Revision of the Structure of the Reported "5-Hydroxydihydrocoumarin"

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CONDENSATION of phenols with αβ-unsaturated nitriles in the presence of zinc chloride and dry hydrogen chloride leads to formation of saturated nitriles which, on hydrolysis, cyclize to dihydrocoumarins.[1] Such reactions have been referred to as "abnormal" Hoesch reactions. With resorcinol, Adams[2] and his co-workers isolated dihydroumbelliferone m.p. 132—134°, but Stephen[3] isolated, besides dihydroumbelliferone, another compound m.p. 224—225°, which was described as 5-hydroxydihydrocoumarin. During our study on the condensation of phenols with methyl acrylate in the presence of aluminium chloride[4] and dry hydrogen chloride at high temperature, with resorcinol, we isolated dihydroumbelliferone† and another compound m.p. 224—225° (compound A) in poor yield, presumably the one described by Stephen *et al.*

Compound A, on dehydrogenation over Pd–C (10%) in diphenyl oxide,[5] afforded a compound melting at 330°, not identical with 5-hydroxycoumarin (lit.[6] m.p. 225—226°). The i.r. spectrum showed no absorption in the hydroxyl region but showed bands at 1760 (lactone), 855, and 870 cm.$^{-1}$ (tetra-substituted aromatic compound). While the observed analytical data agreed with those calculated for 5-hydroxydihydrocoumarin, mass-spectral results (*M* 218) indicated its molecular formula to be $C_{12}H_{10}O_4$. The structure was established by n.m.r. and by synthesis.

Dihydroumbelliferone (II), on treatment with methyl acrylate in the presence of aluminium chloride and dry hydrogen chloride at 150—160°, afforded a material (III) which after subsequent decomposition and purification melted at 224—225°. This was found to be identical with compound A (i.r. spectrum and undepressed mixed m.p.). Compound (III) on dehydrogenation yielded the same compound (IV) m.p. 330°, *M* 214, isolated before from compound A. The i.r. spectrum showed bands at 1740 (α-pyrone), 1625 (olefinic stretch), and 800—810 cm.$^{-1}$ (tetra-substituted aromatic); u.v. (acetonitrile) λ_{max} 274, 338, and 355 mμ (log ε 5·1, 4·8, and 4·7). All these observations indicated the presence of a coumarin ring system. The n.m.r. spectrum could not be determined, due to insolubility in common solvents.

The n.m.r. spectrum of compound A reveals two distinct singlets at 6·82 (due to H_B) and at 7·10 p.p.m. (due to H_A), uncoupled with each other,

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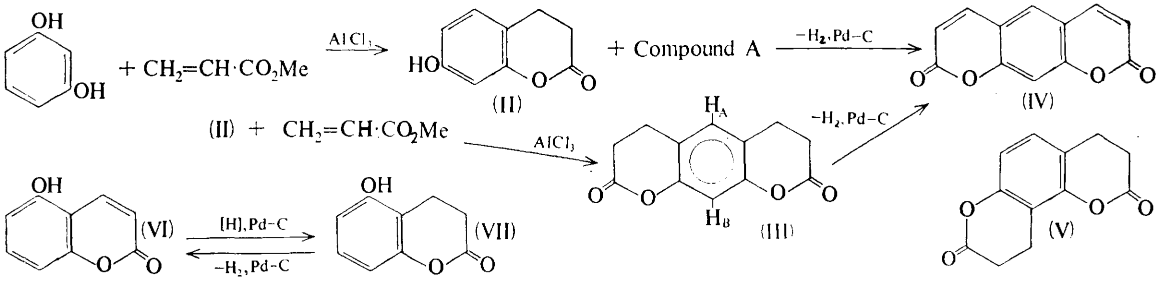
† Satisfactory elemental analysis was obtained for each new compound; all were homogeneous (t.l.c.).



for the two *para*-aromatic protons; the other eight protons appeared in the region 2·6—3·2 p.p.m. Hence for compound A structure (III) is preferred to (V).

Catalytic reduction by Pd–C (10%) of an authentic sample of 5-hydroxycoumarin (VI) (prepared by the method of Shah *et al.*[6]) gave 5-hydroxydihydrocoumarin (VII) m.p. 170—172°, i.r. maxima at 3448 (hydroxyl) and 1728 cm.$^{-1}$ (lactone). Dehydrogenation over Pd–C gave back (VI) m.p. 224—225°.

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