4,6-Diacetyl-3-methyl-N-methylaniline (II). IR spectrum: 1660 (CO), 3310 cm^{-1} (NH). PMR spectrum (CCl_4): 2.39 (3H, s, CH_3), 2.48 (6H, s, $COCH_3$), 2.92 (3H, d, J = 5 Hz, NCH_3), 6.37 (1H, s, aromatic), 8.17 (1H, s, aromatic), 9.17 ppm (1H, broad s, NH).

3-Acetyl-6-methyl-2-methylamino-4-phenyl-5-cyanopyridine (IVa). IR spectrum: 1580 (CO), 2220 (CN), 3380 cm^{-1} (NH). PMR spectrum (CCl_4): 1.53 (3H, s, 6-CH_3), 2.02 (3H, s, $COCH_3$), 3.05 (3H, d, J = 5 Hz, NCH_3), 4.92 (1H, broad s, NH), 7.25-7.67 ppm (5H, m, aromatic).

3-Acetyl-6-methyl-2-methylamino-5-cyanopyridine (IVb). IR spectrum: 1600 (CO), 2225 (CN), 3325 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 2.92 (3H, s, CH_3), 3.04 (3H, s, $COCH_3$), 3.58 (3H, d, J = 6 Hz, NCH_3), 8.63 (1H, s, aromatic), 10 ppm (1H, broad s, NH).

The results of elementary analysis were in agreement with the calculated values.

NEW METHOD FOR THE SYNTHESIS OF 5-AMINO-6-NITROPYRIMIDINES

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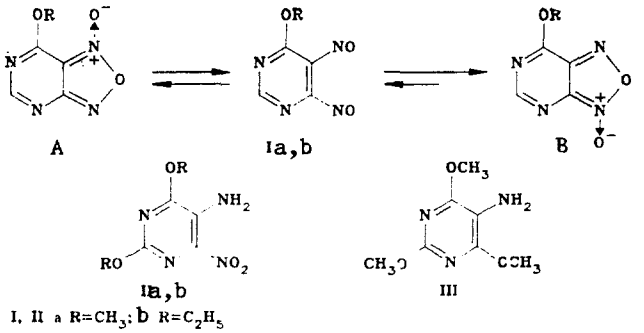
UDC 547.854'793.1.04

Pyrimidines that contain a nitro group in the 4(6) position are a class of compounds to which little study has been devoted; this is explained by the fact that they are difficult to obtain [1].

We have found that 2,4-dialkoxy-5-amino-6-nitropyrimidines IIa, b are formed in the reaction of 7-methoxyfuroxano[3,4-d]pyrimidine (Ia) with sodium methoxide and 7-ethoxyfuroxano[3,4-d]pyrimidine (Ib) with sodium ethoxide. Pyrimidine IIb was also obtained from Ia and sodium ethoxide. The formation of these substances is possible only if nucleophilic attack is realized at isomeric form B, which contains an N-oxide group in the 3 position of the ring. Under the reaction conditions A → B isomerization evidently occurs with subsequent opening of the 1,2,5-oxadiazole ring and simultaneous substitution of hydrogen in the 2 position of the pyrimidine ring.

7-Ethoxyfuroxano[3,4-d]pyrimidine (Ib). This compound was obtained from 5-nitro-4-hydrazino-6-ethoxypyrimidine in analogy with pyrimidine Ia [2]. The yield was 42%, and the product had mp 63-64°C. UV spectrum (in methanol), λ_{max} (log ε): 247 (3.73), 354 nm (3.49). PMR spectrum ($CDCl_3$), δ: 1.42 (3H, t, CH_3), 4.66 (2H, q, CH_2), 8.61 ppm (1H, s, CH).

5-Amino-2,4-dimethoxy-6-nitropyrimidine (IIa). This compound was obtained in 32% yield and had mp 170-171°C. UV spectrum (in methanol), λ_{max} (log ε): 413 nm (3.86). PMR spectrum ($CDCl_3$), δ: 3.89 (3H, s, OCH_3), 4.10 (3H, s, OCH_3), 6.35 ppm (2H, broad s, NH_2).



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5-Amino-6-nitro-2,4-diethoxypyrimidine (IIb). This compound had mp 128-130°C. UV spectrum (in methanol), λ_{max} (log ε): 415 nm (3.62). PMR spectrum ($CDCl_3$), δ: 1.36 (3H, t, CH_3), 1.42 (3H, t, CH_3), 4.34 (2H, q, CH_2). 4.53 (2H, q, CH_2), 5.88 ppm (2H, broad s, NH_2).

The structure of IIa was also proved by a chemical method. The previously described [3] 5-amino-2,4,6-trimethoxypyrimidine (III) was obtained when it was refluxed with an equimolar amount of sodium methoxide as a result of nucleophilic substitution of the nitro group; the product had mp 104-105°C and was obtained in 73% yield. UV spectrum (in methanol), λ_{max} (log ε): 2.79 nm (3.93). PMR spectrum ($CDCl_3$), δ: 3.03 (2H, broad s, NH_2), 3.79 (3H, s, OCH_3), 3.86 ppm (6H, s, OCH_3).

The molecular masses of 6-nitropyrimidines IIa, b determined by mass spectrometry and the results of elementary analysis of the compounds obtained were in agreement with the calculated values.

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FORMATION OF A CONDENSATION SIDE PRODUCT IN THE SYNTHESIS OF 2-BENZYL-4-METHYL-6-CHLOROPYRIMIDINE

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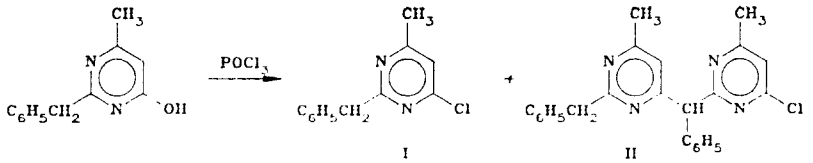
UDC 547.853'855

A general method for obtaining chloropyrimidines is refluxing hydroxypyrimidines in excess phosphorus oxychloride, in individual cases in the presence of N,N-dialkylanilines [1].

In the synthesis of 2-benzyl-4-methyl-6-chloropyrimidine by refluxing the corresponding hydroxypyrimidine with an eightfold excess of phosphorus oxychloride, in addition to the formation of chloropyrimidine I (27%), we obtained, in 44% yield, **2-benzyl-4-methyl-6-[α-4-methyl(6-chloro-2-pyrimidinyl)benzyl]pyrimidine (II)** with mp 195-197°C and R_f 0.54 [Silufol UV 254, benzene–acetone (6:1)]. Mass spectrum, m/z (relative intensity, %): 402 (6), 400 (17), 220 (15), 219 (36), 218 (47), 217 (100), 183 (37), 182 (27), 117 (26), 91 (49), 90 (17).



We do not exclude the possibility that Wintersteiger and coworkers [2] and Ochiai and Janai [3] in their studies of the synthesis of 2-benzyl-4-methyl-6-chloropyrimidine also observed the side process, as evidenced indirectly by the fact that, despite the low yields (50-56%), they avoided prolonged refluxing (no more than 5-7 min). However, a condensation product was not isolated, and the transformed that we noted has not been previously described.

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