

PHOTOINDUCED REACTIONS. LII. PHOTOREARRANGEMENT OF 3-HYDROXYFLAVONES.<sup>1</sup>

Teruo Matsuura, Tadashi Takemoto and Ruka Nakashima

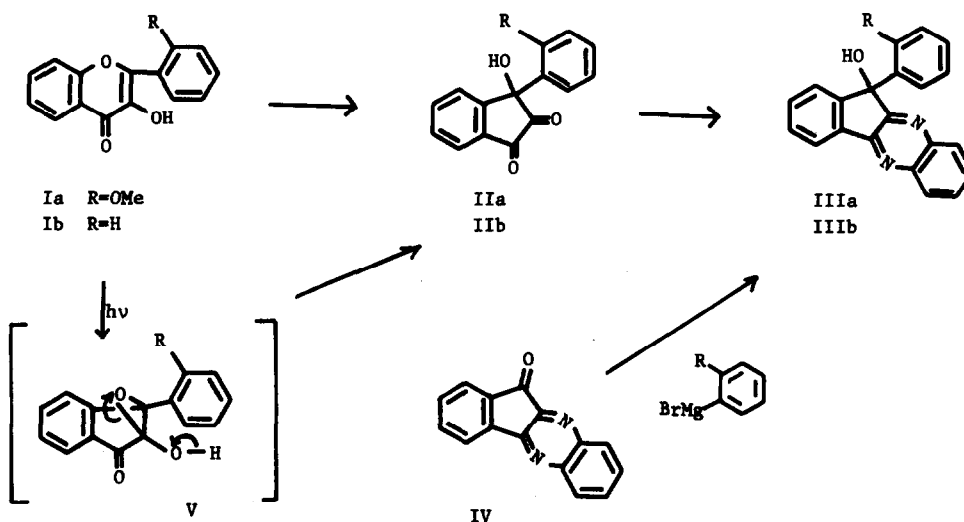
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan  
(Received in Japan 19 February 1971; received in UK for publication 30 March 1971)

Relatively few attention has been given to the photochemical reaction of flavonoids:<sup>2</sup> all the reports were concerned with photochemical oxidation. We wish to report a novel photorearrangement of 3-hydroxyflavones leading to 3-aryl-3-hydroxy-1,2-indandiones.

Irradiation of a solution of 3-hydroxy-2'-methoxyflavone (Ia) in isopropyl alcohol-benzene with a high-pressure mercury lamp through Pyrex gave a crystalline isomer, m.p. 188-189°, in essentially quantitative yield, which was characterized as a monoacetate, m.p. 187-188°. The spectral data of the isomer [ $m/e$  268 ( $M^+$ );  $\lambda_{\max}^{KBr}$  1730-1740, 1770, 3420  $cm^{-1}$ ;  $\nu_{\max}^{EtOH}$  273 nm ( $\epsilon$  9600);  $\delta^{TMS}$  3.37s (3H, OMe), 7.05s (1H, OH), 6.8-8.1m (8H, aromatic protons)] suggested that its structure is assigned as IIa. Treatment of IIa with *o*-phenylenediamine gave a crystalline quinoxaline derivative IIIa (96% yield), m.p. 222-223°, the structure of which was confirmed by a synthesis from 11H-indeno[1,2-b]quinoxalin-11-one (IV)<sup>4</sup> and *o*-anisylmagnesium bromide.

Similar irradiation of 3-hydroxyflavone (Ib) gave an isomer IIb as a noncrystalline solid. The product was converted into a quinoxaline derivative IIIb, m.p. 244-245°, which was identical with an authentic sample of 11-hydroxy-11-phenyl-11H-indeno[1,2-b]quinoxaline.<sup>4</sup>

The present result provides the first example of the photorearrangement of flavonoids. A possible mechanism involving a 2,3-epoxy-2-hydroxy-1-indanone intermediate V, which may be formed by a formal [ $2 + \pi_2$ ] cycloaddition analogous to the transformation of 2-cyclohexenones into bicyclo[3.1.0]hexan-2-ones,<sup>5</sup> is shown in Figure. The conversion of V into II may occur thermally, similar to that of an acetoxyepoxide into an  $\alpha$ -acetoxyketone.<sup>6</sup>



## References

1. Part LI: K. Omura and T. Matsuura, *Synthesis*, in the press.
2. A. C. Waiss, Jr., and J. Corse, *J. Am. Chem. Soc.*, **87**, 206 (1965); A. C. Waiss, Jr., R. E. Lundin, A. Lee and J. Corse, *ibid.*, **89**, 6213 (1967); T. Matsuura, H. Matsushima and H. Nakashima, *Tetrahedron*, **26**, 435 (1970); T. Matsuura and H. Matsushima, *ibid.*, **26**, 435 (1970); T. Matsuura and H. Matsushima, *ibid.*, **26**, 435 (1970); T. Matsuura and H. Matsushima, *ibid.*, **26**, 435 (1970).
3. Satisfactory microanalyses and spectral data were obtained for all new compounds except IIB which could not be isolated in a pure form.
4. B. D. Pearson, R. A. Mitsch and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 1674 (1962).
5. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, GmbH, Weinheim, 1970, p. 89 and references cited therein.
6. H. J. Shine and E. G. Hunt, *J. Am. Chem. Soc.*, **80**, 1958 (1958).