Photochemical Dimerization of Flavones

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Summary Irradiation of the flavones (**1a**) and (**1b**) in the presence of sodium sulphite in MeOH–H_2O gave the flavanone dimers (**2**) and (**3**).

The photochemical reactions of flavonoids have been studied extensively, and some interesting photo-oxygenations have been reported.[1] However, photoreduction of flavonoids has not hitherto been described. We now report that irradiation of flavones in the presence of sodium sulphite affords flavanone dimers.

Irradiation (450 W high-pressure Hg lamp; Pyrex filter) of 6-methylflavone (**1a**) in MeOH–H_2O in the presence of a fivefold excess of Na_2SO_3 under N_2 for 5 h gave compounds (**2a**) (64% yield) and (**3a**) (30% yield):† (**2a**) m.p. 239 °C; ν(KBr) 1690, 1620, 1490, 1300, 1230, 990, and 910 cm^{-1}: λ_{max} (MeOH) (log ε) 220 (4·20), 256 (3·68), and 333 (3·22) nm; δ($CDCl_3$) 2·20 (6H, s, 6-Me), 3·30 (2H, d, *J* 16 Hz, 3-CH_2), 3·95 (2H, d, *J* 16 Hz, 3-CH_2), and 6·7—7·55 (16H, m, ArH); (**3a**) m.p. 290 °C; δ($CDCl_3$) 2·19 (6H, s, 6-Me), 3·07 (2H, d, *J* 16 Hz, 3-CH_2), 3·65 (2H, d, *J* 16 Hz, 3-CH_2), and 6·9—7·6 (16H, m, ArH).

Compounds (**2a**) and (**3a**) were found by molecular weight determination and field desorption mass spectrometry‡ to be flavanone dimers. The ^1H and ^{13}C n.m.r.

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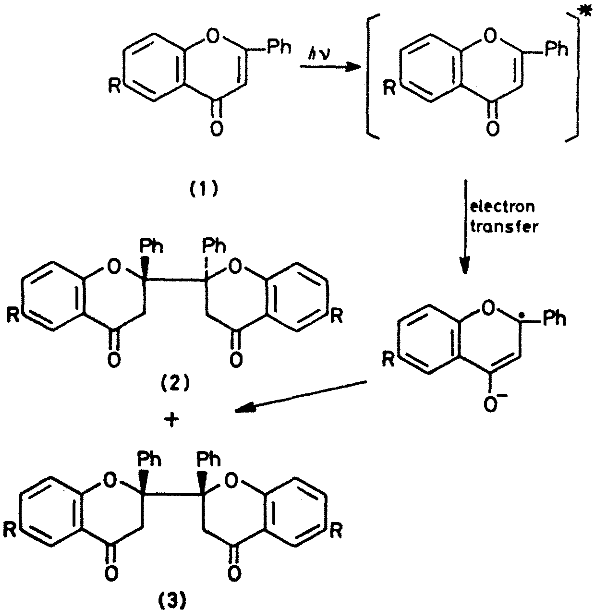
† Satisfactory elemental analyses were obtained for all new compounds.

‡ Mass spectrum of (**2a**) *m/e* 474 (M^+, $C_{32}H_{26}O_4$), 339·1420 ($C_{24}H_{19}O_2$, $M^+ - C_8H_7O$), 237·0908 ($C_{16}H_{13}O_2$, $M^+/2$), and 135·0442 ($C_8H_7O_2$); (**3a**) *m/e* 474 (M^+, $C_{32}H_{26}O_4$), 339·1371 ($C_{24}H_{19}O_2$, $M^+ - C_8H_7O_2$), 237·0922 ($C_{16}H_{13}O_2$, $M^+/2$), and 135·0429 (C_8H_7O). M^+ peaks are only detected in field desorption spectra.



(1)

(2)

+

(3)

a; R = Me
b; R = H

spectra of (**2a**) and (**3a**) showed no flavanone 2-H signal or ^{13}C-2-H coupling, so we conclude that these compounds are joined together at the C-2 positions.

In the ^{1}H n.m.r. spectrum of (**3a**) the methylene protons appear at higher field than those in (**2a**) ($\Delta\delta = 0{\cdot}2$—$0{\cdot}3$ p.p.m.) and this shift may be due to the shielding effect of the aromatic ring.§ Dreiding models show that the CH_2 protons of the *meso*-isomer of the dimer are more shielded by the phenyl group than in the (±)-isomer, so we assume that (**2a**) might be the (±)- and (**3a**) the *meso*-isomer. *X*-Ray analysis of these compounds is now under investigation.

Under the same conditions the flavone (**1b**) gave (**2b**), m.p. 222 °C (62% yield), and (**3b**), m.p. 284 °C (23% yield), whose spectral data are consistent with flavanone dimer structures.

The mechanism of this photoreaction is not clear, but we tentatively postulate that the formation of the dimer involves an intermediate anion radical resulting from electron transfer to the excited flavone from the sulphite.¶ The anion radical then abstracts a proton from the solvent and is ultimately dimerized by either a concerted or stepwise process.

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§ ^{1}H N.m.r. spectroscopy using the chiral shift reagent Eu(tfac)$_3$ led to no conclusions about the stereochemistry.

¶ It has been reported that irradiation of the sulphite ion led to the formation of the SO_3^- radical anion and an electron. $SO_3^{2-}.H_2O \longrightarrow SO_3^- + e^-$ (L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1968, **72**, 1800).

[1] T. Matsuura, H. Matsushima, and H. Sakamoto, *J. Amer. Chem. Soc.*, 1967, **89**, 6213; A. C. Waiss, R. E. Ludin, A. Lee, and J. Corse, *ibid.*, p. 6213; T. Matsuura and H. Matsushima, *Tetrahedron*, 1968, **24**, 6615; T. Matsuura, T. Takemoto, and R. Nakashima, *Tetrahedron Letters*, 1971, 1539; A. Schönberg and G. D. Khandelwal, *Chem. Ber.*, 1970, **103**, 2786; N. Ishibe, S. Yutaka, J. Masui, and Y. Ishida, *J.C.S. Chem. Comm.*, 1975, 241.