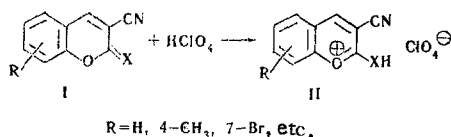


SYNTHESIS OF BENZOPYRYLIUM SALTS
WITH FUNCTIONAL AMINO AND CYANO GROUPS

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The reaction of chromene derivatives (I) with perchloric acid in nitromethane or glacial acetic acid gives high yields of previously undescribed substituted benzopyrylium salts with vicinal amino and cyano groups (II, X = NH):



Perchlorates II were isolated by dilution of the reaction mass with ether and were purified by recrystallization from nitromethane. The structure of the compounds obtained was proved by conversion of the pyrylium salts to the corresponding coumarins, for example, by hydrolysis of 7-bromo-2-amino-3-cyanobenzo[b]pyrylium perchlorate (II, X = H, R = 7-Br) to 7-bromo-3-cyanocoumarin (I, X = O, R = 7-Br), and was confirmed by the IR spectra (of KBr pellets), which contain absorption bands that correspond to the stretching vibrations of the amino (3090-3140 cm⁻¹) and nitrile (2240 cm⁻¹) groups and the deformation vibration of the pyran ring (1590-1680 cm⁻¹).

EXPERIMENTAL

2-Amino-3-cyanobenzo[b]pyrylium Perchlorate. This compound was obtained in 81% yield and had mp 236-238°C (dec.). Found: C 44.5; 44.5; H 2.9; 3.0; Cl 13.2; 13.4; N 10.8; 11.0%. C₁₀H₇ClN₂O₅. Calculated: C 44.4; H 2.6; Cl 13.1; N 10.3%.

4-Methyl-2-amino-3-cyanobenzo[b]pyrylium Perchlorate. This compound was obtained in 82% yield and had mp 208-210° (dec.). Found: C 46.5; 46.9; H 3.6; 3.7; Cl 12.5; 12.6; N 10.1; 10.1%. C₁₁H₉ClN₂O₅. Calculated: C 46.4; H 3.2; Cl 12.5; N 9.8%.

7-Bromo-2-amino-3-cyanobenzo[b]pyrylium Perchlorate. This salt was obtained in 85% yield and had mp 235-237° (dec.). Found: C 34.6; 34.8; H 2.0; 1.9; Br + Cl 33.0; 33.3; N 8.3; 8.3%. C₁₀H₆BrClN₂O₅. Calculated: C 34.6; H 1.7; Br + Cl 33.2; N 8.1%.

2-Amino-3-cyanobenzo[f]chromylium Perchlorate. This compound was obtained in 96% yield and had mp 286-288° (dec.). Found: C 52.6; 52.8; H 3.0; 3.2; Cl 11.0; 11.0; N 9.0; 8.9%. C₁₄H₉ClN₂O₅. Calculated: C 52.4; H 2.8; Cl 11.1; N 8.7%.

7-Bromo-3-cyanocoumarin. A mixture of 0.5 g of II (X = NH, R = 7-Br), 4 ml of ethanol, 0.2 ml of acetic acid, and 0.2 ml of 70% perchloric acid was refluxed for 1 h. The resulting precipitate was recrystallized from alcohol to give 0.21 g (60%) of a product with mp 206°. IR spectrum (of KBr pellets) $\nu_{C=O}$ 1745, $\nu_{C=N}$ 2240 cm⁻¹. Found: C 47.9; 47.9; H 1.6; 1.8; Br 31.8; 32.0; N 5.6; 5.8%. C₁₀H₄BrN₂O₂. Calculated: C 48.0; H 1.6; Br 31.9; N 5.6%.

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