Photochemical Transformations of 2,2-Disubstituted Chromenes

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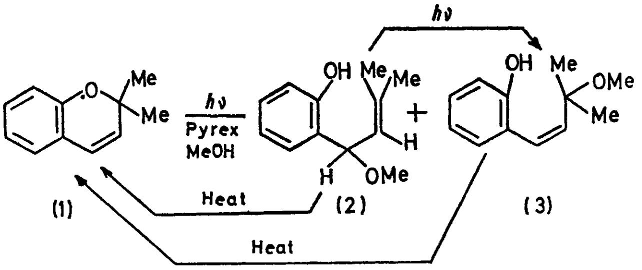
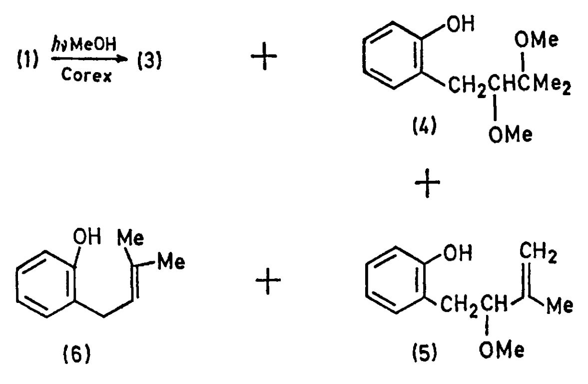
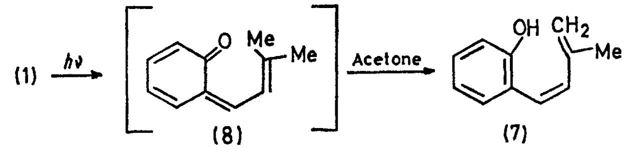
Summary Irradiation of 2,2-disubstituted chromenes give products derived from an *o*-quinoneallide intermediate, the fate of which depends on the nature of the substituent groups as well as the photolysis conditions.

In connection with the photoisomerization of cyclohexa-1,3-dienes to bicyclo[3,1,0]hex-2-enes,[1] we have studied the photochemistry of 2*H*-benzopyrans, since this system appeared to offer a possible synthesis of oxa-bicyclo[3,1,0]hex-2-ene derivatives. Although rearrangements of this type have been recently reported for nitrogen analogues,[2] no structurally related oxacyclic diene has been shown to undergo an analogous rearrangement. We now report preliminary observations on the photochemical reactivity of the 2,2-dimethyl- and 2,2-diphenyl-chromene systems.

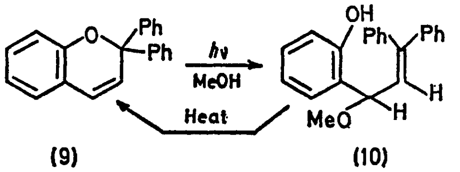


Irradiation of 2,2-dimethylchromene[3] (1) in methanol through Pyrex using a 550-W Hanovia lamp gave two major products whose relative yields varied with time of irradiation. When a 0·018M-solution of (1) was irradiated for 5 h, *ca.* 50% of starting material was consumed and the two products, isolated by preparative t.l.c., were shown to be methanol adducts (2) (70%) and (3) (30%). Irradiation for an additional 6 h gave a mixture containing mainly (3) with traces of (2), suggesting that at least part of (3) is formed from the secondary photoisomerization of (2). Both adducts revert to starting material when left in the dark; they were identified by their spectral data.‡





Irradiation of (1) (3 h) in methanol using a Corex filter gave a mixture of four products: (3) (4%), (4) (19%), (5) (8%), and (6) (17%). Photoadduct (4) was shown to be a secondary product resulting from further irradiation of ether (3). This compound corresponds to the anti-Markovnikov addition of methanol across the C=C double bond of (3).[4]



In contrast to the complex behaviour in the direct irradiation of (1), xanthone-sensitized photolysis gave only allylic ether (3) (90%). Photolysis of (1) in neat acetone, however, afforded the phenol (7) as sole photoproduct. Irradiation of (1) in benzene both with and without benzophenone sensitization likewise produced (7).

The results obtained are best rationalized in terms of an *o*-quinoneallide intermediate (8), the fate of which depends on experimental conditions. The primary mode of reaction [*i.e.* formation of (2) and (3)] corresponds to 1,4 and 1,6 addition of methanol. Allylphenol (6) is apparently formed by 1,4-photoreduction of (8) (Corex filter).[5] In inert solvents such as acetone (or benzene), the primary reaction path corresponds to a photoinduced 1,7-sigmatropic hydrogen shift.

The photochemistry of the related 2,2-diphenylchromene (9), was relatively simple. Irradiation in methanol gave a single photoadduct (10) which was unstable at room temperature and slowly reverted to (9) when left in the dark. Irradiation of (9) in benzene (Pyrex) produced a deep red colour which slowly disappeared in the dark at room temperature. N.m.r. analysis of the photolysate after removal of the solvent indicated that only starting chromene was

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‡ Complete spectroscopic and degradative details will be given elsewhere.

present. Attempts to trap the red species with methanol in the dark failed. We can only suggest that thermal reversion of the labile-*o*-quinoneallide intermediate is more rapid than 1,4-addition of methanol.

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[2] A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, 1970, **92**, 1778; T. DoMinh and A. M. Trozzolo, *ibid.*, p. 6997; P. Beak and J. L. Miesel, *ibid.*, 1967, **89**, 2375; B. Singh, *ibid.*, 1968, **90**, 3943; 1969, **91**, 3670; D. R. Arnold, V. Y. Abraitys, and D. Mclead, jun., *Canad. J. Chem.*, 1971, **49**, 923; L. J. Altman, M. F. Semmelhack, R. B. Hornby, and J. Vederas, *Chem. Comm.*, 1968, 686.

[3] R. L. Shriner and A. G. Sharp, *J. Org. Chem.*, 1939, **4**, 575.

[4] For a related case of anti-Markovnikov addition of methanol across a double bond see S. S. Hixson, *Tetrahedron Letters*, 1971, 4211.

[5] Similar reductions of *o*-quinoneallide intermediates have been observed: J. Kolc and R. S. Becker, *J. Phys. Chem.*, 1967, **71**, 4045.