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NOVEL PHOTOREORGANISATION OF 4-OXO-4*H*-1-BENZOPYRANS: SYNTHESIS OF PYRANOBENZOPYRONES

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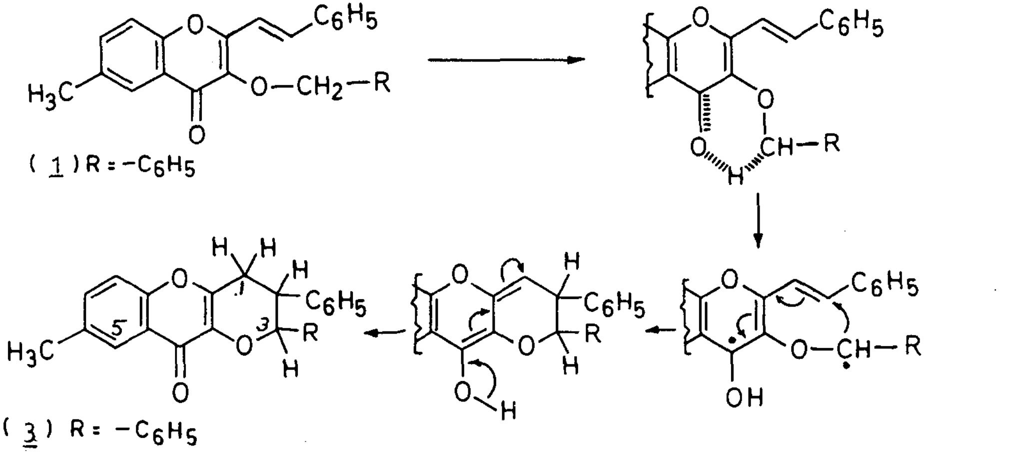
Summary. 2-Styryl- and 2-furyl-3-benzyloxy-4-oxo-4*H*-1-benzopyran on photolysis in benzene and MeOH, respectively, yield 2,3-pyranobenzopyrones via H-abstraction.

2-Methyl-3-methoxy-4-oxo-4*H*-1-benzopyran[1] on photolysis yields a dimeric oxetanol; in contrast 2-phenyl-3-methoxy (or benzyloxy) derivatives produce angular tetracyclic compounds[2]. These reactions invoke the intermediacy of γ-hydrogen abstraction, producing 1,4-biradicals in turn. In this communication, we report an interesting and novel photoreorganisation of two benzopyrans namely 2-styryl- (1) and 2-furyl-3-benzyloxy-4-oxo-4*H*-1-benzopyrans (2) to 2,3-pyranobenzopyrones (3 and 4).

The 2-styryl derivative (1) on irradiation (benzene, pyrex filter) isomerised to (3), yield 20%; m.p. 188-89°; $M^{+\cdot}$ 368 (100%); IR (Nujol), 1640 cm^{-1} (C=O); PMR ($CDCl_3$), δ 2.45 (3H, s, CH_3), 3.10-3.35 (2H, m, C_1-2H's), 3.45-3.62 (1H, m, C_2-H), 5.0 (1H, d, J = 8.8 Hz, C_3-H)[3], 7.10-7.50 (12H, m, Arom Hs), 8.10 (1H, s, broad; C_5-H).

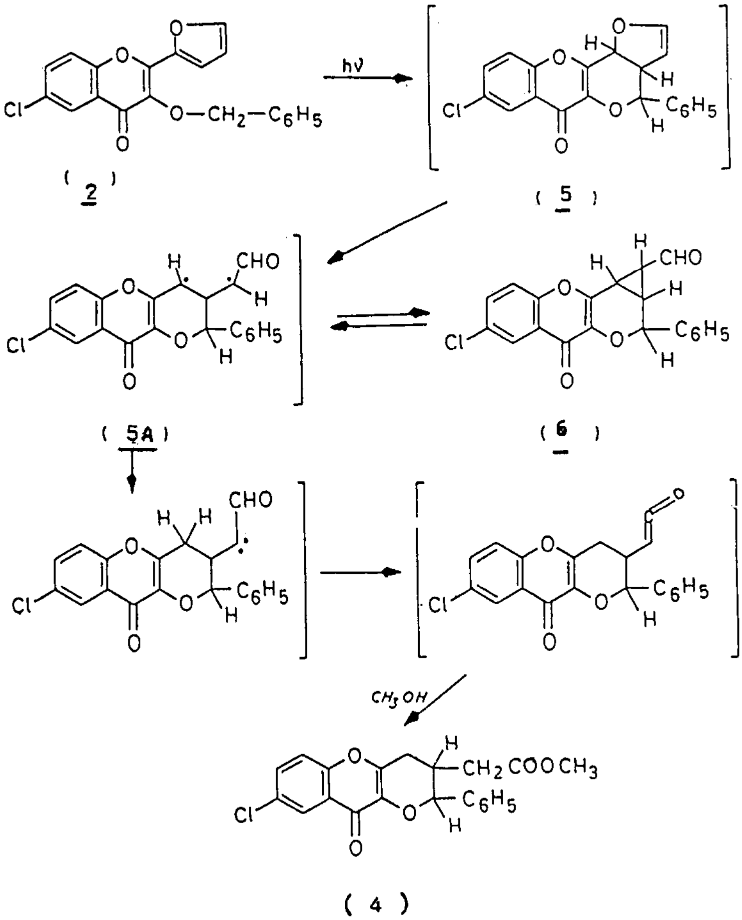


(1) R = $-C_6H_5$

(3) R = $-C_6H_5$

Stilbenes and their heteroanalogues are known to photocyclise exclusively to multiringed angular carbocyclic and heterocyclic compounds.[4] This is the first example as far as we know where a styryl derivative has been converted into a linearly fused ring compound.

On photolysis (2) in MeOH (pyrex filter) gave (4), yield 8%; m.p. 193-95°; $M^{+\cdot}$ 384 (86%); IR (Nujol), 1640 cm^{-1} (C=O), 1735 cm^{-1} ($COOCH_3$); PMR ($CDCl_3$), 2.31-2.43 (2H, s, CH_2COOCH_3), 2.60-3.20 (3H, m, C_1 and C_2-H's),



3.84 (3H, s, $-OCH_3$), 5.01 (1H, d, J = 6 Hz, C_3-H)[3], 7.25-7.48 (6H, m, C_9-H and C_3-C_6H_5), 7.57 (1H, dd, C_8-H), 8.22 (1H, d, C_6-H).

The obtension of (4) can be visualised to occur through the possible initial cyclisation of (2) to dihydrofuryl derivative (5) in a fashion shown for compound (1) which under the photolytic conditions can cleave to a bi-radical (5A). This either can clip to produce cyclopropylaldehyde (6) through a ring contraction and ring expansion[5] process or can rearrange to ketene preceded by carbene[6]; then consequential addition of MeOH leads to tricyclic ester (4). The proposed mechanism finds support from the observation that an irradiation of (2) in benzene solvent led exclusively to (6), yield 16%; m.p. 150-51°; M^{+} 352/354[7]; IR (Nujol), 1640 cm^{-1} (C = O) and 1695 cm^{-1} (-CHO); PMR ($CDCl_3$), 2.56-2.79 (2H, m, C_6-H and C_3-H), 2.95-3.06 (1H, m, C_1-H), 5.57 (1H, s, C_4-H), 7.21-7.41 (6H, m, C_{10}-H and C_4-phenyl), 7.57 (1H, dd, C_9-H), 8.16 (1H, d, C_{10}-H), 9.80 (1H, d, C_1-CHO)[8].

It is of interest to mention here that both (1 and 2) provide an easy route to the synthesis of 2,3-pyranobenzopyrones. Although literature abounds in the methods towards the construction of 5,6 or 6,7 or 7,8-pyranobenzopyrones[9], no method seems to be available for the synthesis of 2,3-pyranobenzopyrones.

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