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On the Synthesis and Structure of 4-Hydroxy-3-phenyl-coumarins and Related 2-Imides

It was reported by CHATTERJEA and ROY[1] that 4-hydroxy-3-phenyl-coumarin and *o*-hydroxyphenyl benzyl ketone (V, III $R = R' = H$) were obtained from *o*-methoxybenzoyl-phenylacetonitrile (I) by means of hydrobromic acid. The author also prepared several methoxy-substituted derivatives by the action of anhydrous aluminium chloride[2] and finds that the action of pyridine hydrochloride under reflux on nitriles of type I (R, R' = H or OMe) causes demethylation of all the methoxy groups and subsequent cyclisation to give intermediate imides (IV; R, R' = H or OH), hydrolysis of which to coumarins (V; R, R' = H or OH) is somewhat difficult when compared with that of ketimines in the Hoesch reaction. Imides of this kind were also obtained[2] by the action of aluminium chloride on I (the methoxy group of which in the *p*-position of carbonyl group was unaffected) and by ester condensation of methyl *o*-methoxybenzoates with phenylacetonitrile. On the other hand, the action of pyridine hydrochloride on esters (II; R, R' = H or OMe) prepared by ethanolysis[3] of I caused cleavage of ester group, decarboxylation, and then demethylation of all the methoxy groups to give ketones (III; R, R' = H or OH). These ketones (III; R, R' = H or OMe) were also obtained by the action of hydrochloric acid[3] on I and II (the methoxy group of which, except when in the *o*-position of carbonyl group, was unaffected).

The infrared spectra of compounds IV and V give indication that the coumarin structures should be replaced by chromone structures, namely 2-amino-(VI) and 2-hydroxy-isoflavones VII respectively. Carbonyl absorption of the compounds is longer than 6 μ (chromones are above[3,4], 4-hydroxycoumarins below[4,5] the 6 μ region).

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[1] J. N. CHATTERJEA and S. K. ROY, J. Indian chem. Soc. *34*, 155 (1957) [Chem. Abstr. *52*, 1987 (1958)]. – Cf. J. N. CHATTERJEA, J. Indian chem. Soc. *34*, 98 (1957) [Chem. Abstr. *51*, 16445 (1957)].

[2] Y. KAWASE, Bull. chem. Soc. Japan *31*, 390, 440 (1958) and unpublished work.

[3] H. L. HERGERT and E. F. KURTH, J. Amer. chem. Soc. *75*, 1622 (1953). – B. L. SHAW and T. H. SIMPSON, J. chem. Soc. *1955*, 655. – G. E. INGLETT, J. org. Chem. *23*, 93 (1958).

[4] C. H. STAMMER *et al.*, J. Amer. chem. Soc. *80*, 137, 140 (1958). – M. YAMAGUCHI, J. japan. Chem. (Kagaku no Ryoiki) Extra Vol. *28*, 124, 126 (1958).

[5] T. R. GOVINDACHARI *et al.*, J. chem. Soc. *1956*, 629. – F. M. DEAN *et al.*, J. chem. Soc. *1957*, 3497.