Reaction of Sulphuryl Chloride with Flavone

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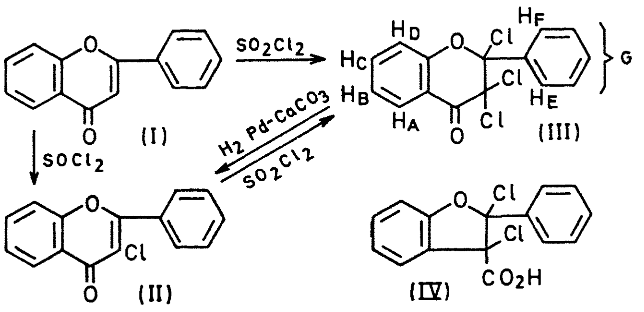
Summary Sulphuryl chloride reacts with flavone and 3-chloroflavone to give 2,3,3-trichloroflavanone which on hydrolysis yields 2,3-dichloro-2-phenylbenzofuran-3-carboxylic acid.

IN a previous communication[1] we reported the formation of 3-chloroflavone[1,2] (II) from flavone (I). We now report that whilst (II) also results from (I) by the action of sulphuryl chloride, the hitherto unknown 2,3,3-trichloro flavanone (III) is obtained by the action on both (I) and (II) of a large excess of sulphuryl chloride in benzene under reflux.



Treatment of (I) or (II) in anhydrous benzene under reflux with an excess of sulphuryl chloride for 15 hr., gave small amounts of a colourless, crystalline non-aromatic compound, $C_6H_6Cl_6$, m.p. 154°, [probably hexachlorocyclohexane (α-isomer) formed by the chlorination of benzene with sulphuryl chloride], and another colourless compound which crystallised as needles from alcohol, $C_{15}H_9Cl_3O_2$, m.p. 114—115° which is assigned the structure 2,3,3-trichloroflavanone (III). The suggested structure is in full agreement with its spectral, analytical, and chemical properties: u.v. λ_{max} (EtOH) 215, 260, 370 nm (log ε 3·33, 4·00, 3·46); i.r. (Nujol) 1720, (CO), 1610, 1585, 1495, 760, 710, 690 (aromatic), 655, 640 (C–Cl) cm^{-1}. As the carbonyl frequency is shifted from 1665 (in flavone) to 1720 cm^{-1} in (III), it is suggested that the latter is probably not a conjugated ketone and that there is αβ-substitution since the i.r. spectrum of flavanone itself shows a carbonyl frequency around 1690 cm^{-1}. Further, the pattern of the u.v. and i.r. curves of (III) and 3,3-dibromoflavanone[3] are similar, the values for the latter being: i.r. (Nujol) 1700 (CO), 1605, 1580, 1495, 770, 710 (aromatic), 650, 630 (C–Br) cm^{-1}; u.v. λ_{max} (EtOH) 214, 260, 325 nm (log ε 4·68, 4·24, 3·79).

The n.m.r. spectrum ($CDCl_3$) of (III) shows the following peaks, δ 8·12 (H$_A$, q, *J* 8·5 and 1·5 Hz), 8·05 (H$_F$, q, *J* 2·5 and 1·0 Hz), 8·00 (H$_E$, q, *J* 3·5 and 1·0 Hz), 7·68 (H$_C$, m), 7·50 (3H, G, br m), 7·30 (H$_B$, m), 7·20 (H$_D$, q, *J* 8·5 and 1·5 Hz) and is in agreement with the suggested structure (III). The mass spectrum of (III), which also supports its structure, consists of the following peaks: at *m/e* 326 (*M*), 291 (*M* ± Cl), 256 (*M* — 2Cl), 228 (loss of CO), 221 (*M* — 3Cl), 136 (PhC ≡ CCl), 120 ($C_7H_4O_2^+$), 105 (benzoyl cation), 92 (benzyl cation), and 51 ($C_4H_3^+$).

In order to confirm the structure of (III), the compound was hydrogenated, in the presence of Raney nickel and Pd–$CaCO_3$ catalysts separately at a pressure of 45 lb./in.^{2} at room temperature to give 3-chloroflavone[1] (II) (mixed m.p., i.r.) in both cases. When this was treated with sulphuryl chloride in anhydrous benzene trichloroflavanone (III) was obtained (mixed m.p., i.r.).

In order to confirm further the structure of (III), it was hydrolysed with alcoholic alkali to give an acid, $C_{15}H_{10}Cl_2O_3$, m.p. 143°. Under the same conditions of hydrolysis, both 3-chloroflavone and 3,3-dibromoflavanone yielded the same 2-benzoylcoumaranone[1] and 3-chloro-6-methylflavone, m.p. 135—136°, obtained by the action of thionyl chloride on 6-methylflavone,[4] afforded 2-benzoyl-5-methylcoumaranone. These results also indicate that the two chlorine atoms in (III) are not in the aromatic ring, as otherwise a halogen substituted 2-benzoylcoumaranone would have resulted.

The above acid has been assigned the structure (IV) on the basis of its properties and spectral data. The i.r. and u.v. data of the acid are: i.r. (Nujol) 3200 (broad OH, CO_2H), 1685 (C=O,CO_2H), 1605, 1575, 1500, 1495, 1485, 760, 705 (aromatic), 655, 640 (C–Cl) cm^{-1}; u.v. λ_{max} (EtOH) 259, 317, (log ε 4·005, 3·46). The mass spectrum of (IV) consists of the following peaks: at *m/e* 308 (*M*), 272 (*M* — HCl); 228 (loss of CO_2), 171 [PhC(Cl)=$\overset{+}{C}$Cl], 136 (PhC≡CCl), 121 (*p*-HO.C_6H_4.$\overset{+}{C}$≡O), 105 (benzoyl cation), 77 (phenyl cation), and 51 ($C_4H_3^+$).

The formation of the dichlorocarboxylic acid (IV) from (III) is a benzilic type of rearrangement.

The above reaction of sulphuryl chloride appears to be a general one, since 6-chloroflavone[5] reacts similarly to give the corresponding tetrachloro-derivative,† $C_{15}H_8Cl_4O_2$, m.p. 183°; i.r. (Nujol) 1725 cm^{-1} (CO). The latter compound on hydrolysis with alkali yields the corresponding trichloro-acid, m.p. 185°.

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† Prepared by Mr. A. R. Bhat in this laboratory.

[1] J. R. Merchant and D. V. Rege, *Tetrahedron Letters*, 1969, 3589.

[2] 3-Chloroflavone has also been prepared by M. S. Newmann and J. L. Ferrari from 3,4-dichlorocoumarin, *Tetrahedron Letters*, 1962, 199.

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