

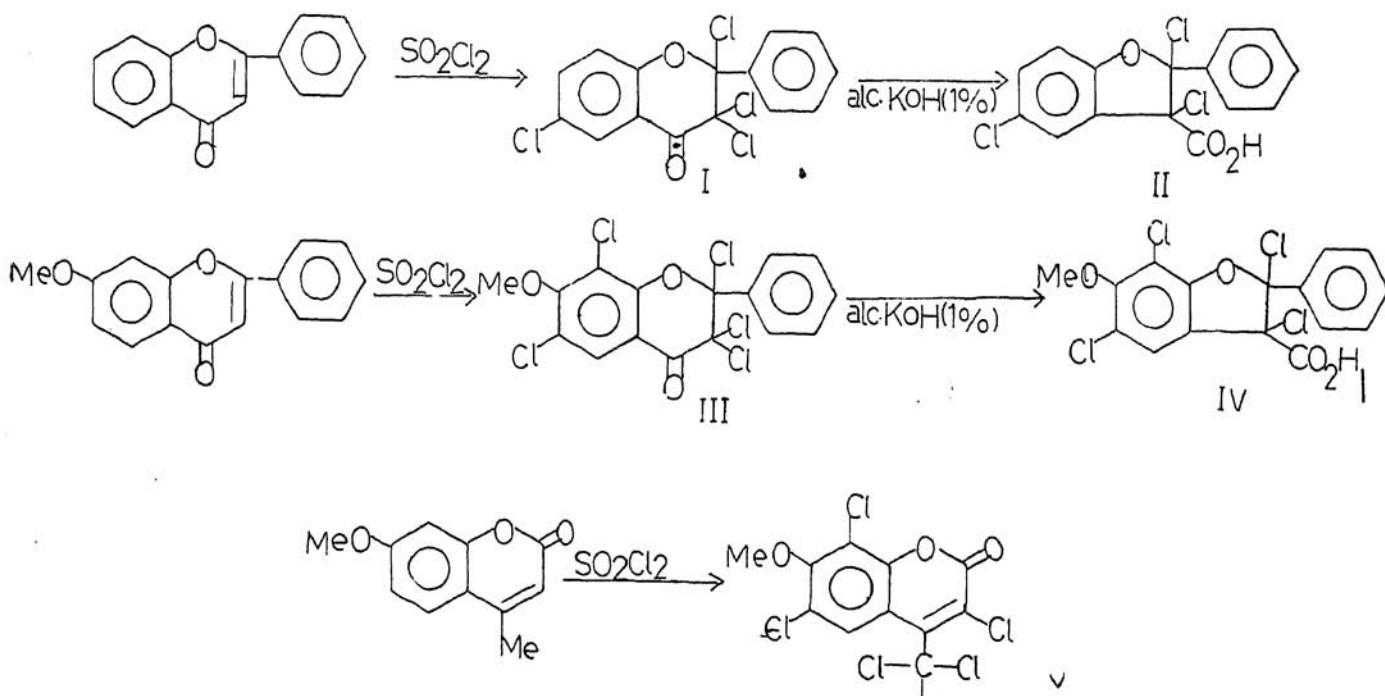
SULPHURYL CHLORIDE—SULPHOLANE A POWERFUL CHLORINATING AGENT

IN connection with our work on the halogenation of benzopyrone derivatives we investigated the reactions of some flavone and coumarin derivatives with sulphuryl chloride in different solvents. Whilst flavone (1 g.) on heating with excess of sulphuryl chloride (20 ml.) in benzene or carbon tetrachloride solution for 15 hour has been reported¹ to yield 2, 3, 3-trichloroflavanone, the same reaction in sulpholane gives a tetrachloroflavanone derivative, m.p. 180–82°. The latter has been assigned the structure as 2, 3, 3, 6-tetrachloroflavanone (I) on the basis of its analytical-spectral data and chemical properties. The i.r. spectrum of (I) showed a band around 1720 cm^{-1} indicating α , β -substitution whereas the n.m.r. spectrum gave signals for only aromatic protons around 6–8.2 δ .

The same compound was also obtained when 6-chloroflavone was heated with excess of sulphuryl chloride in benzene solution. The structure of (I) was further confirmed by its hydrolysis with alcoholic KOH to afford the previously reported² trichloro-carboxylic acid (II). The use of sulpholane for higher halogenation was also observed in the case of 7-methoxyflavone when a pentachloroflavanone derivative (III), m.p. 185–86° was isolated whilst other solvents under similar conditions yielded di-, tri- and tetra-chloro derivatives^{1b}.

The structure (III) was fully consistent with its analytical and spectral data. Its i.r. (KBr) showed a C=O band around 1760 cm^{-1} whilst ether bands were obtained at 2850, 1250 and 1020 cm^{-1} . The n.m.r. spectrum (CDCl_3) showed a singlet at 4.0 δ corresponding to $-\text{OCH}_3$ protons whereas the aromatic protons were obtained as a multiplet in the region 6 to 8.2 δ . On alcoholic alkaline hydrolysis (III) yielded a tetrachloro acid IV, m.p. 145–46°, an observation in complete agreement with our previous findings².

We next investigated the reaction of coumarin with sulphuryl chloride in sulpholane medium. In this case 3, 6-dichlorocoumarin, m.p. 163–64°



(Reported³ m.p. 167–68°) was isolated. Its structure was established by its alkaline KMnO_4 oxidation to give 5-chlorosalicylic acid, m.p. 166–67°, (Reported⁴ m.p. 167–68°). It is of interest to mention that halogenation of coumarin with sulphuryl chloride in carbon tetrachloride gave only 3-chlorocoumarin, m.p. 118–19° (Reported⁵ 122–23°). The higher halogenation power of sulphuryl chloride-sulpholane medium was also evident in the reaction with 7-methoxy-4-methylcoumarin when a hexachloro compound, m.p. 150–53° was obtained which from its analytical and spectral data was assigned the structure (V).

It can thus be seen that sulphuryl chloride in sulpholane is strong chlorinating agent, and may be utilized for the preparation of polyhalogenated compounds.

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