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REACTION OF THIONYL CHLORIDE WITH FLAVONE

J. R. Merchant and D. V. Rege

Department of Chemistry
Institute of Science
Madam Cama Road, Bombay-32, INDIA

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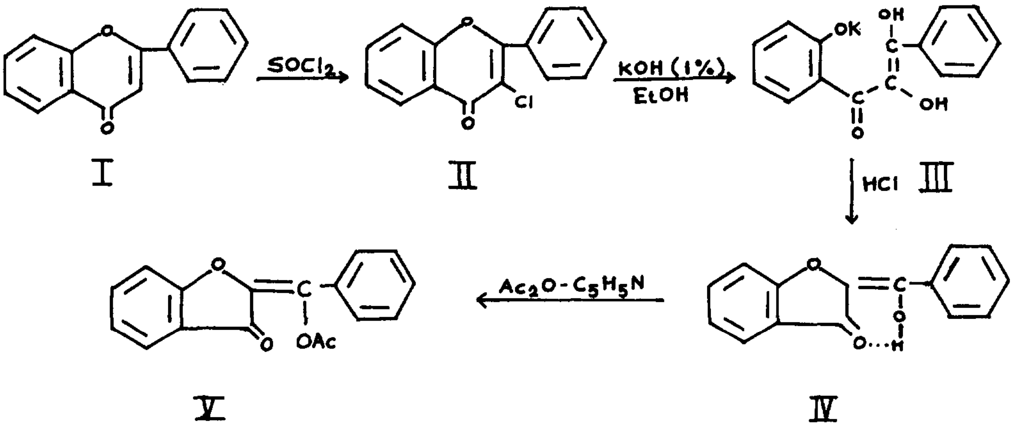
In connection with some work on flavanoids we investigated the reaction of thionyl chloride with flavone at different temperatures Whilst, no reaction occurred at room temperature, with excess of thionyl chloride at elevated temperature, a compound identified as 3-chloroflavone (II) was obtained. It may be mentioned that whilst 3-bromoflavone is known in literature, it has been synthesised by a different method. The action of thionyl chloride as a chlorinating agent in this case to yield the hitherto unknown II has not been reported so far and is described here.

Refluxing flavone (I) in anhydrous benzene with thionyl chloride for 15 hrs. furnished a crystalline 3-chloroflavone, $C_{15}H_9O_2Cl$ m.p. 125° in 70% yield. The suggested structure of 3-chloroflavone (II) is in full agreement with its spectral analytical data, and chemical properties, ir (nujol) :1670, 1615 (conjugated CO), 1610, 1515, 1495, 755, 690 (aromatic), 645 (C -Cl) cm^{-1}; $UV\lambda_{max}^{EtOH}$ 249, 305 mμ (logε , 4.78, 4.42); nmr (CCl_4): δ8.15 (1H d, J = 8.5 c/s); δ 7.82 (2H, b.m.); δ 7.45 (6H, b.m.). A comparison of the nmr spectrum of II with that of flavone indicates, the disappearance of C_3 proton, which in flavone appeared at δ 6.65 (1H, S). This is in agreement with the spectral data of 3-bromoflavone[1]. 3-Chloroflavone showed the usual colour changes with aqueous alkali and was recovered unchanged in catalytic hydrogenation.

In order to confirm the structure of II, it was refluxed with alcoholic KOH (1%) and acidified with dilute HCl, when a halogen free product $C_{15}H_{10}O_3$ (IV) (M.W. 238 M.s.) m.p. 82-83° was obtained. It gave an olive green colouration with neutral $FeCl_3$ solution and was soluble in aqueous sodium bicarbonate. Its spectral data are as follows : ir (nujol) 1616 (chelated CO), 1575, 1530, 875, 750, (aromatic) cm^{-1}; $UV\lambda_{max}^{EtOH}$ 241, 257, 328, 348.5 mμ (logε , 3.99, 3.98, 4.08, 4.15); nmr (CCl_4 : δ 11.85 (1H, S, due to bonded OH group); δ 8.35 (2H, d , J = 8.5 c/s); δ 7.75(1H, d, J = 8.5 c/s); δ 7.40 (6H, b.m.). It was identified (m.mp and ir) as 2-benzoyl coumaranone previously reported[1,2]. The formation of IV could be explained on the basis of the scheme outlined. The latter was converted to an enol acetate (V), on treatment with acetic anhydride and pyridine. Its ir spectrum showed bands at 1765 (ester CO); 1660 (CO), 1600, 1575 (aromatic) cm^{-1}. The bands appearing at 1616 cm^{-1} in the enol IV which is a characteristic absorption due to intramolecular chelated carbonyl group[3] was shifted to 1660 cm^{-1} in its acetate V, providing further evidence to the structure IV.



The above reaction of thionyl chloride with flavone appears to be a general one, since 7-methoxyflavone also reacts to afford the corresponding chloro derivative, m.p. 119°.

Further work on other substituted flavones is in progress and results will be forthcoming.

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