

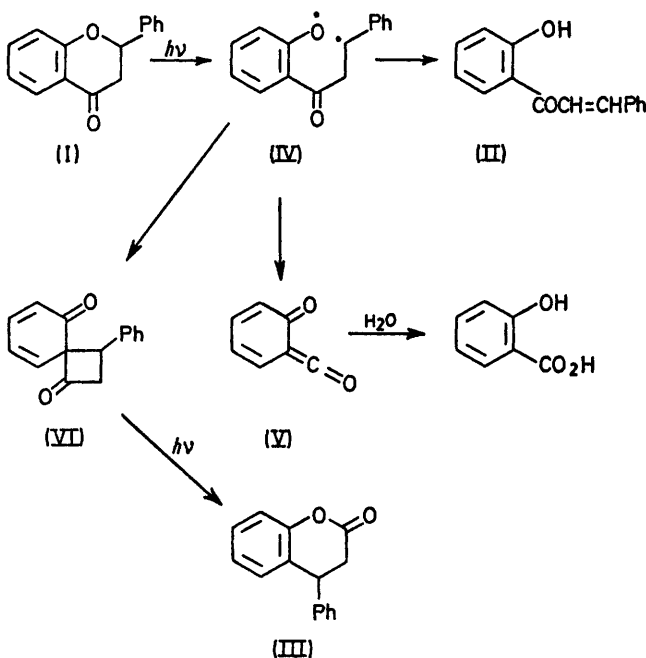
The Photochemistry of Flavanone

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Summary On u.v. irradiation, flavanone rearranges to 4-phenyldihydrocoumarin and 2'-hydroxychalcone, and undergoes fragmentation to yield a highly reactive keto-keten.

IN a reaction analogous to the photo-Fries rearrangement of aromatic esters,¹ various simple aromatic ethers undergo a



light induced rearrangement to *o*- and *p*-substituted phenols.^{2,3} It was therefore of interest to extend our study²

to cyclic ethers where the potential migrating group is attached to the aromatic ring, and we now report a rearrangement of flavanone (I).

Irradiation (Rayonet reactor fitted with 2537-A source, quartz, 0.7% solution w/v) of (I) in benzene (12 h, 37% reaction) produced 2'-hydroxychalcone (II, 20%), 4-phenyldihydrocoumarin (III, 13%, identical with authentic sample⁴), and salicylic acid (4%). We believe that the initial product of the photolysis is the diradical (IV), in analogy with the behaviour of simple aryl ethers.^{2,3} Intra-molecular hydrogen abstraction then leads to 2'-hydroxychalcone (II), while fragmentation gives the keto-keten (V) which reacts with water to yield salicylic acid. It has recently been suggested that the intermediate (V) is produced on photolysis of both 2-phenyl-1,3-benzodioxan-4-one⁵ and 2,3-dihydrobenzofuran-2,3-dione.⁶ We also suggest that the rearrangement of (I) to 4-phenyldihydrocoumarin (III) proceeds through (IV) and the dienone (VI), which yields the product in a further photo-rearrangement. The conversion of (I) into (III) is analogous to the light induced rearrangement of isothiochroman-4-one to thiochroman-3-one, for which an intermediate similar to (VI) has been suggested.⁷

Evidence for the intermediacy of (V) in the formation of salicylic acid was obtained by repeating the photolysis of (I) in benzene containing 5% methanol. Methyl salicylate was produced in 9% yield.

This work was supported by a grant from the Australian Research Grants Committee.

(Received, 21st February 1972; Com. 285.)

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