Photochemical Rearrangement of 4-Phenyl-3-chromanone

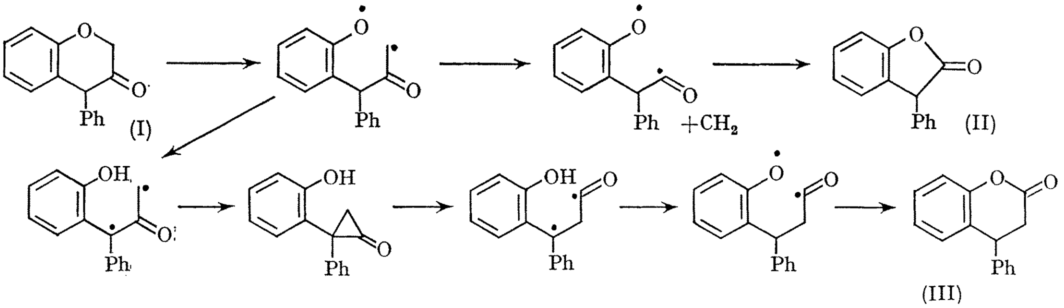
By P. K. GROVER and NITYA ANAND*
(*Central Drug Research Institute, Lucknow, India*)

Summary On photolysis, 4-phenyl-3-chromanone rearranges to 4-phenyldihydrocoumarin.

A RECENT publication by Maheshwari and Berchtold[1] on photolysis of cyclic, saturated β-keto-sulphides prompts us to record our observation on the photolysis of 4-phenyl-3-chromanone (I).

We observed[2] that (I) rearranges under pyrolytic conditions to 3-phenyl-2-coumaranone (II). Since photolytic reactions are higher-energy processes than pyrolytic reactions, it was of interest to subject (I) to photolysis. When (I) was photolysed in ethanol for 4 hr. with a Hanovia 450 w mercury lamp using a Vycor filter, the major product (*ca.* 35%) was 4-phenyldihydrocoumarin (III), identical in all respects with an authentic sample.[3] The coumaranone (II) was not formed.

The following mechanisms shown in the Scheme are suggested for the pyrolytic ring-contraction and the photolytic transformation. In the pyrolytic ring-contraction, the loss of CH_2 is postulated. Loss of CH_2 has been implicated by Leary and Oliver[4] in the photolytic demethylation of 2-methoxybenzophenones. In the mass spectrum of (I) (molecular-ion peak 224) a strong peak at 210 is indicative of the loss of CH_2 and the formation of (II). The mass spectrum of (I) was much more complex than that of (II), apparently consisting of peaks due to (I) and (II).



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[1] K. K. Maheshwari and G. A. Berchtold, *Chem. Comm.*, 1969, 14.
[2] P. K. Grover and Nitya Anand, *Indian J. Chem.*, 1969, 7, 196.
[3] J. D. Simpson and H. Stephen, *J. Chem. Soc.*, 1956, 1382.
[4] G. Leary and J. A. Oliver, *Tetrahedron Letters*, 1968, 299.