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STUDIES ON THE N-OXIDES OF π-DEFICIENT N-HETEROAROMATICS—XXX[1]

PHOTOCHEMISTRY OF ACRIDINE 10-OXIDES (2):[2] SYNTHESIS AND REACTION OF DIBENZ[*c,f*]-1,2-OXAZEPINES

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Abstract—The dibenz[*c,f*]-1,2-oxazepines **IId** and **IIe** were obtained as the major products from 9-cyano- and 9-chloroacridine 10-oxides (**1d** and **1e**) by irradiation (≥300 nm) in benzene, and found to undergo a variety of isomerization reactions under mild conditions in the dark. Existence of the same species (**IIa–IIe**) in the irradiated solution of acridine 10-oxide (**1a**) and its methylated derivatives (**1b** and **1c**) was also confirmed by UV spectroscopy as well as by some trapping experiments.

The direct isolation of **IId** and **IIe** not only constitutes the first synthesis of 1,2-oxazepine derivatives but also gives experimental support to the previously suggested mechanism (Chart 1) for the photolyses of acridine 10-oxides and the related N-oxides.

In Part I of this series,[2] we reported the photochemical isomerization of acridine 10-oxides (**1**) and showed that a variety of photo-products (**2–8**) which were isomeric with the parent N-oxides were formed by the irradiation in an aprotic solvent, whereas the solvent addition products (**9**) were formed concomitantly with these rearrangement products in a protic solvent. At the same time, a mechanism including the oxaziridine (**I**: a primary photo-product from **1**) and the 1,2-oxazepine (**II**: the valence bond tautomer of **I**) as possible intermediates was proposed and a number of the products were classified into two groups, B and C, on the basis whether the direct precursors of them were the oxaziridine species (**I**) [B-type products: **2–4**], or the 1,2-oxazepine species (**II**) [C-type products: **5–9**]. The results obtained are summarized in Chart 1, in which the products isolated carry Arabic numerals (**1**, **2**, ...) and the presumed intermediates carry Roman numerals (**I**, **II**, ...).

The formation of an oxaziridine species (e.g. **I**) from the excited N-oxide was well accepted as a primary process in the photochemistry of aromatic amine oxides irrespective to their ring systems and the tautomerization of this species to the 1,2-oxazepine (e.g. **II**) was also suggested in the photolysis of monocyclic azine N-oxides.[3] However, the actual isolation of oxaziridine or 1,2-oxazepine species has never been successful. This is in strong contrast to the photolysis of 1-iminopyridinium ylides in which 1,2-diazepines (corresponding to the 1,2-oxazepines in a formal sense) were isolated as stable products.[4]

During the photolysis of acridine 10-oxides, we noticed the presence of a very unstable species in the irradiated solution of some N-oxides (**1a–1c**) and speculated that they should be one of the intermediates, **I** or **II**, as assumed in the previously proposed mechanism.[2] Hence, in order to obtain these reactive intermediates, careful photolyses of **1a–1c** and the related N-oxides (**1d–1e**) were reinvestigated.

The study along this line has now led us to a successful isolation of the 1,2-oxazepines (**IId** and **IIe**) by photolysis of 9-cyano- and 9-chloroacridine 10-oxides (**1d** and **1e**). Furthermore, the thermal reactions of these oxazepines has now allowed us to confirm the correctness of the previously proposed mechanism (Chart 1). The isolation of the 1,2-oxazepines also has provided direct support for the intermediacy of the oxaziridine species in the N-oxide photochemistry, because the former (**II**) is the valence bond tautomer of the latter species (**I**).

EXPERIMENTAL RESULTS

The presence of an unstable intermediate was first observed in the photolysis of 9-methylacridine 10-oxide (**1c**) in benzene.[5] Thus, if the reaction was monitored by visible spectroscopy (≥360 nm region), the absorption maxima of **1c** at 443 and 468 nm disappeared gradually and were replaced by a new absorption maximum at 408 nm. This spectrum did not coincide with the spectrum of any photo-product (**2–11**) obtained in our previous work.[2] Furthermore, the product was found to be unstable and reverted slowly to the N-oxide (**1c**) on standing in benzene in the dark. Isolation of this product was unsuccessful due to the ease with which it isomerized back to **Ic** (the isomerization was accelerated either by heating or by concentration). Actually, in the preparative scale experiment, more than 65% of the starting N-oxide (**1c**) was recovered by the usual work-up from the irradiated solution of **1c** in which no N-oxide was contained as checked by visible spectroscopy. As will be shown later, the structure of this product was the 1,2-oxazepine (**IIc**).

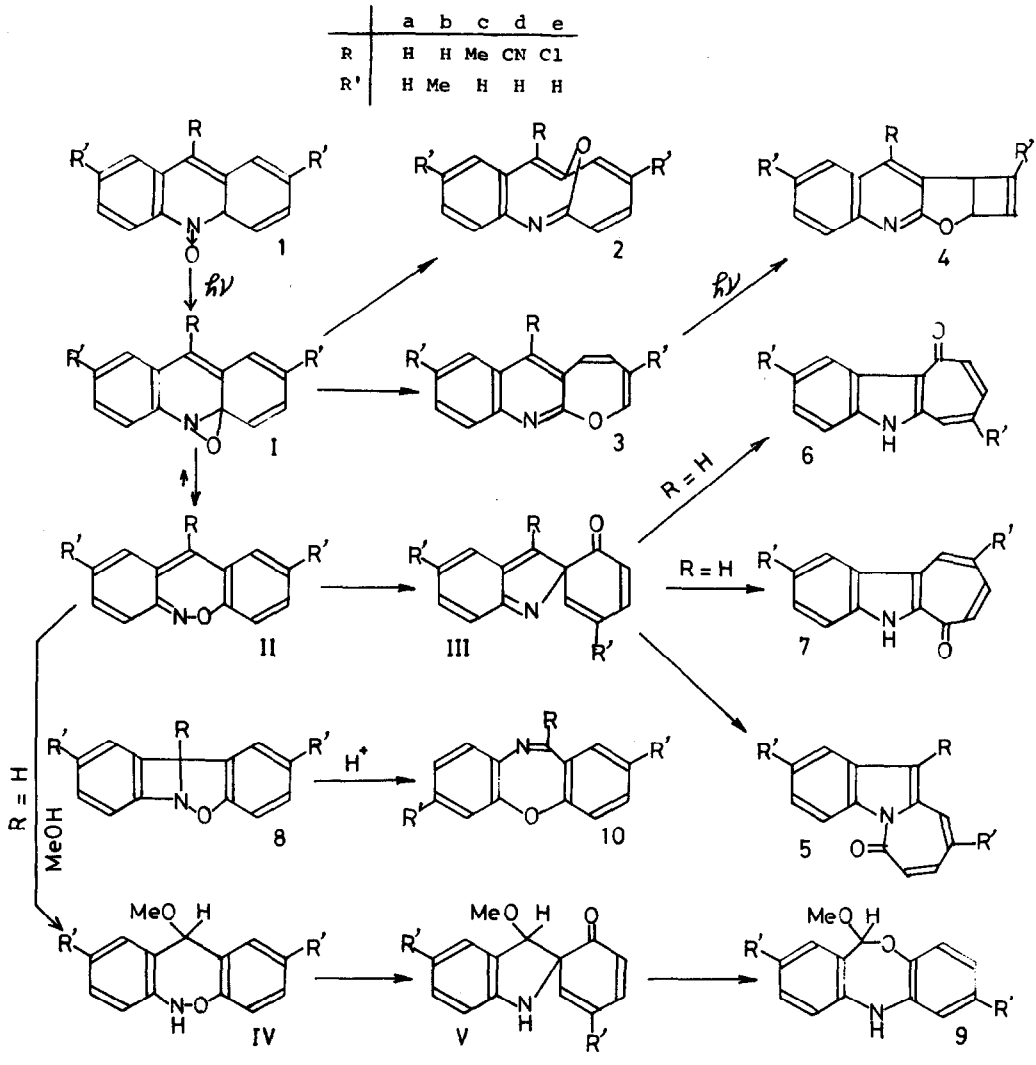


Chart 1.

The formation of such unstable intermediate was also observed in the photolysis of acridine 10-oxide (**1a**) and the trapping of this species (**IIa**) was successful in several ways. Thus, **1a** was irradiated in benzene until all of the N-oxide was consumed (the reaction was followed by visible spectroscopy) and the irradiated solution was subjected to three independent treatments: (1) the solution was stirred at room temperature for 5 hr in the dark after the addition of methanol containing 1% potassium hydroxide, (2) the solution was flashed with hydrogen chloride gas for one min, and (3) the solution was stirred at room temperature for 20 hr after the addition of excess LAH. After these treatments, each solution was concentrated and the products were separated to give the products listed in Table 1. From the treatment 1, the methanol addition product (**9a**) was obtained in a good yield. By the treatment 2, the indolotropone (**6a**) was isolated as a main product. The third treatment afforded *o* - amino - *o'* - hydroxydiphenylmethane (**12**) in an appreciable amount. Though the formation of **9a** and **6a** is compatible with either the oxaziridine (**Ia**) or the 1,2-oxazepine structure (**IIa**), the formation of **12** is only explained from the latter structure (**IIa**). Next, the irradiated solutions of the methylated N-oxides (**1b** and **1c**) containing the same kind of unstable intermediates (each of them showed an absorption maximum at around 400 nm) were subjected to similar treatments and the results are shown in Table 1. As mentioned, the irradiated solution of **1c** resulted in recovery of the N-oxide (**1c**) by the treatment 1, whereas that of **1b** afforded after treatment 1 or 2 a variety of the stable isomerization products whose structures have been determined previously.[2]

The results obtained indicate that the reactive intermediates from **1a–1c** should be the dibenz[*c,f*]-1,2-oxazepines (**IIa–IIc**). Since a 1,2-oxazepine ring has 8π-electrons and thus belongs to an antiaromatic system, it can reasonably be expected that the introduction of an electron withdrawing group in the ring would stabilize the system and make possible the isolation of the corresponding 1,2-oxazepines. Accordingly, photolyses of 9-cyano- and 9-chloroacridine 10-oxides (**1d** and **1e**) were carried out[6] in benzene until all of the N-oxides had been consumed. The solvent was removed and the residue treated with n-pentane. The pentane soluble portion afforded *ca.* 50% (in each case) of orange crystals (**IId** and **IIe**). The UV spectra of both compounds showed two maxima at around 220 and 405 nm (the longer

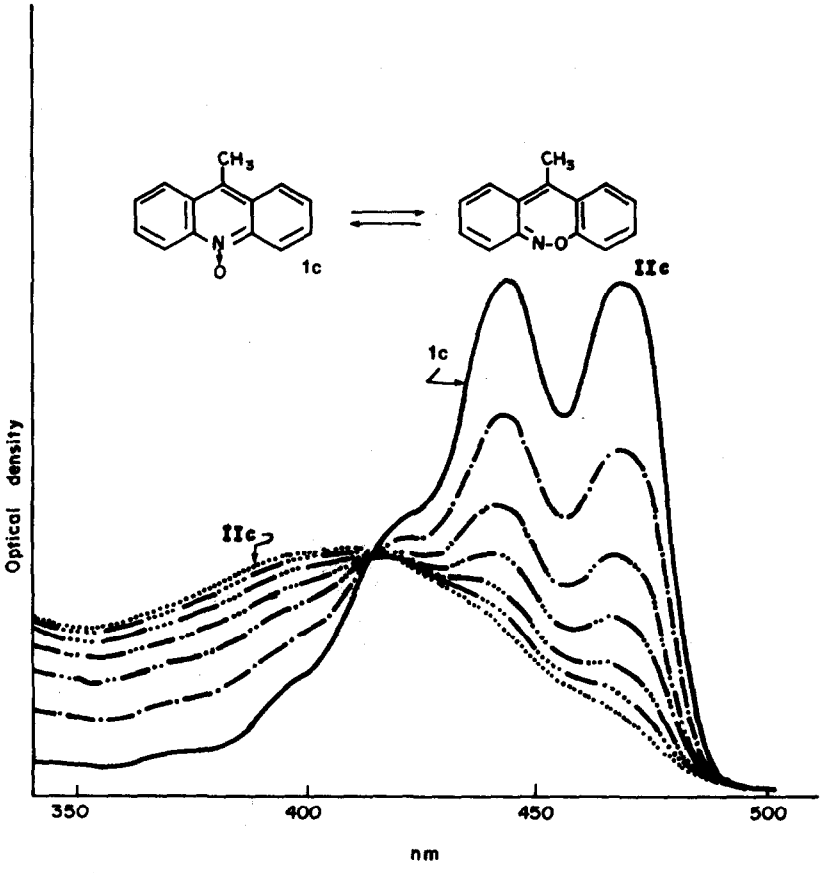


Fig. 1. Photochemical formation of IIc and its thermal revertion to 1c.

wavelength absorption maxima of these compounds resembled quite closely the unstable products obtained from 1a–1c) and their NMR spectra were in good accordance with the 1,2-oxazepine structures (IId and IIe). Chemical reactions of IId and IIe provided further supporting evidence for their structures. Thus, by column chromatography over silica gel, IId afforded 11-cyano-oxepinol[2,3-*b*]quinoline (3d), 1-cyanobenz[*c*]-2-aza[1,6]oxido[10]annulene (2d), and 11-cyano-6-oxo-6H-azepinoindole (5d). The structures of these products were determined unequivocally by direct comparison of their spectral properties and by mixed m.p. determinations with the respective authentic samples obtained in our previous work.[7]

The 11-chloro derivative (IIe) showed almost the same spectral and chemical properties as IId but readily isomerized to the starting N-oxide (1e). Thus, IIe gave 1e in 81% yield on heating in an aprotic solvent and the rate of the reaction was increased with increasing polarity of the solvent (acetonitrile > benzene > cyclohexane). Such a facile reversion to the N-oxide was not observed in IId and thus, by heating in aqueous acetonitrile, IId gave a variety of the stable rearranged products. The formation of these products was also observed either in glc (OV-17, at 220°) or by column chromatographic separation (silica gel) of IId. Some typical isomerization reactions of IId and IIe are summarized in Chart 2 and Table 2.

Reduction of IIe with LAH gave the diphenylmethane (12) which was identical with the product obtained from IIa under a comparable conditions.

Table 1. Trapping experiments for the primary photo-products IIa ~ IIe of 1a ~ 1c

Comp.	Reaction	Product (%)								
		1	2	3	5	6	7	8	9	11
1a	basic MeOH	5			2	10	9.5		62	
	HCl				2	62	11			
1b	basic MeOH	14	19	39	2.5		18			
	HCl	16			3	48	14			
1c	basic MeOH	68			8			5		3
	HCl	7			7					

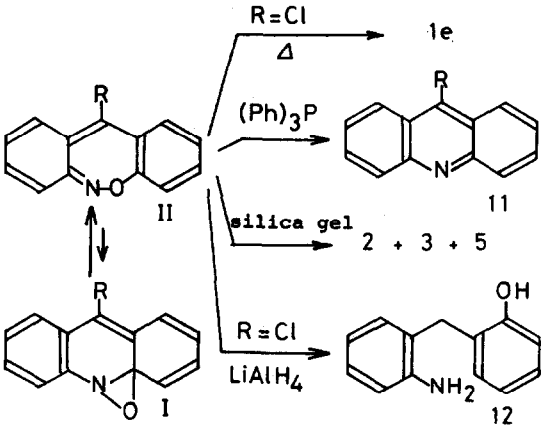


Chart 2.

It should be noted that both **IId** and **IIe** were deoxygenated giving a very high yield of the corresponding acridines (**11d** and **11e**).

DISCUSSION

It is obvious from the comparison of spectral data and chemical reactions between the unstable photo-products (**IIa–IIc**) obtained from **1a–1c** and the isolated orange crystals (**IId** and **IIe**), that these have essentially the same structure. Though both structures, **I** and **II**, are compatible with the spectral data and chemical reactivities, we prefer structure **II** for these photoproducts for the following reasons:

(1) It is well known that oxepine and benzene oxide exist as an equilibrated mixture and the proportion of each depends upon the polarity of solvent.[6] In more polar the solvents, the equilibrium shifts to the oxide side. As 1,2-oxazepine and the oxaziridine are isoelectronic with oxepine and benzene oxide, this equilibration could also be possible in the present case. The polarity effect of the solvent on the rate of reversion of **IIe** to **11e** (*vide supra*) and the results of the previously reported photolysis of acridine 10-oxides showing that the B-type products are formed in greater amounts by irradiation in a polar solvent than in an apolar solvent,[2] are in good accordance with equilibration between **I** and **II**.

(2) Though the existence of oxaziridine species in the photolysis of aromatic amine oxides is well documented, the participation of the 1,2-oxazepine species is only suggested in the monocyclic azine N-oxides, but not in the bicyclic N-oxides. This seems reasonable, because in the latter series, the tautomerization of the corresponding oxaziridine (**A**) to the 1,2-oxazepine (**B**) results in the loss of one benzenoid system, whereas such loss is not expected in the case of monocyclic azine N-oxide (e.g. **C** and **D**). The same argument then suggests that the valence bond tautomerization of **I** to **II** may occur because the loss of one benzenoid system would be compensated by the gain of the other benzenoid system in the isomerization.

(3) The reduction of **IIa** and **IIe** affording the diphenylmethane derivative (**12**) is only compatible with the structure **II**.

Finally, comment was made on the possible tautomerization of the 1,2-oxazepines (**IId** and **IIe**) to the oxaziridines (**Id** and **Ie**). As no spectral changes were observed by changing the solvent used for UV spectra, such equilibration is considered to favour the 1,2-oxazepine side in the present case. This is quite reasonable, as compared with the benzene oxide-oxepine equilibration, the introduction of a N atom into the oxepine π-lattice would stabilize the energy of the 1,2-oxazepine system. In accordance with this explanation, the 1,2-diazepines so far isolated showed no tendency to tautomerize to the corresponding diaziridine species.[4]

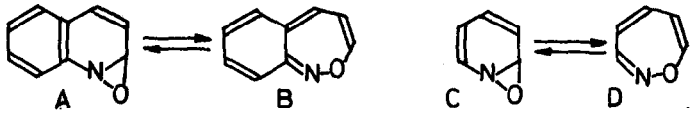
Table 2. Reactions of dibenz[*c,f*][1,2]oxazepines **IId** and **IIe**

Comp.	Reaction	Product (%) 1	2	3	5	11
IId	silica gel column		15	67	5	1.5
	heating in aq. MeCN	1	13	53	7	
	Ph_3P			2	3	94
IIe	silica gel column	37.5	7	36	8.5	
	heating in benzene	81			4	4
	Ph_3P	10				85

CONCLUSION

The isolation of the 1,2-oxazepine species (**II**) from the photolyzate of some acridine 10-oxides supports the mechanism of photochemical isomerization of acridine 10-oxides (**1**). Thus, the oxaziridine (**I**) derived from the photo-excited N-oxide (**1**) tautomerizes to the more stable 1,2-oxazepine (**II**). However, the oxazepine (**II**) is in general not stable enough to be isolated and undergoes further thermal rearrangements to the isomeric products or reacts with the solvent to give the addition products. Two oxazepines (**IId** and **IIe**) which are stable enough to be isolated isomerized to a variety of end products under quite mild conditions (Table 2). It should be noted that oxazepines (**II**) having a Me or a Cl group at the 11-position tend to give the N-oxides in the larger proportion as verified in the present work. This fact and the formation of acridines from **II** by treatment with triphenylphosphine indicates a possible minor equilibration of **II** to the oxaziridine (**I**).

It is surprising that except for the obviously photochemical pathways (designated by $\xrightarrow{h\nu}$ in Chart 1), almost all the other pathways (designated by $\longrightarrow$) can proceed under thermal conditions. We may therefore conclude that all the essential pathways after oxaziridine formation can be explained by the thermal reac-



tions of the two equilibrated intermediates (I and II).

Since the 1,2-oxazepines obtained in the present work are valence bond tautomers of the oxaziridine species, the present results demonstrate clearly that a similar mechanism including the oxaziridine species as a primary photo-product is operating in the photo-chemical isomerization of mono- and bicyclic amine N-oxides.

Recently, Krishnan *et al.* have reported that the oxaziridine species obtained from phenanthridine rearranges spontaneously to phenanthridone.[9] Kaneko *et al.* have demonstrated that the irradiation of a variety of aromatic amine N-oxides in the presence of triphenylphosphine results in almost exclusive deoxygenation.[10] Though these two recent reports seem to provide supporting evidence, the actual isolation of the 1,2-oxazepines has provided direct proof for the existence of the oxaziridine species.

EXPERIMENTAL

M.ps were determined in a capillary tube and are uncorrected. UV spectra were measured on a Hitachi Model-323 spectrometer. IR spectra were obtained on a DS-403G-JASCO spectrometer for KBr discs. NMR spectra were obtained with a JNM-PS-100-JEOL or C-60 HL spectrometer using TMS as an internal standard and chemical shifts are given in δ values with coupling constants in Hz. Mass spectra were determined on a Hitachi RMU-7M double focus mass spectrometer at 70 eV. Irradiation was carried out in a quartz immersion well with a Hanovia high pressure mercury arc lamp (200 or 400 W) using Pyrex filter. All of the previously characterized stable photo-products obtained in the present work were identified with the respective authentic samples[2,7] by mixed m.p.d. and by comparison of the spectral data.

Irradiation of acridine 10-*oxide* **1a** *and trapping of the primary photo-product* **IIa**

A soln of **1a** (500 mg) in benzene (600 ml) was irradiated by means of a 200 W lamp. The irradiation was monitored periodically by measuring the visible spectrum of a dilute soln (in benzene) of the mixture and terminated when most of the N-oxide was consumed (4 hr). The irradiated soln was subjected to the following reactions.

(1) *Treatment with basic methanol.* To the soln was added 1% KOH–MeOH (100 ml) and the mixture was allowed to stand at room temp. for 5 hr. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and the organic layer was washed with water, dried ($MgSO_4$) and evaporated. The residue was chromatographed on alumina. Elution with benzene yielded **5a** (10 mg) m.p. 109–110° and **9a** (310 mg) m.p. 105–106°. Elution with CH_2Cl_2 gave **1a** (25 mg) and **7a** (48 mg) m.p. 250–252°. The water washing was made weakly basic by the addition of AcOH and extracted with $CHCl_3$. Drying over $MgSO_4$ and evaporation afforded **6a** (52 mg) m.p. 285–286°. All of the products were identified with the respective authentic samples[2] by mixed m.p.d.

(2) *Treatment with dry HCl gas.* The irradiated soln was flashed with dry HCl gas for a min. After evaporation of the solvent, $NaHCO_3$aq was added to the residue to neutralize the mixture. The mixture was then extracted with $CHCl_3$. Crystals which were insoluble in both solvents were filtered off to give **6a** (230 mg). The $CHCl_3$ layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel. Elution with benzene gave **5a** (11 mg) and elution with CH_2Cl_2 yielded **7a** (55 mg) and **6a** (79 mg).

(3) *Reduction with* LAH_4. The irradiated soln was added dropwise to a suspension of LAH_4 (1 g) in THF (200 ml) and the mixture was stirred ar room temp. for 20 hr. Excess of the reagent was decomposed by adding sat Na_2SO_4aq. After adding dry ice to make the soln weakly basic, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over $MgSO_4$ and evaporated. The residue was then chromatographed on silica gel. Elution with 10% MeOH–CH_2Cl_2 gave **12** (180 mg) as a viscous oil which was converted to the diacetate **13**, m.p. 118–120° by the action of Ac_2O; UV λ_{max} (95% EtOH) 235 nm (shoulder peak, log ϵ = 3.83); IR 3280, 1750, 1655, 1220 cm^{-1}; mass spectrum: *m/e* 283 (M^+), 241, 223, 93; NMR ($CDCl_3$) 1.90 (3 H, s), 2.30 (3 H, s), 3.80 (2 H, s), 7.4–6.8 (7 H, m), 7.93 (1 H, d, J = 7.0). (Found: C, 71.97; H, 6.30; N, 5.10. Calc. for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94%).

Irradiation of 2,7-*dimethylacridine* 10-*oxide* **1b** *and trapping of the primary photo-product* **IIb**

A soln of **1b** (1 g) in benzene (1.8 l.) was irradiated until most of the N-oxide was consumed (200 W, 4 hr). The irradiated soln was divided into two portions and each soln was subjected to the following reactions.

(1) *Treatment with basic methanol.* To the soln was added MeOH (100 ml) containing 1 ml Et_3N and the whole was stirred at room temp. for 20 hr. The soln was evaporated and the residue was chromatographed on silica gel. Elution with benzene gave **5b** (12 mg) m.p. 125–126° and **2b** (95 mg) m.p. 137–139°. Elution with benzene–CH_2Cl_2 (1:1 v/v) gave **3b** (195 mg) m.p. 157–159°, and with $CHCl_3$ afforded **7b** (90 mg) m.p. 232–235° and **1b** (70 mg). All of the products were identified with authentic samples.[2]

(2) *Treatment with dry HCl gas.* The soln was flashed with dry HCl gas for a min. After the same work-up as described above, **6b** (240 mg) m.p. >290° was obtained from the $CHCl_3$-insoluble portion. The $CHCl_3$–soluble portion was chromatographed on silica gel with benzene to give **5b** (15 mg). Elution with $CHCl_3$ yielded **1b** (80 mg) and **7b** (70 mg).

Irradiation of 9-*methylacridine* 10-*oxide* **1c** *and trapping of the primary photo-product* **IIc**

A soln of **1c** (1 g) in benzene (1.8 l.) was irradiated for 1 hr by a 450 W lamp. This irradiated soln was divided into two portions and each was subjected to the following reactions.

(1) *Treatment with basic methanol.* To the soln was added 100 ml of MeOH containing 1 ml Et_3N and the whole was stirred at room temp. for 18 hr. The crystals isolated after concentration of the soln to about 20 ml yielded **1c** (290 mg). The portion soluble in benzene was chromatographed on alumina. Elution with benzene afforded successively **5c** (41 mg); m.p. 116–117°, **8c** (25 mg); m.p. 89–90°, and **11c** (16 mg) and elution with CH_2Cl_2 yielded **1c** (51 mg). All the products were identified with a sample obtained previously.[2]

(2) *Treatment with dry HCl gas.* The soln was flashed with HCl gas and the whole was stirred at room temp. for 18 hr. After similar work-up, the products were separated by silica gel chromatography. Elution with benzene gave **5c** (35 mg) and that with 5% MeOH–CH_2Cl_2 yielded **1c** (36 mg).

Irradiation of 9-*cyanoacridine* 10-*oxide* **1d** *and the synthesis of* 11-*cyanodibenz[c,f][1,2]oxazepine* **IId**

A soln of **1d** (3 g) in benzene (1.8 l.) was irradiated for 3 hr (450 W). After evaporation of the solvent under a reduced pressure the residue was extracted with n-pentane (three times, each 50 ml) at room temp. Evaporation of the combined pentane fraction under a reduced pressure at room temp. gave an orange crystalline solid (1.8 g), which by recrystallization from ether–pentane afforded **IId** (1.5 g), m.p. 105–109°; IR 2220, 1600, 760,

740 cm^{-1}; UV λ_{max} (cyclohexane) 224 and 400 nm (log ϵ = 4.50 and 3.68 resp.); NMR (C_6D_6) 5.85 (1 H, t.d, J = 7 and 2), 6.0 (1 H, t.d, J = 7 and 2), 6.6–7.3 (5 H, m), 7.5 (1 H, d.d, J = 8 and 2). (Found: C, 76.15; H, 3.71; N, 12.68. Calc. for $C_{14}H_8N_2O$: C, 76.36; H, 3.66; N, 12.72%). The pentane insoluble portion was chromatographed on silica gel. Elution with benzene yielded successively **5d** (288 mg); m.p. 201–204°, **3d** (78 mg); m.p. 137–138°, and **11d** (38 mg). Elution with CH_2Cl_2 gave **1d** (396 mg). The structures of **1d**, **3d** and **5d** were established by the mixed m.p.d. with the authentic samples obtained previously.[7]

Isomerization of **IId** *by chromatography on silica gel.* Compound **IId** (370 mg) dissolved in a small volume of benzene was loaded on a silica gel column (30 g) and allowed to remain in the upper part of the column for 24 hr. After that time, the column was eluted with benzene and then with CH_2Cl_2 to give successively **2d** (55 mg), **5d** (19 mg), **3d** (249 mg) and **11d** (5 mg).

Thermal isomerization of **IId**.[11] A soln of **IId** (300 mg) in aqueous MeCN (1:1 v/v; 50 ml) was heated at 60° for 30 min. During that time, the orange color of the oxazepine faded completely. After evaporation of the solvent, the aqueous soln was extracted with $CHCl_3$ and the organic layer was dried over Na_2SO_4. The residue obtained by evaporation of the solvent was chromatographed on silica gel with benzene to give **2d** (39 mg), **5d** (21 mg), **3d** (159 mg) and **1d** (3 mg).

Treatment of **IId** *with triphenylphosphine.* To a soln of **IId** (100 mg; 0.45 mmole) in CH_3CN (30 ml) was added triphenylphosphine (180 mg; 0.68 mmole) and the mixture was allowed to stand at room temp. for 2 hr. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with hexane–benzene (1:1 v/v) gave triphenylphosphine (64 mg) and **5d** (3 mg). Elution with benzene gave **3d** (2 mg) and **11d** (88 mg). Triphenylphosphine oxide (119 mg) was obtained by elution with CH_2Cl_2.

Irradiation of 9-chloroacridine 10-*oxide* **1e** *and synthesis of* 11-*chlorodibenz*[c,f][1,2]*oxazepine* **IIe**

A soln of **1e** (1 g) in benzene (600 ml) was irradiated for 1.5 hr by a 450 W lamp. After evaporation of the solvent under a reduced pressure at room temp., the residue was treated with n-pentane as described. The pentane extract gave **IIe** (510 mg), m.p. 51–54° (recrystallized from n-pentane); IR 1595, 755, 732 cm^{-1}; UV λ_{max} (95% EtOH) 216 and 410 nm (log ϵ = 4.43 and 3.71 resp.); mass spectrum: *m/e* 229 and 231 (M^+); NMR (C_6D_6) 5.95 (1 H, t.d, J = 6 and 2), 6.20 (1 H, t.d, J = 6 and 2), 6.65–7.40 (6 H, m), 7.55 (1 H, d.d, 8 and 2). (Found: C, 68.31; H, 3.63; N, 6.28. Calc. for $C_{13}H_8NOCl$: C, 67.98; H, 3.51; N, 6.10%). The pentane insoluble portion was chromatographed on silica gel. Elution with hexane-benzene (1:1 v/v) yielded **5e** (157 mg), m.p. 149–151° (recrystallized from ether); IR 1673, 1633 cm^{-1}; UV λ_{max} (95% EtOH) 275, 284 and 430 nm (log ϵ = 4.50, 4.56 and 3.67, resp.); NMR ($CDCl_3$) 6.45 (1 H, d, J = 13.0), 6.32 (1 H, d.d, J = 12 and 8), 6.87 (1 H, d.d, J = 13 and 8), 7.4–7.6 (3 H, m), 7.75 (1 H, m), 9.0 (1 H, m). (Found: C, 67.98; H, 3.64; N, 6.49. Calc. for $C_{13}H_8$ NOCl: C, 67.98; H, 3.51; N, 6.10%). Elution with benzene gave **3e** (45 mg) m.p. 86–87° (recrystallized from ether); IR 1640, 1575, 1485, 765, 738 cm^{-1}; UV λ_{max} (95% EtOH) 226 and 320 nm (log ϵ = 4.69 and 4.09 resp.); NMR ($CDCl_3$) 5.70 (1 H, t, J = 6), 6.25 (1 H, d.d, J = 12 and 6), 6.50 (1 H, d, J = 6), 7.05 (1 H, d, J = 12), 7.90 (1 H, d.d, J = 7 and 2), 8.17 (1 H, d.d, J = 7 and 2), 7.4–7.8 (2 H, m). (Found: C, 67.87; H, 3.55; N, 6.23. $C_{13}H_8NOCl$: C, 67.98; H, 3.51; N, 6.10%). Elution with $CHCl_3$ gave **11e** (10 mg) and **1e** (184 mg).

Isomerization of **IIe** *by chromatography on silica gel.* Chromatography of **IIe** (280 mg) on silica gel (30 g) with benzene in the manner as described gave **5e** (24 mg) and a semi-crystalline compound **2e** (20 mg), mass spectrum: 229 and 231 (M^+); UV λ_{max} (95% EtOH) 275 and 360 nm. Though recrystallization was unsuccessful for the latter product, similarity of the UV spectrum with those of **2a–2d** indicated the benz[*c*]-2-aza[1,6]oxido[10]annulene structure. Further elution with benzene afforded **3e** (100 mg). Elution with CH_2Cl_2 afforded **1e** (105 mg).

Thermal isomerization of **IIe**.[12] A soln of **IIe** (130 mg) in benzene (50 ml) was refluxed until the orange color of **IIe** faded completely (3 hr). Evaporation of the solvent followed by column chromatography on silica gel afforded **5e** (5 mg), **11e** (5 mg) and **1e** (105 mg).

Treatment of **IIe** *with triphenylphosphine.* To a soln of **IIe** (100 mg, 0.45 mmole) in MeCN (30 ml) was added triphenylphosphine (180 mg, 0.68 mmole) and the mixture was allowed to stand at room temp. for 2 hr. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with hexane–benzene (1:1 v/v) gave triphenylphosphine (70 mg). Elution with $CHCl_3$ afforded **11e** (79 mg), triphenylphosphine oxide (110 mg) and **1e** (10 mg).

Reduction of **IIe** *with LAH.* A soln of **IIe** (100 mg) in ether (20 ml) was added to a suspension of LAH (40 mg) in ether and the whole was stirred at room temp. for 20 hr. Excess LAH was decomposed by adding wet Na_2SO_4 and the mixture was dried with Na_2SO_4. The residue obtained after evaporation of the solvent was chromatographed on alumina. Elution with 5% MeOH–CH_2Cl_2 afforded **12** (23 mg) as an oil, which was converted to the diacetate, m.p. 118–120°. The identity of this product with **13** obtained from **1a** was assubred by mixed m.p.d.

The solvent effects of the thermal isomerization of **IIe** *to* **1e**. A soln of **IIe** (1.2×10^{-4} mole/l.) in MeCN, benzene, or cyclohexane, was heated at 50°. Almost quantitative formation of **1e** was observed in the former two solvents. By visible spectroscopy, the half life of **IIe** in each solvent was determined: 140 min for MeCN and 515 min for benzene. In cyclohexane, **IIe** was stable and no spectral change was observed after 10 hr's heating.

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[11]The glc chromatogram (OV-17 at 220°) of **IId** showed four peaks whose relative retention times were the same with those of **11d**, **3d**, **2d** (and/or **5d**) and **1d** (the compounds **2d** and **5d** showed the same relative retention time).

[12]The glc chromatogram of **IIe** under the same condition as above showed five peaks whose relative retention times were the same with those of **11e**, **2e**, **3e**, **5e** and **1e**.