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A POSSIBLE OXAZIRIDINE INTERMEDIATE IN THE PHOTOREARRANGEMENT REACTION OF 6-CYANOPHENANTHRIDINE 5-OXIDE

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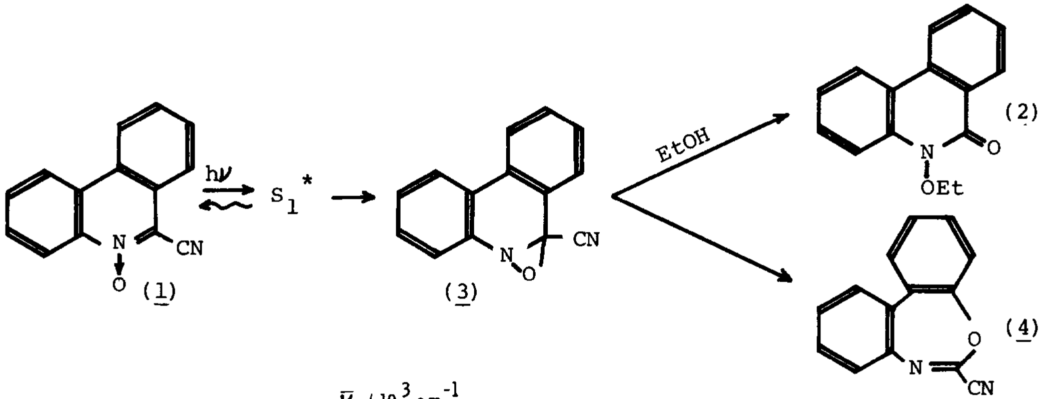
[Summary] Nanosecond spectroscopy and low temperature matrix stabilization technique present evidence of a possible oxaziridine intermediate in the photorearrangement reaction of 6-cyanophenanthridine 5-oxide in ethanol solution to form 5-ethoxyphenanthridine.

Since an oxaziridine intermediate has been proposed in numerous investigations of the photorearrangement reaction of aromatic amine oxides,$^{1)}$ some attempts to confirm the intermediate have been carried out by flash and/or laser photolysis.$^{2,3)}$ Lohse reported very rapid formation of isoquinolone within the duration of a ruby laser pulse (ca. 20 ns) in the photorearrangement reaction of isoquinoline 1-oxide.$^{2)}$ Recently, Kawata and Kokubun reported a transient intermediate in the photorearrangement of quinoxaline 1,4-dioxide.$^{4)}$

In the photolysis of 6-cyanophenanthridine 5-oxide (1) in ethanol, Kaneko et al. reported the formation of 5-ethoxyphenanthridine (2) suggesting an oxaziridine intermediate (3).$^{5)}$ They suggested that the oxygen walk process from 3 leading to the corresponding oxazepine (4) was inhibited, and thus 3 should have a longer lifetime than the oxaziridine from α-cyanoquinoline or isoquinoline N-oxide. This paper describes evidence for a possible oxaziridine intermediate (3) in the photorearrangement of 6-cyanophenanthridine 5-oxide (1) on the basis of the nanosecond transient spectroscopy and the low temperature matrix stabilization of the intermediate.$^{6)}$

The aerated ethanol solution of 1 shows no transient absorption at 400-600 nm by the first single pulse excitation of a nitrogen gas laser (337 nm, FWHM

5 ns, and a peak power ca. 80 kw).7,8) However, a transient absorption band at 470 nm appears by the second and subsequent laser pulse excitations (ca. 2Hz), and increases in intensity with the number of pulsing.9) Figure 1 shows the transient absorption spectrum obtained by the 10th pulse excitation. The spectrum is not ascribed to the $T_n \leftarrow T_1$ absorption of 1, but to that of 2. These preliminary results seem to suggest that 2 is not formed within the duration of a laser pulse, but formed up to the subsequent laser pulses which lead to the formation of T_1 of 2. Neither transient absorption nor fluorescence due to 2 was detected in the stirred ethanol solution of 1 at room temperature by the repeated pulse excitation.10) The fact may be attributable to the escape of 2 or a precursor of 2 (X) from a focussed laser beam (ca. 0.5mm diameter). Here, X is tentatively ascribed to the oxaziridine intermediate, 3.



(1) (3) (2) (4)

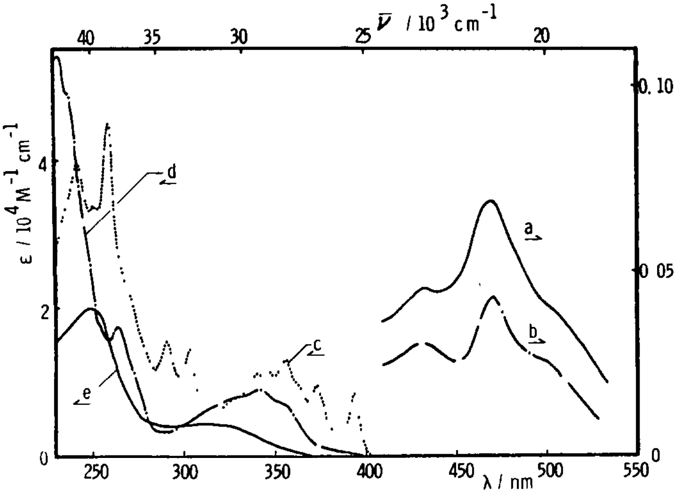


Fig. 1.(a) Transient spectrum of an aerated ethanol soln. of 1 after the 10th pulse, and (b) that of 2 after a single pulse at room temperature. (c) Absorption spectrum of the soln. of 1 at 77°K, and (d) that of 2, and the soln. after prolonged irradiation at 77°K and raising the temperature to room temperature. (e) Depicted absorption spectrum of 3 (see text).

The transient absorption at 385 nm obtained by a ruby laser photolysis (347 nm, FWHM ca. 20 ns) of the aerated ethanol solution of 1 shows strong burn and recovery of the absorption consisting of short and long components.[11)] The short component of recovery may be owing to $S_1 \rightarrow S_0$ of 1, of which decay time corresponds to the fluorescence lifetime. The decay rate constant of the long component of recovery was obtained to be $2.6 \times 10^6\ s^{-1}$ (rise time of absorption is 380 ns). Figure 2 shows an oscillogram exhibiting the long component of rise of absorption at 385 nm. No change of the rate constant in the same photolysis of the de-aerated solution excludes an possibility that the rise of absorption reflects the decay of the triplet state of 1, $T_1 \rightarrow S_0$. Furthermore, since the absorption due to the oxaziridine intermediate (substituted biphenyl conjugate) may be neglected in this wavelength region, it is suggested that the rise of absorption may be ascribed to the formation of 2 from oxaziridine, 3.

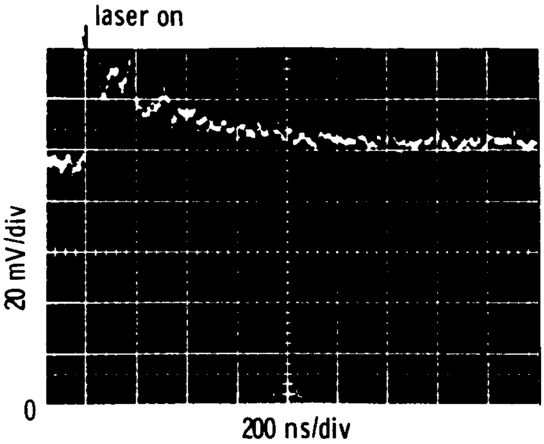


Fig. 2. An oscillogram of the transient absorption (monitored at 385 nm) reflecting rapid burn and recovery (out of scale) of the ground state of 1, and slow rise of 2 (rise time of 2 is 380 ns).

The de-aerated ethanol solution of 1 was irradiated with a steady light source (337 ± 10 nm) at 77°K. The decrease of both fluorescence and absorption due to 1 in intensity was observed, while no corresponding increase of the spectra due to 2 is detected at 77°K. When the temperature of this solution was raised to room temperature, the spectra of 2 appeared,[12)] of which increase in intensity well corresponds to the consumption of 1. The results demonstrate that there is a stable non-fluorescent intermediate in 1 → 2 at 77°K.

The absorption spectrum of this intermediate was depicted from the glassy ethanol solution of 1 after irradiation at 77°K, as shown in Fig. 1. Although, this spectrum is similar to that of oxazepine (4), the spectrum (λ_{max} 250, ε *ca*. 20,000 and 312 nm, *ca*. 4,400 $M^{-1}cm^{-1}$) may be ascribed to the oxaziridine intermediate, 3. It is because no formation of 4 was confirmed in the solution after raising temperature to room temperature. The transient spectroscopy as well as the low temperature matrix stabilization of the intermediate in the photorearrangement reaction of some other aromatic amine oxides are in progress.

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(9) The similar behabior was observed in the fluorescence signal of 2 (385 nm). No fluorescence of 1 was detected at this monitoring wavelengh.

(10) The transient absorption and fluorescence due to isoquinolone were observed in the aerated ethanol solution of isoquinoline 1-oxide in the same experimental set-up (see Ref. 2).

(11) The ruby laser photolysis was carried out at the Department of Chemistry, Tohoku University. The authors are indebted to Dr. K. Kikuchi for the technical advise in the measurement of the transient spectra.

(12) The spectrum of 1 appeared in a small extent by raising the temperature of almost completely photolysed solution (at 77°K) to room temperature. Then, the rearrangement of 3 → 2 may be a major path, though a minor process 3 → 1 occurs.

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