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SIDE-CHAIN HALOGENATION OF 2-METHYLCHROMONES WITH THIONYL CHLORIDE.[1]

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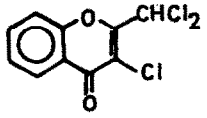
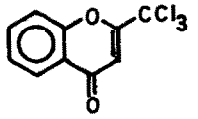
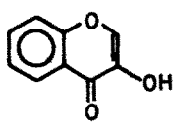
The reaction of 2-methylchromone with thionyl chloride in boiling benzene affords a crystalline trichloro compound (A) $C_{10}H_5O_2Cl_3$, m.p.118°, which on the basis of spectral data could have the structure I or II [u.v. $\lambda_{max}^{CH_3OH}$, 225,300 nm (log ε 3.85,3.72); i.r. (nujol), 1650,1610 cm^{-1} (conjugated CO); n.m.r. ($CDCl_3$) δ 8.21 (1H,d,C_8 J = 8 c/s; δ 7.56 (3H,b.m.); δ 6.96 (1H s)].



I



II

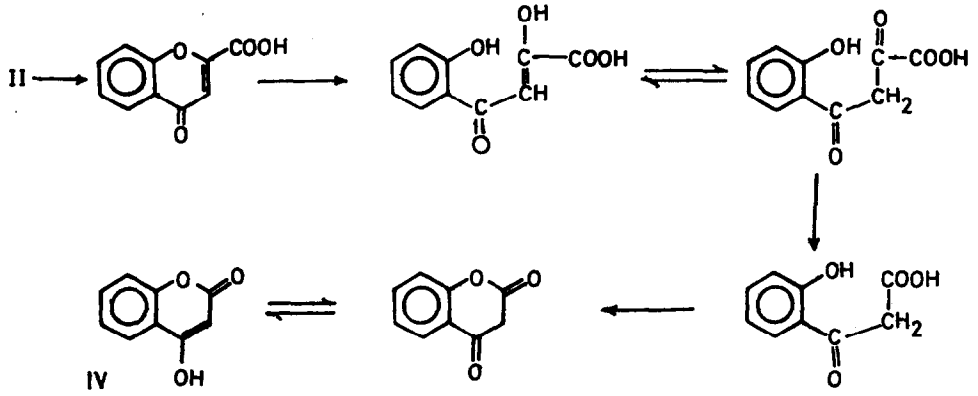


III

Hydrolysis of A with alcoholic alkali gave a halogen free crystalline substance, (B) $C_9H_6O_3$(M.W. 172 M.S.) m.p. 210°, which was isolated after chromatography (silica gel) in poor yields. It was soluble in sodium bicarbonate and gave a brown colouration with neutral $FeCl_3$, which disappeared quickly. The i.r. spectrum (KBr) showed bands at 2746, 2794 (OH) 1672 (conjugated C=O) and also at 1705 cm^{-1}. The n.m.r. (DMSO) showed peaks at δ 7.85 (1H, H_5, q, J = 8.5 c/s, J = 2 c/s); δ 7.65 (1H, H_7, q, J = 8.5 c/s, J = 1 c/s); δ 7.35 (2H, $H_{6,8}$ m); δ 5.59 (1H, H_3, s).

In the mass spectrum peaks were observed at m/e 120 (M - CH_2CO); m/e 92 (M - $C_3H_2O_2$) and at m/e 63 ($C_5H_3^+$). On the basis of this evidence, the hydrolysis product B could have either the structure III or IV. Comparison

with authentic samples of III[2] [m.p. 178-80°, u.v. λ_{max}^{MeOH} 235,275,315 nm (log ε 4.26,3.59,3.99); i.r.(KBr) 3286,3094(OH); 1637,1607 cm^{-1} (bonded CO); n.m.r. (DMSO) δ 9.08 (1H, S_3 OH), δ 8.23 (1H,H_2,s), δ 8.16 (1H,H_5,q,J = 8 c/s, J = 2 c/s), δ 7.58 (3H,$H_{6,7,8}$ bm)] and IV[3] showed it to be identical with IV.



The trichloro compound A thus has the structure II.

Also, 7-chloro-4-hydroxycoumarin[4], m.p. 248° is formed by the hydrolysis of 7-chloro-2-trichloromethyl chromone, m.p. 110°, obtained by the reaction of 7-hydroxy-2-methylchromone with thionyl chloride. The spectral data of all are in complete agreement with their structures.

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