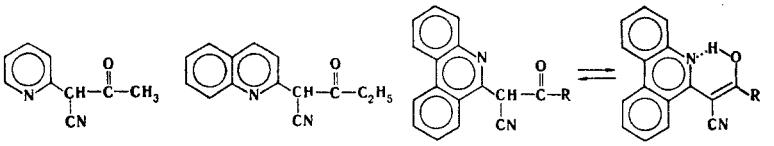
REACTION OF α-CYANOMETHYL DERIVATIVES OF AZAHETEROCYCLES WITH CARBOXYLIC ACID ANHYDRIDES

F. S. Babichev and Yu. M. Volovenko

UDC 542.951:547.836

We have found that 2-cyanomethylpyridine or 2-cyanomethylquinoline, on heating at 130-140°C for 30-60 min with a two- to threefold excess of a carboxylic acid anhydride, form acyl derivatives at the methylene group, i.e., ω-acyl-2-cyanomethylpyridines (I) [mp 176° (from ethanol), 88% yield] or ω-acyl-2-cyanomethylquinolines (II)] mp 168° (from ethanol), 92% yield]. However, it was recently reported [1, 2] that 6-cyanomethylphenanthridine is acylated by anhydrides at the nitrogen atom to give 5-acyl-6-cyanomethylene-5,6-dihydrophenanthridine.



I II III a,b

III a $R=CH_3$; b $R=C_6H_5$

According to our data, C-acylation occurs in this case also to give ω-acyl-6-cyanomethylphenanthridines [IIIa, mp 215° (from propyl alcohol), 93% yield; IIIb, mp 254° (from propyl alcohol), 88% yield]. A broad signal of the hydroxyl proton of the enol form is observed at 16.82 ppm in the PMR spectrum of a $CDCl_3$ solution of IIIa, in addition to the signal of a CH_3 group at 2.58 ppm. This proton is readily exchanged with D_2O, after which its signal vanishes. Yet another proof in favor of structure IIIa is the presence of a 7-H doublet with $J=8$ Hz at 9.33 ppm. Its considerable paramagnetic shift is due to the induced magnetic field of the rigidly fixed nitrile group. The chemical shift of the proton of the hydroxyl group in the spectrum of IIIb is 16.90 ppm, whereas the chemical shift of the 7-H proton is 9.50 ppm.

Absorption of a chelated hydroxyl group at 2960-3120 cm^{-1} is observed in the IR spectra of chloroform solutions of III. The narrow strong band at 2190 cm^{-1} corresponds to the absorption of a nitrile group attached to a double bond.

The empirical formulas of I-III were confirmed by the results of analysis for nitrogen.

LITERATURE CITED

1. E. V. Grishina, É. R. Zakhs, and V. P. Martynova, Khim. Geterotsikl. Soedin., 138 (1974).
2. E. V. Grishina, É. R. Zakhs, and V. P. Martynova, Khim. Geterotsikl. Soedin., 1110 (1974).

T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 1005, July, 1975. Original article submitted December 10, 1974.