The Photolysis of 2-Hydroxychalcone and Its Possible Implication in Flavonoid Biosynthesis

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Summary The photolysis of 2-hydroxychalcone in alcoholic solvents using 3500 Å light yields the corresponding 2-alkoxy-flav-3-ene together with small quantities of flavone.

CHALCONES have been shown to be precursors for many classes of flavonoid compounds,[1] and results obtained by Grisebach[2] using labelled chalcones have shown that the branching which leads to flavonoids in different oxidation states occurs after the formation of a C_{15} intermediate. One of the major remaining problems in flavonoid biosynthesis is the role of sunlight,[3] exposure to light being essential for the formation of anthocyanins. We have investigated the photolysis of a number of chalcones and report the results of the photolysis of 2-hydroxychalcone (I). The photolysis of (I) in ethanol for 8 hr. gave a mixture of three products in the ratio 1 : 97 : 1 as determined by g.l.c. analysis. The major product, m.p. 75—76, 96% yield, was identified as 2-ethoxyflav-3-ene (III; R = Et) on the basis of the following evidence. The mass spectrum showed a molecular ion at *m/e* 252 followed by loss of EtO, 252 → 207 (m^* 170) as the major fragmentation pattern. The 100 MHz n.m.r. spectrum was definitive; it consisted of a triplet at δ 1·07 (*J* 9 Hz, 3H), a multiplet at 3·50 (14 lines, 2H), a doublet at 5·75 (*J* 9 Hz, 1H), a doublet at 6·69 (*J* 9 Hz, 1H), and a multiplet at 6·85—7·70 (9H). These lines can be assigned as follows. The triplet to the methyl of the ethyl group, the 14 line multiplet to the methylene group which is attached through oxygen to an asymmetric centre,† the doublets are an AB system associated with the two olefinic protons, while the remaining multiplet is due to the aromatic protons. In addition, (IIIa) was smoothly converted into a flavylium salt by the addition of acid. This compound (IIIa) has previously been prepared[4,5] by the action of ethanolic alkali on flavylium chloride. Photolysis in methanol gives (IIIb) in 95% yield. The flav-3-enes are considered to be formed from the pseudo-base as shown in the Scheme. One other component, flavone, 1% yield, was formed in a parallel reaction. The third component has not been identified but

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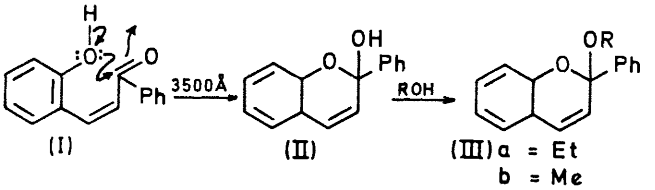
† This multiplet appears as 10 lines at 60 MHz as previously reported (ref. 4).

a trace of a flavylium salt, *m/e* 207, formed by a decomposition of (IIIa or b) on the g.l.c. column or detector has been isolated.‡



SCHEME

This work suggests a novel route to flavylium salts *via* the photocyclisation of 2-hydroxy-chalcones to flav-3-enes. Since the formation of anthocyanins (flavylium salts) directly parallels exposure to sunlight then it is possible that (I) may be an important intermediate in this process. The flav-3-enes so formed are unstable and could be smoothly converted into anthocyanins. Additionally, the direct formation of flavone from a chalcone (I) lends weight to the recent results reported by Wong.[6]

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‡ The flavylium salt was formed after several consecutive injections. It caused a decrease in the peak area due to the flav-3-ene but did not affect the area under the other two peaks.

[1] H. Grisebach, "Biosynthetic Patterns in Microorganisms and Higher Plants," Wiley, New York, 1967.
[2] H. Grisebach, "Chemistry and Biochemistry of Plant Pigments," ed. T. W. Goodwin, Academic Press, London, 1965, p. 279.
[3] For a review see H. W. Siegelman in the "Biochemistry of Phenolic Compounds," ed. J. B. Harbourne, Academic Press, London, 1964.
[4] J. A. Van Allan, G. A. Reynolds, and T. H. Regan, *J. Org. Chem.*, 1967, **32**, 1897.
[5] D. Hill and R. Melhuish, *J. Chem. Soc.*, 1935, 1161.
[6] E. Wong, *Chem. Comm.*, 1968, 395.