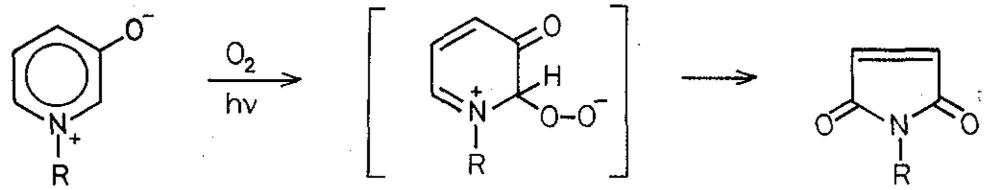
HETEROCYCLES, Vol. 5, 1976

PHOTO-OXIDATION OF 1-METHYL-3-OXIDO-5-PHENYLPYRIDINIUM[1,2]

Julie Banerji, Nicholas Dennis, and Alan R. Katritzky*
School of Chemical Sciences, University of East Anglia, Norwich, England

Dipolar peroxide intermediates of type III, IV are supported for the photo-oxidation of 3-oxidopyridiniums by the isolation of unsymmetrical dimer X.

Mori *et al.*[3] have recently studied the photo-oxidation of 1-methyl-3-oxidopyridinium (I): they isolated *N*-methylmaleimide (V) and 3-hydroxy-*N*-methyl-2-pyridone (VII) and postulated that the dipolar species III was an intermediate. We have now similarly found that 3-oxido-1-phenylpyridinium (II) yields *N*-phenylmaleimide (VI) presumably *via* the analogous dipolar structure IV.



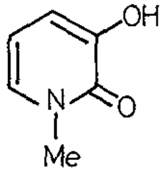
I R = Me
II R = Ph

III R = Me
IV R = Ph

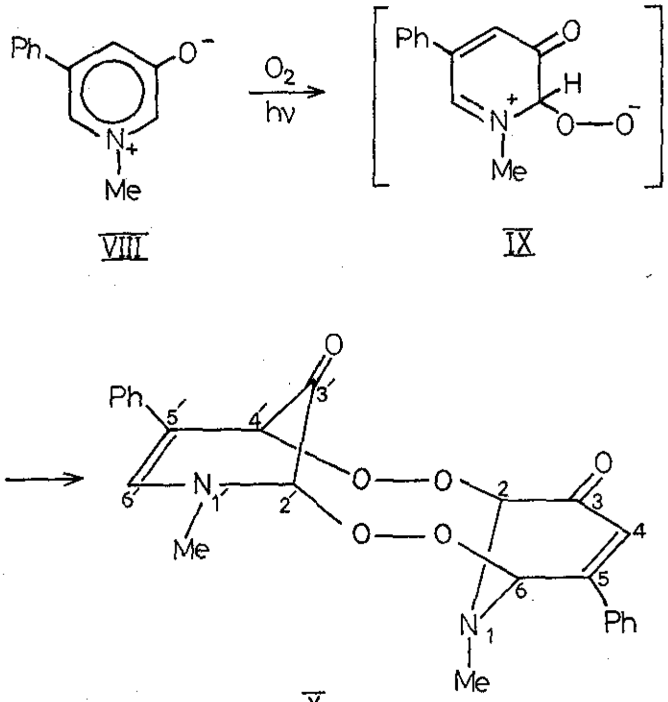
V R = Me
VI R = Ph

Evidence for the intermediacy of dipoles of types III, IV in these photochemical transformations is obtained from the oxidative irradiation of the 1-methyl-5-phenyl compound[4] VIII: in this series the dipole IX dimerises to produce the unsymmetrical dimer X[5] the structure of which was proved by spectral data. Thus, the ir showed two ν(C=O) at 1765 (saturated) and 1680 (unsaturated), ν(C=C) at 1625 (enamine system) and 1600 cm^{-1} (aromatic ring), with no absorption in the OH/NH region. The mass spectrum exhibited a base peak at *m/e* 217.0743 corresponding to the fragment, $C_{12}H_{11}NO_3$ derived from compound X by dedimerisation under electron impact. This $M^+/2$ ion underwent facile loss of CO to fragment *m/e* 189.

The nmr spectrum displayed two methyl singlets at δ 2.63 and 2.65, and a ten-proton singlet at δ 7.47 for the phenyl ring protons. The bridgehead protons, H-2 and H-6 form a doublet ($J_{2,4}$ 1.5 Hz) and a double doublet ($J_{2,6}$ 0.2 Hz, $J_{4,6}$ 1.5 Hz) at



VII



VIII IX

X

δ 6.52 and 7.54 respectively. The remaining set of bridge-head protons at H-2' and H-4' exhibit doublets ($\underline{J}_{2',4'}$ 1.5 Hz) at δ 6.54 and 6.62 respectively. These assignments were confirmed by extensive spin-spin decoupling experiments.[6]

It is of interest that the unsymmetrical dimer X is formed rather than either of the symmetrical alternatives. We believe that the dimerisation is probably a two-step reaction, and that the second step determines the orientation.

FOOTNOTES AND REFERENCES

1 Contributed in honour of the 70th birthday of Dr. Ken'ichi Takeda.

2 1,3-Dipolar Character of Six-membered Aromatic Rings, Part XXIII. For Part XXII see N. Dennis, B.E.D. Ibrahim, and A.R. Katritzky, Synthesis, 1976, 105.

3 A. Mori, S. Ohta, and H. Takeshita, Heterocycles, 1974, 2, 243.

4 N. Dennis, A.R. Katritzky, and R. Rittner, J.C.S. Perkin I, in press.

5 Cubes (from diethyl ether), mp 93°C (Found: C, 66.0; H, 5.1; N, 6.3. $C_{24}H_{22}N_2O_6$ requires C, 66.3; H, 5.1; N, 6.4%).

6 The olefinic protons, H-4 and H-6' form a doublet ($\underline{J}_{2,4}$ 1.5 Hz) and a singlet at δ8.56 and 8.21 respectively.

Received, 22nd June, 1976