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# Radical Anion of Nitrile Ylide by Dual Beam Irradiation of 3-(4-Biphenylyl)-2H-azirine at Low Temperature

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Photolysis and the successive γ-radiolysis of 3-(4-biphenylyl)-2H-azirine at 77 K resulted in the formation of a novel intermediate with an absorption maximum at 425 nm, which was produced by one-electron reduction of the nitrile ylide. The intermediate was also produced by photochemical ring-opening of the azirine radical anion.

Recently, dual beam irradiation processes have been the focus of attention because of their potential utility of generating highly active species which often lead to novel reaction pathways.[1] We report here the formation of a novel intermediate from 3-(4-biphenylyl)-2H-azirine (**1**) by combination of radiolysis and photolysis at low temperature.

**1** **2**

Photoirradiation of a 2-methyltetrahydrofuran (MTHF) solution of **1** (0.5 mmol $dm^{-3}$) at 77 K by a 450 W Xe-lamp for 10 minutes gave a broad absorption spectrum with a maximum at 410 nm as shown in Fig. 1 (curve a).[2] The absorption spectrum was very similar to that obtained by laser flash photolysis of **1**,[3] and the fact suggests that photoirradiation of **1** in a 77 K matrix induces ring-opening of **1** resulting the nitrile ylide (**2**) which has a 1,3-dipole structure as shown in the above equation.[4] The lifetime of **2** was over than a few seconds at room temperature,[3] and the stability at 77 K is sufficient for successive irradiation of γ-ray.

It is well-known that radiolysis of a MTHF solution results in the formation of solvated electrons which efficiently induce one-electron reduction of a solute.[5] γ-Ray irradiation of the matrix-isolated **2** at 77 K induced change of the absorption spectrum of **2** to a sharp spectrum with a maximum at 425 nm (Fig. 1, curve b). On the contrary, γ-ray irradiation of a MTHF solution of **1** (0.5 mmol $dm^{-3}$) at 77 K, by which the formation of the radical anion (**1**$^{\cdot-}$) is expected, gave a quite different absorption spectrum with maxima at 450 and 710 nm (Fig. 1, curve c). From these results, the species with an absorption maximum at 425 nm must be produced by one-electron reduction of the nitrile ylide (**2**). Since the formation of radical anion of **1** (**1**$^{\cdot-}$, $\lambda_{max}$ 450 and 710 nm) was not detected in the spectrum of $\gamma$ -ray irradiated **2**, it was presumed that the photochemical conversion of **1** to **2** was complete or the trapping of solvated electrons by **2** was superior to that by **1**.

$\gamma$-Radiolysis and the successive photolysis of **1** was also carried out in a 77 K MTHF matrix. Photoirradiation of **1**$^{\cdot-}$ by a Xe-lamp induced decrease of the absorption of **1**$^{\cdot-}$ and the formation of another species. The resulting spectrum (Fig. 1, curve d) is similar to

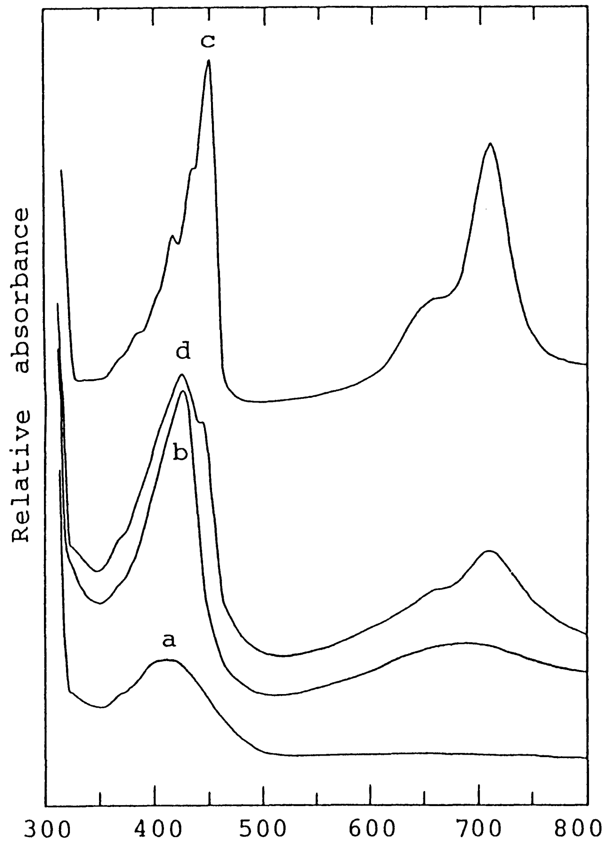


Fig. 1. Absorption spectra of the intermediates isolated in 77 K MTHF matrices; curve-a, photoirradiation (>300 nm) of **1**; curve-b, $\gamma$-ray irradiation (dose, $1\times10^2$ Gy) of the photoirradiated **1**; curve-c, $\gamma$-ray irradiation of **1**; curve-d, photoirradiation of $\gamma$-ray irradiated **1**; [**1**]=0.5 mmol dm$^{-3}$ in all experiments.

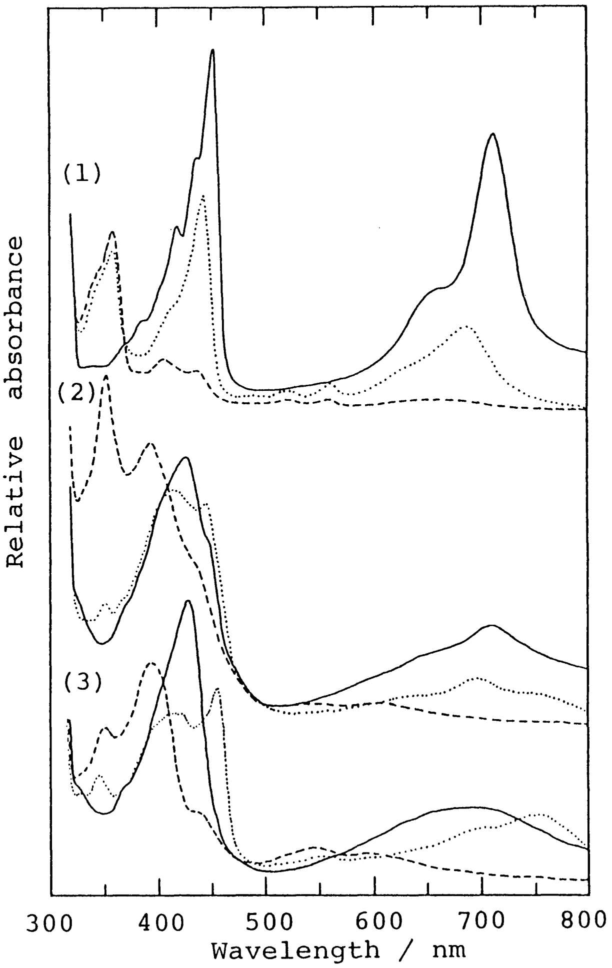
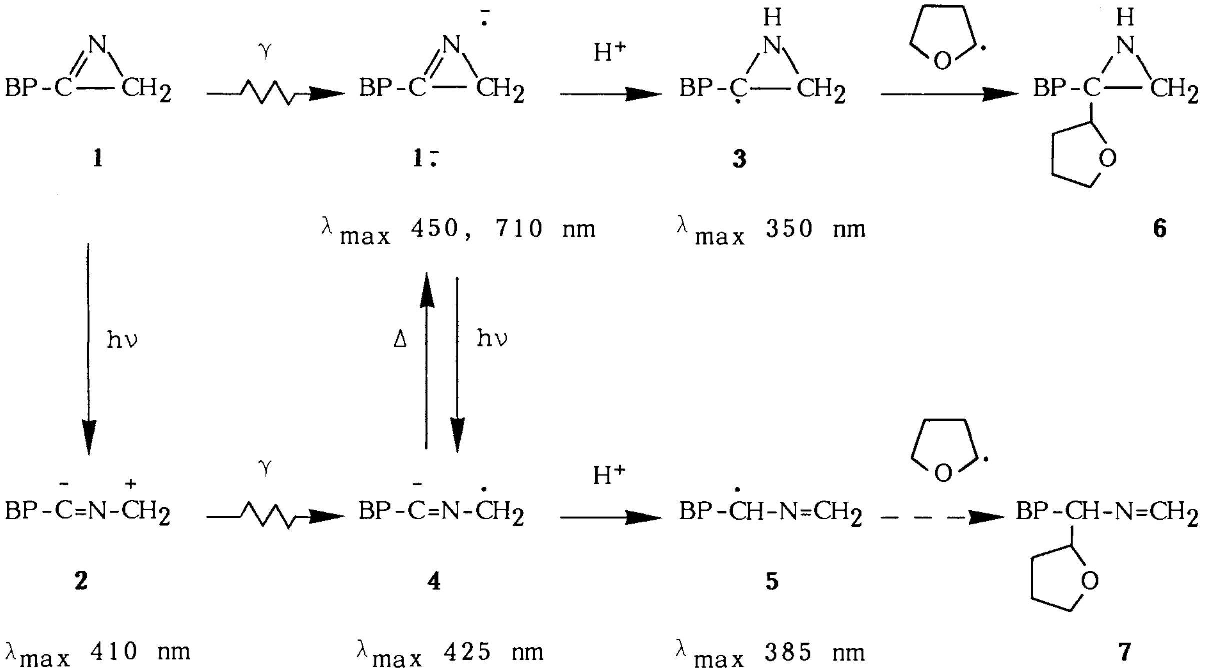


Fig. 2. Changes in absorption spectra induced by annealing of the matrices (77 K, ——; after slight annealing, ····; after further annealing, ----); (1), $\gamma$-ray irradiation (curve c in Fig. 1); (2), $\gamma$-ray irradiation → photoirradiation (curve d in Fig. 1); (3), photoirradiation → $\gamma$-ray irradiation (curve b in Fig. 1).

that of γ-ray irradiated **2** (Fig. 1, curve b), in spite of slight absorption due to remaining **1**$^{\cdot-}$. This result demonstrates that not only one electron reduction of **2**, but also photoirradiation of **1**$^{\cdot-}$ induced formation of the new transient species with an absorption maximum at 425 nm.

The following reaction of the species was observed by annealing of the matrix. Figure 2 shows spectral changes before (solid lines) and after annealing (dotted and dashed lines). Annealing of **1**$^{\cdot-}$ induced decay of **1**$^{\cdot-}$ and simultaneous formation of a new absorption band at 350 nm (Fig. 2, (1) dashed line). The latter absorption band was observed after γ-ray irradiation of an EtOH matrix of **1** at 77 K without annealing. Thus, the 350 nm band is assigned to be a radical (**3** in Scheme 1) produced by protonation of **1**$^{\cdot-}$, i.e., neutralization of **1**$^{\cdot-}$ by MTHF radical cation.[5] On the contrary, upon annealing of the species with an absorption maximum at 425 nm, which were produced by photoirradiation of **1**$^{\cdot-}$ or γ-ray irradiation of **2**, decrease of the parent band and slight recovery of **1**$^{\cdot-}$ were observed initially (Fig. 2, (2) and (3) doted lines), and stable two absorption bands at 350 nm and 385 nm were observed after annealing (dashed lines). The former is supposed to be the radical **3** and the latter is also supposed to be another neutral radical. These results indicate that both photoirradiation of **1**$^{\cdot-}$ and γ-ray irradiation of **2** give an identical anionic species (**4**) with an absorption maximum at 425 nm, which gives a radical with an absorption maximum at 385 nm by the protonation. Recovery of the radical anion (**1**$^{\cdot-}$) and formation of the radical (**3**) upon annealing of **4** suggests the competitive thermal reaction of **4** into **1**$^{\cdot-}$.



Scheme 1.

$\gamma$-Ray irradiation of a THF solution of **1** (50 mmol dm$^{-3}$) at room temperature afforded a THF adduct (**6**) in the yield of 33% (G=1.6),$^{6)}$ and the structure of **6** demonstrates that the precursor radical **3**, therefore **1**$^{\cdot-}$ also keeps a three-membered ring structure. The estimated structure of **2**, in which a positive charge localizes on the terminal carbon, suggests that one-electron reduction of **2** results in the neutralization of the positive site to afford a novel transient species **4**, that is a radical anion of the nitrile ylide. Protonation of both anionic species, **1**$^{\cdot-}$ and **4**, afforded the radicals **3** ($\lambda_{max}$ 350 nm) and **5** ($\lambda_{max}$ 385 nm), respectively. Although the solvent adduct of **5** was not isolated at present.

References

1) A. Bromberg, K. H. Schmidt, and D. Meisel, J. Am. Chem. Soc., **106**, 3056 (1984); T. Ebbesen, J. Phys. Chem., **92**, 4581 (1988); J. A. Schmidt and E. F. Hilinski, J. Am. Chem. Soc., **110**, 4036 (1988); M. A. Fox, E. Gaillard, and C. Chen, ibid., **109**, 7088 (1987); A. Ishida, H. Ito, and S. Takamuku, Chem. Lett., **1991**, 1537.

2) The azirine (**1**) was synthesized according to the previous paper (Ref. 3). All solvents were distilled from $CaH_2$ before use. Steady state $\gamma$-ray irradiation of low temperature matrix experiments was carried out with a $^{60}Co$ source ($2.6\times10^{14}$ Bq; dose, $1\times10^{2}$ Gy). Low temperature matrix spectra were measured with a multichannel spectro-photometer (Otsuka Electronix, MCPD-100). The irradiated sample at 77 K was set in a vacant quartz dewar which was pre-cooled to 77 K and then, an absorption spectrum was measured and recorded every 3 seconds until no transient absorption was observed. An annealing of the matrix was completed after about 5 minutes. Irradiation for product analysis was carried out with the same source. A 50 mmol dm$^{-3}$ THF solution of **1** was irradiated for 4 h. The product was isolated by column chromatography on alumina and analyzed by NMR and MS.

3) I. Naito, A. Ishida, K. Yamamoto, S. Takamuku, K. Isomura, and H. Taniguchi, Chem. Lett., **1989**, 1615.

4) A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore Jr., Pure Appl. Chem., **33**, 269 (1973); A. Padwa, R. J. Rosenthal, W. Dent, P. Filho, N. J. Turro, D. A. Hrovat, and I. R. Gould, J. Org. Chem., **49**, 3174 (1984).

5) W. H. Hamill, "Radical Ions," ed by E. T. Kaiser and L. Kevan, John Wiley, New York (1968), p. 321.

6) **5**; pale yellow oil, $^{1}H$ NMR ($CDCl_3$) $\delta$ = 7.30-7.57 (m, 9H), 4.19 (m, 1H), 3.77-3.80 (dd, J=4, 7 Hz, 2H), 2.05 (s, 2H), 1.78-1.84 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ = 140.87-139.52 (m, Ph), 129.26-126.35 (m, Ph), 81.47 (d, $\underline{C}H-O$), 69.02 (t, $\underline{C}H_2-O$), 43.86 (s, Ar-$\underline{C}$-N), 32.45 (t, $\underline{C}H_2$ of THF), 26.17 (t, $\underline{C}H_2$ of THF), 25.89 (t, $\underline{C}H_2-N$); MS (m/e, relative intensity), 265 (46, $M^+$), 264 (100), 236 (36), 220 (22), 208 (26), 194 (28), 180 (38), 167 (58), 152 (22), 71 (20).

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