SYNTHESIS OF PYRYLOCYANINES BY THE PYRYLATION REACTION

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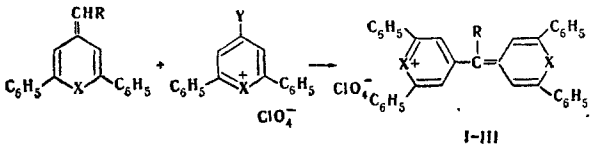
In connection with our investigations of the pyrylation reaction [1, 2], we have applied it to the pyrylation of arylidene- and heterylidenepyrans, as a result of which the pyrylocyanines (I-III) with various heteroatoms have been obtained.



I-III

I X=O; II X=S; III X=Se; Y=H, Cl; a $R=C_6H_5$; b $R=\alpha$-C_4H_3S; c $R=3,4$-$(CH_3O)_2C_6H_3$

Good results (simplicity of application, high yields and purity of the condensed products) are given by the use both of γ-unsubstituted salts by a reaction described in 1968 [1] and also of chlorine-substituted salts by a method described in 1971 [2]. Pyrylation by γ-unsubstituted pyrylium cations takes place when a mixture of the components is boiled in dimethylformamide, while in the case of chlorine-substituted derivatives the medium used is nitromethane. Both methods make it possible to vary the substituents and the heteroatoms of the pyrylocyanines widely. The following pyrylocyanines have been obtained in this way with yields of 85-99% (the empirical formula, the yield in %, and the melting point in °C are given): Ia, $C_{41}H_{29}ClO_6$, 84, 301; IIa, $C_{41}H_{29}ClO_4S_2$, 96, 278; Ib, $C_{39}H_{27}ClO_6S$, 99, 310; IIIa, $C_{41}H_{29}ClO_4Se_2$, 87, 238; and others. The pyrylocyanines obtained are brightly colored crystalline substances with a metallic luster sparingly soluble in the usual organic solvents and soluble in dimethylformamide, acetonitrile, and nitromethane. They were purified by recrystallization from nitromethane. Their structure was shown by the IR spectra and (in some cases) by independent synthesis by Strzelecka's method [3]. Their compositions were confirmed by the results of elementary analysis.

LITERATURE CITED

1. S. V. Krivun, Dokl. Akad. Nauk SSSR, 180, 615 (1968).
2. S. V. Krivun, S. N. Baranov, and A. I. Buryak, Khim. Geterotsikl. Soedin., 1320 (1971).
3. H. Strzelecka, Ann. Chim., 201 (1966).

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