SYNTHESIS OF 2,4-DIAMINO-5-ACETYL(ETHOXYCARBONYL)PYRIMIDINES FROM β-DICARBONYL COMPOUNDS AND DICYANDIAMIDE AND THEIR USE FOR BUILDING A PYRIMIDO[4,5-d]PYRIMIDINE SYSTEM

V. A. Dorokhov, M. F. Gordeev,
A. V. Komkov, and V. S. Bogdanov

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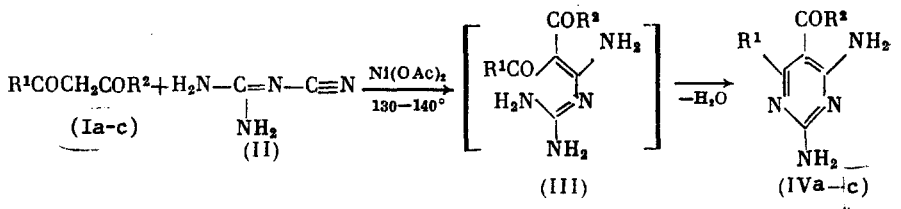
2,4-Diamino-5-acetyl(ethoxycarbonyl)-6-methyl(phenyl)pyrimidines were obtained by the reaction of acetylacetone and β-ketocarboxylic acid esters with dicyandiamide in the presence of $Ni(OAc)_2$. It was shown that annelation of the pyrimidine ring with this compound provides a convenient method for building the pyrimido[4,5-d]-pyrimidine system. New derivatives of 2-aminopyrimido[4,5-d]pyrimidine, 7-amino-3H-pyrimido[4,5-d]-pyrimidin-4-one, and 7-amino-1H,3H-pyrimido[4,5-d]-pyrimidine-2,4-dione were synthesized.

We have recently shown that nickel acetylacetonate $Ni(acac)_2$ effectively catalyzes the addition of active-methylene β-dicarbonyl compounds (DCC) to cyanamide [1] and its monosubstituted derivatives [2]. We used the reaction of DCC with N-cyanoamidines [3], and also with (benzimidazol-2-yl)cyanamide [4, 5] in the presence of Ni(2+) acetate or β-ketoenolates for the preparation of functionalized derivatives of 4-aminopyrimidine and 2-aminopyrimido-[1,2-a]benzimidazole.

In continuation of these investigations, we found in the present work that the reaction of acetylacetone (Ia) and β-ketocarboxylic acid esters (Ib, c) with dicyandiamide (II) in the presence of $Ni(OAc)_2$ leads to 6-substituted 5-acetyl(ethoxycarbonyl)-2,4-diaminopyrimidines (IVa-c). Optimal yields of (IV) (33-38%) are reached when the reaction is carried out in a DCC medium using an equimolar amount of $Ni(OAc)_2$



(1)

$R^1 = R^2 = Me$ (a), $R^1 = Me$, $R^2 = OEt$ (b), $R^1 = Ph$, $R^2 = OEt$ (c).

It is known that the reactions of DCC and (II) in the presence of basic catalysts (NaOH or NaOEt) give to the corresponding derivatives of (pyrimidin-2-yl)cyanamide [6-9], i.e., compound (II) usually behaves with respect to the DCC as an amidine type dinucleophile. Thus, under the influence of $Ni(OAc)_2$, the course of the process sharply changes in the direction of the formation of a carbon–carbon bond, i.e., an addition of the DCC to the nitrile group of (II) takes place.

As in the reaction of DCC with N-cyanoamidines [3] or (benzimidazol-2-yl)cyanamide [4, 5], reaction (1) possibly includes the addition of Ni(2+) β-ketoenolates, generated from DCC and $Ni(OAc)_2$, to the C≡N bond of (II) and the formation of the corresponding keteneaminals (III) which cyclize into (IV) with splitting off of water.

The structure of pyrimidines (IVa-c) was confirmed by the IR, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry data (see the experimental part).

The 2,4-diaminopyrimidine derivatives find application as antimicrobial preparations [10]. The pyrimidines (IV) synthesized in the present work are also of interest as starting compounds for building condensed heterocyclic compounds. We have examined some of the

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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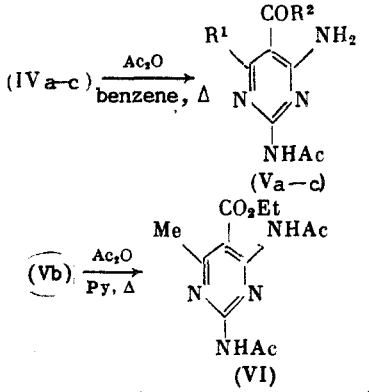
possibilities of using pyrimidines (IV) in the synthesis of pyrimido[4,5-d]pyrimidine derivatives. The latter are structurally similar to purines and are isomeric with pteridines; in compounds of this type, antiallergic [11], diuretic, herbicidal, etc., types of biological activity have been detected [12].

The annelation of the pyrimidine ring to heterocycles containing vicinal amino and acyl (ethoxycarbonyl) groups can be carried out by conventional methods, including, respectively, the reactions with isocyanates and cyclization of the ureas formed by the action of bases or conversion of the initial heterylamines into N-heteryl-N',N'-dimethylamidines and condensation of the latter with ammonia or amines [13].

However, to use these systems it is necessary that the reactions of (IV) should proceed regioselectively at the NH_2 group in the 4-position, and hence, the NH_2 group at the 2-position should preliminarily be protected. In fact, during the direct action of phenyl isocyanate or dimethylformamide dimethylacetal (DMF DMA) on (IV), mixtures of products are formed from which pyrimido[4,5-d]pyrimidines cannot be obtained in satisfactory yields. Therefore the corresponding 2-acetylaminopyrimidines (Va-c) were synthesized from compounds (IVa-c).

Boiling of (IVa-c) with Ac_2O in benzene gives (Va-c) in yields of 56-71%. The reaction of (Vb) with a excess of Ac_2O in a boiling pyridine results in the formation of the diacetyl derivatives (VI), which was isolated in a 47% yield.

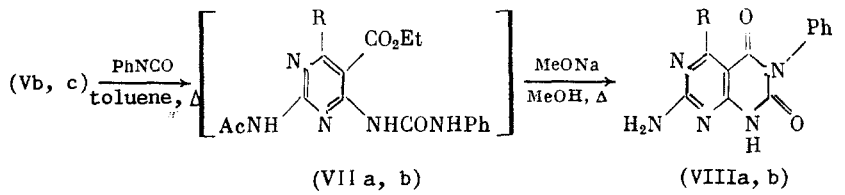


(2)

$R^1 = R^2 = Me$ (a), $R^1 = Me$, $R^2 = OEt$ (b), $R^1 = Ph$, $R^2 = OEt$ (c).

The regiodirectivity of the monoacetylation reaction of (IV) was found by means of ^{13}C NMR spectra of compounds (IV)-(VI). The assignment of signals in the ^{13}C NMR spectra was based on the values of the chemical shifts (CS), the SSCC and their multiplicity. The strongest-field signal of the pyrimidine ring (94.66-110.6 ppm) was assigned to the C^5 atom, considering its disposition between the carbon atoms and the presence of an electron-donor group NH_2 in the 4-position. The signal of the C^6 atom is a quartet ($J \sim 6$ Hz) as a result of a spin–spin coupling (SSC) with the CH_3 group protons, while the signals of the carbonyl groups are quartets ($J \sim 6$ Hz) or triplets ($J \sim 3$ Hz), respectively, as a result of an SSC with CH_3 or OCH_2 group protons. The assignment of the C^2 and C_4 signals in (Vb) is based on a comparison of the spectra of (IVb) and (Vb). On transition from the monoacetyl derivative (Vb) to the diacetyl derivative (VI), the signal of the C^5 atom undergoes a very substantial shift to the weak field (of 11.35 ppm), which indicates the acetylation of (Vb) at the NH_2 group in the 4-position (cf.: the transition from (IVb) to (Vb) is accompanied by a weak field shift of this signal by 4.85 ppm only). Further transformations confirmed that monoacetylation products of compounds (IV) have in fact the structure (V) (the acylation of 2,4-diamino-5-(aryl)methylpyrimidines also proceeds at the NH_2 group in the 2-position of the heterocyclic ring [14]).

Treatment of pyrimidines (Vb, c) with phenyl isocyanate in boiling toluene and subsequent heating with MeONa in MeOH leads to 5-substituted 7-amino-3-phenyl-1H,3H-pyrimido [4,5-d]pyrimidine-2,4-diones (VIIIa, b) in yields of 94 and 52%, respectively (the intermediate formation of urea (VIIa) was confirmed by mass spectrometry)

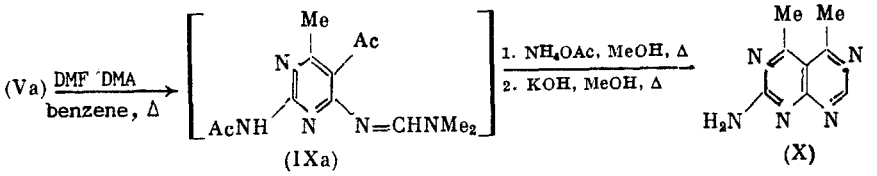


(3)

R = Me(a), Ph (b).

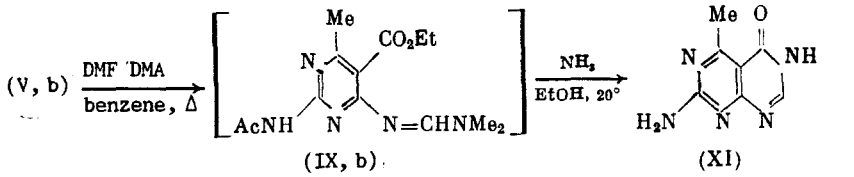
Functionalized pyrimido[4,5-d]pyrimidines of a similar type were synthesized previously by condensation of (5-dimethylamino)methylene-6-iminouracils with guanidine or thiourea [15], but derivatives with a substituent in the 5-position cannot be obtained by this method.

Reaction of pyrimidine (Va) with DMF DMA in boiling benzene with a subsequent heating with NH_4OAc, and then with KOH in MeOH gave 2-amino-4,5-dimethylpyrimido[4,5-d]pyrimidine (X) in a yield of 57%



(4)

In a similar way, 3H-pyrimido[4,5-d]pyrimidin-4-one (XI) was synthesized from (Vb) in a 71% yield. In this case, the cyclization of amidine (IXb) was carried out using an excess of an NH_3 solution in EtOH, while the acetyl protection was removed in the course of the process. The intermediately formed amidine (IXb) was characterized by its PMR spectrum



(5)

The synthesis of 7-amino-3H-pyrimido[4,5-d]pyrimidin-4-one from 2,4-diamino-5-aminocarbonylpyrimidine using dimethylformamide diethylacetal was described previously in [16].

The pyrimido[4,5-d]pyrimidine derivatives (VIII, X, XI) are colorless or yellowish crystalline substances, which are sparingly soluble in water and in most organic solvents. Their structure was confirmed by the IR, PMR, and mass spectral data.

In the mass spectra of these compounds there are intense peaks of molecular ions. The mass spectra of 1H,3H-pyrimido[4,5-d]pyrimidine-2,4-diones (VIII) reveal fragmentation with the formation of $[M - H]^+$, $[M - PhNCO]^+$, $[M - PhNCO - HCN]^+$, and $[M - PhNCO - HCN - CO]^+$ ions. In the mass spectra of (X) signals are observed of the $[M - H]^+$, $[M - Me]^+$, $[M - HCN]^+$, $[M - MeCN]^+$, and $[M - NH_2CN]^+$ ions, while in the spectra of (XI) – the peaks of the $[M - HCN]^+$ and $[M - HCN - CO]^+$ ions are observed.

The IR spectra of compounds (IX), (XI) contain intense absorption bands of the carbonyl groups in the 1680-1685 cm^{-1} region, while the spectra of (VIII) have bands at 1725-1730 cm^{-1} also.

The method for the preparation of 5-acetyl(ethoxycarbonyl)-2,4-diaminopyrimidines (IV) and pyrimido[4,5-d]pyrimidine derivatives (VIII), (X), (XI) from readily available DCC and dicyandiamide, described in the present article, represents a novel example of building up heterocyclic systems using the strategy of chelate organic synthesis (see also [3, 5] and the literature cited therein).

EXPERIMENTAL

The PMR spectra were recorded on a "Bruker WM-250" spectrometer and the ^{13}C NMR spectra on a "Bruker AM-300" spectrometer, the IR spectra were run on a UR-20 spectrophotometer, and and the mass spectra were obtained on a "Varian MAT CH-6" mass spectrometer.

The analytical TLC was carried out in a $CHCl_3$–EtOH, 10:1 eluent.

2,4-Diamino-5-ethoxycarbonyl(acetyl)pyrimidines (IVa-c). A mixture of 1.01 g (12 mmoles) of (II) and 2.12 g (12 mmoles) of $Ni(OAc)_2$ in 10 ml of DCC (Ia-c) was stirred for 4-5 h in an argon atmosphere at 130-140°C (the course of the process was monitored by IR spectroscopy from the disappearance of the νC≡N band). After cooling to ~20°C, the reaction mixture was filtered from the precipitate that separated out, which was washed with ethyl acetate (in the synthesis of (IVa)) or $CHCl_3$ (in the syntheses of IVb, c)). The solvent was removed from the combined filtrates at 70-80°C (1 torr), and the residue was chromatographed on a column with SiO_2 40/100 μm. The eluents for (IVa) were $CHCl_3$ and then ethyl acetate; for (IVb) – $CHCl_3$; for (IVc) – benzene, and then $CHCl_3$. Compounds (IVa, b) were obtained in a crystalline state, and (IVc) in the form of oil, which crystallized on treatment with a 5:1 hexane–Et_2O mixture.

2,4-Diamino-5-acetyl-6-methylpyrimidine (IVa), yield 33%, mp 205-207°C (H_2O). R_f 0.22. Mass spectrum, m/z: 166 $[M]^{+\cdot}$. Found: C 50.08; H 6.00; N 33.36%. $C_7H_{10}N_4O$. Calculated: C 50.59; H 6.07; N 33.72%. IR spectrum ($CHCl_3$, ν, cm^{-1}): 3548, 3505, 3435, 3345 (NH), 1635 (CO), 1620, 1590, 1570. PMR spectrum (DMSO-d_6, δ, ppm): 7.64 br. s (NH_2), 6.68 br. s (NH_2), 2.42 s (Me), 2.40 s (Me). ^{13}C NMR spectrum (DMSO-d_6, δ, ppm): 198.67 (CO), 169.39 (C^6), 164.00, 161.81 (C^2, C^4), 105.70 (C^5), 32.69 (COMe), 20.46 (Me).

2,4-Diamino-5-ethoxycarbonyl-6-methylpyrimidine (IVb), yield 38%, mp 166-167°C (benzene). Lit. [17]: 165-166°C. R_f 0.37. Mass spectrum, m/z: 196 $[M]^+$. IR spectrum ($CHCl_3$, ν, cm^{-1}): 3545, 3510, 3435, 3375 (NH), 1675 (CO), 1610, 1595, 1575. PMR spectrum (DMSO-d_6, δ, ppm): 7.25 br. s (NH_2), 6.64 br. s (NH_2), 4.19 q (CH_2), 2.38 s (Me), 1.27 t ($MeCH_2$). ^{13}C NMR spectrum (DMSO-d_6, δ, ppm): 170.11 (C^6), 167.49 (CO), 164.50, 162.13 (C^2, C_4), 94.66 (C^5), 59.85 (CH_2), 26.16 (Me), 14.20 ($MeCH_2$).

2,4-Diamino-5-ethoxycarbonyl-6-phenylpyrimidine (IVc), yield 35%, mp 188-189°C (benzene). R_f 0.47. Mass spectrum, m/z: 258 $[M]^+$. Found: C 60.32; H 5.39; N 21.57%. $C_{13}H_{14}N_4O_2$. Calculated: C 60.45; H 5.46; N 21.69%. IR spectrum ($CHCl_3$, ν, cm^{-1}); 3545, 3515, 3435, 3385 (NH), 1680 (CO), 1615, 1595, 1560. PMR spectrum ($CDCl_3$, δ, ppm): 7.45-7.22 m (Ph), 6.90 br. s (NH_2), 5.95 br. s (NH_2), 3.87 q (CH_2), 0.70 t (Me). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 171.19 (C^6), 168.06 (CO) 164.77, 162.07 (C^2, C^4), 141.35, 128.40, 127.73, 127.47 (Ph), 96.55 (C^5), 60.09 (CH_2), 13.16 (Me).

4-Amino-2-acetylamino-5-acetyl(ethoxycarbonyl)pyrimidines (Va-c). A mixture of 1 mmole of (IVa-c) and 0.19 ml (2 mmoles) of Ac_2O in 4 ml of benzene was boiled for 5 h. The reaction mixture was allowed to stand for 10 h at 20°C, the crystals that separated out were filtered and compounds (Va-c) were obtained.

4-Amino-5-acetyl-2-acetylamino-6-methylpyrimidine (Va), yield 56%, mp 199-200°C (benzene). Mass spectrum, m/z: 208 $[M]^{+\cdot}$. Found: C 51.44; H 5.57; N 27.38%. $C_9H_{12}N_4O_2$. Calculated: C 51.91; H 5.81; N 26.91%. IR spectrum (KBr, ν, cm^{-1}): 3370, 3275, 3200 (NH), 1685 (CO), 1620, 1575, 1538. PMR spectrum ($CDCl_3$, δ, ppm): 9.35 br. s (NH), 7.71 br. s (NH_2), 2.62 s (Me) 2.56 s (2Me).

4-Amino-2-acetylamino-6-methyl-5-ethoxycarbonylpyrimidine (Vb), yield 71%, mp 212-213°C (benzene). Mass spectrum, m/z: 238 $[M]^{+\cdot}$. Found: C 50.39; H 6.18; N 23.42%. $C_{10}H_{14}N_4O_3$. Calculated: C 50.41; H 5.92; N 23.52%. IR spectrum (KBr, ν, cm^{-1}): 3388, 3268, 3184 (NH), 1688, 1676 (CO), 1634, 1552. PMR spectrum (DMSO-d_6, δ, ppm): 10.08 br. s (NH), 7.52 br. s (NH_2), 4.27 q (CH_2), 2.45 s (Me) 2.22 s (Me), 1.30 t (Me). ^{13}C NMR spectrum (DMSO-d_6, δ, ppm): 169.77, 169.52 (C^6, COMe), 166.76 (CO), 163.69 (C^4), 157.02 (C^2), 99.51 (C^5), 60.63 (CH_2), 25.44 (Me), 25.04 (Me), 14.03 ($MeCH_2$).

4-Amino-2-acetylamino-6-phenyl-5-ethoxycarbonylpyrimidine (Vc), yield 67%, mp 214-215°C (benzene). Mass spectrum, m/z: 300 $[M]^{+\cdot}$. Found: C 59.95; H 5.46; N 18.56%. $C_{15}H_{16}N_4O_3$. Calculated: C 59.99; H 5.37; N 18.66%. PMR spectrum (DMSO-d_6, δ, ppm): 10.21 br. s (NH), 7.57-7.30 m (Ph and NH_2), 3.92 q (CH_2), 2.22 s (Me), 0.77 t ($MeCH_2$).

2,4-Diacetylamino-6-methyl-5-ethoxycarbonylpyrimidine (VI). A mixture of 0.100 g (0.4 mmole) of (Vb) and 0.16 ml (1.6 mmoles) of Ac_2O in 3 ml of Py was boiled for 7 h. The solvent was evaporated in vacuo, the residue was chromatographed on a column with SiO_2 (eluent $CHCl_3$) to yield 0.055 g (47%) of (VI), mp 168-169°C (benzene–hexane, 1:1). Mass spectrum, m/z: 280 $[M]^+$. Found: C 51.13; H 5.66; N 19.88%. $C_{12}H_{16}N_4O_4$. Calculated: C 51.42; H 5.75; N 19.99%. IR spectrum (KBr, ν, cm^{-1}): 3380, 3220, (NH), 1710, 1680 (CO),

1590, 1565. PMR spectrum ($CDCl_3$, δ, ppm): 10.90 br. s (NH), 9.36 br. s (NH), 4.37 q (CH_2), 2.66 s (Me), 2.59 s (Me), 2.35 (Me), 1.40 t ($\underline{Me}CH_2$). ^{13}C NMR spectrum (DMSO-d_6, δ, ppm): 169.97 (C^6), 169.37, 168.44 (2 $\underline{C}OMe$), 165.02 ($\underline{C}O$), 156.73, 156.38 (^2C, C^4), 110.86 (C^5), 60.66 (CH_2), 24.82 (Me), 23.80 ($\underline{Me}$), 23.48 (Me), 13.93 ($\underline{Me}CH_2$).

7-Amino-5-methyl(phenyl)-3-phenyl-1H,3H-pyrimido[4,5-d]pyrimidine-2,4-diones (VIIIa, b). A mixture of 0.6 mmole) of (Vb, c) and 0.10 ml (0.9 mmole) of phenyl isocyanate in 5 ml of toluene was boiled in an argon atmosphere. The solvent was evaporated under vacuum, and (VIIa, b) was obtained (mass spectrum of (VIIa), m/z: 357 $[M]^{+\cdot}$). A 0.065 g portion (1.2 mmoles) of MeONa in 4 ml of MeOH was added to compounds (VIIa, b), and the mixture was boiled for 2 h. Acetic acid was added to the mixture at 20°C to pH ~6, the solvent was evaporated in vacuo, the residue was washed with 30 ml of H_2O, and then with 10 ml of acetone and 10 ml of hexane, to give compounds (VIIIa, b).

7-Amino-5-methyl-3-phenyl-1H,3H-pyrimido[4,5-d]pyrimidine-2,4-dione (VIIIa), yield 94%, mp >360°C. Mass spectrum, m/z (I, %): 269 (76) $[M]^{+\cdot}$, 268 (32) $[M - H]^+$, 150 (100) $[M - PhNCO]^+$, 123 (95) $[M - PhNCO - HCN]^+$, 95 (35) $[M - PhNCO - HCN - CO]^+$. Found: C 57.55; H 4.25; N 25.65%. $C_{13}H_{11}N_5O_2$. Calculated: C 57.99; H 4.12; N 26.01%. IR spectrum (KBr, ν, cm^{-1}): 3310, 3160 (NH), 1725, 1680 (CO), 1630, 1560. PMR spectrum (DMSO-d_6, δ, ppm): 11.66 br. s (NH), 7.57-7.30 m (3H Ph and NH_2), 7.23 d (2H Ph), 2.58 s (Me).

7-Amino-3,5-diphenyl-1H,3H-pyrimido[4,5-d]pyrimidine-2,4-dione (VIIIb), yield 52%, mp >360°C. Mass spectrum, m/z (I, %): 331 (81) $[M]^{+\cdot}$, 330 (100) $[M - H]^+$, 302 (7) $[M - CO]^+$, 254 (9) $[M - Ph]^+$, 212 (24) $[M - PhNCO]^+$, 185 (44) $[M - PhNCO - HCN]^+$, 157 (35) $[M - PhNCO - HCN - CO]^+$. Found: C 64.87; H 4.13; N 20.82%. $C_{18}H_{13}N_5O_2$. Calculated: C 65.25; H 3.95; N 21.14%. IR spectrum (KBr, ν, cm^{-1}): 3300, 3205, (NH), 1730, 1680, (CO), 1630, 1610, 1550. PMR spectrum (DMSO-d_6, δ, ppm): 11.81 br. s (NH), 7.63 br. s, 7.55 br. s (NH_2), 7.52-7.28. (8H, arom), 7.22 d (2H Ph).

2-Amino-4,5-dimethylpyrimido[4,5-d]pyrimidine (X). A mixture of 0.208 g (1 mmole) of (Va) and 0.40 ml (3 mmoles) of DMF DMA in 5 ml of benzene was boiled for 1 h in an argon atmosphere. The solvent was evaporated, 2 ml of $CHCl_3$ was added to the residue and the mixture was filtered through SiO_2 (eluent $CHCl_3$). The solvent was evaporated under vacuum and the residue was boiled in 5 ml of MeOH with 0.390 g (5 mmoles) of NH_4OAc. The mixture was evaporated under vacuum and the residue was boiled for 1 h with 0.110 g (2 mmoles) of KOH in 5 ml of MeOH. MeOH was evaporated under vacuum and the residue was washed with 20 ml of H_2O, and then with 10 ml of acetone and 10 ml of hexane. Yield, 0.110 g (57%) of (X), mp 303-304°C (EtOH). Mass spectrum m/z (I, %): 175 (100) $[M]^{+\cdot}$, 174 (49) $[M-H^+]$, 160 (24) $[M - Me]^+$, 148 (45) $[M - HCN]^+$, 134 (16) $[M - MeCN]^+$, 133 (16) $[M - NH_2CN]^+$. Found: C 54.76; H 5.13; N 39.57%. $C_8H_9N_5$. Calculated: C 54.84; H 5.18; N 39.98%. IR spectrum (KBr, ν, cm^{-1}): 3330, 3110 (NH), 1665, 1580, 1530. PMR spectrum (DMSO-d_6, δ, ppm): 8.84 s (CH=), 7.54 br. s (NH_2), 2.87 s (Me), 2.83 s (Me).

7-Amino-5-methyl-3H-pyrimido[4,5-d]pyrimidin-4-one (XI). A mixture of 0.120 g (0.5 mmole) of (Vb) and 0.27 ml (2.0 mmoles) of DMF DMA in 5 ml of benzene was boiled for 1.5 h in an argon atmosphere. The solvent was evaporated under vacuum to give compound (IXb) (PMR spectrum ($CDCl_3$, δ, ppm): 8.60 s (CH=), 8.43 br. s (NH), 4.35 q (CH_2), 3.13 s, 3.07 s (Me_2N), 2.47 s (Me), 2.35 s (Me), 1.37 t ($\underline{Me}CH_2$)). A saturated solution (5 ml) of NH_3 in EtOH was added to compound (IXb) and the mixture was stirred for 58 h at 20°C. The precipitate that separated out was filtered off and washed with 10 ml of $CHCl_3$. Yield, 0.063 g (71%) of (XI), mp >360°C (butanol). Mass spectrum, m/z (I, %): 177 (100) $[M]^{+\cdot}$, 150 (23) $[M - HCN]^+$, 122 (15) $[M - HCN - CO]^+$. Found: C 47.06; H 4.07%. $C_7H_7N_5O$. Calculated: C 47.46; H 3.98%. IR spectrum (KBr, ν, cm^{-1}): 3288, 3120 (NH), 1684 (CO), 1608, 1572, 1532. PMR spectrum (DMSO-d_6, δ, ppm): 12.08 br. s (NH), 8.15 s (CH=), 7.37 br. s (NH_2), 2.70 s (Me).

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SYNTHESIS OF BORON CHELATES FROM N-(PYRID-2-YL)- AND (N-4-METHYLPYRID-2-YL) CYANOACETAMIDES AND THEIR TAUTOMERIC TRANSFORMATIONS

V. S. Bogdanov, S. V. Baranin,
A. Dib, I. P. Yakovlev, and
V. A. Dorokhov

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Chelate complexes in which the boron atom is bound to the pyridine N atom and the O atom of the deprotonated ligand were synthesized by reaction of N-(pyrid-2-yl)- and N-(4-methylpyrid-2-yl) cyanoacetamides. A new type of intrachelate tautomeric transformation was discovered: the complexes obtained can exist in solutions in the form of two tautomers, which are derivatives of acetimidic acid or the corresponding ketene N,O-acetals.

The complexation with the participation of 2-acylaminopyridines (AAP) have been relatively little investigated. Complexes of 2-acetylaminopyridine (HL) with divalent metal compounds having the composition of $X_2M(HL)_2$ (M = Ni, Cu, Co, Mn, Zn) and $X_2M(HL)$ (where M is Cd) have been described [1, 2]. In the course of our previous investigations on the structure and reactivity of cyclic tetracoordinated boron compounds, we have synthesized chelates (I) in which deprotonated AAP are the ligands [3].

Complexes of this type are characterized by the presence of a delocalized system of π-electrons in the boron-containing ring and their structure is more accurately depicted by the structural formula (I').

Boron chelates were recently obtained with a ligand from the AAP group, which formally corresponds to the product of the addition of ethyl cyanoacetate to N-(pyrid-2-yl) cyanoacetamide at the C≡N bond [4, 5]. According to the ^1H and ^{13}C NMR spectral data in DMSO-d_6, these chelates have the structure (II), in which the boron-containing ring differs in its structure from that in (I).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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