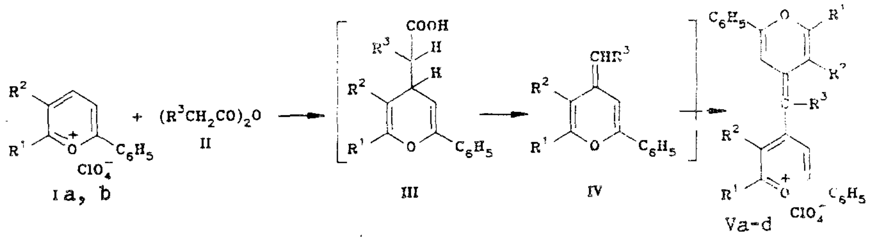
FORMATION OF CYANINES FROM PYRYLIUM SALTS AND ALIPHATIC ACID ANHYDRIDES

A. I. Pyshchev, L. I. Butenko,
É. T. Oganesyan, and V. V. Krasnikov

UDC 547.814.04

We found that when pyrylium salts I with a free γ-position are boiled for a short time with aliphatic acid anhydrides II in the presence of weak bases (sodium acetate, triethylamine), cyanines V are formed in satisfactory yields.



Ia $R^1=C_6H_5$, $R^2=H$, b $R^1=R^2=(CH)_4$; Va—c $R^1=C_6H_5$, d $R^1-R^2=(CH)_4$; a-c $R^2=H$, a,d $R^3=H$, b $R^3=CH_3$, c $R^3=C_2H_5$

The formation of cyanines can be attributed by the formation of a carbanion from the acid anhydride through the action of a base, attack on this by a free electrophilic center of the pyrylium cation, oxidation, and decarboxylation of the pyran intermediate III to pyranylidene IV. The synthesis of cyanines from the latter have been thoroughly investigated [1].

The formation of a meso-carbon fragment derived from an aliphatic acid anhydride is convincingly confirmed by the PMR spectra of cyanines, obtained by using propionic and butyric anhydrides.

We should note the unusual character of the reaction of pyrylium salts with such weak nucleophiles as the carboxylic acid anhydrides, and also the fact that when the reactions are carried out under similar conditions and with the participation of analogous reagents, products of a different type are formed [2]. Compounds Va, d are identical with compounds described in [3] with respect to their melting points and UV spectra.

Compound Vb. mp 268-270°C, PMR spectrum ($CDCl_3$): 2.25 (s, 3H, CH_3), 7.6-8.1 ppm (m, 24H).

Compound Vc. mp 250-251°C, PMR spectrum ($CDCl_3$): 1.25 (t, 3H, CH_3), 2.3 (q, 2H, CH_2), 7.17-8.3 ppm (m, 24H).

The elemental analysis corresponds to the structures given above.

LITERATURE CITED

1. A. I. Tolmachev and M. A. Kudryashova, Khim. Geterotsikl. Soedin., No. 2, 178 (1977).
2. F. Krohnke and K. Dickore, Chem. Ber., 92, 46 (1959).
3. J. A. Van Allan and J. A. Reynolds, J. Heterocycl. Chem., 9, 669 (1972).

Scientific Research Institute of Physical and Organic Chemistry of Rostov State University, Rostov-on-Don 344006. Pyatigorsk Pharmaceutical Institute, Pyatiogorsk 357500. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1563, November, 1989. Original article submitted January 25, 1989.

0009-3122/89/2511- 1311$12.50