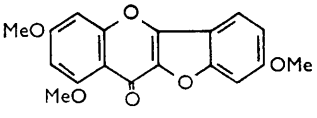
Acid Cleavage of 6-Methoxy-2-(2,4,6-trimethoxybenzoyl)coumaran-3-one

By **Rhys Bryant** † and **D. L. Haslam**, Department of Chemistry, The University, Manchester 13

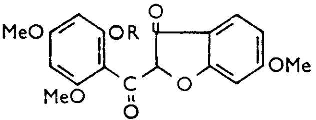
Under acidic conditions 6-methoxy-2-(2,4,6-trimethoxybenzoyl)coumaran-3-one did not demethylate to give the expected 6-methoxy-2-(2-hydroxy-4,6-dimethoxybenzoyl)coumaran-3-one, but cleaved to give 1,3,5-trimethoxybenzene and 6-methoxycoumaranone.

CHROMONO(2′,3′:3,2)BENZOFURANS (I) are readily prepared[1] by acid cyclisation of 2-(2-hydroxybenzoyl)-coumaran-3-ones (II; R = H). The latter compounds may be prepared[2] by a four-stage synthesis from 2-hydroxy-ω-(2-methoxycarbonylphenoxy)acetophenones (III). A more convenient synthesis of 2-(2-hydroxybenzoyl)-coumaranones would appear to be by demethylation of 2-(2-methoxybenzoyl)coumaranones (II; R = Me).

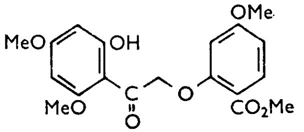
We have investigated the action of a variety of Lewis acids on the methoxy-compound (II; R = Me), but failed to bring about demethylation. Instead, with mild reagents (anhydrous aluminium chloride in refluxing ether, or acetic acid–hydrochloric acid), the compound cleaved to give 6-methoxycoumaran-3-one (IV) and 1,3,5-trimethoxybenzene. The cleavage presumably takes place by electrophilic attack of the Lewis acid (here denoted by H$^+$) at the aromatic carbon atom (V) giving a carbonium ion (VI). The corresponding acid would then undergo decarboxylation to the coumaranone (IV).



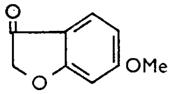
(I)



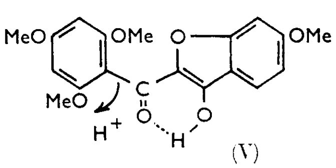
(II)



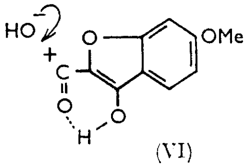
(III)



(IV)



(V)



(VI)

EXPERIMENTAL

Ultraviolet spectra (for chloroform solutions) were measured using Unicam SP800, Perkin-Elmer 137, or Cary 14 spectrophotometers. Infrared spectra were recorded in Nujol using a Unicam SP200 spectrometer. Nuclear magnetic resonance spectra were obtained using a Varian A60 instrument.

6-Methoxy-2-(2,4,6-trimethoxybenzoyl)coumaran-3-one (II; R = Me).—This *compound* was prepared from ω-chloro-2,4,6-trimethoxyacetophenone[3] and methyl 2-hydroxy-4-methoxybenzoate[4] according to the method of Bryant and Haslam.[2] It had m. p. 174—175° (EtOH–CHCl$_3$), $\lambda_{\text{max.}}$ 244, 262 (infl.), and 352 mμ (ε 7900, 6800, and 21,500), $\nu_{\text{max.}}$ 1610 cm.$^{-1}$ (CO) (Found: C, 63·5; H, 5·1; OMe, 35·1%. $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·1; 4OMe, 34·6%).

Attempted Demethylation of 6-Methoxy-2-(2,4,6-trimethoxybenzoyl)coumaran-3-one (II; R = Me).—The coumaranone (II) (2 g.) and anhydrous aluminium chloride (0·746 g.) in ether (sodium-dried) were stirred and heated under reflux 1 hr., stirred overnight, and then heated under reflux for a further 3 hr. The ether was removed and the residue warmed for 30 min. with a mixture of glacial acetic acid (20 ml.) and conc. hydrochloric acid (10 ml.). The liquid was extracted into ether, washed with aqueous sodium hydrogen carbonate, dried (MgSO$_4$), and evaporated. The residual red oil (1·6 g.) was chromatographed on a column of silicic acid (Mallinckrodt A.R., 100 mesh). Elution with chloroform gave two fractions: (i) 351 mg., which crystallised from hexane, m. p. 54—55° (Found: C, 64·2; H, 7·1. Calc. for $C_9H_{12}O_3$: C, 64·3; H, 7·2%). The m. p. was undepressed when mixed with authentic 1,3,5-trimethoxybenzene. The n.m.r. spectrum in deuteriochloroform indicated 3 identical aromatic protons (τ 3·9) and 9 methoxy-protons (τ 6·25); (ii) 368 mg. material which on crystallisation yielded 6-methoxycoumaran-3-one,[5] m. p. 122—124° (EtOH) (Found: C, 65·3; H, 5·4; OMe, 19·0. Calc. for $C_9H_8O_3$: C, 65·85; H, 4·9; OMe, 18·9%).

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† *Present address:* Mead Johnson Research Center, Evansville, Indiana 47721, U.S.A.

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