gaussian 98[24] program package on a DEC Alpha workstation computer. The calculations of excited states were performed at the INDO/S level of theory on the geometry optimized with the semiempirical method of the PM3 level of theory by the WinMOPAC program package.

Supporting Information Available: Preparation of compounds **1b**, **1c**, and **8**. Lists of observed and calculated IR frequencies of compounds **1a**, **2**, and **3**. Geometry and selected structural data of **2** and **3** optimized with B3LYP/6-31G(d). UV−vis spectra recorded in Ar matrixes. Molecular orbitals of **1a** and **1c** and excited states of **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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