SYNTHESIS OF PYRYLIUM AND PYRIDINIUM DERIVATIVES OF BENZOFURAN

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Recently, one of us and co-workers developed a general method for the annexation of pyrylium and pyridinium rings to compounds of the furan [1], thiophene [2], and indole [1] series. In the present communication, we have demonstrated that this method can be successfully used for the synthesis of the heretofore unknown benzofuro[3,2-c]pyrylium salts and the corresponding hard-to-obtain benzofuro[3,2-c]pyridines. We were able to realize the synthesis of 2,9-dialkylbenzofuro[3,2-c]pyrylium perchlorates (I) in good yields (66-75%) by the acylation of 2-acetonylbenzofuran (II), obtained by the reduction [3] of the product of the alkaline condensation of 2-formylbenzofuran with nitroethane via the following scheme:

This route was used to obtain the following compounds. 2,9-Dimethylbenzofuro[3,2-c]pyrylium perchlorate was obtained in 66% yield as shiny, colorless crystals with mp 161°C (from glacial acetic acid). Found: C 51.8; H 3.8; Cl 11.7%. $C_{13}H_{11}ClO_6$. Calculated: C 52.3; H 3.7; Cl 11.9%. IR spectrum (cm⁻¹): 1652, 1600, 1582, 1534, 1454, 1404, and 1083. 2-Ethyl-9-methylbenzofuro[3,2-c]pyrylium perchlorate was obtained in 75% yield as cream-colored crystals with mp 148°C (from glacial acetic acid). Found: C 53.5; H 4.4; Cl 10.8%. $C_{14}H_{13}ClO_6$. Calculated: C 53.8; H 4.2; Cl 11.4%. IR spectrum (cm⁻¹): 1650, 1602, 1580, 1530, 1470, 1094.

The benzofuro[3,2-c]pyrylium salts obtained react with alcoholic ammonia to give high yields of the corresponding benzofuro[3,2-c]pyridines (III).

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