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THE REACTION BETWEEN MESITYL OXIDE AND 4-HYDROXYCOUMARIN

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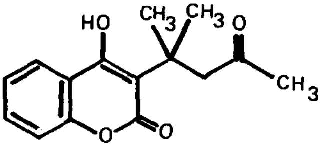
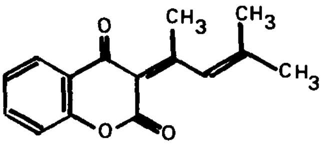
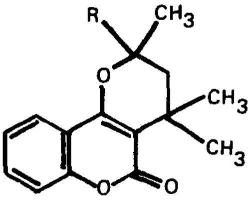
Two products have been obtained (1) from the reaction between 4-hydroxycoumarin and mesityl oxide; the structure (I) was assigned to the acidic, heptane insoluble product, $C_{15}H_{16}O_4$ (m.p. 212°), and the structure (II) to the neutral, heptane soluble product $C_{15}H_{14}O_3$ (m.p. 93°). The conversion of (I) into a ketal (III, $R = OCH_3$) by the action of methanolic hydrogen chloride was also observed.



(I)



(II)



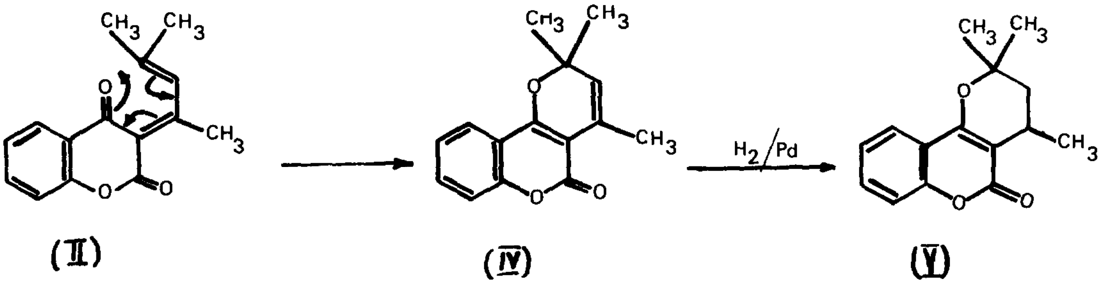
(III)

In the i.r. spectrum of the acid there is a ν_{max} C=O at 1668 cm^{-1} due to the carbonyl group in the side chain, hydrogen-bonded to the hydroxyl group of the coumarin residue. The u.v. spectrum is typical of a 3-substituted 4-hydroxycoumarin showing maxima at 318 (7,500), 304 (11,300), 281 (13,300) and 269 nm. (ε 12,100). The acid is insoluble in chloroform but can be dissolved in trifluoroacetic acid to give (III, R = OH), when the n.m.r. spectrum (60 Mc./sec.) shows singlets at 8.95 (3H), 8.75 (3H) and 8.27 τ (3H) and an AB multiplet H_A = 7.78, H_B = 7.16 τ (J_{AB} = 15.0 c./sec.). Thus the spectroscopic evidence confirms that the acid (I) is 3-(α,α-dimethyl-β-acetylethyl)-4-hydroxycoumarin.

The i.r. and u.v. spectra of the neutral product show that it is not a simple 4-hydroxycoumarin and the n.m.r. spectrum is inconsistent with the structure (II). In addition, catalytic hydrogen of the neutral compound results in the consumption on one (and not two) moles of hydrogen and gives rise to an oily product with the u.v. spectrum of a simple coumarin derivative and which has ν_{max} C=O (liq.) at 1712 $cm.^{-1}$

The n.m.r. (CCl_4) of the oil suggests that it is 2,2,4-trimethylpyrano[5,6-c]coumarin (V) as there are signals at 8.63 (3H s), 8.45 (3H s), 8.60 τ (3H d, J = 6.5 c./sec.) and an ABX pattern H_A = 7.92, H_B = 8.35 τ (J_{AB} = 13.9 c./sec., J_{AX} = 6.7 c./sec. and J_{BX} = 10.0 c./sec.). There are also complex multiplets at 7.15)1H) and 2.2 - 3.0 τ (3H).

This indicates that the neutral product must be (IV) which is probably formed from the initial adduct (II), by an electrocyclic reaction similar to that observed with β-ionone (2).



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