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Photochemical Reactions of 6-Cyanophenanthridine 5-Oxide[1,2]

Chikara Kaneko, Reiko Hayashi (née Kitamura), Masami Yamamori, Kunihiro Tokumura, and Michiya Itoh

Faculty of Pharmaceutical Sciences, Kanazawa University[3]

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The photolysis of 6-cyanophenanthridine 5-oxide (**1**) in various solvents was reported. In addition to the expected 6-cyanodibenz[*d*,*f*][1,3]oxazepine (**2**), two new types of rearrangement products: 5-alkoxyphenanthridin-6(5H)-ones (**9**), as a major product from **1** by irradiation in methanol or ethanol, and 5-cyanophenanthridin-6(5H)-one (**3**), as a by-product in the photolyses using an aprotic solvent, were obtained in the present experiments.

In order to account for the formation of these products (**3** and **9**), reasonable assumptions that the oxygen walk process from the oxaziridine species (**11**) leading to the oxazepine (**2**) is relatively inhibited to occur and thus **11** has a longer life time as compared to the related oxaziridines derived from α-cyanated bicyclic amine N-oxides were proposed.

A mechanistic rationalization and characteristic features in the photochemical rearrangement reactions of **1** are discussed in detail, together with the structure determinations of the photoproducts.

Keywords——photochemical rearrangement; dibenz[*d*,*f*][1,3]oxazepine 6-carbonitrile; 5-substituted phenanthridin-6(5H)-ones; 2-amino-2′-hydroxybiphenyls; solvent effect; oxaziridines from aromatic amine N-oxides

In the photochemical isomerization of quinoline 1-oxides (A) to either carbostyrils (B) or benz[*d*][1,3]oxazepines (C), the following reaction pathways (a and b) including an oxaziridine (D) as a common intermediate have been widely accepted.[4] If the substituent (X) has a low affinity for electrons, such as a hydrogen atom or alkyl group, irradiation of these N-oxides in a hydroxylic solvent resulted in an almost exclusive formation of the 2-oxo-com-

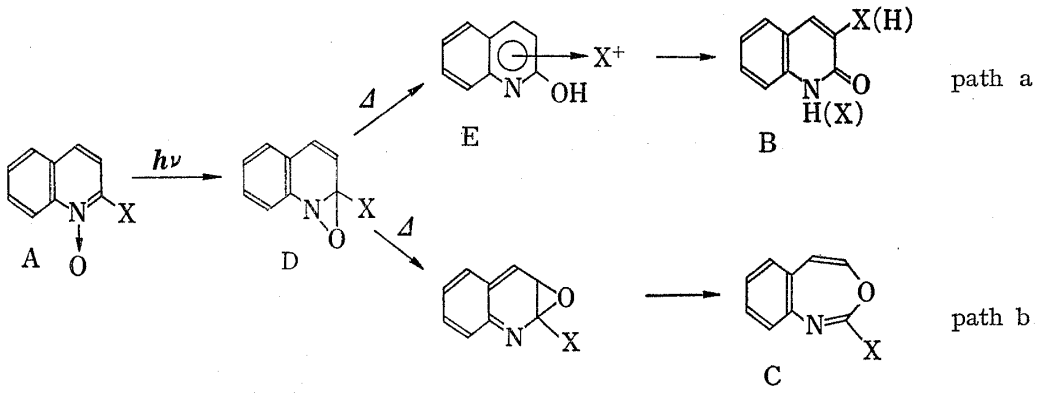
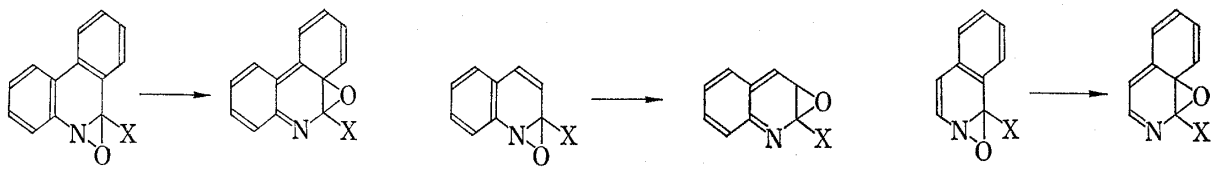


Chart 1

1) Studies on the N-Oxides of π-Deficient N-Heteroaromatics. XXVIII. Part XXVII: R. Kitamura, H. Fujii, K. Hashiba, M. Somei, and C. Kaneko, *Tetrahedron Lett.*, **1977**, 2911.
2) A part of this work was presented at the 45th Meeting of Hokuriku Branch, Pharmaceutical Society of Japan, Kanazawa, November 1977.
3) Location: *13–1, Takara-machi, Kanazawa 920, Japan.*
4) For recent reviews on this topic: *a*) C. Kaneko, *Yuki Gosei Kyokai Shi* (*J. Syn. Org. Chem. Japan*), **26**, 758 (1968); *b*) M. Ishikawa and C. Kaneko, *Kagaku no Ryoiki, Suppl.*, **92**, 149 (1970); *c*) G.G. Spence, E.C. Taylor, and O. Buchardt, *Chem. Rev.*, **1970**, 231; *d*) F. Bellamy and J. Streith, *Heterocycles*, **4**, 1391 (1976).

pounds (B) from D *via* a carbonium ion rearrangement of the substituent (X) as indicated by path a.[5] Competing with the above pathway, there is an another path leading to the oxazepines (C) from the same intermediate (D) *via* a suprafacial 1,5-oxygen shift as indicated in path b. Both of these pathways are considered as thermal by nature and thus, if the substituent has a high affinity for electrons such as a cyano[6] or trifluoromethyl group,[7] no carbonium ion rearrangement is possible for these substituents due to an instability of the corresponding π-complex (E) [a possible transition state species from D to B] and hence the oxazepines (C) are the sole rearrangement products for these N-oxides (A: X=CN or CF_3) irrespective of the kind of the solvents used for irradiation.

Based on the knowledge on the photochemical isomerization reactions of quinoline and related bicyclic amine N-oxides, it seems reasonable to assume that a 1,5-oxygen shift (this pericyclic reaction[8] is conventionally termed as an oxygen walk process) from the oxaziridine (G) derived from phenanthridine 5-oxides to H may be more difficult than the 1,5-oxygen shifts from the oxaziridines (D and F) derived from the bicyclic amine N-oxides to I and J. It is because that while one benzenoid system is lost in the latter species (D and F), the former species loses two benzenoid systems simultaneously in the oxygen walk process.



G H D I F J

Chart 2

In an expectation of finding some new rearrangement pathways hitherto unobserved in bicyclic amine N-oxides, irradiation of 6-cyanophenanthridine 5-oxide (**1**) was carried out in a variety of solvents. Such an expectation is reasonable by the reasons that the N-oxide (**1**) would give photochemically the oxaziridine (G: X=CN)[9] from which no carbonium ion rearrangement (path a) of the cyano group is possible and also the other possible rearrangement pathway (path b) should be prohibited to occur to some extent and thus, if new pathways hitherto unobserved in the photochemistry of bicyclic amine N-oxides are not available, an actual isolation of the oxaziridine species could be expected.[10]

The results obtained revealed the presence of two new rearrangement pathways for **1** and are described in this paper.

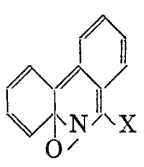
5) 2-Unsubstituted quinoline 1-oxides afforded the corresponding carbostyrils in substantial quantity even by photolyses in an aprotic solvent. This fact indicates that a zwitterionic species may also play an important role in path a.

6) M. Ishikawa, C. Kaneko, I. Yokoe, and Sa. Yamada, *Tetrahedron*, **25**, 295 (1969).

7) C. Kaneko, S. Hayashi, and Y. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2145 (1974).

8) *a*) C. Kaneko, Sa. Yamada, and M. Ishikawa, *Tetrahedron Lett.*, **1970**, 2329; *b*) C. Kaneko, Sa. Yamada, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 2818 (1975).

9) Both the experimental facts[a-c] and MO calculations[d] suggest that an oxaziridine of type G should be formed from **1** regiospecifically and none of type G′ formed; *a*) M. Ishikawa, Sa. Yamada, H. Hotta, and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **14**, 1102 (1966); *b*) E.C. Taylor and G.G. Spence, *Chem. Commun.*, **1966**, 767; *c*) E.C. Taylor and G.G. Spence, *ibid.*, 1102 (1968); *d*) C. Kaneko, Sa. Yamada, I. Yokoe, and T. Kubota, *Tetrahedron Lett.*, **1970**, 2333.



G′

10) All attempts to observe oxaziridines in the photolysis of quinoline 1-oxides, as well as other aromatic amine N-oxides, have been unsuccessful.[4] The arguments against oxaziridines as intermediates in the photochemistry of isoquinoline[a] and pyridazine N-oxides[b] were put forward based on the experiments using flash photolysis techniques: *a*) C. Lohse, *J. Chem. Soc. Perkin Trans. II*, **1972**, 229; *b*) K.B. Tomer, N. Harrit, I. Rosenthal, O. Buchardt, P.L. Kumler, and D. Creed, *J. Am. Chem. Soc.*, **95**, 7402 (1973).

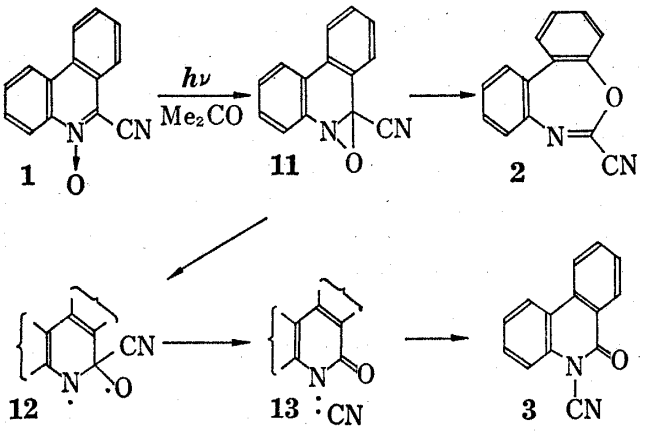


Chart 3

Results of Preparative-scale Photolyses and Discussions

Irradiation of 6-cyanophenanthridine 5-oxide (**1**) in acetone resulted in the formation of two rearrangement products, 6-cyanodibenz[*d*,*f*][1,3]oxazepine (**2**) and 5-cyanophenanthridin-6(5H)-one (**3**) in the respective yields of 78 and 13%, together with 3% of 6-cyanophenanthridine (**4**).[11] The structure of the major product (**2**) was supported by elemental analysis, infrared (IR) (2225 cm^{-1}), and other spectral data. By treatment with aqueous methylamine in ether at room temperature for a few min, **2** was converted to the N-substituted 2-amino-2′-hydroxybiphenyl (**5**) in a quantitative yield. The structure of **5** was determined from both IR [3290 (NH), 3000—2500 (hydrogen bonded OH), and 2225 cm^{-1} (CN)] and nuclear magnetic resonance (NMR) [δ: 9.32 (s, 1H), 8.24 (s, 1H), and 2.64 (s, 3H)] as well

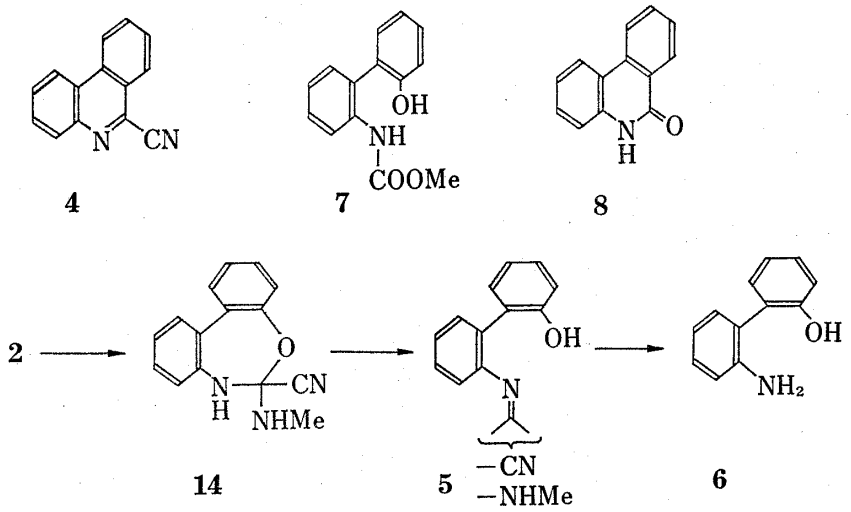


Chart 4

as its hydrolysis to 2-amino-2′-hydroxybiphenyl (**6**) in refluxed methanol in the presence of hydrochloric acid. Obviously, the formation of **5** can be explained by assuming the intermediacy of the addition product (**14**) formed by a nucleophilic attack of the amine at the 6-position of **2**.[12] The formation of 2-methoxycarbonylamino-2′-hydroxybiphenyl (**7**) [ν_{max}^{KBr}: 3300, 1680, and 742 cm^{-1}; δ: 10.02 (s, 1H), 7.78 (s, 1H), and 3.56 (s, 3H)] from **2** in methanol (room temperature for 22 hr) can also be explained by a similar mechanism. The structure of the minor rearrangement product (**3**) was again supported by elemental analysis, a close similarity of its ultraviolet (UV) spectrum with that of phenanthridin-6(5H)-one (**8**), and the presence of 2225 (CN) and 1700 cm^{-1} bands in the IR spectrum and finally determined by its conversion to **8** in refluxed ethanol in the presence of hydrochloric acid. The use of other

11) Irrespective of the kind of solvents used for irradiation, **4** was formed as a minor product. The formation of a simple deoxygenation product is quite common in the N-oxide photochemistry.[4]

12) A similar addition product was assumed as an intermediate for the reactions of benz[*d*][1,3]oxazepines with amines: C. Kaneko and I. Yokoe, *Tetrahedron Lett.*, **1967**, 5355.

aprotic solvents such as dichloromethane, benzene, and acetonitrile also gave the same rearrangement products (**2** and **3**).

Though the use of *t*-butanol as an irradiation solvent also gave the same products, the use of a primary alcohol resulted in the formation of 5-alkoxyphenanthridin-6(5H)-ones (**9**) as the major products, whose N-substituent was obviously derived from the alcohol used as a solvent. In this case, none of 5-cyanophenanthridin-6(5H)-one (**3**) was detected in the photolyzate. The structures of the N-alkoxyphenanthridones (**9a** and **9b**) were determined by elemental analyses, IR, NMR, and a close similarity of their UV spectra with that of **8** (Table I). Intervension of a diradical species (**12** and **13**) is also suggested in the photolysis in ethanol, because phenanthridin-6(5H)-one (**8**) was isolated in *ca.* 2% yield. The formation

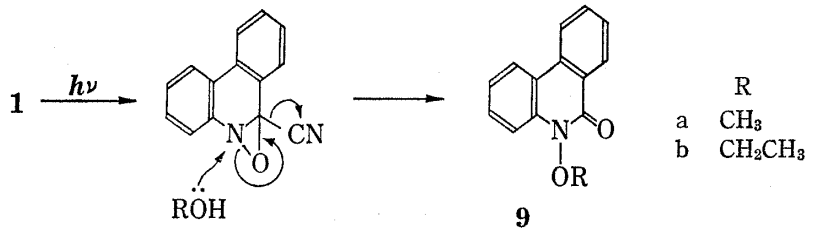


Chart 5

of **8** would be caused by abstruction of a hydrogen atom from ethanol by 5,6-dihydro-6-oxophenanthridin-5-yl radical formed from the radical pair (**13**) by the escape of the cyano radical.

Since 6-cyanophenanthridine 5-oxide (**1**) can be considered as a benzo-analog of either 2-cyanoquinoline- or 1-cyanoisoquinoline N-oxide, we can formally expect only the oxazepine (**2**) as a sole rearrangement product under these conditions. Therefore, it seems worth discussing the mechanisms for the formation of **3** and **9**, both of which belong to new types of product previously unobserved in the N-oxide photochemistry.

The formation of the former product (**3**) may be explained by assuming an initial homolytic fission of the N–O bond in the oxaziridine (**11**) to give the diradical (**12**) and its rearrangement to **3** as shown in Chart 3.[13] An ionic rearrangement pathway like path a (Chart 1) is highly improbable both from the kind of solvent (aprotic) and from the nature of rearrangement group (CN).

The mechanism for the formation of 5-alkoxyphenanthridin-6(5H)-ones (**9a** and **9b**) by irradiation in methanol or ethanol will then be considered. Since the oxazepine (**2**) gives **7** in methanol at room tenperature either in dark or under irradiation and thus can not be the precursor of **9**, the formation of **9** can reasonably be explained by assuming the intervension of the oxaziridine (**11**) as shown in Chart 5. A similar mechanism has been proposed by us[14] for the formation of N-aminocarbostyrils when 2-cyanoquinoline 1-oxides were irradiated in dichloromethane in the presence of an alkylamine and these experiments were regarded as a trapping of an oxaziridine species by amines.

As briefly discussed in the introductory part, we think that the reason for the formation of these two rearrangement products (**3** and **9**) from **1** is that the two rearrangement paths corresponding to path a and b (Chart 1) are both prohibited to occur from this oxaziridine (**11**). If this explanation is correct, then it becomes reasonable to assume that the oxaziridine (**11**) should have a relatively longer life time than those of the oxaziridine (D and F: X=CN) derived from the bicyclic amine N-oxides.

In order to support this conclusion, irradiation of **1** in dichloromethane was carried out in the presence of methyl- or dimethylamine. As a result, the expected 5-alkylamino-

13) A mechanism involving such diradical species (**12** and **13**) has been proposed to account for the formation of some photo-products in the photolyses of 6-alkyl- and -arylphenanthridine 5-oxides.[9c]

14) C. Kaneko, I. Yokoe, and M. Ishikawa, *Tetrahedron Lett.*, **1967**, 5237.

phenanthridin-6(5H)-ones (**10a** and **10b**) were obtained in the respective yields of 90 and 88%. These structures were deduced from a similarity of their UV spectra with that of **8** (Table I) and supported by other spectral data. Under the identical reaction condition with

Table I. UV Spectra of Phenanthridin-6(5H)-one and Its 5-Substituted Derivatives in CH_3OH

Comp.	λ_{max}: nm (log ε)	Comp.	λ_{max}: nm (log ε)
3	227 (4.60)	**9b**	231 (4.66)
	233 (4.69)		236 (4.65)
	255 (4.09)		253, sh (4.19)
	263 (4.11)		263 (4.21)
	275 (4.01)		325, sh (3.87)
	291 (3.66)		340 (3.95)
	302 (3.76)		356, sh (3.84)
	321 (3.87)	**10a**	233 (4.62)
	330, sh (3.79)		238 (4.64)
8	224, sh (4.59)		251, sh (4.30)
	230 (4.67)		260 (4.28)
	237 (4.63)		295, sh (3.63)
	249 (4.19)		312, sh (3.73)
	258 (4.28)		326 (3.90)
	309 (3.78)		340 (3.83)
	323 (3.95)	**10b**	231 (4.66)
	337 (3.80)		237 (4.63)
9a	231 (4.65)		250 (4.17)
	236 (4.63)		259 (4.27)
	253, sh (4.16)		300, sh (3.67)
	263 (4.20)		310, sh (3.73)
	325, sh (3.85)		323 (3.89)
	340 (3.95)		337 (3.82)
	356, sh (3.85)		

the formation of **10a**, 2-cyanoquinoline 1-oxide and its 4-methyl derivative afforded the lesser amounts (*ca.* 40%) of 1-methylaminocarbostyrils and 1-cyanoisoquinoline 2-oxide did not give any 2-methylaminoisocarbostyril.[14] A comparison of these results seems to indicate that the life time of the oxaziridine species whose carbonium ion rearrangement path is blocked should decrease in the order of G>D>F (X=CN).

Though recently an argument against oxaziridine as intermediate in the photochemistry of isoquinoline 2-oxides was put forward after their flash-spectroscopic studies,[10a] the above conclusion suggests that the oxaziridine (**11**) should be a much nicer candidate for such study.

Preliminary experiments with nanosecond flash photolysis of **1** in ethanol showed that **9b** was not formed within 5 ns. A further application of the flash photolysis technique to the photochemistry of **1** is now being carried out and the details of which will be published separately.

Experimental

The melting points were determined in a capillary tube and are uncorrected. IR spectra were determined with a JASCO-IRA-2 spectrometer, UV spectra with a Hitachi Model 323 spectrometer, NMR spectra with a JEOL-JNM-C-60H or -JNM-PS-100 spectrometer and the chemical shifts are in δ-units. Mass spectra (MS) were recorded on a JEOL-JMS-01SG spectrometer using in all cases a direct sample insertion into the ion source. For spectroscopic data, the following abbreviations are used: d=doublet, d-d, doublet of doublets, m=multiplet, s=singlet, sh=shoulder peak, and t=triplet.

Photolyses were carried out in an immersion apparatus equipped with 400 W Toshiba high pressure mercury lamp with a Pyrex filter and cooled internally with running water. Irradiation was runned in argon until all of the N-oxide had been consumed under stirring.

6-Cyanophenanthridine 5-Oxide (1)——The N-oxide (**1**) [mp 215—217°. UV $\lambda_{max}^{methanol}$ nm (log ε): 240 (4.50), 257 (4.54), 287 (4.05), 298 (3.96), 344 (4.03), 354 (4.05)] was prepared from phenanthridine[15] by the reported procedure.[16]

Irradiation of 6-Cyanophenanthridine 5-Oxide (1) in Acetone——A solution of 1.0 g of the N-oxide (**1**) in 450 ml of acetone was irradiated for 30 min. The solvent was evaporated under a reduced pressure and the residue was chromatographed over silica gel. Elution with hexane–ether (9: 1 v/v) gave crystalline fractions which after recrystallization from hexane–ether afforded 6-cyanodibenz[*d*,*f*][1,3]oxazepine (**2**) (778 mg), mp 103—104.5°. IR ν_{max}^{KBr} cm^{-1}: 2225, 1648. UV $\lambda_{max}^{acetonitrile}$ nm (log ε): 244 (4.39), 314 (3.67). MS *m/e*: 220 (M^+). *Anal.* Calcd. for $C_{14}H_8N_2O$: C, 76.36; H, 3.66; N, 12.72. Found: C, 76.14; H, 3.73; N, 12.68.

Elution with hexane–ether (1: 1 v/v) gave 6-cyanophenanthridine[16] (**4**) (25 mg), mp 136—137° (methanol). Further elution with hexane–ether (1: 2 v/v) and ether gave, after recrystallization from acetone–methanol, 5-cyanophenanthridin-6(5H)-one (**3**) (131 mg), mp 188.5—189°. IR ν_{max}^{KBr} cm^{-1}: 2225, 1700. NMR ($CDCl_3$) δ: 8.46 (1H, d-d, J=8 and 1.5 Hz), 8.24 (2H, m), 7.35—8.0 (5H, m). MS *m/e*: 220 (M^+). *Anal.* Calcd. for $C_{14}H_8N_2O$: C, 76.36; H, 3.66; N, 12.72. Found: C, 75.98; H, 3.70; N, 12.48.

Irradiation in an other aprotic solvent (benzene, acetonitrile, or dichloromethane) or in *tert*-butanol resulted in the same product distribution.

Hydrolysis of 5-Cyanophenanthridin-6(5H)-one (3)——The phenanthridone (**3**) (49 mg) was suspended in ethanol (15 ml) containing 5 ml of concd HCl and the reaction mixture was refluxed for 42 hr. The residue obtained after evaporation of the solvent was recrystallized from acetone–methanol to give 32 mg of phenanthridin-6(5H)-one (**8**), mp 288—290°. The structure of **8** was determined by mixture melting point determination with the authentic sample.[9a]

Reaction of 6-Cyanodibenz[*d*,*f*][1,3]oxazepine (2) with Methylamine——The oxazepine (**2**) (198 mg) was dissolved in 20 ml of ether. After addition of 0.2 ml of 40% aqueous methylamine solution, the reaction mixture was stirred for 10 min at room temperature. Evaporation of the solvent under a reduced pressure, followed by recrystallization from methanol, afforded the compound (**5**) (223 mg), mp 154—155°. IR ν_{max}^{KBr} cm^{-1}: 3290 (NH), 3000—2500 (a hydrogen bonded OH), 2225, 1625, 757. UV $\lambda_{max}^{methanol}$ nm (log ε): 244 (4.28), 285 (3.92). NMR (DMSO-d_6) δ: 9.32 (1H, s), 8.24 (1H, s), 6.7—7.5 (8H, m), 2.64 (3H, s); the former two signals disappeared by addition of D_2O. MS *m/e*: 251 (M^+). *Anal.* Calcd. for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.87; H, 5.08; N, 16.55.

The crude compound (**5**) obtained from 376 mg of **2** by the above procedure was dissolved in 50 ml of methanol containing 10 ml of 20% HCl. The whole was refluxed for 14 hr. After evaporation of methanol, the residue was made alkaline by addition of saturated aqueous $NaHCO_3$ solution. Extraction with CH_2Cl_2, evaporation after drying over Na_2SO_4, and recrystallization from aqueous ethanol (1: 1 v/v) afforded 2-amino-2′-hydroxybiphenyl (**6**) (276 mg), mp 92.5—93°. UV $\lambda_{max}^{methanol}$ nm (log ε): 286 (3.77); the maximum shifted to 306 nm by addition of 10% KOH solution. IR ν_{max}^{KBr} cm^{-1}: 3370, 757. NMR ($CDCl_3$) δ: 6.7—7.45 (8H, m), 3.8 (2H, broad s). MS *m/e*: 185 (M^+). *Anal.* Calcd. for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.76; H, 6.03; N, 7.38.

Reaction of 6-Cyanodibenz[*d*,*f*][1,3]oxazepine (2) with Methanol——A solution of **2** (88 mg) in 25 ml of methanol was kept standing at room temperature for 22 hr. By this time, no starting material (**2**) was detected in the reaction mixture (thin-layer chromatography). The residue obtained after evaporation of the solvent was chromatographed over silica gel. Elution with hexane–ether (2: 1 v/v) afforded crude 2-methoxycarbonylamino-2′-hydroxybiphenyl (**7**) (65 mg). Recrystallization from methanol afforded the pure sample of **7**, mp 155—156°. UV $\lambda_{max}^{methanol}$ nm: 281. IR ν_{max}^{KBr} cm^{-1}: 3300, 1680, 742. NMR (DMSO-d_6) δ: 10.02 (1H, s), 7.78 (1H, s), 7.62 (1H, broad d, J=8 Hz), 6.7—7.5 (7H, m), 3.56 (3H, s). By the acid hydrolysis under the condition as described above, this compound (**7**) also afforded **6**.

Irradiation of 6-Cyanophenanthridine 5-Oxide in Methanol or in Ethanol——The N-oxide (**1**) (498 mg) was dissolved in 450 ml of methanol and irradiated for 35 min. Evaporation followed by recrystallization from methanol gave 228 mg of 5-methoxyphenanthridin-6(5H)-one (**9a**). The mother liquor after concentration was chromatographed over silica gel to give at first (elution with hexane–ether 2: 1 v/v) 6-cyanophenanthridine (**4**) (15 mg) and then (elution with ether) a further amount (138 mg) of **9a**. 5-Methoxyphenanthridin-6(5H)-one (**9a**) was recrystallized from methanol, mp 231—234°. IR ν_{max}^{KBr} cm^{-1}: 1660. NMR (DMSO-d_6) δ: 8.50 (1H, broad d, J=8 Hz), 8.30 (1H, d-d, J=8 and 1.5 Hz), 7.0—8.0 (6H, m), 3.90 (3H, s). MS *m/e*: 225 (M^+). *Anal.* Calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.51; H, 5.03; N, 5.98.

Irradiation in ethanol under an identical condition as above gave the deoxygenated product (**4**) (2%) and 5-ethoxyphenanthridin-6(5H)-one (**9b**) (60%), mp 244—246° (methanol). IR ν_{max}^{KBr} cm^{-1}: 1660. NMR (DMSO-d_6) δ: 8.56 (1H, broad d, J=8 Hz), 8.28 (1H, broad d, J=8 Hz), 7.0—8.0 (6H, m), 4.16 (2H, q, J=7 Hz), 1.38 (3H, t, J=7 Hz). MS *m/e*: 239 (M^+). *Anal.* Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N,

15) E.C. Taylor and N.W. Kalenda, *J. Am. Chem. Soc.*, **76**, 1699 (1954).
16) E. Hayashi and H. Ohki, *Yakugaku Zasshi*, **81**, 1033 (1961).

5.85. Found: C, 75.16; H, 5.52; N, 5.67. In this case, phenanthridin-6(5H)-one (**8**) (2%) was also obtained, whose fraction was eluated between those of **4** and **9b** in the column chromatography.

Irradiation of 6-Cyanophenanthridin-5-Oxide (1) in Dichloromethane in the Presence of Methyl- or Dimethylamine——A solution of the N-oxide (**1**) (495 mg) in a mixture of 285 ml of CH_2Cl_2 and 40 ml of 40% methylamine solution was irradiated for 15 min.[17] After the irradiation, organic layer was separated and aqueous layer was extracted with CH_2Cl_2. The combined CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated. The residue obtained in a usual manner was chromatographed over silica gel. Elution with hexane–ether (2: 1 v/v) gave a crystalline fraction (460 mg) which by recrystallization from ether to give 5-methylaminophenanthridin-6(5H)-one (**10a**), mp 88—89.5°. IR ν_{max}^{KBr} cm^{-1}: 3260, 1640. NMR ($CDCl_3$) δ: 8.56 (1H, d-d, J=8 and 1.5 Hz), 8.31 (1H, d-d, J=8 and 1.5 Hz), 8.28 (1H, d-d, J=8 and 1.5 Hz), 8.00 (1H, d-d, J=8 and 1.5 Hz), 7.2—7.9 (4H, m), 6.12 (1H, q, J=6 Hz; this signal disappeared by addition of D_2O, 2.81 (3H, d, J=6 Hz). MS *m/e*: 224 (M^+). *Anal.* Calcd. for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.49. Found: C, 75.13; H, 5.42; N, 12.36. Phenanthridin-6(5H)-one (**8**) was also isolated in a small amount (9 mg) from the more polar fractions.

Use of 40 ml of 50% dimethylamine solution instead of the methylamine solution resulted in the formation of 88% of 5-dimethylaminophenanthridin-6(5H)-one (**10b**) and 1% of **8**. The compound (**10b**) was recrystallized from hexane–ether, mp 104—104.5°. IR ν_{max}^{KBr} cm^{-1}: 1645. NMR ($CDCl_3$) δ: 8.58 (1H, d-d, J=8 and 1.5 Hz), 8.40—8.16 (3H, m), 7.90—7.25 (4H, m), 3.16 (6H, s). *Anal.* Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.48; H, 6.03; N, 11.48.

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17) An efficient stirring was maintained before and during the irradiation.