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LETTERS TO THE EDITOR

Synthesis of 2,4,6(1*H*,3*H*,5*H*)-Pyrimidinetrione-5-carboxaldehyde

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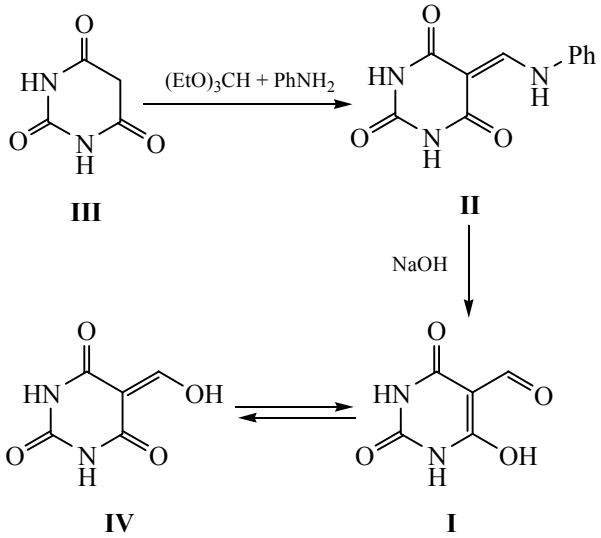
Continuing our research [1] in the field of pyrimidine-5-carboxaldehydes, we faced the necessity to synthesize pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione-5-carboxaldehyde **I**. Among the methods, described for obtaining **I** [2, 3], we have chosen the one, based on the alkaline hydrolysis of 5-phenylaminomethylenepyrimidine-2,4,6 (1*H*,3*H*,5*H*)-trione **II**, which, in turn, can be prepared by three-component condensation of pyrimidine-2,4,6(1*H*,3*H*,5*H*)trione **(III)**, triethoxymethane and aniline.



III **II** **IV** **I**

Unlike the original procedure [3] that implies performing this syntheses in ethylene glycol at 150–180°C, we carried out the reaction in the absence of solvent at 110–115°C with simultaneous removal of ethanol formed during the reaction. As s result we obtained aminomethylene ketone **II** in chromatographically pure form. In the ^{1}H NMR spectrum of **II** there are characteristic signals of protons of the aromatic ring in 7–8 ppm region, as well as those of pyrimidine NH near 11 ppm.

To obtain the target aldehyde **I** we carried out alkaline hydrolysis of aminomethylene ketone **II** in diluted aqueous sodium hydroxide solution with simultaneous steam distillation of the liberated aniline. As in the case of **II**, aldehyde **I** was extracted from the reaction mixture in chromatographically pure form and did not require recrystallization. ^{1}H NMR spectrum of **I** contains a signal of a methine proton at 9.4 ppm, as well as a signal of low intensity at about 9.9 ppm, belonging to the OH group at C^6, and the broadened signal of hydroxymethyl group in the 6–7 ppm region. The latter points to an existence of aldehyde **I** in a mixture with its prototropic tautomer, 5-hydroxymethylenepyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(IV)**.

Pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione-5-carboxaldehyde (I). Through a suspension of 19.9 g of aminomethylene ketone **II** in 5% aqueous sodium hydroxide solution acute steam was passed until all aniline was distilled off. The cooled reaction mixture was filtered, the solid was transferred into 600 ml of water, and to the suspension formed concentrated hydrochloric acid was added dropwise under vigorous stirring until pH 3–4 was achieved. The precipitate was filtered off, washed with water and ethanol and after drying at 80°C for 6 h gave 8.2 g (61%) of aldehyde **I**, mp > 300°C, R_f 0.44. ^{1}H NMR spectrum, δ, ppm: 9.38 s (1H, CH), 9.90 s (2H, NH). Found, %: C 37.56; H 2.32; N 17.33. $C_5H_4N_2O_4$. Calculated, %: C 38.47; H 2.58; N 17.95.

5-Phenylaminomethylenepyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (II). A mixture of 12.8 g of methylene ketone **III**, 14.8 g of triethoxymethane, and 9.3 g of aniline was kept under stirring at 110–115°C until ethanol distillation ceased. Solidified reaction mixture was ground with 70 ml of ethanol, filtered off, and washed with ethanol. After drying at 80°C for 6 h 19.9 g (86%) of aminomethylene ketone **II** was

obtained, mp > 300°C, R_f 0.51. Analytical sample was crystallized from glacial acetic acid, washed with ethanol, and dried in a vacuum over phosphorus pentoxide. ^{1}H NMR spectrum, δ, ppm: 7.21–7.46 m (5H, Ph), 8.53 d (1H, CH), 10.73 s (1H, NH), 10.89 s (1H, NH), 11.86 d (1H, N*H*Ph).

^{1}H NMR spectra were recorded on a Bruker WM-400 spectrometer (400.13 MHz) in DMSO-d_6 with residual solvent protons as internal reference. TLC was carried out on Silufol UV-254 plates using 2-propanol–25% aqueous ammonia, 3:1 mixture, as eluent, spot visualization with UV-light. Elemental analysis were performed on a Leco CHNS-932 analyzer.

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