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PHOTOREACTION OF PHENAZINE-5-OXIDE

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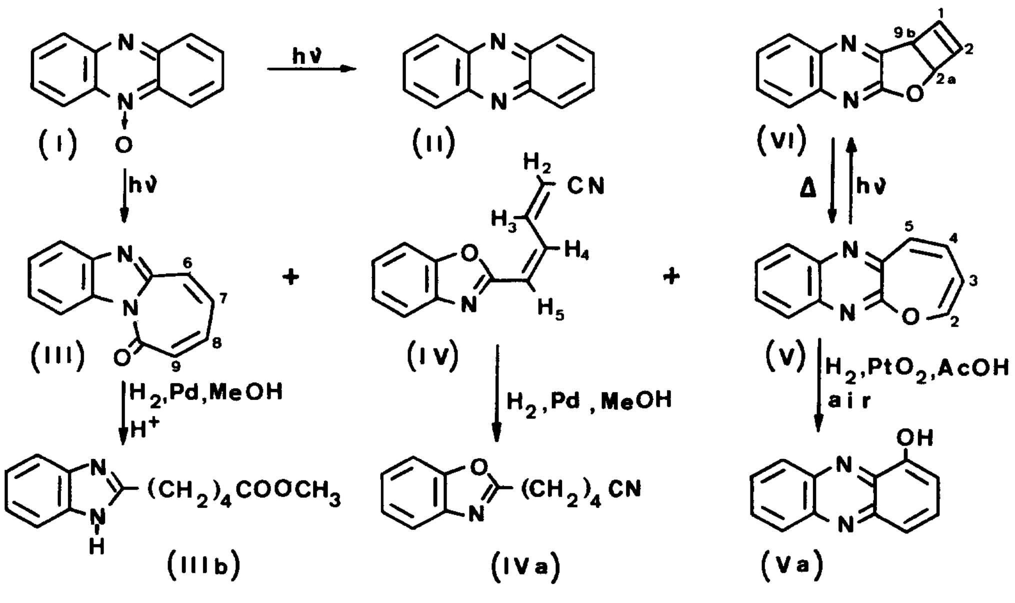
Although the photochemical reactions of aromatic amine *N*-oxides[1] have been extensively studied, no study on phenazine-5-oxide has been reported. Rees and Waite[2] observed that solutions of phenazine-5-oxide were photodecomposed but no effort was made to isolate or identify the photoproduct which they assumed to be phenazine.

We wish to report that irradiation of phenazine-5-oxide (I) gave two main reactions, deoxygenation to phenazine (II) and rearrangement. The following isomers of I have been isolated: 10-oxo-azepino[1,2-a]benzimidazole (III), (Z,Z)-5(2-benzoxazolyl)-2,4-pentadienenitrile (IV) and oxepino [2,3-b] quinoxaline (V). The E,E (IV'), the E,Z (IV") stereoisomers of IV and 2a,9b-dihydrocyclobuta[4,5]furo[2,3-b]quinoxaline (VI) were also obtained. The presence of 2,7-epoxy-1,8-benzodiazecine (VIII) has been ascertained.



In a typical run, 300 ml of 0.003 M nitrogen (oxygen) flushed solution of I in benzene (methanol) were irradiated with a medium-pressure mercury lamp (Hanau TQ 150), with a Pyrex filter, for 20 min. The separation of the reaction products was achieved by silica-gel column chromatography, eluant benzene:ethyl acetate (7:3). In Table I the yields of unchanged starting material and of compounds II-VI are reported.

TABLE I (% yields and UV data)

	Nitrogen flushed		Oxygen flushed		UV data (cyclohexane)
	Benzene	Methanol[a]	Benzene	Methanol	λ max nm (log ε)
I	37	traces	38	37	
II	3	68	1	16	
III	38	3	42	12	236(4.23) 243(4.24) 272(4.34) 399(3.76)
IV(+IV'+IV")[b]	6	traces	4	3	(IV) 256(4.17) 337(4.34)
V	6	1-2	6	6	222(4.38) 362(3.86)
VI	traces	1	traces	1	245(4.35) 249(4.41) 330(4.00) 346(4.02)

[a] A small amount of 5(2-benzimidazolyl)-2,4-pentadienoic acid methyl ester (VII) was isolated.

[b] UV data. IV': 254(3.35) 341(4.35) 361(4.17); IV": 248(3.89) 341(4.35) 361(4.17)

Quantum yields for the conversion of I into II (methanol, 7.10^{-4} M) ϕ_{400}=0.04 and for I into III (benzene, 7.10^{-4} M) ϕ_{400}=0.02.

The structures of the new compounds, suggested by physical data[3], were confirmed by chemical methods.

III - Yellow needles, m.p. 176-177°(ethanol), ν_{CO} 1675 cm^{-1}, $\delta\left[(CD_3)_2CO\right]$ 6.75(d,H_9) 7.25(d,H_8,$J_{8,9}$=13) 8.75(q,H_1) and m/e 196(M^+) 168(base peak, M^+-CO). Catalytic hydrogenation gave the 6,7,8,9-tetrahydro-derivative (IIIa), white plates, m.p. 50-51°(petroleum ether), ν_{CO}1710 cm^{-1}. Methanolysis of IIIa gave the known IIIb[4] in quantitative yield.

IV-IV'-IV" - The catalytic reduction of these three stereoisomers gave the known IVa[6].

IV-almost white plates, m.p. 81°(ethanol), ν_{CN}2218 cm^{-1}, δ(CCl_4) 6.6(d;H_5) 5.6 (d,H_2) 8.5(t,H_3,$J_{2,3}$=$J_{3,4}$=$J_{4,5}$=11).

IV'-light yellow plates, m.p. 166-168°(ethanol), ν_{CN}2218, $\nu_{C\text{-}H}$ trans 996 cm^{-1}, δ(CCl_4) 6.75(d,H_5,$J_{4,5}$=15) 5.6(d,H_2,$J_{2,3}$=14.5).

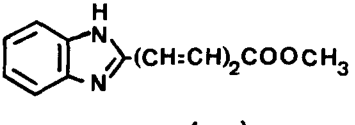
IV"-light yellow powder, m.p.120°, ν_{CN} 2215, $\nu_{C\text{-}H}$ trans 992 cm^{-1}, δ(CCl_4) 6.8 (d,H_5,$J_{4,5}$=16) 5.45(d,H_2,$J_{2,3}$=11).

V - Yellow crystals, m.p. 95-96°(ethanol), $\delta(CCl_4)$ 6.4(d,H_2,$J_{2,3}$=6) 5.5(t,H_3,$J_{3,4}$=6) 6.1(q,H_4,$J_{4,5}$=11,5) 6.7(d,H_5). Catalytic reduction of V (PtO_2,AcOH) and air reoxydation gave 1-hydroxyphenazine (Va). Irradiation in benzene or methanol of V gave VI in quantitative yield.

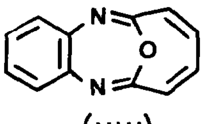
VI - White plates, m.p.139-140°(ethanol), $\delta(CDCl_3)$ 4.5(d,H_{9b}) 5.6(t,H_{2a}) 6.3(d,H_2) 6.6(t,H_1,$J_{1,2a}$=$J_{2a,9b}$=3). On strong heating VI reconverted to V.

VII - White crystals, dec. 215°($EtNO_2$), ν_{NH} 2550-2800 and ν_{CO} 1705 cm^{-1}, λ_{max} (EtOH)(log ε) 261(3.89) 347(4.20), δ(DMSO) 6.3(d,H_2,$J_{2,3}$=14.5) 12.9(N-H). Catalytic hydrogenation of VII gave IIIa.

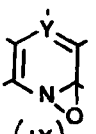
Preparative TLC of the mother liquor of IV' gave a small amount (~1% of the reacted I) of a thermally unstable product which we did not succeed in isolating in the pure state. Its NMR and UV spectra were consistent with the structure VIII. Heating in methanol gave III and VII; phenazine was formed on catalytic reduction.



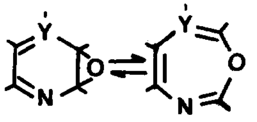
(VII)



(VIII)



(IX)



(X)

Y=C,N

Deoxygenation to phenazine (II). This reaction is the main one in methanol owing to the well known photoreductive properties of alcohols. It was suggested that the lowest triplet state[7,8] was responsible for the formation of the parent amine from the N-oxides as well as the singlet state[9]. Although great care must be taken in interpreting oxygen quenching results, the data reported in Table I suggest that in the case of II the triplet state is operating because of the strong decrease in deoxygenation when the photoreaction was performed in the presence of oxygen.

Rearrangements. With the exception of the nitriles (IV), the photoproducts arising from phenazine-5-oxide are analogous to those obtained by Kaneko et al from 9-cyano[10] and 2,7-dimethylacridine-10-oxide[11] and, limitedly to the analogues of III and VIII from the benzophenazine-N-oxides[12]. The authors suggested that in such cases, as well as in other photoisomerizations of azine-N-oxides, the first intermediate was an oxaziridine (IX) from which the V and VIII - like compounds could arise through a thermally allowed 1,9 and 1,5 suprafacial shift and a valence tautomerization. We think that this pathway is conceivable in our case too.

The formation of the III - like compound in the case of 9-cyanoacridine-

10-oxide was explained by C. Kaneko *et al* through an annulene (X) and, more recently, through a spiro compound in the cases of benzophenazine-5-oxide and 2,7-dimethyl acridine-10-oxide. With regard to phenazine-5-oxide, the above mentioned properties of VIII suggest that it can be an intermediate of III even if it is too stable to account for the formation of all the III obtained. A second competitive mechanism seems to concur to the formation of III[13]. In our case we have no evidence to support a hypothetical spiro intermediate.

As regards the formation of the nitriles (IV), no example of ring-opening reactions of this type has been reported in the photochemistry of aromatic *N*-oxides. As the formation of the nitriles is not oxygen sensitive in a significant way IV can rise from the same excited state involved in the formation of the other rearrangement products. We hypothesize that also the first intermediate is the same, i.e. a true or a quasi-oxaziridine[8] from which a 1,3-suprafacial shift with $\pi_s^2 + \sigma_a^2$ is conceivable to give the benzoxazole ring. Nevertheless a radical pathway has to be considered too.

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