anhydrides of these types sometimes form not N-acyl but N-phosphoryl salts. Thus, in the reaction of benzo[f]quinoline with indole in the presence of a mixture of phenylsulfonylacetamide and phosphorus oxychloride we obtained the corresponding N-phosphorylated derivative of 1,2-dihydrobenzo[f]quinoline (VI), mp 153-155°C, yield 34% (the results of elementary analysis corresponded to the calculated figures), which was also formed by the reaction of quinoline with indole in the presence of $POCl_3$ in an inert solvent.

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THE QUESTION OF THE TAUTOMERISM OF 3-AMINO-1-HYDROXYETHYL-2-PYRAZOLINE

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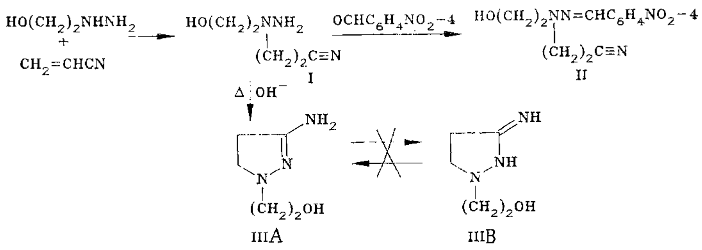
UDC 547.773'234.22

According to [1], acrylonitrile forms with β-hydroxyethylhydrazine a compound with a cyclic structure — 3-amino-1-hydroxyethyl-2-pyrazoline, which exists in equilibrium with the imino-hydrazine tautomer. The proof of this was based on the presence of eight signals in its ^{13}C NMR spectrum. Nevertheless, it is known [2] that 3-amino-2-pyrazolines usually exist solely in the "amidrazone" tautomeric form as do, incidentally, their linear analogs [3].

We have found that the primary product of the condensation of β-hydroxyethylhydrazine with acrylonitrile (I) has a linear structure. Yield 60%, bp 148-150°C (0.2 mm), R_f 0.49 [chloroform—methanol (8:1)]. IR spectrum (1% solution in $CHCl_3$): 2240 cm^{-1} ($C{\equiv}N$). PMR spectrum (DMSO-d_6), ppm: 2.50-2.8 (m, 6 H, 3 CH_2), 3.67 (t, 2 H, OCH_2, J = 6.0 Hz), 3.96 (br.s., 3 H, NH_2, OH). ^{13}C NMR spectra ($CDCl_3$), ppm 14.9 (CH_2CN), 54.8 and 58.6 ($2CH_2N$), 61.5 (OCH_2), 11.87 ($C{\equiv}N$).



A chemical confirmation of this structure was the formation of the p-nitrobenzylidene derivative (II) with 80% yield, mp 69-70°C (from water). The results of elementary analysis corresponded to the calculated figures. PMR spectrum (DMSO-d_6), ppm: 2.87 (t, 2 H, CH_2CN), 3.5-3.9 (m, 6 H, 3 CH_2), 4.86 (t, 1 H, OH, J = 5.0 Hz), 7.49 (s, 1 H, $CH{=}N$), 7.7-8.2 (m, 4 H, C_6H_4).

S. M. Kirov Academy of Military Medicine, Leningrad. Translated from Khimiya Geterotsiklicheskaya Soedinenii, No. 9, p. 1282, September, 1984. Original letter submitted December 6, 1983.

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When compound (I) was heated in methanol in the presence of alkali, 3-amino-1-hydroxyethyl-2-pyrazoline (III) was formed with a yield of 70%, bp 139-141°C ($4 \cdot 10^{-2}$ mm), R_f 0.34 [~~chloroform~~-methanol (8:1)]. IR spectrum (1% solution in $CHCl_3$); 1630 cm^{-1} (C=N). PMR spectrum ($CDCl_3$), ppm: 2.76 (t, 2 H, CH_2CH_2O, J = 5.0 Hz), 3.78 (t, 2 H, OCH_2, J = 5.0 Hz), 4.34 (br.s., 3H, NH_2, OH), 2.44 and 3.08 (4 H, A_2B_2 system of methylene groups of the ring, J_{AB} = 9.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), ppm: 32.5 (C-4), 55.5 (C-5), 59.7 (NCH_2), 61.8 (OCH_2), 155.6 (C=N). The spectral characteristics of compound (III) did not change with time.

Thus, it can be stated that, in actual fact, as was to be expected from information given in the literature [2, 3], the tautomerism (IIIA) $\rightleftarrows$ (IIIB) does not take place. By analogy, form (IIIA) is the most preferred. The reason for the doubling of some signals in the ^{13}C NMR spectrum described in [1] is apparently that the work was carried out with a mixture of compounds (I) and (III).

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A NEW APPROACH TO THE SYNTHESIS OF ISOQUINOLINO CROWN ETHERS

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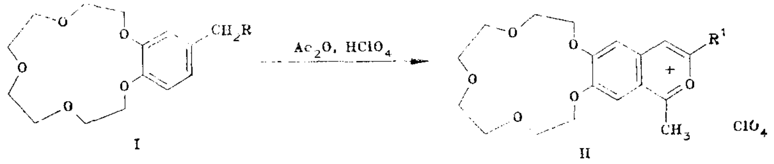
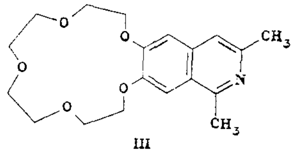
UDC 547.833.6'814'898

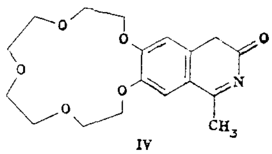
The synthesis of isoquinolino-15-crown-5s based on the reaction of 6,7-dihydroxyisoquinolines with 1,11-dichloro-3,6,9-trioxaundecane [1] is known. Using benzo-15-crown-5 as an example, we have shown that crown derivatives of isoquinoline can be obtained from substituted benzo crown ethers (I) by the intermediate formation of the crown-2-benzopyrylium salts (II) using the acid-catalyzed heterocyclization reaction developed by us previously [2].



I a) $R=COCH_3$; b) $R=CN$; II a) $R^1=CH_3$; b) $R^1=NHCOCH_3$

Under the action of ammonia, compounds (IIa, b) were converted into the corresponding isoquinoline (III) and isoquinolone (IV), which may be of interest in the synthesis of biologically active substances.


III


IV

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