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LETTERS TO THE EDITOR

Specificity of Acid Hydrolysis of 2-Benzylidenehydrazino-4,6-dimethylpyrimidine

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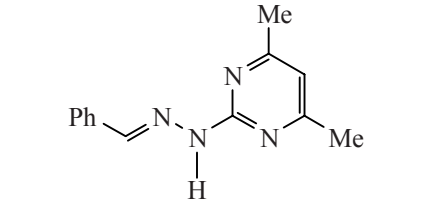
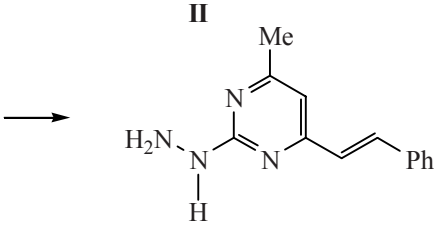
We examined a procedure for the synthesis of 2-hydrazino-4,6-dimethylpyrimidine (**I**), which differs from the traditional method [1]. The procedure is based on acid hydrolysis of readily accessible 2-benzylidenehydrazino-4,6-dimethylpyrimidine (**II**). Compound **II** can be obtained by high-temperature condensation of benzylideneaminoguanidine with pentane-2,4-dione under solvent-free conditions. However, the hydrolysis of benzylidenehydrazine **II** gave no expected product **I**, but resulted in partial formation of 2-hydrazino-4-methyl-6-(2-phenylethenyl)-pyrimidine (**III**) despite continuous removal of liberated benzaldehyde from the reaction zone.



II



III

The structure of styryl-substituted pyrimidine **III** was confirmed by spectral and analytical data. Its ^{1}H NMR spectrum contained a broadened singlet at about δ 4.1 ppm due to protons in the primary amino group, and protons at the exocyclic double C=C bond resonated as doublets at δ 6.9–7.0 and 7.7–7.8 ppm. In the IR spectrum of **III** we observed absorption bands corresponding to N–H bending vibrations (1636 cm^{-1}), stretching vibrations of double bond conjugated with aromatic ring (1581 cm^{-1}), and out-of-plane bending vibrations of C–H bonds at the *trans*-ethylene bond (968 cm^{-1}). Compound **III** displayed in the UV spectrum a very strong asymmetric absorption band with its maximum at λ 297 nm (logε 4.33) and a shoulder at about λ 340 nm (logε 4.12), originating from π–π and *p*–π* transitions in the entire conjugation system. The presence of an unsubstituted hydrazino group in molecule **III** was confirmed by the formation of a brightly colored condensation product with ninhydrin.

2-Benzylidenehydrazino-4,6-dimethylpyrimidine (II). A mixture of 16.2 g of benzylideneaminoguanidine and 10 g of pentane-2,4-dione was heated to 135°C and was vigorously stirred for 30 min at that temperature. The resulting semicrystalline material was ground with 300 ml of water, and the precipitate was filtered off, washed with water, recrystallized from 70% ethanol, and dried for 10 h at 70°C. Yield 11 g (49%), mp 164°C; published data [2]: mp 161°C; R_f 0.74. ^{1}H NMR spectrum, δ, ppm: 2.31 s (6H, Me), 6.49 s (1H, CH), 7.25–7.68 m (5H, Ph), 8.05 s (1H, NH), 10.91 s (1H, CH=N).

2-Hydrazino-4-methyl-6-(2-phenylethenyl)pyrimidine (III). A solution of 4.52 g of benzylidenehydrazine **II** in dilute (1:1) hydrochloric acid was heated to the boiling point, and direct steam was passed through the solution over a period of 2 h with simultaneous removal of liberated benzaldehyde. The mixture was filtered, the filtrate was evaporated to dryness under reduced pressure, the residue was dissolved in 60 ml of water, and the solution was filtered and made persistently alkaline by adding 25%

aqueous ammonia. An oily material separated and was ground with 20 ml of water, and the precipitate was filtered off and dried in air. We thus isolated 0.76 g (17%) of crude pyrimidine **III**. An analytical sample was obtained by double recrystallization from benzene, followed by recrystallization from benzene–hexane (5 : 4) and drying under reduced pressure. Yield 178 mg (3.9%), mp 154°C, R_f 0.83. ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, Me), 4.13 br.s (2H, NH_2), 6.57 s (1H, CH), 6.97 d (1H, CH=CH), 7.28–7.60 m (5H, Ph), 7.76 d (1H, CH=CH), 7.81 br.s (1H, NH). Found, %: C 69.09; H 6.31; N 24.33. $C_{13}H_{14}N_4$. Calculated, %: C 69.00; H 6.24; N 24.76.

The ^{1}H NMR spectra were recorded on a Bruker AC-400 spectrometer at 400.13 MHz using DMSO-d_6 as solvent and reference. The IR spectra were measured in KBr on a Shimadzu FTIR-8400S instrument. The UV spectra were obtained on an SF-26 spectrophotometer from solutions in ethanol with a concentration of ~10^{-4} M. The elemental composition was determined on a Leco CHNS-932 CHN analyzer. The purity of the products was checked by TLC on Silufol UV-254 plates using butan-1-ol–acetic acid–water (1 : 1 : 1) as eluent; spots were visualized under UV light.

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