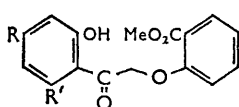


953. *Chromono(2',3':3,2)benzofurans*

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PHILBIN, WHEELER, and ÓCINNÉIDE¹ reported the synthesis of some chromono(2',3':3,2)-benzofurans by the drastic demethylation of 2'-methoxyflavonols; no yield was recorded. The attempted cyclisation of 2'-hydroxyflavonols under similar conditions failed.¹

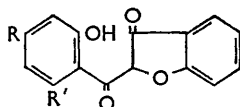
We now report the synthesis of chromono(2',3':3,2)benzofurans (VI—VIII) by a ready acid-catalysed dehydration of 2-2'-hydroxybenzoylcoumaran-3-ones (IV—V).



(I); R = OH, R' = H

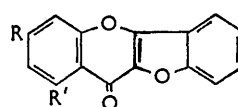
(II); R = R' = OMe

(III); R = R' = OH



(IV); R = OH, R' = H

(V); R = R' = OMe



(VI); R = OH, R' = H

(VII); R = OMe, R' = H

(VIII); R = R' = OMe

2,4-Dihydroxy- ω -(2-methoxycarbonylphenoxy)acetophenone² (I) with potassium carbonate in acetone gave 2-(2,4-dihydroxybenzoyl)coumaran-3-one (IV). Under similar conditions, 2,4,6-trihydroxy- ω -(2-methoxycarbonylphenoxy)acetophenone² (III) failed to

¹ E. M. Philbin, T. S. Wheeler, and F. ÓCinnéide, *Chem. and Ind.*, 1961, 715.

² R. Bryant and D. L. Haslam, *J.*, 1965, 2361.

condense. However, 2-hydroxy-4,6-dimethoxy- ω -(2-methoxycarbonylphenoxy)acetophenone (II) readily afforded 2-(2-hydroxy-4,6-dimethoxybenzoyl)coumaran-3-one (V). Treatment of the 2-2'-hydroxybenzoylcoumaranones (IV and V) with methanolic hydrogen chloride gave respectively, 7'-hydroxy- (VI) and 5',7'-dimethoxychromono(2',3':3,2)benzofuran (VIII). 7'-Methoxychromonobenzofuran (VII) was obtained by methylation of compound (VI).

Experimental.—Ultraviolet spectra (in chloroform solutions) and infrared spectra (in Nujol) were measured with Unicam S.P. 800 and 200 spectrometers, respectively.

2-(2,4-Dihydroxybenzoyl)coumaranone (IV).—2,4-Dihydroxy- ω -(2-methoxycarbonylphenoxy)acetophenone ² (2.06 g.) was stirred and refluxed for 3 hr. in acetone (100 ml.) containing potassium carbonate (10 g.). The solvent was removed and the product dissolved in water. The solution was acidified, and extracted with ether. The extract was dried (Na₂SO₄) and evaporated to yield the dihydroxybenzoylcoumaranone (1.6 g., 90%), yellow needles (ethanol-water), m. p. 210—212° λ_{\max} 297 and 367 m μ (ϵ 7,900 and 25,500, respectively); ν_{\max} 1625 (CO) and 3200 cm.⁻¹ (OH) (Found: C, 66.2; H, 3.6. C₁₅H₁₀O₅ requires C, 66.8; H, 3.7%).

7'-Hydroxychromono(2',3':3,2)benzofuran (VI). The above dihydroxybenzoylcoumaranone (1.0 g.) was refluxed for 7 hr. in methanol (70 ml.), previously saturated with dry hydrogen chloride. 7'-Hydroxychromono(2',3':3,2)benzofuran (0.328 g., 35%) was precipitated. It was recrystallised as orange needles (ethanol-chloroform), m. p. 315—317°, λ_{\max} 252, 271, and 316 m μ (ϵ 14,900, 7,450, and 29,600, respectively), ν_{\max} 1655 cm.⁻¹ (Found: C, 71.9; H, 3.4. C₁₅H₈O₄ requires C, 71.4; H, 3.2%).

7'-Methoxychromono(2',3':3,2)benzofuran (VII). 7'-Hydroxychromono(2',3':3,2)benzofuran (100 mg.) was methylated with methyl iodide-potassium carbonate in the usual way. The methoxy-compound crystallised from ethanol in almost colourless needles, m. p. 213—214°; λ_{\max} 255, 268 and 318 m μ (ϵ 15,750, 4,980, and 32,000, respectively); ν_{\max} 1660 cm.⁻¹ (CO) (Found: C, 72.2; H, 3.9; MeO, 11.3. C₁₆H₁₀O₄ requires C, 72.2; H, 3.8; MeO 11.7%).

2-Hydroxy-4,6-dimethoxy- ω -(2-methoxycarbonylphenoxy)acetophenone (II). 2,4,6-Trimethoxy- ω -(2-carboxyphenoxy)acetophenone ² (13.9 g.) was refluxed for 5 min. with a mixture of glacial acetic acid (170 ml.) and 40% hydrobromic acid (70 ml.). Dilution with water precipitated ω -(2-carboxyphenoxy)-2-hydroxy-4,6-dimethoxyacetophenone as white needles (10.9 g., 82%), m. p. 215—217° (ethanol-chloroform); λ_{\max} 295 m μ (ϵ 24,600); ν_{\max} 1725 (CO) and 3220 cm.⁻¹ (OH) (Found: C, 61.4; H, 4.8; MeO, 18.7. C₁₇H₁₆O₇ requires C, 61.4; H, 4.85; 2MeO, 18.7%). Methylation of this carboxylic acid (10.9 g.) yielded 2-hydroxy-4,6-dimethoxy- ω -(2-methoxycarbonylphenoxy)acetophenone (4.02 g., 35%), white needles, m. p. 95—97° (ethanol); λ_{\max} 293 m μ (ϵ 23,600); ν_{\max} 1710 cm.⁻¹ (CO) (Found: C, 61.2; H, 4.95; MeO, 26.0. C₁₈H₁₈O₇ requires C, 62.4; H, 5.2; 3MeO, 26.9%).

2-(2-Hydroxy-4,6-dimethoxybenzoyl)coumaran-3-one (V). 2-Hydroxy-4,6-dimethoxy- ω -(2-methoxycarbonylphenoxy)acetophenone (4.0 g.) was condensed by using potassium carbonate in acetone, as described above. The 2-2'-hydroxybenzoylcoumaranone (V) was obtained as yellow prisms (2.0 g., 57%), m. p. 113—115°; λ_{\max} 304 and 363 m μ (ϵ 3,780 and 4000); ν_{\max} 1625 (CO) and 3200 cm.⁻¹ (OH) (Found: C, 64.8; H, 4.4; MeO, 19.4. C₁₇H₁₄O₆ requires C, 65.0; H, 5.0; 2MeO, 21.0%).

5',7'-Dimethoxychromono(2',3':3,2)benzofuran (VIII). 2-(2-Hydroxy-4,6-dimethoxybenzoyl)-coumaranone (3 g.) was refluxed for 3 hr. in methanolic-hydrogen chloride. The solvent was removed, and the residue dissolved in chloroform. The solution was washed with 5% sodium hydroxide, dried (Na₂SO₄), and chromatographed on alumina (Peter Spence type 0). 5',7'-Dimethoxychromono(2',3':3,2)benzofuran (1.1 g., 38%) was obtained as salmon-coloured needles, m. p. 262—263° (ethanol-chloroform); λ_{\max} 259, 309 and 330 m μ (ϵ 25,500, 20,500 and 17,300, respectively); ν_{\max} 1660 cm.⁻¹ (CO) (Found: C, 68.8; H, 4.0; MeO, 20.5. C₁₇H₁₂O₅ requires C, 68.9; H, 4.1; 2MeO, 21.0%).