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PHOTOCHEMICAL SYNTHESIS OF NATURALLY OCCURRING β-DIKETONES

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Summary: Photochemical syntheses of pongamol, ovalitenone, and milletone from the corresponding 2'-methoxychalcone epoxides are reported.

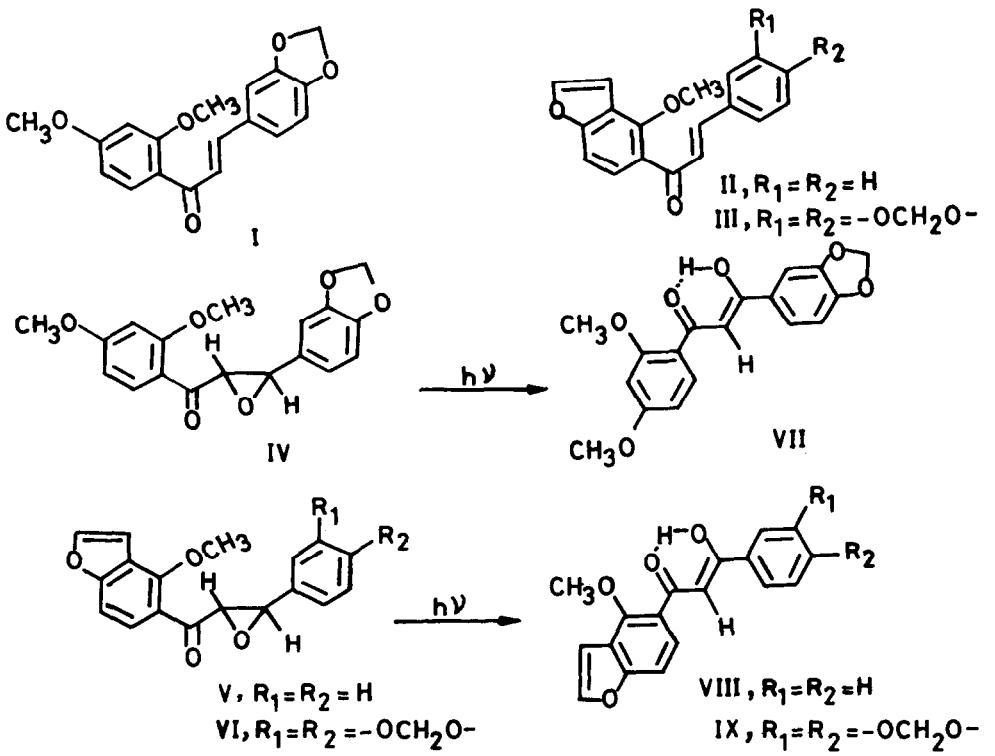
Photochemical investigations have shown that 2,3-epoxy-3-phenylpropiophenones (chalcone oxides) gave the corresponding 1,3-diphenylpropane-1,3-diones (dibenzoylmethanes)[1]. This apparent 1,2-shift has been observed by a number of workers with related epoxy-ketones[2-4] and with 2'-hydroxychalcone[5]. In this paper we report photochemical syntheses of Pongamol[6] (VIII), Ovalitenone[7] (IX) and Milletenone[8] (VII) from the corresponding 2'-methoxychalcone epoxides in good yield (~75%). The chalcones required are 2',4'-dimethoxy-3,4-methylenedioxychalcone (I), Ovalitenin-A[7] (II) and 2'-methoxy-3,4-methylenedioxy-furano (2",3"-3',4')chalcone[9] (III). These were converted into the epoxides (IV-VI) using alkaline H_2O_2[10]. The spectral characteristics of 2'-methoxy-3,4-methylenedioxy-furano(2",3"-3',4')chalcone epoxide (VI) are given below. Chalcone epoxides (IV), m.p. 136° and (V), m.p. 117° had spectral data consistent with their structures.

2'-Methoxy-3,4-methylenedioxy-furano(2",3"-3',4')chalcone epoxide (VI)

M.p. 133-4°, λ_{max}^{MeOH} (log ε): 240(4.5), 290(sh) nm. ν_{max}^{KBr} : 1650,1045 & 930 cm^{-1}. PMR (90 MHz, $CDCl_3$, δ): 4.0(br, s, 4H, -OMe & H-α), 4.35(d, 1H, J = 2Hz, H-β), 6.1(s, 2H, $-OCH_2O-$), 6.5(d, 1H, J = 2Hz, H-3"), 7.0(d, 1H, J = 2 Hz, H-2"), 7.75(d, 1H, J = 10 Hz, H-5'), 8.3(d, 1H, J = 10 Hz, H-6') and 6.95(m, 3H, H-2,5 & 6).

Photolysis of chalcone epoxides (IV-VI)

The epoxide (200 mg) was dissolved in benzene (50 ml) and the solution after flushing with nitrogen was irradiated using low wavelength photochemical reactor (Engelhard Hanovia) for 1 hr. at room temperature. The solvent was removed under reduced pressure and the residual mass was chromatographed



(column & preparative TLC) over silica gel. The products identified by comparison with the authentic samples were the β-diketone (75%), the corresponding acetophenone and aldehyde. The spectral characteristics of synthetic pongamol (VIII) are given below. Ovalitenone (IX) and Milletenone (VII) had spectral data consistent with those reported for the corresponding authentic samples.

Pongamol: M.p. 128-29°, λ_{max}^{MeOH}(log ε): 245(4.37), 345(4.33) nm. ν_{max}^{KBr}: 1600, 1550 cm^{-1}. PMR: 4.0(s, 3H, -OMe), 6.9(d, 1H, J = 2Hz, H-3"), 7.0(d, 1H, J = 10 Hz, H-5), 7.0 - 7.5(m, 6H, H-2',3',4',5',6' & one olefinic proton), 7.5(d, 1H, J = 2Hz, H-2"), 7.8(d, 1H, J = 10 Hz, H-6), [4.5(s, 1/3H), 3.8(s, ½H) due to protons of diketo and olefinic forms (enol)]; identical with an authentic sample[6].

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