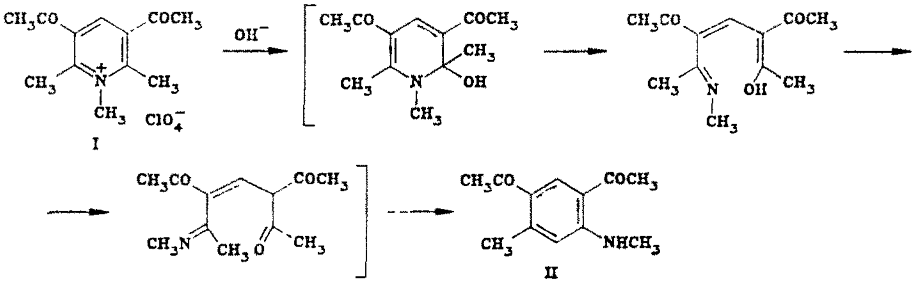
RECYCLIZATION OF 3,5-DIACETYL- AND 3,5-DICYANOPYRIDINIUM SALTS UNDER THE INFLUENCE OF BASES

G. P. Shkil', R. S. Sagitullin, D. Mutsenietse, and V. Lusis

UDC 547.821.3'821.412.04

We have established that the accessible 3,5-diacetylpyridinium quaternary salt I is converted to aliphatic-aromatic amino diketone II in good yield on heating in aqueous alcoholic alkali.

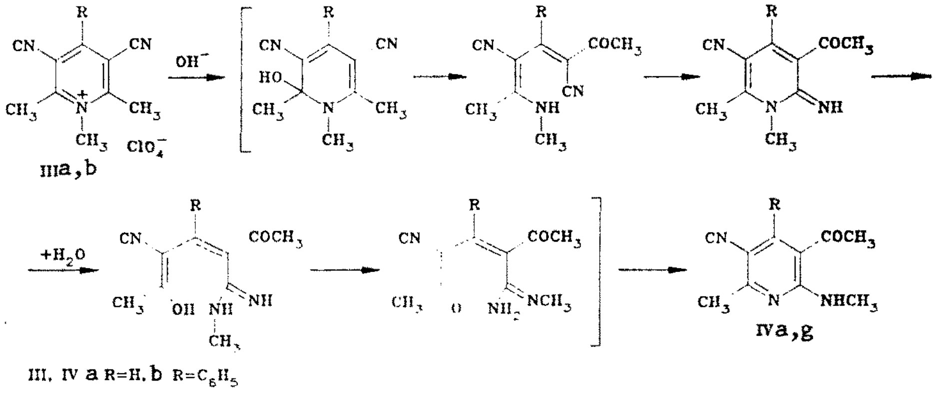


The yields of the corresponding amino diketones decrease sharply when a substituent (CH_3, C_6H_5) is present in the 4 position of the starting quaternary salt.

Under similar conditions 3,5-dicyanopyridinium quaternary salts III undergo double rearrangement to give 3,5-functionally substituted 2-methylaminopyridines IV. The concluding step of the transformation is the Dimroth amidine rearrangement.

A solution of 3 g of NaOH in 20 ml of 50% ethanol was added to a solution of 3 g (9.3 mmoles) of I in 10 ml of 50% ethanol, and the mixture was heated for 1 h on a water bath. It was then cooled, and II [mp 142-143°C (from alcohol), 83% yield] was removed by filtration. Pyridines IVa [mp 224-225°C (from chloroform), 61% yield] and IVb [mp 142-143°C (from alcohol), 86% yield] were similarly obtained.

Pyridinium perchlorates I and IIIa, b were obtained by alkylation of the corresponding pyridines with dimethyl sulfate with subsequent exchange of the anion. The previously unknown **3,5-diacetyl-1,2,6-trimethylpyridinium perchlorate (I)** had mp 122-123°C and the following PMR spectrum (DMSO): 2.66 (6H, s, 2,6-CH_3), 2.79 (6H, s, 3,5-$COCH_3$), 4.07 (3H, s, 1-CH_3), 8.86 ppm (1H, s, 4-H).



Omsk State University, Omsk 644077. Institute of Organic Synthesis, Latvian Academy of Sciences, Riga 226006.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 848-849, June, 1990. Original article submitted September 4, 1989.

0009-3122/90/2606-0709$12.50 ©1990 Plenum Publishing Corporation

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

G. Ya. Remennikov, I. A. Dyachenko, V. V. Pirozhenko,
and V. M. Cherkasov

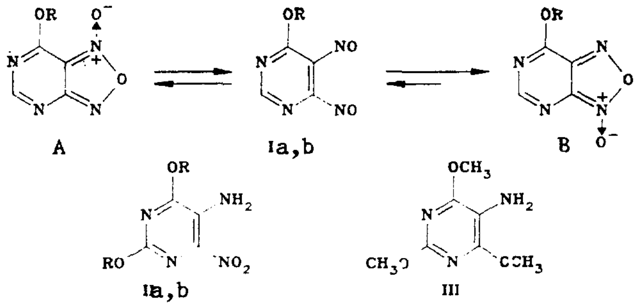
UDC 547.854'793.1.04

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).



A

Ia,b

B

IIa,b

III

I, II a R=CH_3; b R=C_2H_5

Institute of Bioorganic Chemistry and Petrochemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 849-850, June, 1990. Original article submitted August 10, 1989.