Tautomeric Control of the Photochemistry of 4-Phenylchroman-3-one

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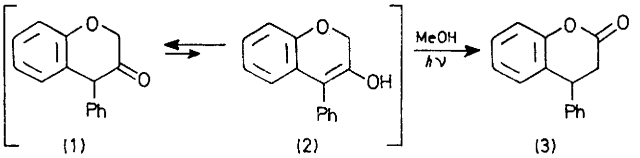
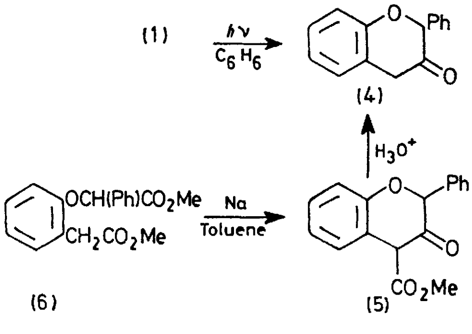
Summary Irradiation of 4-phenylchroman-3-one in benzene gave 2-phenylchroman-3-one as the only photoproduct; the mechanism involves β-scission and recoupling of the diradical produced through the aromatic ring to give a transient spirocyclohexadienone which gives the product by a 1,3-sigmatropic shift.

WE have recently shown[1] that the photoisomerization of 4-phenylchroman-3-one (**1**) to 4-phenyldihydrocoumarin (**3**)[2] involves the prior enolization of (**1**) into its enol tautomer (**2**) which is subsequently converted into (**3**) on exposure to u.v. light with methanol as the solvent. In view of these results, we have examined the photochemistry of (**1**) in a nonpolar solvent where the concentration of (**2**) would be negligible.[†]



We now report a novel rearrangement which occurs when the chromanone (**1**) is irradiated in benzene or MeCN. Under these conditions (250 mg in 125 ml benzene; Pyrex filter; 15 h) the only product isolated (60%) besides starting material (15%) was 2-phenylchroman-3-one (**4**). Extended irradiation of (**1**) did not enhance the degree of conversion but only increased the amount of polymer formed. The possibility that starting material in the crude photolysate was derived by photoisomerization of the final photoproduct was eliminated by the finding that (**4**) did not give (**1**) on extended irradiation in benzene. The assignment of 2-phenylchroman-3-one (**4**) as the photoproduct was based on its spectroscopic properties:[‡] i.r. 5·80 μm; u.v. (MeOH) 305 nm (ε 650); τ ($CDCl_3$) 6·38 (s, 2H) and 4·80 (s, 1H), and was further confirmed by comparison with an authentic sample prepared by treating the chromanone (**5**) with aqueous acid. The β-ketoester (**5**) was synthesized, in turn, from a Dieckmann condensation of the acetate (**6**) with sodium in refluxing toluene.



The photochemical formation of the chromanone (**4**) from (**1**) can be rationalized according to the mechanism outlined in the Scheme. Initial n–π^* excitation followed by β-scission and recoupling through the aromatic ring leads transiently to the spirocyclohexadienone (**7**), which can either revert to starting material or give the final product by a 1,3-sigmatropic shift. The first step of the proposed mechanism has precedence since related β-scissions of n–π^* excited ketones have been reported.[3] Zimmerman has explained these reactions by a simple AO resonance model for the excited carbonyl group.[4] He suggested that the n–π^* excited state can eject a group in the α-position either as a radical or as an anion. The conversion of (**1**) into (**7**) is also analogous to the light-

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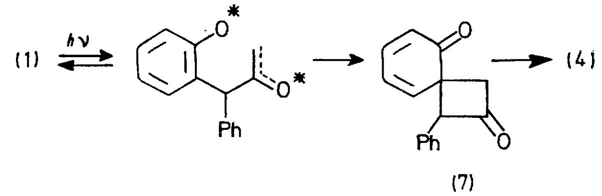
[†] The amount of the enol form of (**1**) present in solution can be estimated from its u.v. spectrum.

[‡] All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given elsewhere.

induced rearrangements of isothiochroman-4-one to thiochroman-3-one[5] and flavone to 4-phenyldihydrocoumarin[6] where intermediates similar to (**7**) have been suggested.



SCHEME

Our present results are especially interesting in view of the fact that the photolysis of (**1**) is solvent dependent. This solvent effect can best be rationalized in terms of the enol content in each solvent. In alcoholic solvents there is a significant (*i.e.* > 1%)amount of the enol form present which can be selectively excited with long-wavelength light. In benzene or acetonitrile, insignificant quantities of the enol tautomer are present in solution† and consequently the photoreaction is due to excitation of the keto-form of the chromanone (**1**).

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