The Photochemistry of Flavanone

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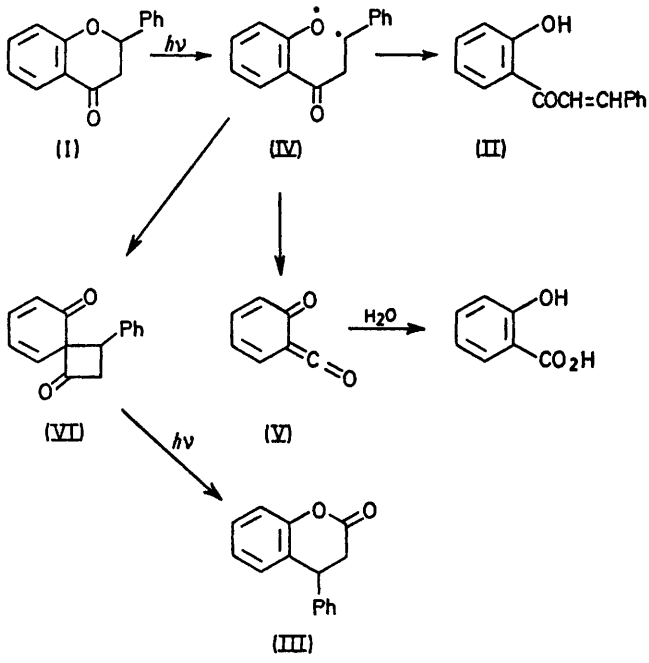
Summary On u.v. irradiation, flavanone rearranges to 4-phenyldihydrocoumarin and 2′-hydroxychalcone, and undergoes fragmentation to yield a highly reactive keto-keten.

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 study[2] 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 sample[4]), 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] Intramolecular 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-one[5] 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.

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