

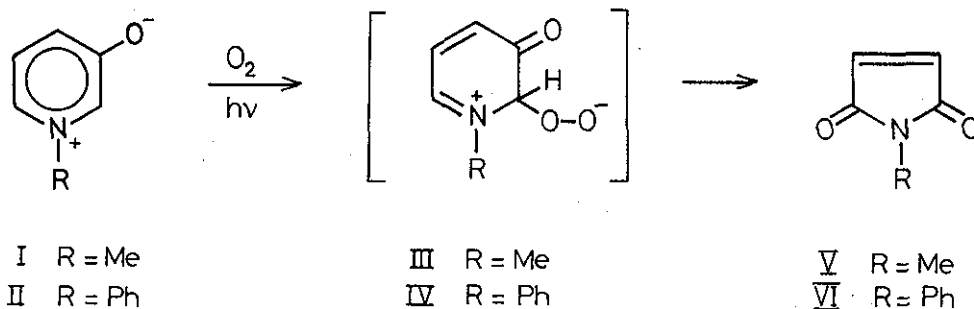
PHOTO-OXIDATION OF 1-METHYL-3-OXIDO-5-PHENYLPYRIDINIUM^{1, 2}

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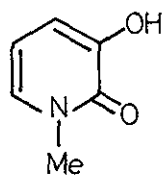
Dipolar peroxide intermediates of type III, IV are supported for the photo-oxidation of 3-oxidopyridiniums by the isolation of unsymmetrical dimer X.

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.

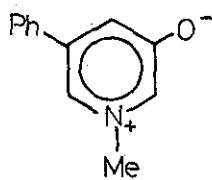


Evidence for the intermediacy of dipoles of types III, IV in these photochemical transformations is obtained from the oxidative irradiation of the 1-methyl-5-phenyl compound⁴ VIII: in this series the dipole IX dimerises to produce the unsymmetrical dimer X⁵ the structure of which was proved by spectral data. Thus, the ir showed two $\nu(\text{C}=\text{O})$ at 1765 (saturated) and 1680 (unsaturated), $\nu(\text{C}=\text{C})$ 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, $\text{C}_{12}\text{H}_{11}\text{NO}_3$ derived from compound X by dedimerisation under electron impact. This $\text{M}^+/2$ ion underwent facile loss of CO to fragment m/e 189.

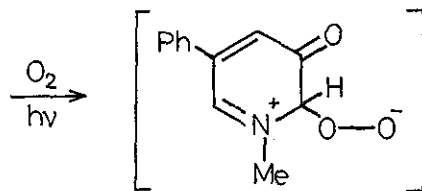
The nmr spectrum displayed two methyl singlets at δ 2.63 and 2.65, and a ten-proton singlet at δ 7.47 for the phenyl ring protons. The bridgehead protons, H-2 and H-6 form a doublet ($J_{2,4}$ 1.5 Hz) and a double doublet ($J_{2,6}$ 0.2 Hz, $J_{4,6}$ 1.5 Hz) at



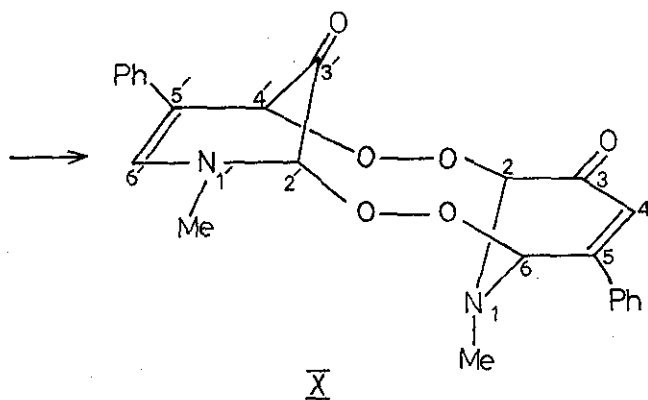
VII



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 ($J_{2',4'}$, 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 ($J_{2,4}$, 1.5 Hz) and a singlet at δ 8.56 and 8.21 respectively.

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