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PHOTOISOMERIZATION OF 1-METHOXYPHENAZINE-N,N-DIOXIDE IN PROTIC AND APROTIC SOLVENTS

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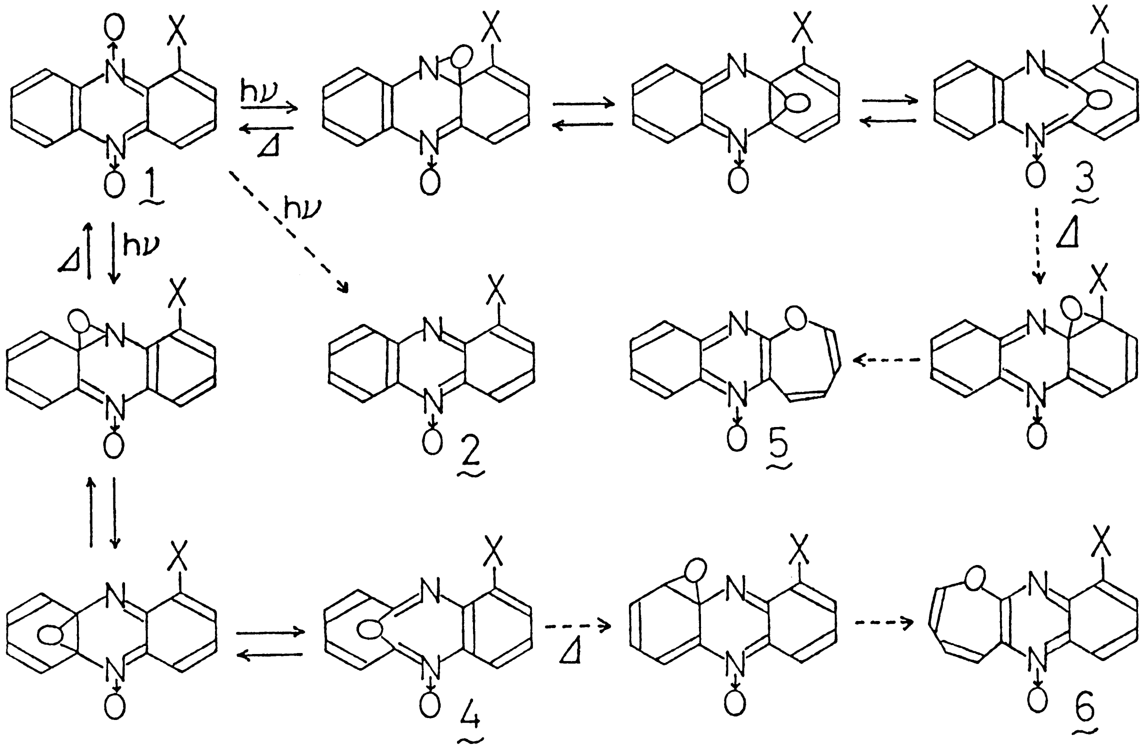
Photoisomerization of 1-methoxyphenazine-N,N-dioxide was investigated in protic and aprotic solvents. It showed photochromism in aprotic solvents. In protic solvents, irreversible photoisomerization occurred and the photoproduct was identified to be the methoxyl derivatives of oxepinoquinoxaline N-oxide.

In the preceding paper,1) we reported the photochromism of phenazine-N,N-dioxide and its chloroderivatives on irradiating with light of wavelength greater than 450 nm of an Ar ion laser or a Xe lamp in protic and aprotic solvents. The structure of the photoproduct was an annulene type compound. In this letter, we report the photoisomerization of 1-methoxyphenazine-N,N-dioxide (**1**). **1** shows photochromism in aprotic solvents, but in contrast to the case of phenazine-N,N-dioxide, the recovery of **1** in the dark is not complete. In protic solvents, not the photochromism but the irreversible photoisomerization of **1** was observed.

Photochromism was observed when **1** in benzene was irradiated with a Y-48 filtered2) 500W Xe lamp. When irradiation was continued till the absorption of **1** completely disappeared and then the irradiated solution was kept in the dark at room temperature, the photoproduct was confirmed spectroscopically to revert to **1** in approximately 70% yield. Besides **1**, 1-methoxyphenazine 5-oxide (**2**)3) and new compounds **5**,4) **6**5) were detected in this system. **2** was considered to be produced directly from **1** by the photochemical process.6) The yield of **1** in the back reaction in such aprotic solvents as acetone, chloroform, tetrahydrofuran and acetonitrile is almost the same as that in benzene. The rate constant and the activation energy of back reaction in benzene are 3.67 x 10^{-5} s^{-1} at 20 °C and 93.7 kJ mol^{-1}, respectively. The absorption spectrum of the photoproduct in aprotic solvents is similar to that of phenazine-N,N-dioxide. All the photoproducts except for 5 and 6 were converted to 2 by adding triphenylphosphine (TP, ≈2 x 10^{-2} mol dm^{-3}) to the photoproducts (≈1 x 10^{-4} mol dm^{-3}) as it was in the case of phenazine-N,N-dioxide. On the basis of the structure of 5 and 6 together with the facts just mentioned, the N→O group located at the position closer to the methyl group participates in the photoisomerization. It is also inferred that the photoproduct is the mixture of two compounds of annulene type, 3 and 4. A tentative mechanism of photoisomerization of 1 in aprotic solvents is presented in Scheme 1. The processes depicted by solid and broken lines are the major and minor ones, respectively.



X = OCH_3

Scheme 1.

The irradiation of 1 in protic solvents (methanol, ethanol) gave three kinds of photoproducts. One of them is 2 (yield, 32.4%) and others are 5 and 6 (yield, 31.2% and 23.5%, respectively). The spectral change observed in the irradiation of an ethanol solution of 1 is shown in Fig. 1. At the initial stage of irradiation (for 4 minutes-irradiation), isosbestic points appear at 434, and 538 nm. Curve e in Fig. 1 was obtained when the ethanol solution of 1 was irradiated for 4 minutes and allowed to stand for 2 hours in the dark. This spectrum is the superposition of those of 1 (the residue on irradiation and the reproduced one by the back reaction), 2, 5, and 6. Their formation was confirmed by TLC. Curve f was obtained on irradiation of the ethanol solution of 1 for 4 minutes followed by the addition of TP to the solution. This spectrum is the superposition of those of 1 (the residue on irradiation) and 2.

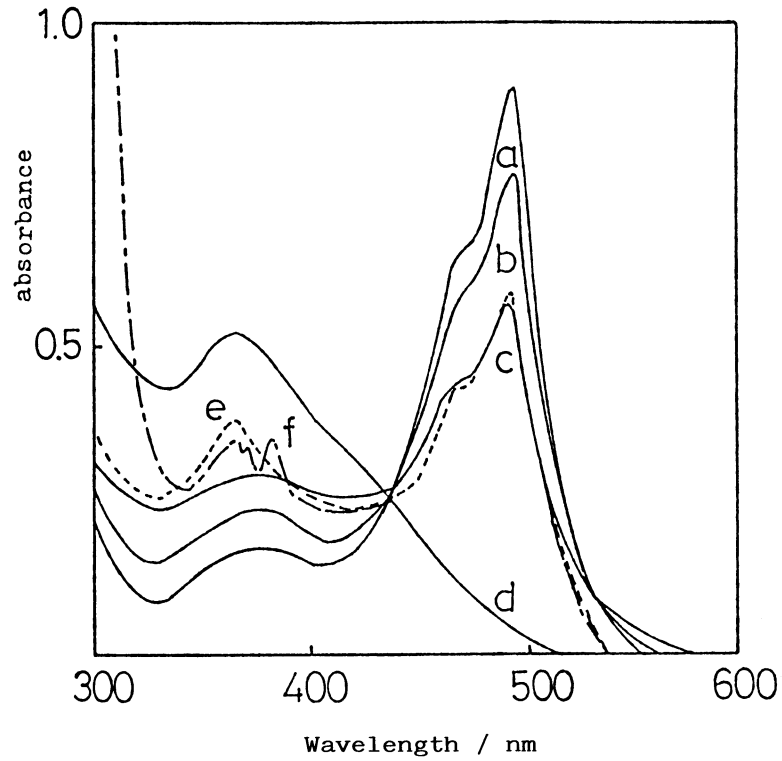
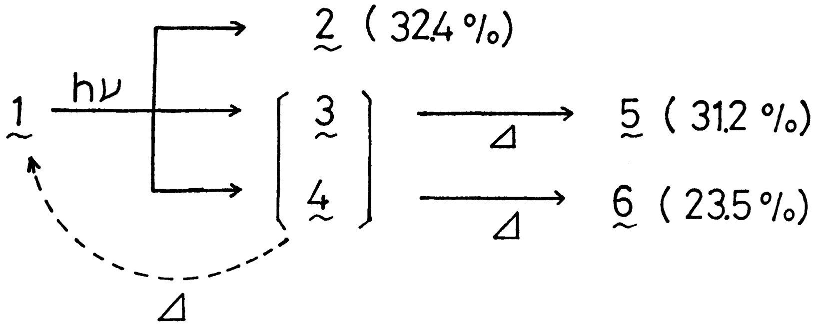


Fig. 1. Spectral change of 1 in ethanol solution irradiated with a Y-48 filtered 500W Xe lamp for various times: curve a, 0 min; curve b, 1 min; curve c, 4 min; curve d, 12 min; curve e ----, absorption spectrum of the 4 min irradiated solution of 1 being allowed to stand for 2 hours in the dark; curve f —·—·, absorption spectrum when TP was added to the 4 min irradiated solution of 1.

Thus, the photoreaction of 1 in protic solvents is considered to proceed via annulene type compounds. 5 and 6 are not formed directly from 1. The sequence of the photoreaction of 1 in protic solvents is shown in Scheme 2. The solid and broken lines indicate the major and minor processes, respectively.

It is concluded that 3 and 4 revert to the starting N,N-dioxide in aprotic solvents but they further undergo the dark reaction to produce 5 and 6 in protic solvents.



Scheme 2 .

References

1) H.Kawata, S.Niizuma, and H.Kokubun, J. Photochem., 9, 436 (1978).

2) Toshiba Y-48 cut-off filter which sharply cuts the light of wavelength shorter than 480 nm (50% Transmittance at 480 nm).

3) I.Yoshioka, Yakugaku Zassi, 73, 23 (1952).

4) 5 : yellow needles, mp 178-179 °C; ^{1}H-NMR($CDCl_3$) δ = 3.18(3H,s), 4.85(1H,d,J = 6.6 Hz), 6.45(1H,dd,J = 6.6, 11.5 Hz), 7.05(1H,d,J = 11.5 Hz), 7.5-7.7(2H,m), 7.9(1H,m), and 8.5(1H,m); ^{13}C-NMR($CDCl_3$) δ = 159.34(s), 155.81(s), 141.19(s), 136.04(s), 134.80(s), 133.23(d), 131.14(d), 129.51(d), 129.25(d), 119.13(d), 114.50(d), 83.83(d), and 56.66(q); MS(m/e) 242 (M^+); IR(KBr) 1660, 1601, 1572, 1356, 1250, and 1110 cm^{-1}; UV(EtOH) 243(ε 4.45), 363(ε 3.86), and 407(ε 3.88) nm; Found: C,64.24; H,4.11; N, 11.40%. Calcd for $C_{13}H_{10}N_2O_2$: C, 64.46; H,; 4.16; N, 11.56%.

5) 6 : yellow needles, mp 179-180 °C; ^{1}H-NMR($CDCl_3$) δ = 4.08(3H,s), 5.74(1H,t,J = 6.0 Hz), 6.44(1H,dd,J = 6.0, 11.7 Hz), 6.49(1H,d,J = 6.0 Hz), 7.12(1H,dd,J = 1.0, 8.1 Hz), 7.31(1H,d,J = 11.7 Hz), 7.58(1H,dd,J = 8.1, 8.7 Hz), and 8.04(1H, dd,J = 1.0, 8.7 Hz); MS(m/e) 242 (M^+); IR(KBr) 1639, 1502, 1453, 1330, and 1105 cm^{-1}; UV(EtOH) 240(ε 4.28), 285(ε 4.19), and 365(ε 4.00) nm; Found: C, 64.54; H, 4.10; N, 11.46%. Calcd for $C_{13}H_{10}N_2O_2$: C, 64.46; H, 4.16; N, 11.56%.

6) G.G.Spence, E.C.Taylor, and O.Buchardt, Chem. Rev., 70, 231 (1970).

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