SYNTHESIS OF BENZOPYRYLIUM SALTS AND CHROMONES BY BISACYLATION OF SOME PHENOLS

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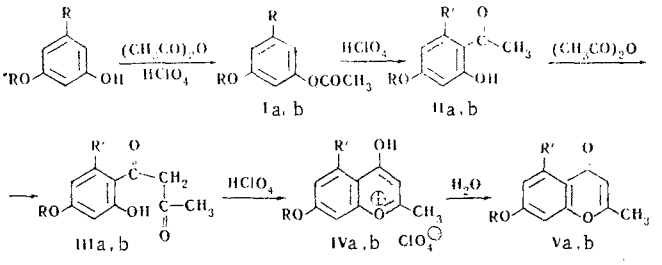
It is well-known that the reaction of phenols with acetic anhydride in the presence of 70% perchloric acid leads only to O-acylation [1], and the formation of pyrylium salts in such reactions has not been observed [2].

We have shown that under more severe conditions (refluxing of the reaction mixture). some phenols (m-phenoxyphenol and phloroglucinol) readily undergo bisacylation to form good yields of 4-hydroxy-2-benzopyrylium perchlorates:



I-Va R′ H, R′ OH; b R=C_6H_5, R′=H

The O-acetyl derivatives (I) of the phenols, which are formed initially, give o-hydroxy ketones II as a result of the Fries rearrangement, and II are reacylated to 1,3-diketones III. Finally, the latterare cyclized to 2-methyl-4-hydroxybenzopyrylium salts IV. Thus the following compounds were obtained in 50% yields by refluxing a mixture of phloroglucinol or m-phenoxyphenol with acetic anhydride and 70% perchloric acid (molar ratios of 1 : 3 : 1) for 40-50 min: 2-methyl-4,5,7-trihydroxybenzopyrylium perchlorate (IVa) [yellow crystals with mp > 300°C (glacial acetic acid). Found: C 41.2; H 3.3; Cl 11.7%. $C_{10}H_9ClO_8$. Calculated: C 41.0; H 3.1; Cl 12.1%. IR spectrum: 3300-3360, 1640, 1590, 1460, and 1120 cm^{-1}] and 2-methyl-4-hydroxy-7-phenoxybenzopyrylium perchlorate (IVb) [mp 230-231° (glacial acetic acid)]. Found: C 54.1; H 3.5; Cl 11.0%. $C_{16}H_{13}ClO_7$. Calculated: C 54.5; H 3.7; Cl 10.5%]. Refluxing of IVa,b in aqueous alcohol gave close to quantitative yields of 2-methyl-5,7-dihydroxychromone (Va) as yellow crystals that melted with decomposition at 290° [from water – dimethylformamide (1.5 : 1)]. According to [3], this compound has mp 290°. Found: C 62.8; H 4.4%. $C_{10}H_8O_4$. Calculated: C 62.5; H 4.2%. IR spectrum: 3280-3300, 1630, 1595, 1500, and 1460 cm^{-1} also produced was 2-methyl-7-phenoxychromone [mp 150° (from alcohol)]. Found: C 76.6; H 4.6%. $C_{16}H_{12}O_3$. Calculated: C 76.2; H 4.7%. IR spectrum: 1640, 1600, 1500 cm^{-1}]. Other phenols (phenol, m- and p-cresols, and resorcinol) react like other aromatic compounds [4] under the conditions of this reaction to give 2-methyl-4,6-diarylpyrylium salts. We plan to submit an additional communication regarding this.

LITERATURE CITED

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