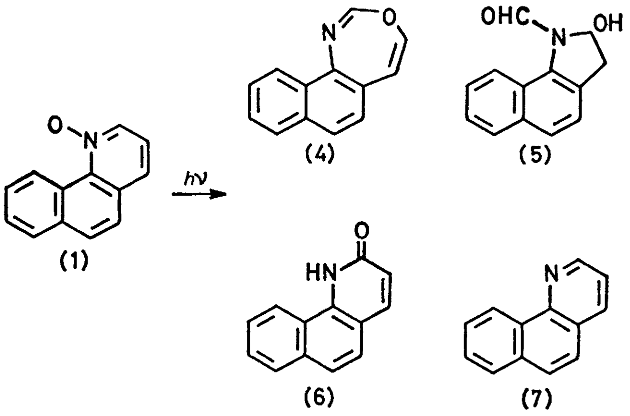
Photochemistry of Some Azaphenanthrene *N*-Oxides

By **Angelo Albini,* Gian Franco Bettinetti,** and **Giovanna Minoli,** Istituto di Chimica Organica dell'Università, Viale Taramelli 10, 27100 Pavia, Italy

1- and 4-Azaphenanthrene *N*-oxides undergo solvent-dependent photoisomerization, yielding naphtho-1,3-oxazepines in aprotic solvents and benzoquinolin-1(2*H*)-ones in water. No ring enlargement but only isomerization to the corresponding lactam is observed to take place in the case of 9-azaphenanthrene *N*-oxide. Measurements of the quantum yield of two photoprocesses (lactam formation and ring enlargement) confirm the difference between the photochemical behaviour of 9- azaphenanthrene *N*-oxide and that of the other two *N*-oxides examined

THE photochemistry and photophysics of heteroaromatic *N*-oxides depends *inter alia* on the number of condensed aromatic nuclei in the molecule.[1] As this increases, the electronic spectra of the heteroaromatic *N*-oxides become less different from those of their carbocyclic analogues and their excited states increasingly acquire π–π* character. Lower quantum yields of reaction and higher quantum yields of fluorescence are observed for phenazine 5-oxide and its derivatives than, *e.g.*, for the series of quinoline 1-oxides.[2] Moreover, the photochemical processes observed in the acridine and phenazine 5-oxide series are in part different from those characteristic of mononuclear and binuclear heteroaromatic *N*-oxides.[2,3]



SCHEME 1

Because of our interest in the photochemistry of heteroaromatic *N*-oxides, it thus seemed worthwhile to turn our attention to the azaphenanthrene *N*-oxides. The only results previously reported concerned the photochemistry of 9-azaphenanthrene *N*-oxide in alcohols.[4] The results obtained for 4-aza- (1), 1-aza- (2), and 9-aza-phenanthrene *N*-oxide (3) are reported here.

The absorption spectra of the three *N*-oxides studied are very similar, and their shape is similar to the spectrum of phenanthrene itself; all three spectra undergo a blue shift in going from aprotic to protic solvents, as is characteristic of heteroaromatic *N*-oxides [$\lambda_{max.}$ 390 nm in cyclohexane and 371 nm in water for compound (1); the corresponding values for compounds (2) and (3) are 388 and 363 nm and 385 and 366 nm, respectively]. Therefore, it would appear that the singlet excited states of these compounds are of similar character (π–π*).

As protic solvents are known to have a strong effect on the photochemistry of heteroaromatic *N*-oxides,[1] the photochemistry of compounds (1)—(3) was investigated for two extreme sets of conditions, *i.e.* in anhydrous hydrocarbons (cyclohexane and benzene) and in water.

The irradiation of compound (1) in cyclohexane followed by removal of the solvent and extraction of the residue with a little cyclohexane gave an almost colourless oil as the main product. The appearance of a strong absorption at 1 668 cm^{-1} in the i.r. spectrum, and of olefinic signals in the n.m.r. spectrum, beside the characteristic losses of CO and HCN from the molecular ion in the mass spectrum [5] and the persistence of the low-field n.m.r. signal due to 10-H, supported the attribution of the structure naphtho[1,2-*d*][1,3]oxazepine (4) to this compound.

Compound (4), as well as other 1,3-oxazepines not bearing a stabilizing phenyl or cyano group in position 2, is very sensitive to moisture and silica gel. If the residue from the irradiation was directly chromatographed on silica gel, no trace of compound (4) was obtained but only its degradation products. The main product among them was 2-hydroxy-2,3-dihydro-1*H*-benz[*g*]indole-1-carbaldehyde (5), a hydration product, the structure of which was established on the basis of analysis and a comparison of its spectroscopic properties with those of known 2-hydroxyindoline-1-carbaldehydes.[1]

TABLE 1

Yield (%) of photoproducts

Substrate	Solvent	Treatment	Products
(1)	Cyclohexane	*c*	(4) 50 [a]
(1)	Cyclohexane	*d*	(5) 23, (6) 14
(1)	Water	*d*	(6) 58, (7) 7
(2)	Cyclohexane	*c*	(8) 70 [a]
(2)	Cyclohexane	*d*	(9) 66, (11) 9
(2)	Water	*d*	(9) 4, (10) 74, (11) 3
(3)	Benzene [b]	*d*	(12) 77, (13) 5
(3)	Water	*d*	(12) 70, (13) 3

[a] Yield determined spectroscopically (see Experimental section). [b] The same results were obtained in cyclohexane. [c] Extraction. [d] Chromatography.

The irradiation of compound (2) under the same conditions, followed by extraction of the residue yielded naphtho[2,1-*d*][1,3]oxazepine (8) as a pale yellow solid.

The u.v., i.r., and n.m.r. spectra of the two naphtho-1,3-oxazepines are very similar, as may be expected from their structures. In this case also, the 1,3-oxazepine is sensitive to silica gel and chromatography of the irradiation mixture afforded as the main product 2-hydroxy-2,3-dihydro-1*H*-benz[*e*]indole-3-carbaldehyde (9), which arises from hydrolysis of the primary product, as confirmed by chromatography of the pure 1,3-oxazepine.

TABLE 2

Relevant spectroscopic characteristics of the photoproducts

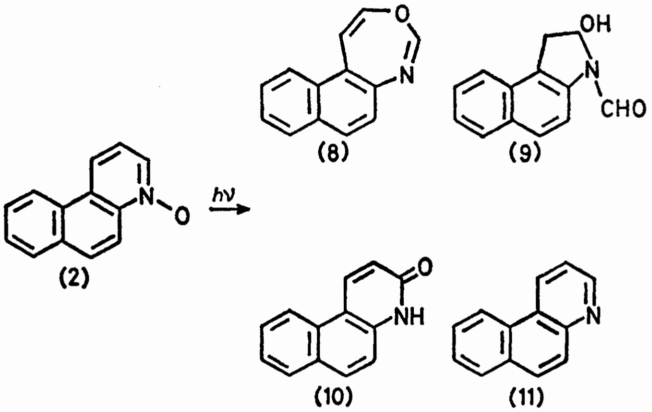
	N.m.r. (δ)				I.r.[a]
	H-1	H-2	H-4 H-5	H-10	($\nu_{max.}$/cm^{-1})
(4) [b]		6.85 (s)	(4) 6.05 (s)	8.4 (dd)	1 668s
(8) [c]	6.2 (d, *J* 6 Hz)	6.6 (d)	(5) 6.7 (s)		1 665s
	H-2	CH_2		CHO	
(5) [b]	6.4 (dd, *J* 2, 6.5 Hz)	3.55 (dd), 3 (dd) (*J* 6.5, 17 Hz)		9.45 (s)	3 240br, 1 640m, 1 670s
(9) [d]	6.1 (dd, *J* 1.5, 6 Hz)	3.4—3.7 (m)		8.9 (s)	3 300br, 1 650s

[a] I.r. of the neat liquid, or in Nujol mull when solid. [b] N.m.r. in $CDCl_3$. [c] N.m.r. in CCl_4. [d] N.m.r. in $(CD_3)_2SO$.

The photochemistry of both (1) and (2) undergoes a complete change when they are irradiated in water. In this solvent benzo[*h*]quinolin-1(2*H*)-one (6) and benzo[*f*]quinolin-1(2*H*)-one (10) were obtained as main products from the *N*-oxides (1) and (2), respectively. These were identical to authentic samples.[6]

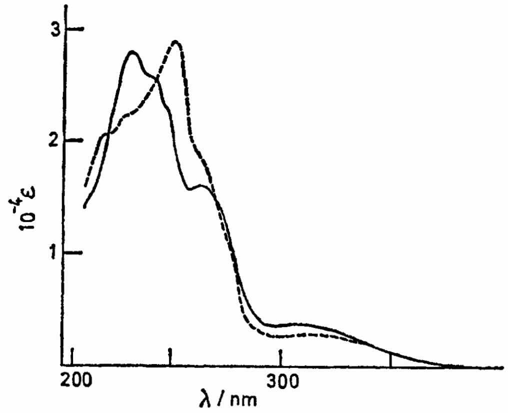
Deoxygenation to give the corresponding azines (7) and (11) is a minor process for both (1) and (2) in aprotic as well as in protic solvents.

As opposed to (1) and (2), the irradiation of 9-azaphenanthrene *N*-oxide (3) in aprotic medium (benzene and cyclohexane) did not yield the expected dibenzo-1,3-oxazepine. Phenanthridone (12) was obtained as the main product, together with a minor amount of the deoxygenation product (13). The same products in about the same yields were obtained on irradiation in water. Similar results were previously obtained in alcohol solvents.[4]

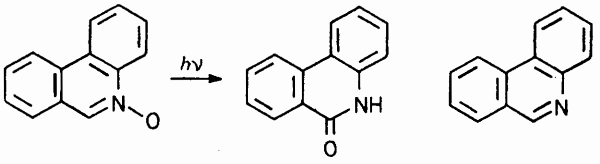


SCHEME 2

The above results show a remarkable difference in the photochemistry of the *N*-oxides (1) and (2) on one hand and (3) on the other. The photochemistry of compounds (1) and (2) resembles that of quinoline 1-oxide. Ring enlargement is the dominant process in aprotic media, while isomerization to the corresponding lactam becomes predominant in water. The two naphtho-1,3-oxazepines formed in aprotic solvents are less unstable than 3,1-benzoxazepine; however, they are strongly moisture sensitive and are decomposed upon silica gel chromatography, yielding the corresponding hydroxybenzoindoline carbaldehydes, as found for 3,1-benzoxazepine.



Absorption spectrum in cyclohexane of the naphtho-oxazepines (4) (——) and (8) (— — —)



(3) (12) (13)

SCHEME 3

As opposed to compounds (1) and (2), the *N*-oxide (3) is photoisomerized to the corresponding lactam both in protic and aprotic media. This contrasts with the photochemical behaviour of most heteroaromatic *N*-oxides, and is similar to that found for nitrones, which are invariably isomerized to the corresponding lactams through an oxaziridine.

TABLE 3

Quantum yield of the photoreactions

		Quantum yield		
N-Oxide	Solvent	*N*-oxide disappearance	Lactam formation	Ring enlargement
(1)	Cyclohexane	0.33	0.045	0.165
(1)	Water	0.16	0.095	0.065
(2)	Cyclohexane	0.22	<0.001	0.15
(2)	Water	0.03	0.025	<0.001
(3)	Cyclohexane	0.54	0.42	
(3)	Water	0.23	0.16	

It was of interest to establish whether this difference is also reflected in a difference in the quantum yield of these reactions. In fact, the data on lactam formation and on the ring enlargement process (see Table 3) confirm the similarity of the behaviour of (1) and (2) with that of quinoline 1-oxide, as the quantum yield of the ring enlargement process for compounds (1) and (2) is close to that measured for the analogous process from quinoline 1-oxide, and the quantum yield of the isomerization to the lactam similarly increases in going from aprotic to protic solvents.

On the other hand, the quantum yield of the isomerization to the lactam from compound (3) is higher than is commonly observed for heteroaromatic *N*-oxides and decreases in protic solvents. Both these characteristics are found in nitrones.[7]

TABLE 4

Analytical data for new compounds [a]

Product	M.p. (°C)	(solvent)	Found (%) C	H	N	Formula	Calculated (%) C	H	N
(5)	125—127	(benzene)	73.2	5.5	6.5	$C_{13}H_{11}NO_2$	73.2	5.6	6.6
(8)	82—84	(light petroleum)	80.1	5.1	7.3	$C_{13}H_9NO$	80.0	4.7	7.2
(9)	192—194	(benzene–cyclohexane)	73.1	5.4	6.3	$C_{13}H_{11}NO_2$	73.2	5.6	6.6

[a] The formula of product (4) was determined mass spectrometrically.

Thus, despite the similarity of the absorption spectra, the singlet excited state of the heteroaromatic *N*-oxides (1) and (2) on one hand and (3) on the other exhibit different chemical reactivity. It would appear that compound (3) behaves as if the excitation energy were confined to the 'nitrone' chromophore, while the increase on conjugation seems not to affect the photochemical reactivity of (1) and (2), which substantially remains that of quinoline 1-oxide.

EXPERIMENTAL

General.—U.v. spectra were recorded on a Perkin-Elmer 200 spectrophotometer, i.r. spectra on a Perkin-Elmer 257 spectrometer, n.m.r. spectra on a Perkin-Elmer R-12 instrument, and mass spectra on a Du Pont 492 B instrument.

The *N*-oxides (1)—(3) were prepared according to the literature methods [6,8] and purified by crystallization to constant m.p. Solvents were distilled before use (cyclohexane and benzene over sodium).

Preparative Irradiations.—Solutions ($1—3 \times 10^{-3}$M) of the *N*-oxides (1)—(3) were irradiated by means of a medium pressure mercury lamp (Hanau TQ 150 W) at 16 °C after purging with nitrogen. The progress of the reaction was followed by t.l.c. and the irradiation was pursued until conversion of the most of the *N*-oxide had taken place. The photolysed solution was then evaporated under reduced pressure and the residue treated as follows. For irradiations in cyclohexane or benzene, the residue was extracted with a little cyclohexane and the unstable naphtho-1,3-oxazepines which were thus obtained were recrystallized or otherwise purified. The yield obtained was spectroscopically estimated by the method described in ref. 9. In separate experiments the residue was chromatographed on silica gel. For the reaction in water, the quinolinones which in part crystallized out during the reaction were filtered off. The solution was extracted with chloroform and the extracts were combined with the precipitate and chromatographed on silica gel. The identification of the new products was based on analytical (Table 4) and spectroscopic data (Table 2).

Measurements.—The quantum yields of the photoreactions were determined at 313 nm by irradiating dilute solutions contained in spectrophotometric 1 cm cells with a super high pressure mercury lamp (Osram 200 W/4, Schott Pil interference filter). Potassium ferrioxalate was used as actinometer. The disappearance of the *N*-oxides (1)—(3) was followed by u.v. spectroscopy at the appropriate wavelength. The reactions were quenched at *ca.* 10% conversion. The product quantum yield was calculated from the quantum yield of disappearance of the *N*-oxides and the product yield in low conversion runs. Low and high conversion runs showed little difference in the product distribution.

This work was supported in part by the C.N.R., Rome, and by the Alexander-von-Humboldt Stiftung, Bonn.

[9/1555 *Received*, 1*st October*, 1979]

REFERENCES

[1] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231; F. Bellamy and J. Streith, *Heterocycles*, 1976, **4**, 1391.

[2] A. Albini, A. Barinotti, G. F. Bettinetti, and S. Pietra, *J.C.S. Perkin II*, 1977, 238.

[3] S. Yamada, M. Ishikawa, and C. Kaneko, *Tetrahedron Letters*, 1972, 971.

[4] M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *Chem. and Pharm. Bull. (Japan)*, 1966, **14**, 1102; E. C. Taylor, B. Furth, and M. Pfau, *J. Amer. Chem. Soc.*, 1965, **87**, 1400.

[5] L. Simonotti, G. Facchetti, G. F. Bettinetti, and A. Albini, *Gazzetta*, 1976, **106**, 49.

[6] M. Colonna and G. Fatutta, *Gazzetta*, 1953, **83**, 622.

[7] K. Koyano, H. Suzuki, Y. Mori, and I. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 3582.

[8] E. Hayashi and Y. Hotta, *J. Pharm. Soc. Japan*, 1960, **80**, 834.

[9] A. Albini, R. Colombi, and G. Minoli, *J.C.S. Perkin I*, 1978, 924.