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The Synthesis of 2,8-Diphenyl-4*H*,10*H*-benzodipyran-4,10-dione

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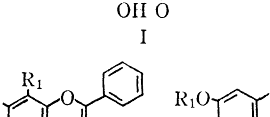
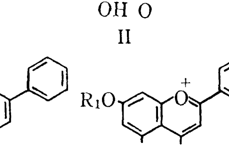
Recently one of the present authors has reported a new flavone, "arthraxin" (I), with a 4*H*,10*H*-benzodipyran-4,10-dione skeleton.[1] Now the unequivocal synthesis of 2,8-diphenyl-4*H*,10*H*-benzodipyran-4,10-dione (II) has been performed in a way which will be described below.

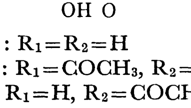
The acetylation of 5,7-dihydroxyflavone (III) with acetic acid in the presence of boron trifluoride affords 8-acetyl-5,7-dihydroxyflavone (IV). The alternative structure V is rejected by means of a study of the NMR spectrum, as is shown in Table 1. From the calculation, based on the analysis in terms of the additive substituent shielding values,[2-4] each proton at H-6 or H-8 can be predicted to have the same value. The difference between the real value of the protons at H-6 and H-8 can be explained as being caused by the ring current of the structure IX. Heating an *o*-hydroxyacetophenone, IV, with benzoic anhydride and sodium benzoate gives the title compound, II. All the spectral data as well as the result of the elemental analysis support this structure.

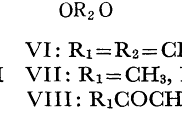
TABLE 1. (δ)

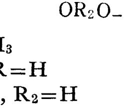
Compound	H-8	H-6	H-3
III	6.55	6.25	6.85
IV		6.35	6.70
VI	6.57	6.36	6.65
VII	6.56	6.38	6.63
VIII	6.86	6.56	6.73


I


II







III: $R_1=R_2=H$ VI: $R_1=R_2=CH_3$
IV: $R_1=COCH_3$, $R_2=H$ VII: $R_1=CH_3$, $R=H$
V: $R_1=H$, $R_2=COCH_3$ VIII: R_1COCH_3, $R_2=H$

Experimental

8-Acetyl-5,7-dihydroxyflavone (IV). Through a solution of 5,7-dihydroxyflavone (III) (0.4g) in acetic acid saturated with boron trifluoride, boron trifluoride gas was passed for 5 hr with stirring. The color of the reaction mixture turned from yellow to brown, and then yellow precipitates appeared. The precipitates were filtered and treated by heating under reflux in 200m*l* of water for 20 min to produce IV as yellow precipitates. This was purified by sillica-gel-column chromatography, using a benzene-ethyl acetate (2:1) mixture, to give pale yellow needles; mp 208 —209°C; UV, 235 (15700), 248 (15200), and 276 (16700) nm (ε); IR (KBr), 3450, 1655, 1605, and 1590 cm^{-1}; NMR ($CDCl_3$), δ 2.85 (s, 3H, $PhCOCH_3$), 6.35 (s, 1H, H-6), 6.70 (s, 1H, H-3), 7.5—8.0 (m, 5H, H-2', 3', 4', 5', 6'), 13.8 (s, IH), 14.3 (s, 1H).

Found: C, 69.04; H, 4.22%. Calcd for $C_{17}H_{12}O_5$: C,68.91; H, 4.08%.

*2,8-Diphenyl-4*H*,10*H*-benzodipyran-4,10-dione (II).* A mixture of 8-acetyl-5,7-dihydroxyflavone (0.5 g), benzoic anhydride (10 g), and sodium benzoate (1 g) was blended in a mortar and then heated in an oil bath at 180°C for 6 hr. The reaction mixture was dissolved in 30 m*l* of ethanol, and to this solution a solution of potassium hydroxide (3.2 g) in water (2 m*l*) was added; the mixture was then heated under reflux for 30 min to decompose a benzene of II. After the ethanol had been evaporated from the mixture, water was added and a stream of carbon dioxide was passed through to give yellow precipitates. The precipitates were filtered, washed with acetone, and then reprecipitated from a benzene-ethyl acetate (1:1) mixture to afford pale yellow powders; mp 275°C (decomp.); UV, 256 (41900) and 287 (40700) nm(ε); IR, 3450, 1655, 1640, and 1585 cm^{-1}; NMR δ 6.85 (s, 1H), 6.95 (s, 1H), 7.30—7.65 (m, 7H), 7.8—8.1 (m, 4H), 12.25 (s, 1H).

Found: C, 75.02; H, 3.79%. Calcd for $C_{24}H_{14}O_5$:C, 75.39; H, 3.69%.

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2) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35,** 731 (1961).
3) P. Diehl, *Helv. Chim. Acta*, **44,** 829 (1961).
4) J. A. Ballantine and C. T. Pillinger, *Tetrahedron*, **23,** 1691 (1967).