SYNTHESIS OF 2-METHYL-2,3-DIHYDROFURO[3,2-*c*]COUMARIN

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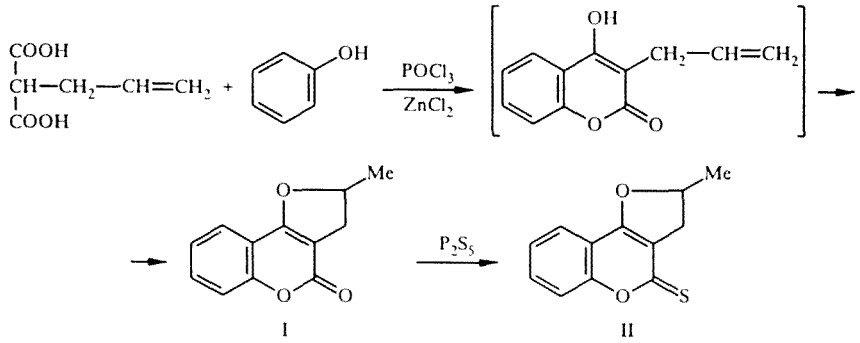
Furocoumarins are an important class of natural products which possess valuable physiological properties [1, 2].

2-Methyl-2,3-dihydrofuro[3,2-*c*]coumarin (I) was synthesized by the reaction of phenol with allylmalonic acid at 60-70°C in the presence of phosphorus oxychloride and zinc chloride. Compound I was apparently formed by cyclization of 3-allyl-4-hydroxycoumarin (the product of the Pechman reaction [3]), as a result of an intramolecular cyclization via the attack of the nucleophilic hydroxyl group on the β-carbon of the allyl group. 2-Methyl-4-thioxy-2,3-dihydrofuro[3,2-*c*]chromene (II) was obtained by the treatment of the furocoumarin (I) with phosphorus pentasulfide in pyridine or xylene.



I II

2-Methyl-2,3-dihydrofuro[3,2-*c*]coumarin (I). Yield 59%. mp 135°C (xylene). R_f 0.76 (1:1 xylene–ethyl acetate). Found, %: C 71.57, H 4.59. Calc. for $C_{12}H_{10}O_3$, %: C 71.29, H 4.98. IR spectrum: 1630 (C=C), 1670 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$ + DMSO): 1.5 (3H, d, CH_3), 3.1 (2H, d, CH_2), 4.5 (H, m, CH), 7.2-8.0 ppm (4H, m, arom.).

2-Methyl-4-thioxy-2,3-dihydrofuro[3,2-*c*]chromene (II). Yield 65%. mp 75°C (petroleum ether). R_f 0.59 (5:1 xylene–ethyl acetate). Found, %: C 66.24, H 4.31, S 14.54. Calc. for $C_{12}H_{10}O_2S$, %: C 66.07, H 4.62, S 14.70. IR spectrum: 1150 (C=S), 1630 cm^{-1} (C=O).

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