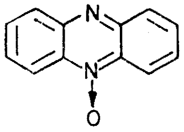
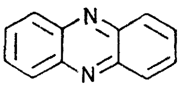
Solvent Effects in the Photoisomerization of Phenazine 5-Oxide

By **Angelo Albini, Gian Franco Bettinetti,** and **Silvio Pietra,*** Istituto di Chimica Organica dell'Università, 27100 Pavia, Italy

The photoisomerization of phenazine 5-oxide in acetonitrile–water mixtures has been investigated. The quantum yields of 10*H*-azepino[1,2-*a*]benzimidazol-10-one (3) and 2-(4-cyanobuta-1,3-dienyl)benzoxazole (4) are closely related to solvent composition in that they decrease strongly with increasing content of water. In acetonitrile ϕ_3 and ϕ_4 are temperature independent. The quantum yield of oxepino[2,3-*b*]quinoxaline (5) is almost independent of the composition of the solvent mixtures. A mechanism is proposed which relates the quantum yield variations to the properties of the excited state.

We have previously [1] found that irradiation of phenazine 5-oxide in benzene gives rise to phenazine (2) and to compounds of isomerization, the lactam (3), the nitrile (4), and the oxepinoquinoxaline (5) with its photoproduct (6). In methanol, the same products have been obtained but with rather different relative yields. Not only does the ratio of phenazine to isomerization products increase greatly but also the ratios among the various photoisomerization products vary. The latter point seemed worthy of further research.


(1)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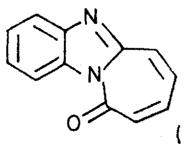
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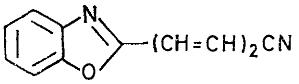
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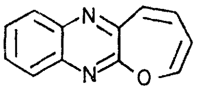
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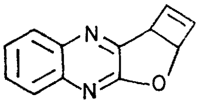
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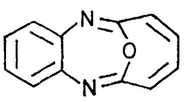
(7)

In this paper we describe the photolysis in mixtures of water and acetonitrile. In acetonitrile–water the yields of the photoisomerization products vary in relation to the quantity of water added. The yields obtained by 30 min irradiation of a 3 × 10^{-3}M solution are given in the Table.

% Yields of the photoproducts of phenazine 5-oxide [a] in MeCN–H_2O

	H_2O in solvent mixture (%)				
Products	0	10	20	40	70
(1)		8	12	20	37
(2)	2	3	4	2	6
(3)	51	25	19	15	6
(4)	13	2	0·5		
(5) + (6)	4	28	46	45	37

[a] In some cases the epoxybenzodiazecine (7) was obtained;[1] however the amounts isolated were so small as to have no effect on the yields of (3).[1]

We measured the *N*-oxide disappearance (ϕ_{-1}) at 364 nm in acetonitrile, in water, and in mixtures of the two solvents. The composition of the corresponding preparative run was established at *ca.* 10% conversion by g.l.c., controlled in some cases by column chromatography. In this way it was possible to estimate the quantum yields for the formation of (3)—(5), having checked that (3) and (4) were stable under the irradiation conditions. Similarly ϕ_{-1} has been measured and ϕ_3—ϕ_5 in acetonitrile at different temperatures have been estimated (Figures 1 and 2). The values of ϕ_3 and ϕ_4 in acetonitrile are practically independent of temperature, while a temperature effect occurs for ϕ_5. At constant temperature, the large variations in ϕ_{-1} are connected with variations in ϕ_3 and ϕ_4 but not ϕ_5 which is slightly dependent on the quantity of water.

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[1] A. Albini, G. F. Bettinetti, and S. Pietra, *Tetrahedron Letters*, 1972, 3657.

Solvent effects in the photoisomerization of azine *N*-oxides are already known[2] and were explained by the hypothesis that an oxaziridine was the primary photoproduct from the *N*-oxides and that all the products were derived from the oxaziridine. This intermediate remained hypothetical until Kaneko's[3] research into acridine *N*-oxides. Kaneko proved its existence and then effected its isolation in the form of the valence-tautomer dibenzo[*c,f*]-1,2-oxazepine. On the other hand, Lohse[4] has ascertained that in the photochemical reaction of isoquinoline *N*-oxides to isoquinolones stable intermediates do not exist.

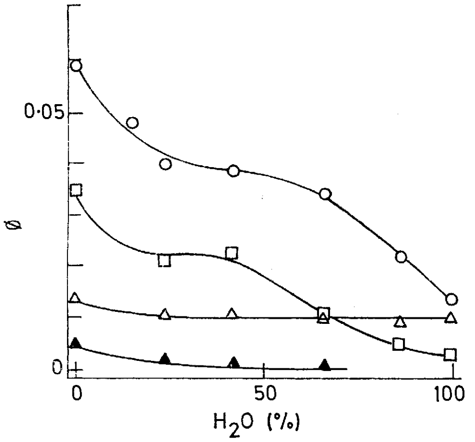


FIGURE 1 Solvent dependence of quantum yields: ○, ϕ_{-1}; □, ϕ_3; ▲, ϕ_4; △, ϕ_5

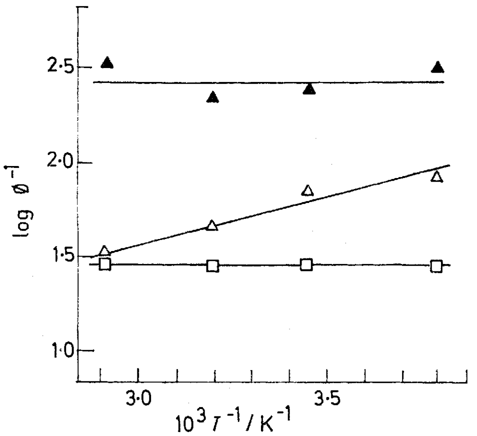
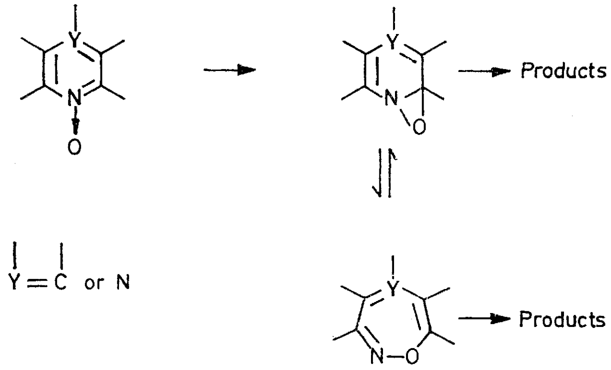


FIGURE 2 Temperature dependence of the quantum yields in MeCN: □, $\log \phi_3^{-1}$; ▲, $\log \phi_4^{-1}$; △, $\log \phi_5^{-1}$

In the case of phenazine 5-oxide, we initially postulated that the primary photoproduct was an oxaziridine or a quasi-oxaziridine.[1] The data we now present lead us to think that there are two very different pathways for photoisomerization, one for (5) and one for (3) and (4) and that the latter does not involve any stable intermediate. The decrease in ϕ_3 and ϕ_4 with the increase in the amount of water would then be caused by variations in the properties of the excited state.

This is supported, even if not proved, by the characteristic way in which the absorption spectrum of (1) varies in acetonitrile–water. The last band of the absorption spectrum of (1) in acetonitrile shows three maxima at $\lambda_{max.}$ 381 (ε 1×10^4), 395 (ε $0{\cdot}955 \times 10^4$), and 418 nm (ε $1{\cdot}065 \times 10^4$ l mol^{-1} cm^{-1}). In water the three maxima are respectively at $\lambda_{max.}$ 383 (ε $1{\cdot}320 \times 10^4$), 397 (ε $0{\cdot}805 \times 10^4$), and 420 nm (ε $0{\cdot}788 \times 10^4$ l mol^{-1} cm^{-1}). In acetonitrile–water the absorbances have intermediate values, but with variations which, especially in those of the last two maxima, are similar to the variations in ϕ_3 (Figure 4).



SCHEME 1

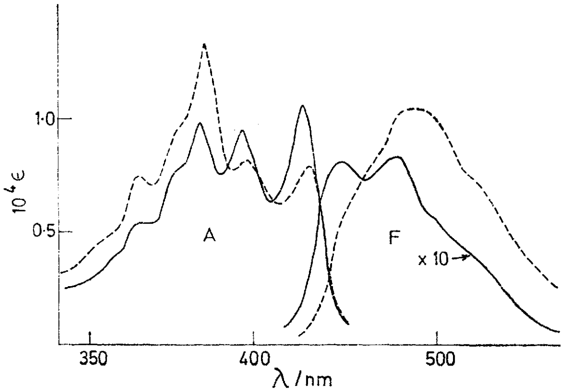


FIGURE 3 Absorption and corrected fluoresence spectra of phenazine 5-oxide (1) in MeCN(——) and in H_2O (– – – –)

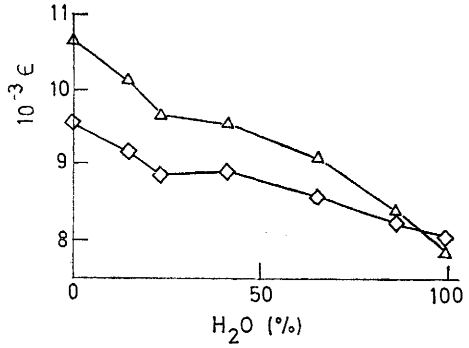


FIGURE 4 Solvent dependence of the absorbance of *N*-oxide (1) at 418—420 (△) and at 395—397 nm (◇)

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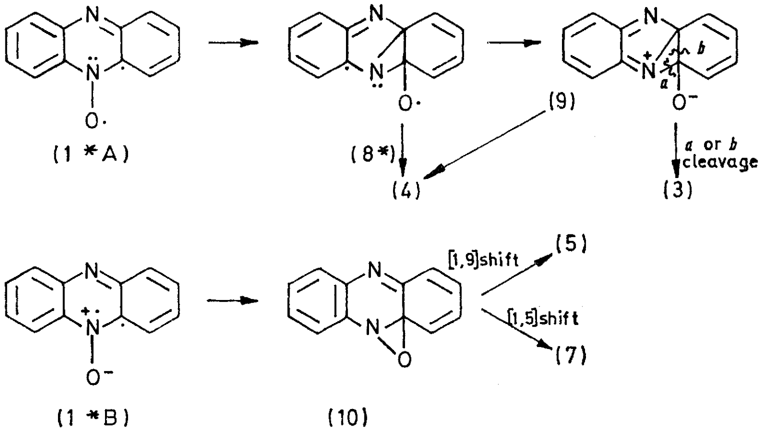
[2] (*a*) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **76**, 231; (*b*) O. Buchardt, K. B. Tomer, and V. Madsen, *Tetrahedron Letters*, 1971, 1311; (*c*) S. Yamada, M. Ishikawa, and C. Kaneko, *ibid.*, 1972, 971.

[3] S. Yamada, M. Ishikawa, and C. Kaneko, *Tetrahedron Letters*, 1972, 977; *J.C.S. Chem. Comm.*, 1972, 1093.

[4] C. Lohse, *J.C.S. Perkin II*, 1972, 229.

It is our opinion that two electronic configurations [tentatively indicated by (1*A) and (1*B) in Scheme 2, in different proportions according to the solvent], contribute to the reactive excited state of phenazine *N*-oxide. Compounds (3) and (4) are only obtained in aprotic solvents (acetonitrile, benzene) which give rise to a significant proportion of (1*A). The bond alteration involving the minimum of electron localization gives (8*). The subsequent step produces (9) from which (3) is obtained, either by direct cleavage of bond *b* or by cleavage of bond *a* through a spiroketone similar to the one proposed by Kaneko [2c] for benzophenazine *N*-oxide.



SCHEME 2

In solvents where there is insufficient (1*A), (3) and (4) are not formed. This is the case for water in which the lowest excited singlet state of phenazine *N*-oxide has undoubtedly more $\pi \longrightarrow \pi^*$ character than in acetonitrile because the fluorescence quantum yield is 0·012 in acetonitrile and 0·17 in water.

The $\pi \longrightarrow \pi^*$ contribution is represented by (1*B) which leads to the formation of (5), presumably *via* an unstable oxaziridine. Our data are compatible with (5) being formed through an excited state. The temperature effect observed for (5) suggests that thermal activation of an intermediate is involved. The M.O. calculations by Kraessig *et al.*[5] also allow us to extend to phenazine *N*-oxide Kaneko's [6] statement for other azine *N*-oxides, *i.e.*, that an oxaziridine is more likely to be formed from the excited state than from the ground state.

EXPERIMENTAL

Phenazine 5-oxide (1) was prepared according to the method of Soule,[7] purified by passing through an alumina column (benzene as eluant), and recrystallized, m.p. 266° (from ethanol). U.v. spectra were recorded with Perkin-Elmer 137 and Beckman DU-2 spectrophotometers. G.l.c. was performed with a Perkin-Elmer 800 gas chromatograph (SE 30 column).

General Procedures.—(a) *Preparative runs.* A 3×10^{-3}M solution of *N*-oxide (1) was irradiated for 30 min with a Hanau TQ 150 medium pressure mercury lamp equipped with a Pyrex filter. The solvent was evaporated at reduced pressure at room temperature and the residue was separated by column chromatography on silica gel [eluant, benzene–ethyl acetate (4 : 1)]. In the case of H_2O-rich mixtures the solution was extracted with ethyl acetate, the solvent evaporated, and the residue worked-up as above.

(b) *Preparative* 10% *conversion runs.* For the 10% conversion experiments the irradiation time range was 3—4 min depending on the quantum yield. The residue, obtained as above, was extracted with isopropyl ether and the extract analysed by g.l.c. The small amount of lactam (3) not extracted by isopropyl ether was determined by i.r. spectral examination of the residue.

Chemical and physical data of the compounds isolated were reported previously.[1]

Measurements.—The quantum yields were determined at 364 nm with a super high pressure mercury lamp (Osram 200 W/4 lamp; Schott PIL interference filter). The half-band width was 6 nm. Ferrioxalate was used as actinometer.[8] The disappearance of the *N*-oxide (1) was followed by u.v. spectroscopy of the maximum at 420 nm corrected for the absorbance of lactam (3). The reaction was quenched at 10% conversion.

The corrected fluorescence spectra were measured with a Perkin-Elmer MPF-2A instrument. The fluoroescence quantum yields were measured relative to quinine sulphate.

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[5] R. Krässig, D. Bergmann, N. Fliegen, F. Kummer, W. Seiffert, and H. Zimmermann, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 617.

[6] C. Kaneko, S. Yamada, and I. Yokoe, *Tetrahedron Letters*, 1970, 2333.

[7] E. C. Soule, U.S.P. 2,332,179 (*Chem. Abs.*, 1944, **38**, 1534).

[8] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.