Selectivity in Photoenolisation of Substituted 3-Aroylchromones

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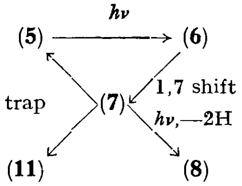
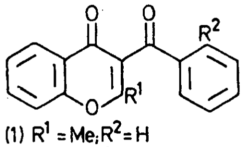
Summary Deuterium labelling studies have shown that 2-methyl-3-aroylchromones do not undergo direct photoenolisation, although the ground state dienol is capable of existence.

Photoenolisation in 2-alkyl-3-benzoylchromones has been extensively studied and it has been demonstrated that 2-methyl-3-benzoylchromone (**1**) does not form a photoenol.[1,2] By contrast, we have now found that 3-(2′-methyl)benzoylchromone (**2**) does undergo photoenolisation. The derived enol (**3**) undergoes further rapid photochemical reaction giving the benzoxanthenone (**4**) (80%).[2] The presence of the methyl groups in isomeric positions would not be expected to alter substantially the energy of the initial excited states (u.v. curves virtually superimposible). Hydrogen transfer, to form an intermediate biradical,[1] is therefore unfavoured for (**1**), the excited state preferring to collapse back to the ground state, whereas for (**2**) hydrogen transfer predominates.

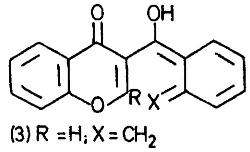


Scheme

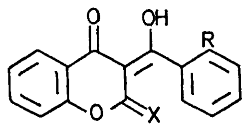
Irradiation of 2-methyl-3-(2′-methyl)benzoylchromone (**5**), m.p. 134—135°,† could give two dienols, (**6**) and (**7**). The product was the benzoxanthenone (**8**) (58%, m.p. 207—210°) which, in contrast to chromone (**1**), appears to form *via* formation of the dienol (**7**). As a result of deuterium labelling experiments, however, it has been shown that this dienol is not formed by a photochemical process but that it probably arises from a thermal, intramolecular 1,7-hydrogen shift from the expected photoenol (**6**), (Scheme). Thus, irradiation of the 2-([$^2H_3$]-methyl)derivative (**9**) in benzene, using a Pyrex filter and a medium pressure mercury lamp, afforded the specifically labelled benzoxanthenone (**10**), containing two deuterium atoms (m.s. and n.m.r. analysis), one of which was present in the methyl group. Further confirmation of the Scheme was obtained on irradiating the chromone (**5**) in the presence of dimethyl butynedioate. The reaction mixture contained some unchanged chromone (**5**), the benzoxanthenone (**8**), and the adduct (**11**) (ratio *ca.* 4 : 6 : 9). The structure of the adduct (**11**), m.p. 165—195° (decomp.) was confirmed by using the labelled chromone (**9**). In this case the adduct (**12**) showed no ^{1}H n.m.r.



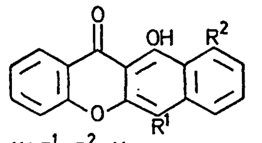
(1) $R^1 = Me; R^2 = H$
(2) $R^1 = H; R^2 = Me$
(5) $R^1 = R^2 = Me$
(9) $R^1 = CD_3; R^2 = Me$



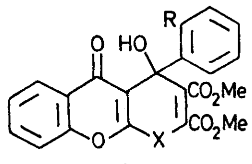
(3) $R = H; X = CH_2$
(6) $R = Me; X = CH_2$



(7) $R = Me; X = CH_2$



(4) $R^1 = R^2 = H$
(8) $R^1 = H; R^2 = Me$
(10) $R^1 = D; R^2 = CH_2D$



(11) $R = Me; X = CH_2$
(12) $R = CH_2D; X = CD_2$

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† All new compounds gave satisfactory analytical and spectral data.

signals corresponding to the methylene group (indicating -CD_2-), and an aromatic methyl group which integrated for two protons (-CH_2D).

The results are thus consistent with formation of an initial dienol (**6**), which undergoes rapid 1,7-hydrogen migration to produce the more stable, ground state dienol (**7**), which then undergoes either further photochemical cyclisation or trapping with the dienophile. The method constitutes a new photochemical route to the benzoxanthenones.[3]

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[1] K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417.

[2] W. A. Henderson and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5424.

[3] D. H. R. Barton, P. D. Magnus, and J. I. Okogun, *J.C.S. Perkin I*, 1972, 1103.