Medium and Substituent Effects on the Photochemistry of Phenanthridine *N*-Oxides. Is an Intermediate of Diradical Character involved in the Photorearrangement of Heterocyclic *N*-Oxides?

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The photochemistry of several 6-substituted phenanthridine *N*-oxides has been investigated, or reinvestigated, in benzene and ethanol. The main processes observed are: (*a*) 1,2-oxygen and substituent shift to yield *N*-substituted phenanthridones (**2**) and (*b*) ring enlargements to dibenzo[*d*,*f*]-1,3-oxazepines (**7**). With 6-diphenylmethylphenanthridine *N*-oxide (**1b**) rearrangement (*a*) predominates and occurs with 45% substituent loss in benzene (but only 2% in ethanol). With the 6-phenyl derivative (**1c**) process (*a*) predominates in ethanol and process (*b*) in benzene and with the 6-*p*-nitrophenyl derivative (**1d**) the latter process predominates in both solvents. With 6-cyanophenanthridine *N*-oxide (**1e**) rearrangement (*b*) predominates in benzene; in the presence of 2,3-dimethylbutene (but not of cyclohexene) addition products are obtained; with dienes deoxygenation is the main process. Medium and substituents may change the nature of the lowest excited singlet state, but more importantly affect the stability of an intermediate of diradical character occurring along the reaction pathway, thus driving it towards rearrangement (*a*) or (*b*). Intermediate diradicals are unambiguously indicated only in particular cases [elimination of a diphenylmethyl radical from (**1b**), alkene addition in the case of (**1e**)] but their role is probably more general.

The *N*-oxide chromophore (=N→O, nitrogen sp^2 hybridized †) is one of the few with which an efficient photorearrangement is associated.[2] Two cases should be distinguished. When the *N*-oxide chromophore is part of an open-chain system, as in the case of nitrones (>C=N→O), the process observed is accounted for by cyclization to an oxaziridine which either is isolated or is the logical precursor to the observed products. On the other hand, in the case of heterocyclic *N*-oxides a large variety of photoprocesses is observed and a general mechanistic pathway has not been elucidated.

In the case of phenanthridine *N*-oxides, as an example, different photochemical reactions are observed depending on the substituents present and the experimental conditions employed. As for the mechanism, some workers considered that a radical or a carbocation was involved in the photoreaction,[3] while others interpreted it in terms of an electrocyclic rearrangement to an oxaziridine.[4] We later proposed the intermediacy of a diradical.[5] In the case of 6-cyanophenanthridine *N*-oxide, an intermediate was actually detected by low-temperature spectroscopy,[4a] but its identification as the corresponding oxaziridine is not straightforward.[2]

In an effort to obtain deeper insight into the mechanism, we investigated the photochemistry of some phenanthridine *N*-oxides carrying substituents which it was thought might permit the elucidation of the pathway followed. Most substrates studied had been previously considered, but product identification was in some case incomplete and the experimental conditions were not homogeneous. The photochemical reactions were examined both in benzene and in ethanol, as the photochemistry of *N*-oxides is often different in aprotic than in protic media. From the results described below, it will be seen that we can now present a unified, although not yet sufficiently detailed, mechanistic picture of this rearrangement.

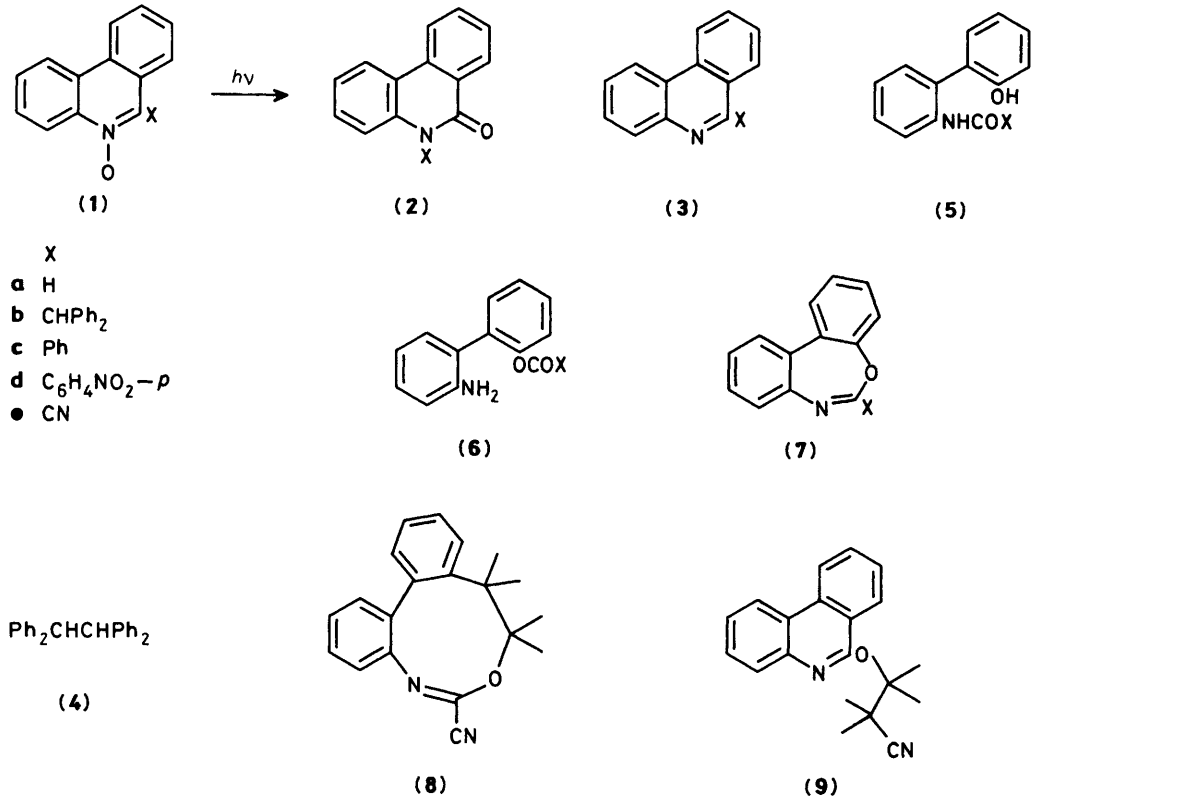
† The photochemistry of amine *N*-oxides (–N→O, nitrogen sp^3 hybridized) essentially involves fragmentations, see ref. 1).

Results

We previously reported that in the case of the parent compound phenanthridine *N*-oxide (**1a**) rearrangement to phenanthridone (**2a**) is the major photoprocess, along with limited deoxygenation to phenanthridine (**3a**) both in protic and aprotic media.[6] Some 6-alkylphenanthridine *N*-oxides have been found to yield the corresponding *N*-alkylphenanthridones,[3,7] as is observed for several other *N*-oxides. However, it has been reported in communication form that 6-diphenylmethylphenanthridine *N*-oxide (**1b**) in benzene yields phenanthridone (**2a**) (17%) with detachment of the substituent and formation of tetraphenylethane (**4**) (16%).[3]

In our hands, irradiation of compound (**1b**) in benzene yielded a complex mixture of products, which was separated by silica gel chromatography (Table 1, Scheme 1). Tetraphenylethane and phenanthridone were obtained in 13 and 29% yield, respectively. The main product, obtained in 37% yield, was identified from its analytic and spectroscopic properties as *N*-diphenylmethylphenanthridone (**2b**), the product expected from the 'normal' migration of the substituent to the nitrogen atom. This compound is not dealkylated either photochemically or during work-up, and thus product (**2a**) is formed through an independent pathway.

Three other products are formed in significant yield, besides the expected phenanthridine (**3b**) (3%). Two of them are shown by elemental analysis to have added one molecule of H_2O. The first of these products is, according to spectroscopy, an amide, the second is a phenolic ester. Both compounds are hydrolysed under suitable conditions to 2-hydroxy-2′-aminobiphenyl. Thus the structures 2′-(2-hydroxyphenyl)diphenylacetanilide (**5b**) and 2-(2-aminophenyl)phenyl diphenylacetate (**6b**) can be assigned. The third compound is obtained in 4% yield, and, when subjected to further chromatography, is partially decomposed to a mixture of products (**5b**) and (**6b**). This decomposition and the spectroscopic properties allow identification of this product as 6-diphenylmethyldibenz[*d*,*f*]-1,3-oxazepine (**7b**), a structure in accord with silica gel-catalysed hydration to products (**5b**) and (**6b**).



(1) (2) (3) (5) (4) (6) (7) (8) (9)

Scheme 1.

Table 1. Products from the irradiation of phenanthridine *N*-oxides (**1a—e**)

Starting material	Solvent	Additive	Products (%)
(**1a**)[a]	Benzene	*b*	(**2a**) (77), (**3a**) (5)
(**1a**)[a]	Ethanol		(**2a**) (70), (**3a**) (3)
(**1b**)	Benzene	*b*	(**2a**) (29), (**2b**) (34), (**3b**) (3), (**4**) (15), (**5b**) (9), (**6b**) (7), (**7b**) (4)
(**1b**)	Ethanol		(**2a**) (2), (**2b**) (95), (**3b**) (2)
(**1c**)	Benzene	*b*	(**2c**) (19), (**3c**) (12), (**5c**) (7), (**7c**) (26)
(**1c**)	Ethanol		(**2c**) (92), (**3c**) (3)
(**1d**)	Benzene	*b*	(**3d**) (15), (**5d**) (14), (**7d**) (30)
(**1d**)	Ethanol		(**3d**) (9), (**5d**) (84)
(**1e**)	Benzene	*c*	(**2a**) (2), (**2e**) (3), (**3e**) (2), (**7e**) (70)
(**1e**)[d]	Benzene	DMB, 0.3M	(**2a**) (11), (**2e**) (3), (**3e**) (18), (**7e**) (trace), (**8**) (35), (**9**) (4)
(**1e**)	Benzene	DMBD, 0.05M[e]	(**2a**) (3), (**2e**) (trace), (**3e**) (32), (**7e**) (28)
(**1e**)	Acetonitrile		(**2e**) (15), (**3e**) (3), (**7e**) (62)
(**1e**)	Acetonitrile	DMB, 0.3M	(**2a**) (3), (**2e**) (16), (**3e**) (5), (**7e**) (trace), (**8**) (20)
(**1e**)	Ethanol	*f*	(**2e**) (3), *N*-ethoxyphenanthridone (55)

[a] From ref. 6. [b] No change, except an increase of some percent in deoxygenation to phenanthridines (**3**) in the presence of 0.3M-DMB. [c] No appreciable change in the presence of 0.3M-cyclohexene. [d] Preliminary communication, ref. 5. [e] Hexa-2,4-diene and cyclohexa-1,3-diene likewise cause an increase in deoxygenation to (**3e**). [f] No appreciable change in the presence of 0.3M-DMB.

Products (**5b**)—(**7b**) are not formed when (**1b**) is irradiated in ethanol, the rearrangement product *N*-diphenylmethylphenanthridone (**2b**) being formed almost exclusively (94%), with minor amounts of dealkylated phenanthridone (**2a**) (2%) and phenanthridine (**3b**) (3%).

For 6-phenylphenanthridine *N*-oxide (**1c**) we confirmed previous reports[3] that the virtually exclusive process in ethanol is rearrangement to the phenanthridone (**2c**), whereas in benzene ring enlargement to the oxazepine (**7c**) is predominant. The latter product is isolated in 26% yield if the mixture is separated by silica gel chromatography, whereas, according to the original communication, it undergoes almost complete hydrolysis when chromatography is carried out on Florisil.

In order to explore the effect of electron-withdrawing substituents we prepared and photolysed 6-(4-nitrophenyl)-phenanthridine *N*-oxide (**1d**). In this case the main product in benzene is the oxazepine (**7d**), accompanied by the amide (**5d**), arising from hydration during work-up and some phenanthridine (**3d**), but no phenanthridone (**2d**). In contrast to the previous case, the phenanthridone is not formed even in ethanol, and compounds (**5d**) and (**7d**) were the main products in that solvent.

Table 2. Absorption spectra of phenanthridines and phenanthridine *N*-oxides

Compound	Solvent	$\lambda_{max.}$/nm (log ε)				Compound	$\lambda_{max.}$/nm (log ε)				
(**3a**)	Benzene	345(3.15)	330(3.15)	300(3.66)	290(3.78)	(**1a**)	380(2.88)	338(4.03)		294(4.15)	282(4.12)
	Ethanol	346(3.33)	331(3.33)	299(3.79)	290(3.85)		367(3.10)	329(4.13)		290(sh,4.07)	
(**3b**)	Benzene	346(3.17)	332(3.26)		293(3.79)	(**1b**)	379(2.87)	340(3.99)		296(4.27)	285(4.25)
	Ethanol	346(3.27)	330(3.33)		290(3.82)		368(3.10)	333(4.05)		285(4.18)	
(**3c**)	Benzene	350(3.36)	334(3.51)		293(4.02)	(**1c**)	384(sh, 3.04)	342(4.01)		298(4.21)	286(4.20)
	Ethanol	350(3.48)	335(3.52)		298(3.92)		366(3.15)	331(4.07)		284(sh, 4.17)	
(**3e**)	Benzene	368(3.18)	350(3.31)	320(3.97)	308(3.98)	(**1e**)	396(3.78)	375(3.86)	357(4.01)	306(4.09)	293(4.13)
	Ethanol	368(3.24)	350(3.34)	320(3.99)	309(3.97)		394(3.61)	373(3.75)	355(3.99)	298(3.94)	287(4.01)

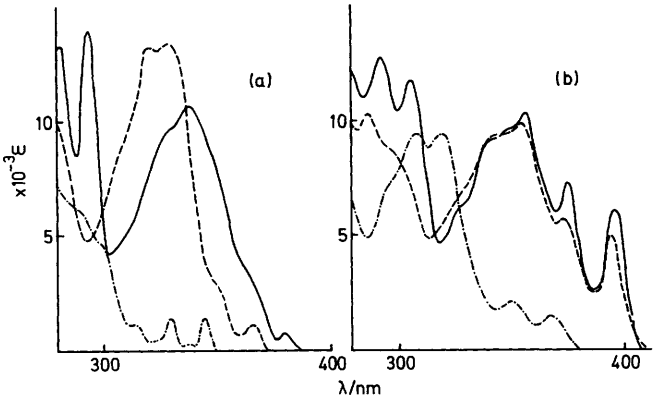


Figure. (a) Absorption spectrum of phenanthridine *N*-oxide in benzene (———) and in ethanol (– – – –) and of phenanthridine in benzene (—·—·—); (b) Absorption spectrum of 6-cyanophenanthridine *N*-oxide in benzene (———) and in ethanol (– – – –) and of 6-cyanophenanthridine in benzene (–·–·–)

From 6-cyanophenanthridine *N*-oxide (**1e**), the main product in benzene is the oxazepine (**7e**) accompanied by minor amounts of *N*-cyanophenanthridone (**2e**) and the phenanthridine (**3e**).[8] In a previous communication we reported that in the presence of 2,3-dimethylbut-2-ene (DMB) the yield of (**7e**) is much reduced, that of (**3e**) enhanced, and two trapping products, the oxazonine (**8**) and the phenanthridyl ether (**9**) are obtained.[5] In order to explore the scope of this reaction, we irradiated this *N*-oxide in the presence of less substituted alkenes, *viz.* cyclohexene and *trans*-but-2-ene and of dienes, *viz.* 2,3-dimethylbuta-1,3-diene (DMBD), hexa-2,4-diene and cyclohexa-1,3-diene. The alkenes (0.3M) hardly affect the photorearrangement of (**1e**). With the dienes, deoxygenation becomes the main process, but no trapping product is obtained.

In view of the results for (**1e**), the *N*-oxides (**1a**—**d**) were irradiated in benzene containing 0.3M-DMB. In no case was a significant change in product distribution observed, except for a small enhancement of the deoxygenation process.

Discussion

A consistent picture of the photochemical reactivity of phenanthridine *N*-oxides is now available. Two main pathways are observed: (*a*) rearrangement to a phenanthridone with a shift of the substituent to the nitrogen in position 6 and (*b*) ring enlargement to a dibenzoxazepine. Process (*a*) takes place with partial substituent loss in the case of *N*-oxides (**1b** and **e**).

The relative importance of processes (*a*) and (*b*) is greatly influenced by the substituent present, as well as by the nature of the solvent, and, in some cases, of an additive.

It is first necessary to relate the change in the chemistry either to a change in the characteristics of the lowest excited state or to an effect on the reactivity of an intermediate, the nature of which remains to be defined. It can be assumed that the reaction involves an excited singlet rather than a triplet state. In no case is the photodecomposition of these phenanthridine *N*-oxides influenced by dissolved oxygen and sensitization experiments using Michler's ketone [with (**1a** or **e**) as substrate] were unsuccessful. In this respect, these substrates are no different from other *N*-oxides, which generally rearrange through the singlet state. However, it is possible that substituents have an effect on the orbital distribution of the lowest (and reactive) excited singlet, and an indication is given by the absorption spectrum (none of these *N*-oxides fluoresces at room temperature).

The absorption spectrum of phenanthridine (**3a**) and its alkyl derivatives is not dissimilar from that of phenanthrene (the lowest excited singlet is an L_b state with low transition probability) and shows negligible solvatochromy. *N*-Oxidation introduces a new low-energy band, which undergoes a *ca.* 10 nm blue shift in protic solvents (Figure (a), Table 2). On the other hand, the spectrum of 6-cyanophenanthridine (**3e**) shows more intense low-energy transitions and the corresponding *N*-oxide (**1e**) shows little difference from (**3e**) and minimal solvatochromy. For the phenyl-substituted *N*-oxides (**1c** and **d**), the spectrum and solvatochromy are intermediate between those of the two previously discussed derivatives. Thus, in the case of *N*-oxide (**1a**) and alkyl derivatives [*e.g.* (**1b**)] the lowest singlet is an $n_0 \longrightarrow \pi$ state, or at any rate involves substantial charge transfer from the oxygen atom to the heterocyclic nucleus, whereas charge transfer is less significant with phenyl or cyano derivatives. Thus, one might expect some difference in the photochemistry, since the nature of the lowest singlet is different.

A classification of the observed photoprocesses indeed shows a similar dichotomy in that rearrangement to lactams is predominant or exclusive with (**1a** and **b**) and ring enlargement predominates with (**1c** and **e**), at least in benzene. The hypothesis that the $n\pi^*$ state is responsible for the first process and the $\pi\pi^*$ state for the second, however, does not fit with the observed effect of the solvent on the photochemistry. In the case of (**1c**), for example, ring enlargement is the main process in aprotic medium, but lactam formation is virtually exclusive in ethanol,† whereas protic solvents are expected to destabilize $n\pi^*$ states, and thus should have the opposite effect according to the hypothesis above.

Moreover, in the rearrangement to the lactam there is a solvent effect. In the case of compound (**1b**), changing from benzene to ethanol not only increases lactam formation *vs.* ring enlargement (from 62 to 98% of the observed products), but, within the former group, also reduces loss of diphenylmethyl

† Lactam formation also increases in the case of (**1b**), whereas with (**1e**) the reaction changes in alcohols, but not towards lactam formation (*N*-alkoxyphenanthridones are formed, see ref. 8).

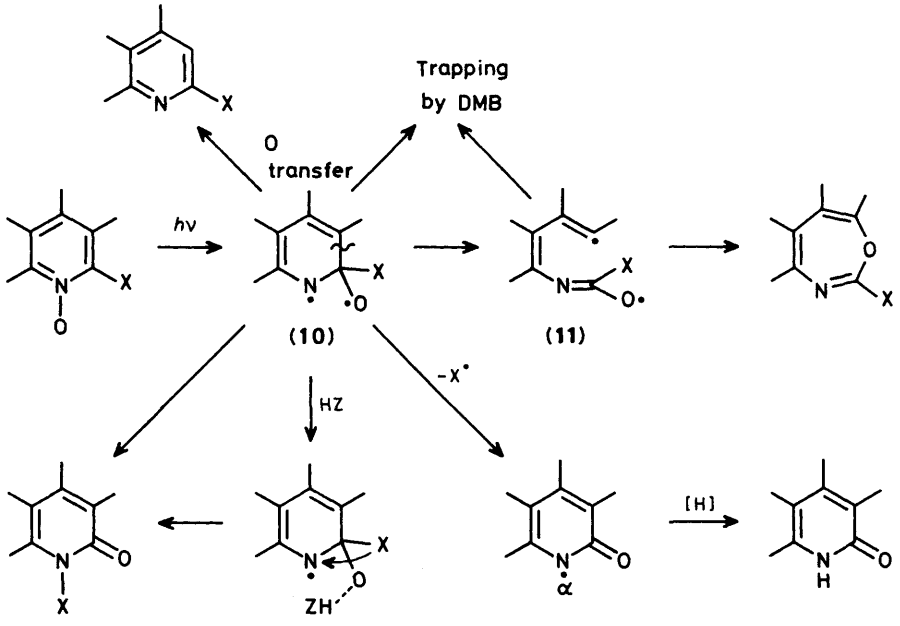
radical: in benzene dealkylated (**2a**) is 45% of total phenanthridone [(**2a**) + (**2b**)], whereas in ethanol it amounts to only 2%. Thus shift of the oxygen to the α-carbon and shift of the substituent to the nitrogen atom appear to take place simultaneously when the oxygen is involved in hydrogen bonding with the solvent, and through a distinct intermediate of diradical character, in aprotic medium. This intermediate is prone to homolytic fragmentation.

As for the *N*-oxides rearranging mainly to oxazepines, *viz.* compounds (**1c**—**e**), in these cases there is no group which could be cleaved as a radical, and conjugating substituents at position 6 'localize' the nitrogen–α–carbon bond so that oxygen rather shifts to the β position, inserting between C_α and C_β and conserving the N=C_α double bond. The *N*-oxide (**1e**) enjoys maximum stabilization as the cyano group lies in the molecular plane [whereas phenyl groups present in compounds (**1c** and **d**) are tilted out of plane] and in this case two different diradical intermediates which occur along the pathway towards the 1,3-oxazepine [see (**10**) and (**11**) in Scheme 2] are also stabilized and trapped by alkenes, yielding products (**8**) and (**9**).

the substituent X at the α position. When conjugation with the substituent is possible, the system N=C<X remains planar during the rearrangement and the oxygen atom 'pivots' over the α-carbon, becoming attached to the α- and β- carbons and yielding a 1,3-oxazepine [process (*b*)]. Otherwise simultaneous 1,2-shifts of the oxygen atom and the substituent take place to yield an *N*-substituted phenanthridone [process (*a*)]. Discrete states of diradical character [(**10**) and (**11**) in Scheme 2] appear to be involved in both processes (*a*) and (*b*), as shown by successful trapping experiments in the case of X = CN, a reaction due to the stabilization of the diradical by the substituent, and by the radical cleavage of the substituent in the case of X = diphenylmethyl.

Hydrogen bonding with the oxygen atom in protic solvents hinders development of the diradical character, thus preventing cleavage of substituent X and in general favouring migration of this group to the nitrogen atom *versus* cleavage of the C_α–C_β bond and thus lactam *versus* oxazepine formation.

Substituents gradually change the reactivity of the intermediate diradical (stabilizaton by coplanar CN > twisted



Scheme 2.

A third indication of the intermediacy of a diradical in the photorearrangement is given by the characteristics of de-oxygenation. Deoxygenation is often observed as a minor pathway in the photochemistry of *N*-oxides and various hypotheses have been formulated about the mechanism (that 'active' oxygen is liberated, that an oxidizing intermediate is formed during rearrangement, that electron transfer is the first step[9]). In the case of phenanthridine *N*-oxides, oxygen transfer to the solvent is minimal for the parent compound and alkyl derivatives (*ca.* 3%) but increases up to 10—15% for those phenanthridine *N*-oxides which mainly rearrange to oxazepines and becomes a major pathway both when transfer to a π acceptor and when hydrogen abstraction are possible [*e.g.* with (**1e**), 32% deoxygenation with 0.05M-dienes, and substantial deoxygenation in neat 2-methyltetrahydrofuran[4a]]. These two reactions can be reasonably attributed to an electrophilic radical, *e.g.* an oxygen-centred radical, in the present case intermediate (**10**).

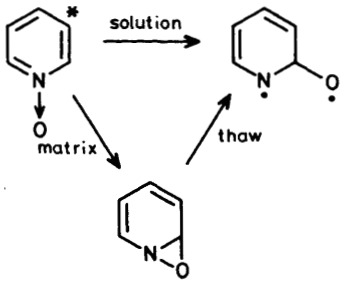
In conclusion, two pathways are open to the excited state of phenanthridine *N*-oxides, and the reaction observed depends on

p-$NO_2C_6H_4$ > C_6H_5; this order decreases the oxazepine yield) rather than reversing the order of different excited states, and the changes in the absorption spectra discussed above are rather parallel to than the cause of the change in photochemistry.

It is interesting to notice the intermediacy of diradicals had already been proposed in earlier studies on compounds (**1b**)[3] and (**1e**),[8] although these had been considered as secondary products from oxaziridines.

However, we measured the quantum yield for reaction for *N*-oxides (**1a** and **e**) and found that this is not affected when the absorbed flux is diminished by a factor of ten. Therefore the hypothesis that an oxaziridine is the primary photoproduct and a second photochemical step leads to a radical does not hold at least at room temperature. It is possible that the structure of an oxaziridine can be assigned to the primary product observed by Tokumura *et al.* in rigid medium at 77 K.[4a] It should be observed, however, that the photoreaction of (**1e**) in glass is extremely slow (quantum yield two orders of magnitude lower than at room temperature), and thus comparison between the inefficient photoreaction in glass and the efficient reaction in

fluid solution can be misleading. Furthermore, the chemistry observed for this intermediate when the glass thaws (*e.g.* deoxygenation, reasonably through hydrogen abstraction, in 2-methyltetrahydrofuran, m.p. −137 °C) is not really that expected from an oxaziridine, possibly indicating that the three-membered ring undergoes spontaneous homolytic splitting to a diradical in fluid solution, even at low temperature. It appears reasonable to postulate that, at least at room temperature, the first minimum, if there is any, along the reaction pathway corresponds to a diradical, rather than to an oxaziridine (Scheme 3).



Scheme 3.

This mechanism fits with what is generally known about *N*-oxide photochemistry. Thus, the importance of the planarity of the –N=C<X structure is confirmed by a great number of examples showing without exception that conjugation with a substituent at the α-position favours the rearrangement to the oxazepine,[2] and there are sparse hints of the intermediacy of a diradical, *e.g.* the radical cleavage of the substituent observed in the case of 1-neopentyl- and 1-benzyl-isoquinoline *N*-oxide[10] and furthermore the observed effect of a magnetic field on the photorearrangement of some *N*-oxides.[11,12]*

In conclusion, Scheme 2 offers a reasonable, although rough, picture of the photorearrangement of phenanthridines, and in general of heterocyclic *N*-oxides. Of course, it would be desirable to have more precise indications about the potential surface and the diradical states encountered along the pathway. Theoretical work would clearly be beneficial to this aim.

Experimental

Synthesis and Purification of the Phenanthridine N-*Oxides*.—Compounds (**1a**),[14] (**1b**),[15] m.p. 101—102 °C (from methanol), (**1c**),[16] and (**1e**)[17] were prepared according to published procedures and purified by crystallization. Compound (**1d**), light yellow needles (from nitroethane), m.p. 241—243 °C, was obtained in 89% yield from the oxidation of (**3d**)[18] (1 g) in acetic acid (3 ml) and 40% H_2O_2 (0.5 ml) for 2 h at 50 °C, then adding a further 0.5 ml and heating 2 h more.

Physical Data.—U.v. spectra were recorded with a Cary 19 spectrophotometer, i.r. spectra for KBr pellets by means of a Perkin-Elmer 197 spectrophotometer, ^{1}H n.m.r. spectra in $CDCl_3$ by means of a Bruker 80 instrument with tetramethylsilane as internal standard, mass spectra by means of a Du Pont DU2 instrument, and elemental analyses by means of a Carlo Erba 1106 analyser. M.p.s are uncorrected.

Photochemical Reaction of 6-*Diphenylmethylphenanthridine* N-*Oxide* (**1b**) *in Benzene*.—A solution of (**1b**) (200 mg) in benzene (200 ml) was irradiated at 17 °C by means of a Helios Italquartz 125 W medium-pressure arc through a Pyrex filter until the starting material had disappeared (t.l.c.). Evaporation of the solvent and chromatography on silica gel eluting first with cyclohexane–ethyl acetate and then with chloroform yielded the following products (in order of elution): 1,1,2,2-tetraphenylethane (**4**) (12 mg, 13%); 6-diphenylmethylphenanthridine (**3b**) (6 mg, 3%); *N*-diphenylmethylphenanthridone (**2b**) (74 mg, 37%), light yellow needles, m.p. 168—170 °C (from cyclohexane) (Found: C; 86.45; H, 5.4; N, 3.8. Calc. for $C_{26}H_{19}NO$: C, 86.4, H, 5.3, N, 3.9%) δ_H 7—7.8 (m, 14 H), 7.85 (dd, 1 H, *J* 8, 1.5 Hz), 8.1—8.4 (m, 3 H), and 8.6 (dd, 1 H, *J* 8, 1.5 Hz); $\nu_{max.}$ 1 638, 1 607, 1 582, 745, and 709 cm^{-1}; 6-diphenylmethyldibenz[*d*,*f*]-1,3-oxazepine (**7b**) (8 mg, 4%), light yellow needles, m.p. 103—105 °C (from cyclohexane); δ_H 7.4—7.7 (m, 11 H) and 7.8—8 (m, 8 H); $\nu_{max.}$ 1 648, 1 598, 1 576, 1 317, 1 278, and 700 cm^{-1}; 2-(2-aminophenyl)phenyl diphenylacetate (**6b**) (15 mg, 7%), needles from benzene, m.p. 190—191 °C (Found: C, 82.1; H, 5.4; N, 3.6. Calc. for $C_{26}H_{21}NO_2$: C, 82.3; H, 5.6; N, 3.7%); δ_H 5 (s, 1 H), 7—7.8 (m, 18 H), and 7.95 (s, br, 2 H); $\nu_{max.}$ 3 240, 3 170, 1 762, 1 190, 738, and 710 cm^{-1}; 2′-(2-hydroxyphenyl)diphenylacetanilide, crystals from benzene, m.p. 109—111 °C (Found: C, 82.1; H, 5.4; N, 3.5. Calc. for $C_{26}H_{21}NO_2$: C, 82.3; H, 5.6; N, 3.7%); δ_H 5 (s, 1 H), 6.7—7.6 (m, 19 H), and 8.25 (dd, 1 H, *J* 8, 1 Hz); $\nu_{max.}$ 3 300br, 1 650, 1 595, 1 580, 1 212, 750, and 698 cm^{-1}; phenanthridone (**2a**) (31.5 mg, 29%).

Photochemical Reaction of 6-*Phenylphenanthridine* N-*Oxide* (**1c**) *in Benzene*.—Irradiation of (**1c**) (200 mg) in benzene (200 ml) and work-up as above yielded the following products: 6-phenyldibenz[*d*,*f*]-1,3-oxazepine (**7c**) (52 mg, 26%), light yellow needles from cyclohexane, m.p. 73—75 °C (Found: C, 84.2; H, 4.9; N, 5.05. Calc. for $C_{19}H_{13}NO$: C, 84.1; H, 4.8; N, 5.15%); δ_H 7.1—7.65 (m, 11 H), 8.25 (d, 1 H, *J* 8 Hz), and 8.3 (d, 1 H, *J* 7 Hz); $\nu_{max.}$ 1 642, 1 595, 1 580, 1 230, 1 205, 1 190, 1 172, 1 018, 760, 710, and 690 cm^{-1}; 6-phenylphenanthridine (**3c**) (22.5 mg, 12%); *N*-phenylphenanthridone[19] (**2c**) (38 mg, 19%); 2-(2-hydroxyphenyl)-*N*-benzoylaniline (**5c**) (15 mg, 7%), needles from benzene, m.p. 228—229 °C (Found: C, 78.65; H, 5.1; N, 10.9. Calc. for $C_{19}H_{15}NO_2$: C, 78.9; H, 5.2; N, 4.8%); δ_H 6.9—7.7 (m, 12 H), 8 (br, 1 H), and 8.55 (dd, 1 H); $\nu_{max.}$ 3 310, 3 140, 1 638, 1 527, 770, 750, 728, 710, and 690 cm^{-1}.

Photochemical Reaction of 6-(p-*Nitrophenyl*)*phenanthridine* N-*Oxide* (**1d**) *in Benzene*.—Irradiation of (**1d**) (200 mg) in benzene (200 ml) and work-up as above yielded the following products: 6-(*p*-nitrophenyl)dibenz[*d*,*f*]-1,3-oxazepine (**7d**), (60 mg, 30%), light yellow needles from cyclohexane, m.p. 157—158 °C (Found: C, 72.3; H, 4.0; N, 8.6. Calc. for $C_{19}H_{12}N_2O_3$: C, 72.1; H, 3.8; N, 8.9%); δ_H 7.2—7.75 (m, 8 H) and 8.2—8.6 (AA′BB′ system); $\nu_{max.}$ 1 655, 1 605, 1 597, 1 350, and 760 cm^{-1}; 6-(*p*-nitrophenyl)phenanthridine (**3d**) (28.5 mg, 15%); 2-(2-Hydroxyphenyl)-*N*-(*p*-nitrobenzoyl)aniline (**5d**) (29.5 mg, 14%), needles from benzene, m.p. 251—252 °C (Found: C, 68.0; H, 4.0; N; 8.1. Calc. for $C_{19}H_{14}N_2O_4$: C, 68.25; H, 4.2; N, 8.4%); δ_H 6.55 (dd, 1 H, *J* 5.5, 3.5 Hz) and 8.3—8.6 (AA′BB′ system + O–H); $\nu_{max.}$ 1 655, 1 605, 1 585, 1 340, and 745 cm^{-1}.

Photochemical Reaction of 6-*Cyanophenanthridine* N-*Oxide* (**1e**) *in Benzene containing* 0.33M-2,3-*Dimethylbutene*.—Irradiation of (**1e**) (200 mg) in benzene (200 ml) and work-up as above yielded the following products: 6-cyanodibenzo[*d*,*f*]-1,3-oxazepine (**7e**), traces;[8] 5,6-dihydro-5,5,6,6-tetramethyl-8-cyanodibenz[*d*,*f*]-1,3-oxazonine (**8**) (89.7 mg, 35%), needles from cyclohexane, m.p. 155—156 °C (Found: C, 78.8; H, 6, 5; N, 9.1. Calc. for $C_{20}H_{20}N_2O$: C, 78.9; H, 6.6; N, 9.2%) δ_H 1.05 (s, 3 H), 1.35 (s, 6 H), 1.65 (s, 3 H), and 6.8—7.6 (m, 8 H); $\nu_{max.}$ 2 220vw, 1 620, 1 250, 1 120, and 760 cm^{-1} (the structure of this product was ascertained by means of a single-crystal *X*-ray analysis,[20]); 6-

* On the other hand no evidence for oxaziridine intermediates has been found despite systematic examination, see ref. 13.

cyanophenanthridine (**3e**) (33.5 mg, 18%); 6-(2-cyano-1,1,2-trimethylpropoxy)phenanthridine (**9**) (11 mg, 4%), needles from hexane, m.p. 118—120 °C (Found: C, 79.0; H, 6.65; N, 9. Calc. for $C_{20}H_{20}N_2O$: C 78.9; H, 6.6; N, 9.2%); δ_H 1.6 (s, 6 H), 2.05 (s, 6 H), 7.5—7.9 (m, 5 H), and 8.4—8.7 (m, 3 H); $\nu_{max.}$ 2 225, 1 610, 1 583, 1 142, 1 128, 760, and 723 cm^{-1} [this compound refluxed in ethanol in the presence of a trace of hydrochloric acid is quantitatively converted into phenanthridone (**2a**)]; *N*-cyanophenanthridone (**2e**), (6 mg, 3%),[8] phenanthridone (**2a**), (19.5 mg, 11%).

Other Photochemical Reactions.—Other photochemical reactions were carried out similarly to the above example, under the conditions and with the results reported in Table 1.

Quantum Yield Measurements.—Quantum yields of photodecomposition at 366 nm were measured for 5×10^{-4} or 10^{-4}M solutions of the *N*-oxides in 1 cm optical path cuvettes on an optical bench. Light from a Osram 200W high-pressure mercury arc was focused and monochromatized by means of an interference filter. Light intensity was measured by ferrioxalate actinometry. An absorbed flux of *ca.* 10^{-7} einstein min^{-1} cm^{-2} was obtained. This could be reduced by means of neutral filters.

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