The dependence of the rate constants in (4a) on [H$^+$] and the distribution of the specific species is derived as follows from the detailed reaction scheme given in Table III.

Let α represent the fraction of the total amount of a species present in a given state of protonation. Then

$$\alpha_{\mathrm{OA}} = 1/(1 + 10^{4.0}[\mathrm{H}^+]) \qquad (5a)$$

$$\alpha_{\mathrm{HOA}} = 1 - \alpha_{\mathrm{OA}} \qquad (6a)$$

$$\alpha_{1,\mathrm{imine}} = 1/(1 + K_4[\mathrm{H}^+] + K_4K_5[\mathrm{H}^+]^2) \qquad (7a)$$

$$\alpha_{2,\mathrm{imine}} = K_4[\mathrm{H}^+]/(1 + K_4[\mathrm{H}^+] + K_4K_5[\mathrm{H}^+]^2) \qquad (8a)$$

$$\alpha_{3,\mathrm{imine}} = K_4K_5[\mathrm{H}^+]^2/(1 + K_4[\mathrm{H}^+] + K_4K_5[\mathrm{H}^+]^2) \qquad (9a)$$

$$\alpha_{1,\mathrm{enamine}} = 1/(1 + K_6[\mathrm{H}^+] + K_6K_7[\mathrm{H}^+]^2) \qquad (10a)$$

$$\alpha_{2,\mathrm{enamine}} = K_6[\mathrm{H}^+]/(1 + K_6[\mathrm{H}^+] + K_6K_7[\mathrm{H}^+]^2) \qquad (11a)$$

$$\alpha_{3,\mathrm{enamine}} = K_6K_7[\mathrm{H}^+]^2/(1 + K_6[\mathrm{H}^+] + K_6K_7[\mathrm{H}^+]^2) \qquad (12a)$$

The enamine/ketimine ratios of the di- and triprotonated adducts are functions of the ratio, R_1, for the monoprotonated adduct and the adduct protonation constants:

$$R_2 = (K_6/K_4)R_1 \qquad (13a)$$

$$R_3 = (K_6K_7/K_4K_5)R_1 \qquad (14a)$$

Applying the relationships defined by eq 5a–14a gives

$$k_{\mathrm{a}} = (k_3 + k_4[\mathrm{H}^+])\alpha_{\mathrm{OA}} + k_5[\mathrm{H}^+]\alpha_{\mathrm{HOA}} \qquad (15a)$$

$$k_{-\mathrm{a}} = k_3/K_3\alpha_{\mathrm{imine}} + k_4/(K_3K_4)\alpha_{2,\mathrm{imine}} + k_5/(K_3K_4K_5)\alpha_{3,\mathrm{imine}} \qquad (16a)$$

$$k_{\mathrm{b}} = k_6\alpha_{1,\mathrm{imine}} + k_7\alpha_{2,\mathrm{imine}} \qquad (17a)$$

$$k_{-\mathrm{b}} = (k_6/R_1)\alpha_{1,\mathrm{enamine}} + (k_7/R_2)\alpha_{2,\mathrm{enamine}} \qquad (18a)$$

$$k_{\mathrm{c}} = k_8 \qquad (19a)$$

The three eigenvalues of (4a) are calculated from the following:

$$\lambda_{1,\mathrm{calcd}} = 2(-P/3)^{1/2} \cos{(\phi/3)} \qquad (20a)$$

$$\lambda_{2,\mathrm{calcd}},\lambda_{3,\mathrm{calcd}} = 2(P/3)^{1/2} \cos{(60° \pm (\phi/3))} \qquad (21a)$$

where

$$\phi = \tan^{-1}\left(\sqrt{-\Delta}/q\sqrt{27}\right) \qquad (22a)$$

$$\Delta = 4P^3 + 27/q^2 \qquad (23a)$$

$$P = b - a^2/3 \qquad (24a)$$

$$q = c - ab/3 + 2a^3/27 \qquad (25a)$$

$$a = -(k_{\mathrm{a}}[\mathrm{ENH}^+] + k_{-\mathrm{a}} + k_{\mathrm{b}} + k_{\mathrm{c}} + k_{-\mathrm{b}}) \qquad (26a)$$

$$b = k_{\mathrm{a}}(k_{-\mathrm{a}} + k_{-\mathrm{b}})[\mathrm{ENH}^+] + k_{-\mathrm{b}}(k_{-\mathrm{a}} + k_{\mathrm{c}}) + k_{\mathrm{a}}(k_{-\mathrm{a}} + k_{\mathrm{b}} + k_{\mathrm{c}})[\mathrm{ENH}^+] \qquad (27a)$$

$$c = -k_{\mathrm{a}}(k_{-\mathrm{a}} + k_{\mathrm{c}})k_{-\mathrm{b}}[\mathrm{ENH}^+] - k_{\mathrm{a}}k_{-\mathrm{a}}k_{-\mathrm{b}}[\mathrm{ENH}^+] \qquad (28a)$$

Owing to the excess of EN, [ENH$^+$] is easily calculated for a given experiment from the total EN, the pK_{a}s of EN and the given pH. The sum of the squares of the differences, $\lambda_{3,\mathrm{obsd}} - \lambda_{3,\mathrm{calcd}}$ and $\lambda_{2,\mathrm{obsd}} - \lambda_{2,\mathrm{calcd}}$, are simultaneously minimized by varying the parameters defined in Table III.

For a detailed discussion of relaxation methods, ref 30 is recommended.

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(30) Manfred Eigen and L. de Maeyer in "Techniques of Organic Chemistry", Vol. VIII, Part II, A. Weissberger, Ed., Wiley, New York, 1963.

Formation and Reaction of Oxaziridine Intermediate in the Photochemical Reaction of 6-Cyanophenanthridine 5-Oxide at Low Temperature

Kunihiro Tokumura, Hitomi Goto, Hironobu Kashiwabara, Chikara Kaneko, and Michiya Itoh*

Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan. *Received January 4, 1980*

Abstract: A stable oxaziridine intermediate in the photorearrangement reaction of 6-cyanophenanthridine 5-oxide was detected by matrix stabilization in ethanol and in 2-methyltetrahydrofuran (MTHF) solutions at 77 K. The oxaziridine intermediate trapped in these glassy solvents at 77 K affords 5-ethoxyphenanthridone and 6-cyanophenanthridine at the temperature allowing thermal reaction with solvent molecules, respectively. Remarkable excitation-wavelength dependence upon the formation of oxaziridine was observed at 77 K. Temperature dependences of the fluorescence quantum yield (ϕ_{f}) of the *N*-oxide and of the quantum yield (ϕ_{r}) of the formation of oxaziridine afford almost the same activation energies in these processes. This fact suggests that the formation of oxaziridine is competitive with the fluorescence decay of the lowest singlet excited state of the *N*-oxide. The photochemical reactions of the oxaziridine in ethanol glass and in MTHF glass at 77 K to form 6-cyano-3,1-dibenzoxazepine are also reported.

Since oxaziridine intermediates have been proposed in numerous investigations of the photorearrangement reactions of aromatic amine oxides,[1] some attempts to confirm this intermediate have been carried out by laser flash photolysis. Lohse[2] reported very rapid formation of isoquinolone within the duration of a ruby laser pulse in the photorearrangement reaction of isoquinoline 2-oxide. He suggested that the reaction cannot include such an intermediate as an oxaziridine. Further, Tomer et al.[3] also reported a mechanism without the formation of a transient oxaziridine in the photorearrangement of 3,6-diphenylpyridazine 1-oxide by ruby laser spectroscopy. On the other hand, some attempts to detect an unstable intermediate in the photorearrangement reaction at low temperature have been reported. Jerina et al.[4] reported oxygen walks and keto tautomers of phenol in the photolysis of arene oxide at low temperature.

Recently, Kaneko et al.[5] reported that the photolysis of 6-cyanophenanthridine 5-oxide (**1**) in ethanol at room temperature

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(1) (a) C. Kaneko, *J. Synth. Org. Chem. Jpn.*, **26**, 758 (1968); (b) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970); (c) F. Bellamy and J. Streith, *Heterocycles*, **4**, 1391 (1976).

(2) C. Lohse, *J. Chem. Soc., Perkin Trans 2*, 229 (1972).

(3) K. B. Tomer, N. Harrit, I. Rosenthal, O. Buchardt, K. L. Kumler, and D. Creed, *J. Am. Chem. Soc.*, **95**, 7402 (1973).

(4) D. M. Jerina, B. Witkop, C. L. McIntosh, and O. L. Chapman, *J. Am. Chem. Soc.*, **96**, 5578 (1974).

(5) C. Kaneko, R. Hayashi (nee Kitamura), M. Yamamori, K. Tokumura, and M. Itoh, *Chem. Pharm. Bull.*, **26**, 2508 (1978).

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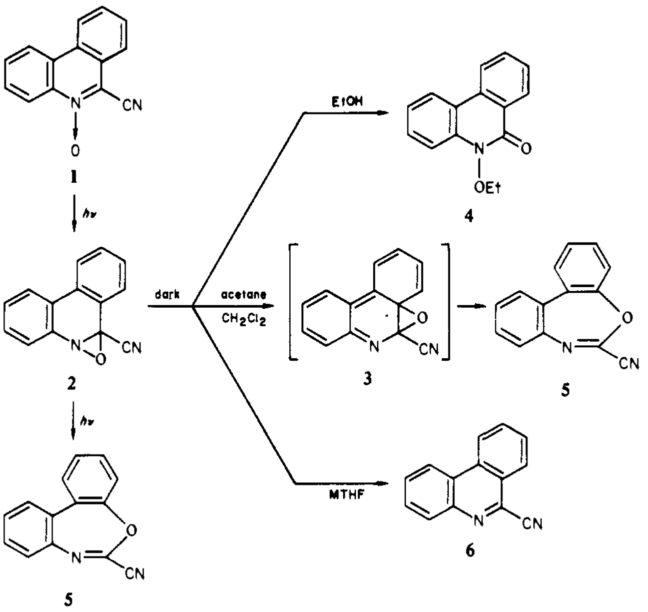
resulted in the formation of 5-ethoxyphenanthridone via a possible oxaziridine intermediate (**2**). It was suggested that the oxygen-walk process (1,5-oxygen shift) of **2** to epoxide intermediate (**3**) proceeds with difficulty, and thus **2** should have a longer lifetime than oxaziridine from 2-cyanoquinoline 1-oxide or 1-cyanoisoquinoline 2-oxide. Very recently, Tokumura, Itoh, and Kaneko[6] reported evidence of the oxaziridine intermediate in the photoreaction of **1** in ethanol on the basis of nanosecond transient spectroscopy, using a nitrogen laser and a ruby laser. They determined a relatively long lifetime (ca. 380 ns) of **2** for the formation of 5-ethoxyphenanthridone (**4**) at room temperature. On the other hand, it was reported[5] that the photolysis of **1** in nonhydroxylic solvents such as acetone, benzene, or dichloromethane at room temperature afforded 6-cyano-3,1-dibenzoxazepine (**5**).

This paper describes evidence for the oxaziridine intermediate (**2**) in the photoreaction of 6-cyanophenanthridine 5-oxide (**1**) in ethanol and in 2-methyltetrahydrofuran (MTHF) by low-temperature matrix stabilization of the intermediate. Further, the formation of **2** shows remarkable excitation-wavelength and temperature dependences. Temperature dependences of the fluorescence quantum yield of **1** and of the quantum yield of the formation of **2** suggest that oxaziridine formation is competitive with fluorescence decay of the singlet excited state of **1**. The oxaziridine trapped in ethanol glass at 77 K gives 5-ethoxyphenanthridone (**4**) at the temperature allowing thermal reaction of **2** with ethanol molecule, while that trapped in MTHF glass at 77 K gives 6-cyanophenanthridine (**6**) by the deoxygenation reaction. Further, the photoreaction of **2** trapped at 77 K both in MTHF and in ethanol affords **5**, which presents a striking contrast to the dark reactions of **2** ($2 \rightarrow 4$, and $2 \rightarrow 6$). Finally, the paper presents direct confirmation of the oxaziridine mechanism in the photorearrangement reaction of aromatic amine oxides.



Experimental Section

Absorption and Emission Spectroscopy. Hitachi 323 and Hitachi MPF-4 spectrophotometers were used for the measurements of absorption and fluorescence spectra, respectively. Low-temperature spectroscopy was carried out for the sample cell immersed in fresh liquid nitrogen in quartz Dewar or blown by cool nitrogen gas. The temperature was monitored by a calibrated thermocouple (constantan–copper). The fluorescence quantum yield (ϕ_f) of **1** at 77 K was estimated to be 0.003 as the relative value of reported ϕ_f (0.13)[7] for phenanthrene in EPA at 77 K.

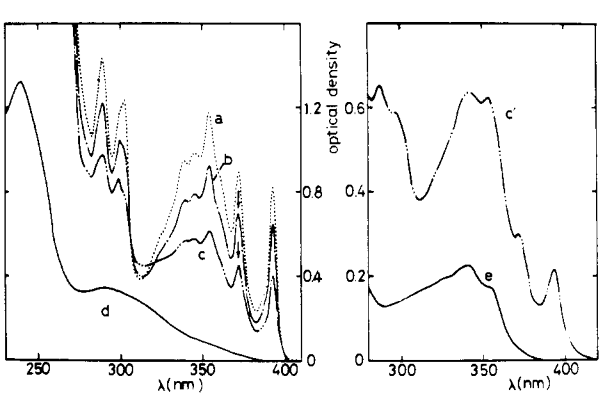


Figure 1. Absorption spectral change of an ethanol solution of **1** (9.1×10^{-5} M) with irradiation (>350 nm) at 77 K: (a) $t = 0$; (b) 15 min; (c) 60 min. (c′) The spectrum of the solution at room temperature obtained by warming up the photolyzed glass exhibiting (c). (d) The depicted spectrum of oxaziridine intermediate (**2**) obtained by subtracting the spectrum of remaining **1** at 77 K from (c). The second band of **2** was depicted by similar processes. (e) The depicted spectrum of 5-ethoxyphenanthridone obtained by substrating the spectrum due to **1** from (c′).

Photolysis. The steady light obtained by passing a xenon arc (150 W) through suitable glass filters was employed as a light source in photolysis. A convex quartz lens was used to irradiate the total volume of glassy solution. Monochromatic steady light[8] from the system of xenon arc (150 W) and grating monochromator in a Hitachi MPF-4 spectrophotometer was also employed as a light source for the photolysis combined with fluorescence measurement and actinometry and for wavelength-dependent photolysis. Sample solutions were used without deaeration except for a special case as follows. The ethanol solution used for low-temperature photolysis was degassed by repeated freeze–thaw cycles in order to prevent ethanol glass from cracking.

Determination of Reaction Quantum Yield. The integrated rate equation[9] for the photoreaction proceeding proportional to light absorption is as follows:

$$\ln\,[e^{2.303D(\lambda)} - 1] = \ln\,[e^{2.303D_0(\lambda)} - 1] - 2303\phi\epsilon(\lambda)I_0t$$

where $D(\lambda)$ and $\epsilon(\lambda)$ are optical density and molar extinction coefficient of reactant at a photoexcitation wavelength, respectively. I_0, ϕ, and t are intensity of incident light, quantum yield, and irradiation time, respectively. Because of no significant absorption due to photoproduct or intermediate at 394 nm, the disappearance of *N*-oxide **1** was monitored by the decrease of the optical density at this wavelength. The intensity (I_0) of monochromatic 394-nm light was estimated to be 2.99×10^{-9} einstein cm^{-2} min^{-1} by modified ferrioxalate actinometry at 293 K, and the values of ϵ(394 nm) of **1** in ethanol and in MTHF were determined to be 6560 and 13 800 M^{-1} cm^{-1}.[10] Thus, ϕ_- for the disappearance of **1**[11] in ethanol and in MTHF at 293 K were obtained to be 0.64 and 0.46 from the slope of the plot (ln $[e^{2.303D} - 1]$ at 394 nm vs. time). By this experimental setup, ϕ for the disappearance of acridine in aerated ethanol was obtained to be 0.045, close to the reported value (0.043).[12]

Materials. 6-Cyanophenanthridine 5-Oxide (1) and 6-Cyanophenanthridine (6). The crystals of **1** (mp 215–217 °C) and **6** (mp 136–137 °C) were prepared from phenanthridine by published procedures. The former was purified by repeated recrystallizations from benzene followed by a silica gel TLC chromatographic technique in order to eliminate fluorescent **6** as impurity.

5-Ethoxyphenanthridine-6(5*H*)-one (5-Ethoxyyphenanthridone, 4) and 6-Cyano-3,1-dibenzoxazepine (5). The crude crystals of **4** (mp 244–246 °C) and **5** (mp 103–105 °C) were obtained from the photolyzed solution of **1** in ethanol and in acetone, respectively, by a silica gel column chromatographic technique followed by crystallization. The purification of the crystals was performed by repeated recrystallization from suitable solvent.

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(6) K. Tokumura, M. Itoh, and C. Kaneko, *Tetrahedron Lett.*, 2027 (1979).

(7) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973, p 46.

(8) Half-width of the exciting light is approximately 5 nm.

(9) S. Kato, S. Minagawa, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **34**, 1026 (1961).

(10) In addition of ethanol, the first band of the *N*-oxide in isopentane exhibits broadening (the decrease of molar extinction coefficient at λ_{max}) and very slight blue shift due to the hydrogen bonding (N→O---HOEt). The equilibrium constant of the hydrogen bonding was evaluated to be ca. 1 M^{-1} at 290 K. Thus, at room temperature, the hydrogen-bonded species is predominant in ethanol while the free species is predominant in MTHF.

(11) The quantum yield, ϕ_-, may correspond to the quantum yield for the formation of oxaziridine intermediate (**2**), as will be mentioned later.

(12) S. Niizuma and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **36**, 1629 (1963).

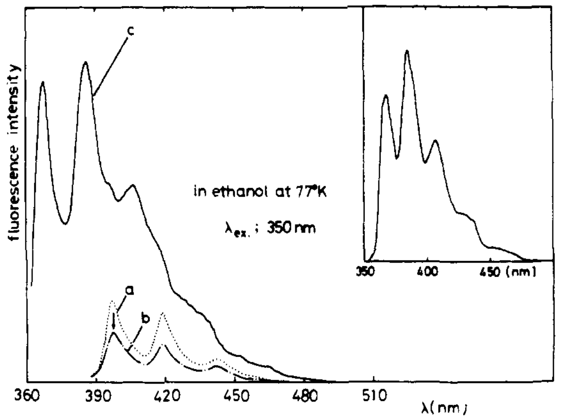

Figure 2. Fluorescence spectral change of an ethanol solution of **1** (3.2×10^{-5} M) with irradiation (350 nm) at 77 K. (a) The spectrum of **1** at 77 K before irradiation. (b) The spectrum after irradiation at 77 K. (c) The spectrum of the ethanol glass at 77 K obtained by warming up the photolyzed glass exhibiting (b) to fluid solution and by the subsequent cooling. An inset is the spectrum of **4** in ethanol at 77 K. All spectra are uncorrected.

Ethanol (Nakarai Chemicals, 99.5 vol %) was used without further purification. 2-Methyltetrahydrofuran (Wako Pure Chemical) was distilled after refluxing for 3 h over $LiAlH_4$.

Results and Discussion

Detection and Dark Reaction of Oxaziridine Intermediate. Photolysis of 6-cyanophenanthridine 5-oxide (**1**) in ethanol was reported to afford almost exclusively 5-ethoxyphenanthridone (**4**) at room temperature,[5] as mentioned before. An ethanol solution of **1** was irradiated with a steady light (>350 nm) at 77 K. The decrease of absorption intensity due to **1** was observed, while no corresponding increase of the spectrum of **4** was detected at 77 K. When the photolyzed glass was warmed up to fluid solution, the spectrum of **4** appeared, whose intensity increase corresponds well to the consumption of **1**, as shown in Figure 1. The fluorescence spectral change corresponding to the absorption spectra was also observed. The fluorescence spectrum of **1** decreased monotonously with irradiation (350 nm)[13] at 77 K, and the fluorescence spectrum of **4** appeared with raising temperature, as shown in Figure 2. The results demonstrate that there is a stable intermediate in **1** → **4** at 77 K. Therefore, the absorption spectrum of this intermediate was determined from the glassy ethanol solution of **1** after irradiation at 77 K, as shown in Figure 1. The spectrum (ϵ_{max}/M^{-1} cm^{-1} [λ_{max}/nm] 27000 [240] and 6900 [290]) is similar to that of 6-cyano-3,1-dibenzoxazepine (**5**) having a substituted biphenyl conjugate system, which also corresponds to the conjugate system of the oxaziridine intermediate (**2**). Therefore, the spectrum depicted may be ascribed to **2**.[14] This assumption is further supported by the fact that no significant formation of **5** was detected in the solution after irradiation at 77 K followed by warming up to fluid solution. Furthermore, the spectrum is quite different from that expected for another possible epoxide intermediate (**3**) having a nonbiphenyl conjugate system.

Detection of oxaziridine was attempted in the photolysis of a MTHF solution of **1** at 77 K. By the same procedures as in the ethanol solution, the decrease in intensity of the absorption spectrum due to **1** was observed at 77 K. When the glassy solution was warmed up to viscous fluid solution, an absorption spectrum of 6-cyanophenanthridine (**6**) appeared. Therefore, the absorption spectrum of the intermediate was obtained by taking account of the absorption due to remaining **1**, as shown in Figure 3. The spectrum obtained is similar to that of **2** trapped in ethanol glass at 77 K.[15] Thus, the intermediate trapped in MTHF glass at 77 K may also be considered as the stable oxaziridine (**2**). The presence of **2** was also confirmed by fluorescence spectroscopy. The fluorescence spectrum of **1** decreased in intensity with irradiation (350 nm) at 77 K. The photolyzed glass was warmed up to fluid solution and then cooled again to form glass at 77 K. The glassy solution obtained in such a way exhibited a fluorescence spectrum of **1** and **6** superimposed, as shown in Figure 4. These facts suggest that **2** is thermally stable in MTHF glass at 77 K, and its conversion to **6** proceeds only at a higher temperature allowing a thermal deoxygenation of **2**. This deoxygenation of oxaziridine affording **6** occurs in MTHF fluid solution, but not in ethanol and in dichloromethane.[16] The significant role of MTHF in this reaction was further demonstrated by the fact that the relative quantum yield of the formation of **6** increased with increasing content of MTHF in the dichloromethane solution of **1**. The deoxygenation reaction of **2** to **6** may be due to the redox reaction between **2** and MTHF molecule, which proceeds in MTHF in preference to the oxygen shift of the oxaziridine. The predominant formation of **6** from **1** in MTHF at room temperature was confirmed by the progressive spectral change of absorption with irradiation (394 nm) of **1** (Figure 5). In contrast to the deoxygenation in the triplet excited state[17] which is usual for various aromatic amine oxides, this deoxygenation reaction is novel in that only the singlet excited state of **1** is involved. Namely, the formation of **6** in direct photolysis of **1**[18] in MTHF can be

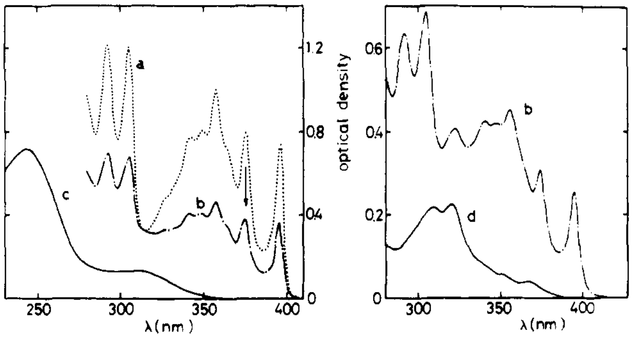

Figure 3. Absorption spectral change of an MTHF solution of **1** (3.7×10^{-5} M) with irradiation (>350 nm) at 77 K; (a) $t = 0$; (b) 60 min. (b′) The spectrum of the solution at room temperature obtained by warming up the photolyzed glass exhibiting (b). (c) The depicted spectrum of **2** obtained by subtracting the spectrum of remaining **1** at 77 K from (b). (d) The depicted spectrum of 6-cyanophenanthridine (**6**) obtained by subtracting the spectrum due to **1** from (b′).

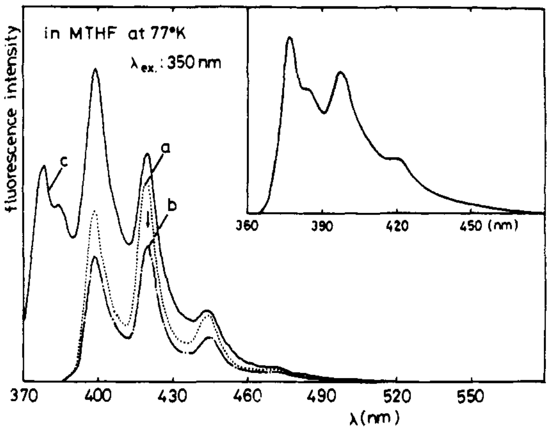

Figure 4. Fluorescence spectral change of an MTHF solution of **1** (2.2×10^{-5} M) with irradiation (350 nm) at 77 K. (a) The spectrum of **1** at 77 K before irradiation. (b) The spectrum after irradiation at 77 K. (c) The spectrum of the MTHF glass at 77 K obtained by warming up the photolyzed glass exhibiting (b) to fluid solution and by the subsequent cooling. An inset is the spectrum of **6** in MTHF at 77 K. All spectra are uncorrected.

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[13] In the excitations at 350 and 320 nm, no other fluorescence was detected. The trapped intermediate seems to be nonfluorescent even at 77 K.

[14] Unfortunately, the IR detection of **2** has been unsuccessful at the present stage, because of insufficient solubility of **1** in ethanol at low temperature.

[15] The first band of the absorption spectrum of **2** exhibits slightly blue shift in the change of solvent from MTHF to ethanol.

[16] In dichloromethane solution, 6-cyano-3,1-dibenzoxazepine was obtained almost exclusively by the photolysis of **1**, as described previously.[5]

[17] P. L. Kumler and O. Buchardt, *Chem. Commun.*, 1321 (1968).

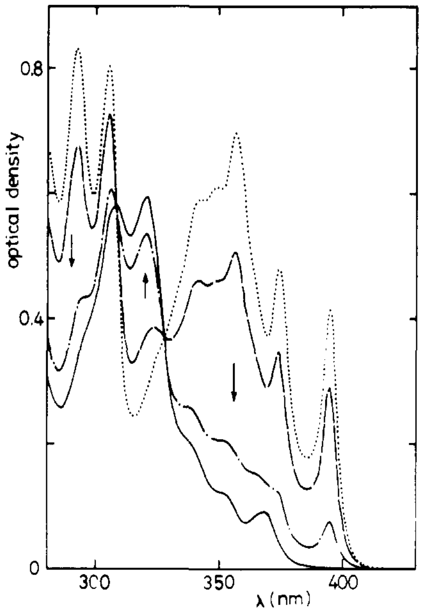
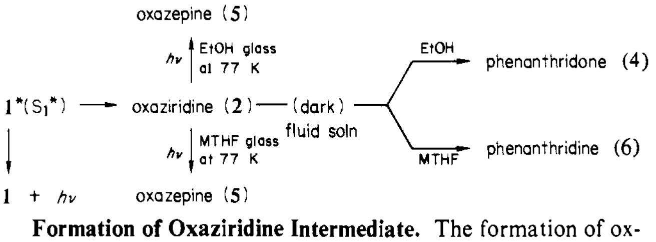


Figure 5. The progressive change in absorption spectrum of a MTHF solution of **1** (3.0×10^{-5} M) with irradiation (394 nm) at room temperature. (irradiation time: 0, 10, 38, and 91 min). The spectrum obtained finally is very similar to that of **6**.

ascribed to the formation of the oxaziridine intermediate and the subsequent deoxygenation of **2**, because of negligible probability of intersystem crossing of **1**.[19]

Photorearrangement Reaction of Oxaziridine Intermediate at 77 K. Once the oxaziridine intermediate (**2**) is trapped in organic glass at 77 K as mentioned in the last section, it is possible to investigate the photochemical behavior of **2**. Hence, the oxaziridine trapped in the MTHF glass at 77 K was further photolyzed by the irradiation of an absorption band of **2** (λ_{max} 313 nm) at 77 K, as shown in Figure 6. When the photolyzed MTHF glass was warmed up to fluid solution, it exhibited the exclusive formation of 6-cyano-3,1-dibenzoxazepine (**5**) and no formation of **6** was detected. The same results as those described above were also obtained in the photolysis of **2** in the ethanol glass at 77 K. Thus, it is reasonable to consider that the photorearrangement reaction of **2** to **5** takes place both in ethanol glass and in MTHF glass at 77 K. On the other hand, it was reported[5] that **5** is formed exclusively in the photolysis of **1** in acetone, benzene, or dichloromethane at room temperature. If the formation of **5** in such inert solvents[20] may be ascribed to the formation of **2** followed by the oxygen-walk process to form **5** (the dark intramolecular reaction of **2**) at room temperature, it is noteworthy that the photolysis of **2** in MTHF or ethanol at 77 K gives the same rearrangement product, **5**, purely by photochemical means.



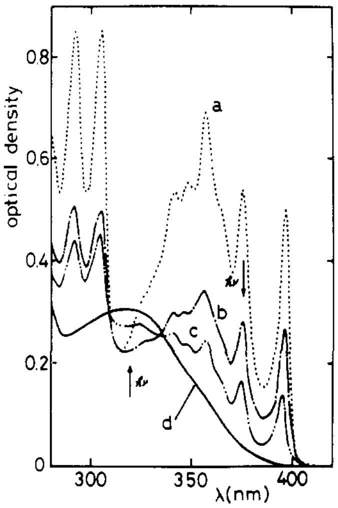
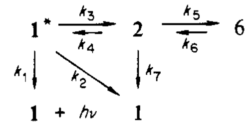


Figure 6. (a) The absorption spectrum of a MTHF solution of **1** (2.5×10^{-5} M) at 77 K. (b) The spectrum of the MTHF glass containing oxaziridine intermediate (**2**) formed with irradiation (375 nm) of **1** and remaining **1**. (c) and (d) The spectra obtained by further irradiation (313 nm) of the absorption band of **2** (the solution exhibiting (b)) at 77 K. The spectrum (d) is almost the same as that of 6-cyano-3,1-dibenzoxazepine in MTHF glass at 77 K.

Formation of Oxaziridine Intermediate. The formation of oxaziridine in the photolysis of **1** at 77 K was described in the preceding sections. In this photolysis at 77 K, a remarkable excitation-wavelength dependence upon the oxaziridine formation was observed. Thus, while neither consumption of **1** nor formation of **2** was detected in the photolysis of glassy ethanol and MTHF solutions by 394-nm irradiation, these were detected by the shorter wavelength (~356 nm) excitation. This wavelength dependence seems to suggest that the reactive state of the formation of **2** is not S_1* but S_2* of **1**. However, this consideration was ruled out by the fact that the quantum yields of the formation of **4** in ethanol and of the deoxygenation of **1** in MTHF at room temperature were independent of the excitation wavelength. The formation of **2** does not occur at 77 K but occurs at room temperature in 394-nm irradiation, as mentioned before. Thus, it seems that an activation energy is required for the formation of **2** from S_1* of **1**. On the other hand, the glassy solution of **1** irradiated at the wavelength shorter than ca. 370 nm affords **2** at 77 K, while no formation of **4** in ethanol nor **6** in MTHF was observed at this temperature. However, if the temperature of the solid solution containing **2** is raised up to ca. 135 K so that the glassy solid solution becomes a very viscous fluid, the dark reactions of **2** leading to the formation of **4** in ethanol and **6** in MTHF occur. These facts imply very low activation energies for the processes **2** → **4** and **2** → **6**.

In the photochemical reaction of **1** leading to **2** and **6** (or **4**), the following scheme involving fluorescence decay of **1*** seems to be reasonable:



where k_1 and k_2 are radiative and nonradiative rate constants of the singlet excited state of **1**, respectively; k_3 and k_5 are rate constants of the formations of **2** and **6** (or **4**), respectively. Here, k_4 and k_6 for their back processes may be neglected. The rate constant of reproduction of **1** from **2**, k_7, may also be neglected, as mentioned in the last section. A MTHF (ethanol) solution of **1** was irradiated (394 nm) at several irradiation times, and progressive decrease of **1** and increase of **6** (or **4**) were determined. Since predominant formation of **6** (or **4**) and no reproduction of **1** from **2** were detected, the formation of **2** from the singlet excited state of **1** may be monitored by the disappearance of **1**. Figure 7 shows plots of ln [exp(2.303D) − 1] against irradiation times at several temperatures above 130 K, where D is the optical density of **1** at 394 nm.[21] The ratios of slopes of the plots may be

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(18) It was confirmed by the triplet sensitization reaction using proflavin that **6** was formed via the triplet excited state of **1**. Therefore, the deoxygenation reaction takes place also in the triplet state without the formation of **2**.

(19) Neither $T_n \leftarrow T_1$ absorption of **1** in the ruby laser and Xe flash photolysis nor phosphorescence of **1** (77 K) was detected. The facts suggest no significant intersystem crossing of singlet excited states of **1**.

(20) No intermolecular reaction of **2** with solvent molecules but intramolecular rearrangement of **2** to form **5** takes place.

(21) The variation of ϵ at 394 nm with temperature was corrected.

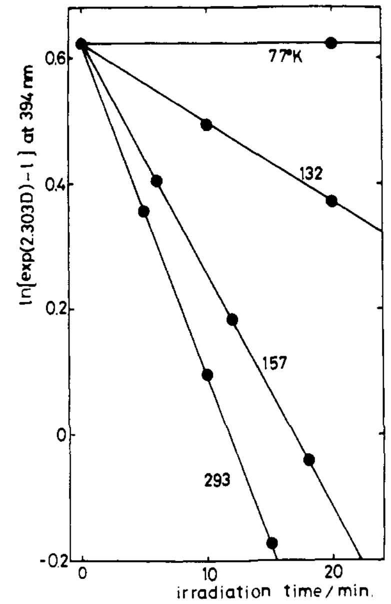

Figure 7. The plots of ln [exp(2.303D) - 1] at 394 nm vs. irradiation times at several temperatures.

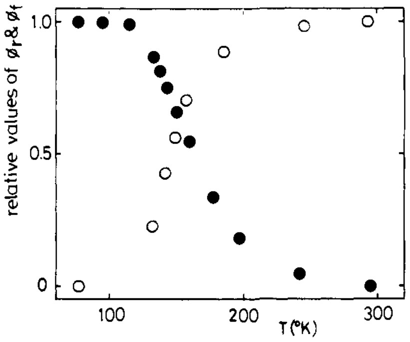

Figure 8. The plots of relative values of ϕ_r (○) and ϕ_f (●) against T.

approximately equal to those of quantum yield for the disappearance of **1** which seems to correspond to the quantum yield (ϕ_r) for the formation of **2**. The relative values of ϕ_r are plotted against temperature, as shown in Figure 8. The value of ϕ_r at 293 K was determined to be 0.46 by actinometry. Then, the values of ϕ_r at several temperatures were determined. On the other hand, ϕ_r is written as

$$\phi_r = k_3/(k_1 + k_2 + k_3) \qquad (1)$$

Assuming that k_1 and k_2 are approximately independent of temperature, and k_3 is expressed by an Arrhenius equation, the following equation is obtained:

$$\ln [\phi_r/(1 - \phi_r)] - \ln [A/(k_1 + k_2)] = -E_a/RT \qquad (2)$$

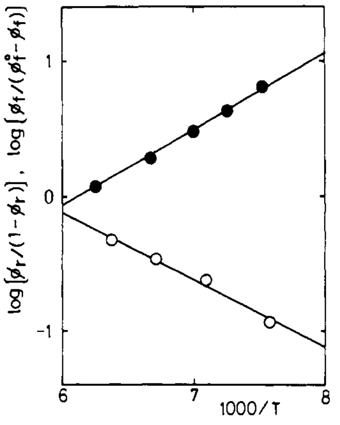

Figure 9. Arrhenius plots of temperature dependences upon the formation of **2** and the fluorescence decay of the singlet excited state of **1**. (○) The plot of log [$\phi_r/(1 - \phi_r)$] against 1000/T. (●) The plot of log [$\phi_f/(\phi_f^0 - \phi_f)$] against 1000/$T$.

where A and E_a are a preexponential factor and an apparent activation energy for the formation of **2**, respectively. Figure 9 shows the plot of log [$\phi_r/(1 - \phi_r)$] vs. $1/T$ exhibiting a linear relationship. Then, the value of E_a was obtained to be ca. 2.3 kcal mol^{-1} in MTHF from the slope of the plot.[22]

The fluorescence quantum yield of **1** is expressed by the equation

$$\phi_f = k_1/(k_1 + k_2 + k_3) \qquad (3)$$

The relative values of ϕ_f at various temperatures are plotted against temperature, as shown in Figure 8. If k_3 is assumed to be negligible in the excitation of the 394-nm band of **1** at 77 K on the basis of no formation of **2**, as mentioned in the last section, the fluorescence quantum yield (ϕ_f^0) at 77 K is expressed by $\phi_f^0 = k_1/(k_1 + k_2)$. Then the ratio of ϕ_f and ϕ_f^0 is expressed by the equation

$$\ln \phi_f - \ln (\phi_f^0 - \phi_f) + \ln [A/(k_1 + k_2)] = E_a/RT \qquad (4)$$

where E_a is the apparent activation energy for the formation of **2**, as mentioned above. Figure 9 exhibits a linear plot of eq 4, of which the slope affords E_a (2.6 kcal mol^{-1} in MTHF). The activation energy obtained from the fluorescence quantum yield is fairly consistent with that of the reaction quantum yield. These temperature dependences of two quantum yields demonstrate that the formation of **2** is a competitive process with the fluorescence decay of the lowest singlet excited state of **1**.

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[22] The activation energy (E_a) in ethanol was also estimated to be 1.4 kcal mol^{-1}.