2,2′-Bipyridine-4-one (6). A mixture of chelate 7 and ligand **6** (~2 : 1, 0.21 g) was heated in a sealed glass tube for 9 h at 160—170 °C with a 6.9 *N* solution of HCl (4 mL) in butanol. Water (2 mL) was added to the reaction mixture. The aqueous layer was separated and water was distilled off *in vacuo* to give 0.17 g of **6** · HCl. The obtained salt was dissolved in water (1 mL) and a 25% aqueous ammonia (0.3 mL) was added to the solution. The solution was extracted many times with $CHCl_3$ to give 0.08 g (62%) of bipyridinone **6**, m.p. 146—147 °C (from acetone). Lit.:[7] m.p. 145 °C. MS, *m/z*: 172 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 6.54 (dd, 1 H, H-5); 7.15(s, 1 H, H-3), 7.37 (dd, 1 H, H-6); 7.74 (d, 1 H, H-3′); 7.80—7.95 (m, 2 H, H-4′, and H-5′); 8.63 (d, 1 H, H-6′). ^{13}C NMR ($CDCl_3$), δ: 113.5 (C—3); 116.8 (C-5); 120.4 (C-3′); 124.8 (C-5′); 137.5 (C-4′); 139.2 (d, C-6, J = 179 Hz); 146.6 (C-2); 149.2 (d, C-6′, J = 179 Hz); 149.7 (C-2′); 178.8 (C=O).

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Heterocyclization of acetylketene *N,S*-acetals with benzoyl cyanamide

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N-Unsubstituted mono- and diacetylketene *N,S*-acetals undergo cyclization with benzoyl cyanamide to form 2-amino-4-methylthiopyrimidine derivatives.

Key words: mono- and diacetylketene *N,S*-acetals, benzoyl cyanamide, 2-amino-4-methylthiopyrimidines.

Mono- and diacylketene *N,S*-acetals are used as convenient building blocks for the synthesis of heterocyclic systems.[1—3]

Previously we have shown that the scope of synthetic application for *N,S*-ketene acetals with unsubstituted NH_2 group can be significantly enlarged.[4—7] The most effective reagents of this type are 3-[amino(methylthio)methylene]pentane-2,4-dione (**1**) (readily obtained from acetylacetone and MeSCN)[8] and its deacetylation product, 1-amino-1-methylthiobut-1-en-3-one (**2**).

In the present work, functionally substituted pyrimidines have been synthesized by heterocyclization of compounds **1** and **2** with benzoyl cyanamide (**3**). Thus, refluxing of *N,S*-acetal **1** and cyanamide **3** in toluene afforded 5-acetyl-2-benzoylamino-6-methyl-4-methylthiopyrimidine (**4**). Debenzoylation of the latter with MeONa in MeOH gave *N*-unsubstituted aminopyrimidine **6** (Scheme 1).

In spite of the presence of the active C-nucleophilic center in molecule **2** (*e.g.*, cyclization of *N,S*-acetal **2** and benzoyl isothiocyanate into 5-acetyl-6-methylthio-2-phenyl-3*H*-pyrimidine-4-thione proceeds with the primary formation of the C—C-bond),[9] compound **2** behaves also as an *N*-nucleophile with respect to cyanamide **3**. The reaction of compounds **2** and **3** in boiling toluene resulted in the condensation product **5**, which was isolated as an oil, identified by ^1H NMR, and converted (without any purification) into crystalline aminopyrimidine **7** by debenzoylation. The structures of functionally substituted pyrimidines **6** and **7** are con-

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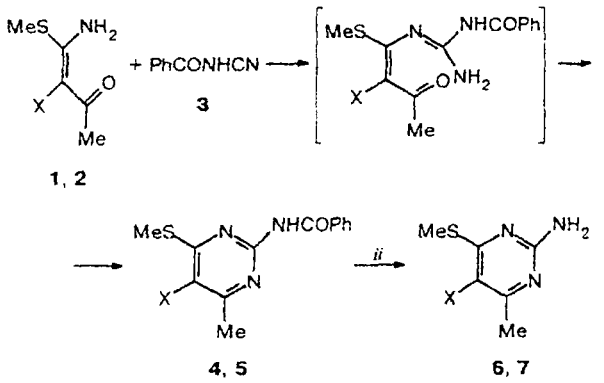
Scheme 1



X = MeCO (**1**, **4**, **6**); H (**2**, **5**, **7**).
Reagents and conditions: *i*. PhMe, Δ; *ii*. MeONa, MeOH, Δ

firmed by spectral methods. Compound **7** has been previously[10] synthesized from 2-amino-4-hydroxy-6-methylpyrimidine in three steps; spectral data have not been given.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 and Bruker AM-300 instruments, respectively. IR spectra were obtained on a Perkin-Elmer 577 instrument, and mass spectra were recorded on a Varian MAT-311A spectrometer (EI, 70 eV). The starting *N,S*-acetals were synthesized by known procedures.[8]

5-Acetyl-2-amino-6-methyl-4-methylthiopyrimidine (6). A mixture of *N,S*-acetal **1** (0.35 g, 2 mmol) and benzoyl cyanamide **3** (0.44 g, 3 mmol) in toluene (10 mL) was refluxed for 3 h. The solvent was evaporated *in vacuo*, and the residue was chromatographed on a SiO_2 column (the eluent was C_6H_6, then a C_6H_6—EtOH mixture, 200 : 1 and 100 : 1). The appropriate fractions were collected and the solvent was evaporated to give 0.42 g (69%) of pyrimidine **4**, m.p. 87—88 °C (from a 1 : 4 benzene—hexane mixture). IR ($CHCl_3$), ν/cm^{-1}: 3424 (NH), 1702 (CO), 1675 sh, 1568, 1534. ^{1}H NMR ($CDCl_3$), δ: 2.40 (s, 3 H, Me), 2.59 (s, 3 H, Me), 2.61 (s, 3 H, Me), 7.40—7.68 (m, 3 H, Ph), 7.88—7.98 (m., 2 H, Ph), 8.55 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 12.81 (SMe), 22.13 (Me), 31.22 (COMe), 127.91 (C-5), 127.51, 128.52, 132.20, 134.21 (Ph), 155.50 (C-2), 162.36 (q, C-6, ^2J = 6 Hz), 165.36 (NCO), 168.03 (q, C-4, ^3J = 3 Hz), 201.64 (q, C=O, ^2J = 6 Hz). MS, *m/z*: 301 $[M]^+$. A mixture of pyrimidine **4** (0.42 g, 1.4 mmol) and MeONa (1.4 mmol) in MeOH (15 mL) was refluxed for 30 min. The solvent was evaporated *in vacuo*, and the residue was chromatographed on a SiO_2 column (the eluent was C_6H_6, then a 1 : 1 C_6H_6—$CHCl_3$ mixture and $CHCl_3$) to give 0.16 g (58%) of pyrimidine **6**, m.p. 153—154 °C (from a 1 : 4 benzene—hexane mixture). Found (%): C, 48.46; H, 5.55; N, 20.96; S, 15.82. $C_8H_{11}N_3OS$. Calculated (%): C, 48.71; H, 5.62; N, 21.30; S, 16.25. IR ($CHCl_3$), ν/cm^{-1}: 3520 and 3415 (NH_2), 1682 (C=O), 1598, 1532. ^{1}H NMR ($CDCl_3$), δ: 2.31 (s, 3 H, Me), 2.47 (s, 3 H, Me), 2.54 (s, 3 H, Me), 5.25 (br.s, 2 H, NH_2). ^{13}C NMR (CDCl), δ: 12.20 (SMe), 22.74 (Me), 31.47 (COMe), 121.41 (C-5), 160.74 (C-2), 163.43 (q, C-6, ^2J = 6.3 Hz), 167.23 (q, C-4, ^3J = 3.0 Hz), 200.46 (q, C=O, ^2J = 6 Hz). MS, *m/z*: 197 $[M]^+$.

2-Amino-6-methyl-4-methylthiopyrimidine (7). Pyrimidine **5** was synthesized in the same way as compound **4** from *N,S*-acetal **2** and benzoyl cyanamide **3** and isolated as an oil in 75% yield by SiO_2 chromatography (the eluent was C_6H_6, then a C_6H_6—$CHCl_3$ mixture, 2 : 1 and 1 : 1). ^{1}H NMR ($CDCl_3$), δ: 2.42 (s, 3 H, Me), 2.59 (s, 3 H, Me), 6.80 (s, 1 H, H-5), 7.45—7.61 (m, 3 H, Ph), 7.88—7.98 (m, 2 H, Ph), 8.55 (br.s, 1 H, NH). Debenzoylation of crude product **5** (similar to the transformation of **4** into **6**) afforded pyrimidine **7** in 56% yield, m.p. 146—148 °C (*cf.*, Ref. 11). IR ($CHCl_3$), ν/cm^{-1}: 3520 and 3410 (NH_2), 1598, 1563. ^{1}H NMR ($CDCl_3$), δ: 2.25 (s, 3 H, Me), 2.48 (s, 3 H, Me), 5.12 (br.s, 2 H, NH_2), 6.40 (s, 1 H, H-5). ^{13}C NMR ($CDCl_3$), δ: 12.20 (SMe), 23.49 (Me), 107.62 (d, C-5, ^1J = 169 Hz), 162.30 (C-2), 165.67 (q, C-6, ^2J = 7.0 Hz), 171.21 (q, C-4, ^3J = 3.0 Hz). MS, *m/z*: 155 $[M]^+$.

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