4,5-Diamino-1-phenyl-1,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one in the synthesis of fused tricyclic systems

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Starting from the substituted 4,5-diaminopyrazolo[3,4-*b*]pyridine, derivatives of a number of tricyclic systems, *viz.*, imidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridine, pyrazolo[3,4-*b*][1,2,5]thiadiazolo[3,4-*d*]pyridine, pyrazolo[3,4-*b*][1,2,3]triazolo[4,5-*d*]pyridine, and [1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridine, were synthesized and reaction schemes for the processes were proposed.

Key words: pyrazolo[3,4-*b*]pyridin-6(7*H*)-one, dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridin-4(3*H*)-one, diazepines, pyrazolo[3,4-*b*][1,2,5]thiadiazolo[3,4-*d*]pyridin-4(3*H*)-one, [1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridine, dimethylformamide diethyl acetal.

One of the most fruitful trends in the development of chemistry of heterocyclic compounds is a creation of new approaches to the synthesis of fused heterocycles, the detailed analysis of properties of which has both the theoretical and practical importance. Many compounds, containing pyrazole and pyridine rings (often the fused ones), are of interest as the prospective biologically active substances. Thus, the new nonglycoside antiherpetic compounds,[1,2] nonpeptide corticotropin-releasing factor inhibitors, active against depressions, anxiety, and other stress pathologies,[3—5] as well as selective GAMK-receptor modulators, showing strong sedative effect and considerable analgesic activity, were discovered among pyrazolopyridines.[6]

Earlier,[7] we synthesized 4,5-diamino-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6(7*H*)-one hydrochloride (**1**). The presence of two amino groups, located at the adjacent positions of pyrazolopyridine (4 and 5), opens wide possibilities for the application of this compound in the heterocyclization reaction for the synthesis of tricyclic systems, including pyrazolo[3,4-*b*]pyridine fragment.

We showed that the reflux of diamine **1** with acetylacetone in ethanol for 2 h (Scheme 1) leads to the imidazole ring closure, resulting in 69% isolated yield of 2-methyl-6-phenyl-5,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridin-4(3*H*)-one hydrochloride (**3**). TLC analysis of the reaction mixture showed the presence of insignificant admixture of diazepine **2**, which upon further heating was completely converted to the final tricyclic compound **4**. Undoubtedly, the initial condensation of diketone at one of the amino groups proceeds to form azomethines **A** and (or) **B**. Further, the addition of the free amino group at the azomethine double bond takes place to form imidazoline ring, the aromatization of which proceeds with elimination of acetone and formation of tricycle **3**.

Based on the data in papers,[8—10] it can be assumed that during the course of the reaction, an equilibrium mixture of the starting compound **1**, the intermediates **A—C**, and diazepine **2** is formed, which further slowly and irreversibly is converted to hydrochloride **3**. Imidazopyrazolopyridine **4** can be further liberated from the latter. In order to confirm our suggestions on the course of cyclization under consideration, we carried out the reaction of the base of the starting diamine **1** with acetylacetone in benzene with the removal of water by distillation. In the reaction mixture, the formation of the product, the structures of which, according to the mass spectrometry data, corresponded to the structure of the diazepine derivative **2** was observed. We also showed that, when it was kept or heated in water or aqueous ethanol for 2 days, a mixture, consisting from imidazole derivative **4** and the starting diamine **1**, was formed according to the TLC data.

Of course, the possibilities for the creation of fused five-membered rings are not limited only to the imidazole derivatives.

The presence of two *ortho*-amino groups in the starting molecule suggests a possibility for the thiadiazole ring closure. Compounds with such structure are of interest due to the presence of the thiadiazole fragment in

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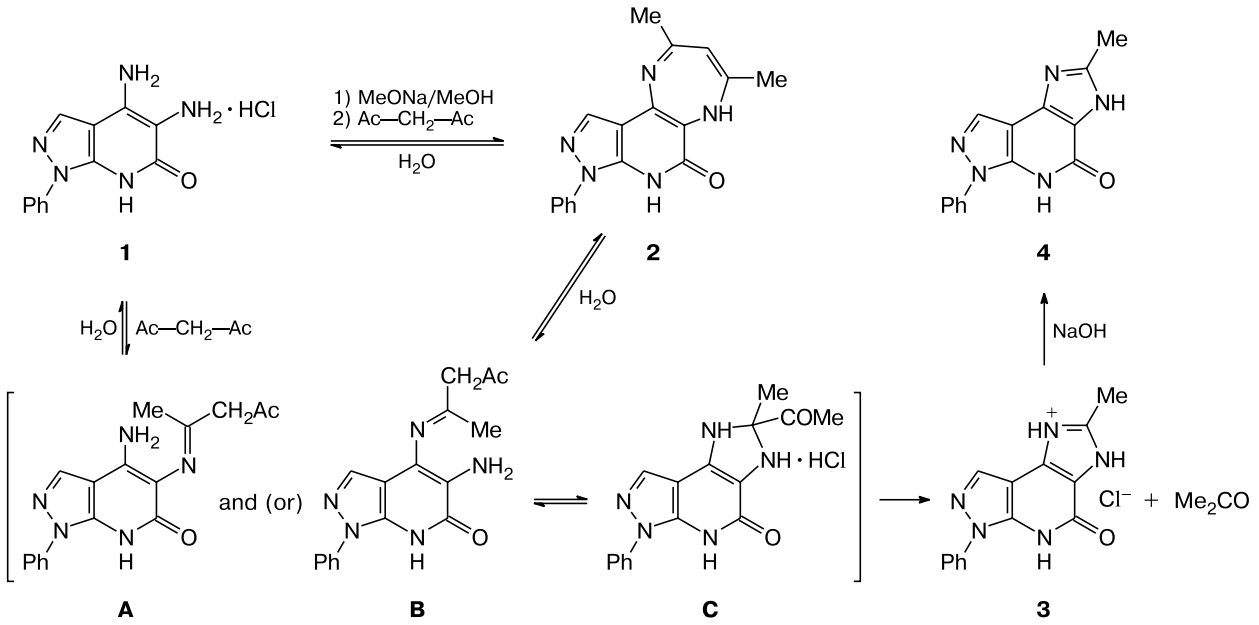
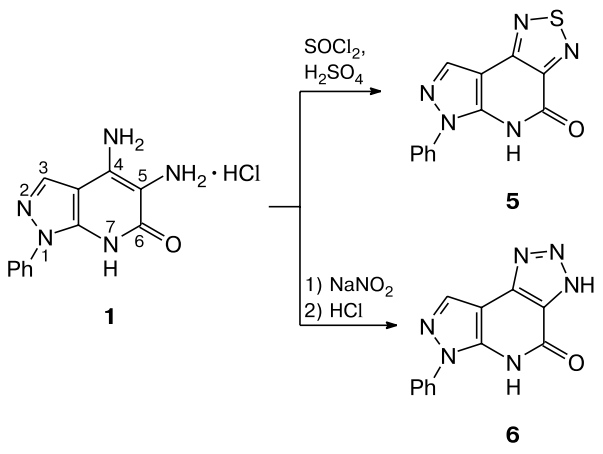
Scheme 1



a number of highly active compounds, showing, for example, the ability to activate the cognitive functions.[11—13] Earlier,[14—16] methods for the synthesis of various thiadiazoles from aromatic diamines with the use of thionyl chloride were described, where it was indicated that inorganic acids increase the conversion. In accordance with this, it was shown that the reflux of diamine hydrochloride **1** in thionyl chloride in the presence of sulfuric acid for 2 days leads to 6-phenyl-5,6-dihydro-4*H*-pyrazolo[3,4-*b*][1,2,5]thiadiazolo[3,4-*d*]pyridin-4(3*H*)-one (**5**) in 78% yield (Scheme 2).

Scheme 2



The reaction of diamine hydrochloride **1** with sodium nitrite for 1 h smoothly afforded 6-phenyl-5,6-dihydropyrazolo[3,4-*b*][1,2,3]triazolo[4,5-*d*]pyridin-4(3*H*)-one (**6**). During this, apparently, the diazotization reaction of 5-amino group initially takes place, the diazonium cation that formed undergoes cyclization with participation of the amino group in position 4, which leads to triazole ring closure.

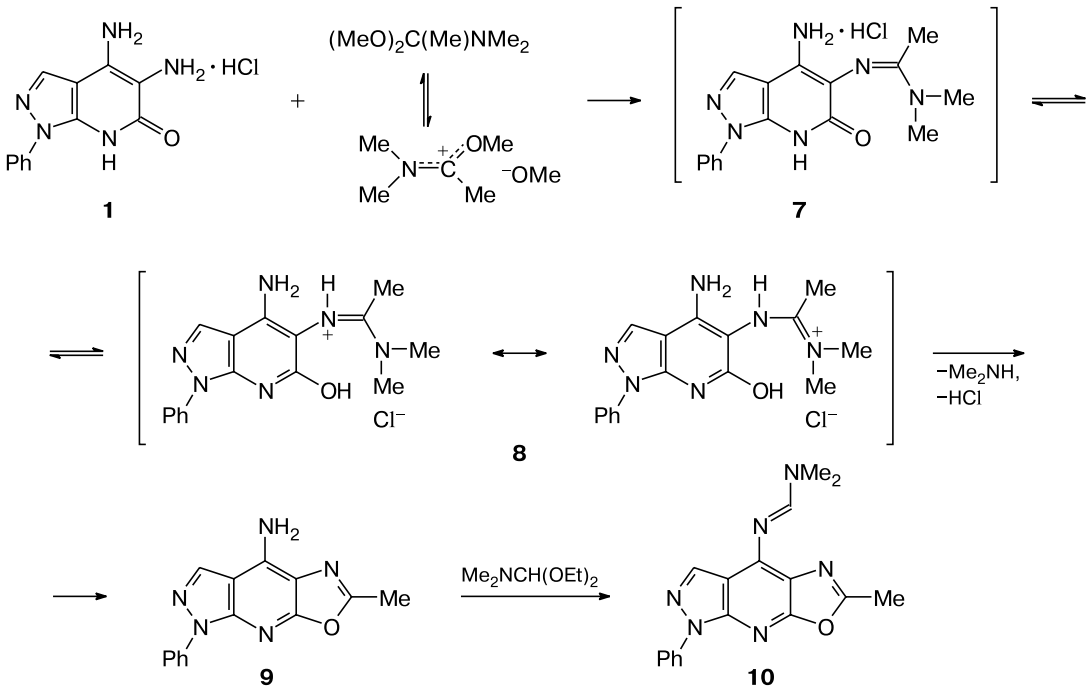
It is known[17] that a variety of heterocyclic compounds can be synthesized based on the use of amide acetals. In this connection, the possibility of involvement of diamine hydrochloride **1** into the reaction with amide acetals was considered in this work.[18] 6-Methyl-1-phenyl-1*H*-[1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridin-4-amine (**9**) was obtained by the reflux of compound **1** with excess of dimethylacetamide dimethyl acetal in methanol (Scheme 3).

In accordance with Scheme 3, the ambident cation,[19] presented in the solution of dimethylacetamide dimethyl acetal in equilibrium with acetal and methoxide anion,[20] undergoes condensation at the amino group of the pyridine ring in position 5 to form amidine **7**, which is a key intermediate in the synthesis of oxazole **9**, forming, probably, through the intermediate compound **8**.

The structure of compound **9** was confirmed also by its conversion to 4-[(dimethylamino)methylidenamino]-6-methyl-1-phenyl-1*H*-[1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridine (**10**) in 80% yield by heating with dimethylformamide diethyl acetal for 30 min.

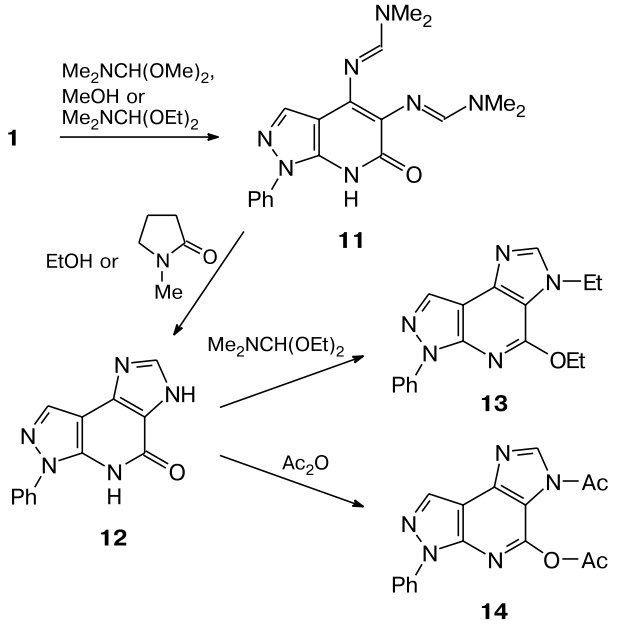
It turned out that the reaction of compound **1** with dimethylformamide dimethyl acetal followed the other direction than it was expected. The reflux of free diamine **1** or its hydrochloride with excess of dimethylformamide dimethyl acetal in methanol for 1 h leads to 4,5-bis[(dimethylamino)methylidenamino]-1-phenyl-1,7-dihydro-

Scheme 3



1*H*-pyrazolo[3,4-*b*]pyridin-6-one (**11**) (Scheme 4). This compound can be obtained more smoothly by the reflux in minimum dimethylformamide diethyl acetal due to the higher activity of the latter comparing with dimethyl acetal.[18] The relatively higher reactivity of diethyl acetal can be explained by the fact that the steric strain in its uncharged form, caused by the nonbonding interactions of alkoxy groups, decreases by going to the ambident cation (presented in equilibrium with acetal and responsible for the high reactivity of amide acetal toward nucleophilic reagents) to a greater extent than for dimethyl acetal.[19] The further research showed that the reflux of bisamidine **11** in minimum aq. ethanol or in anhydrous *N*-methylpyrrolidone-2 leads to compound, to which, based on the spectral data, the structure of 6-phenyl-5,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridin-4(3*H*)-one (**12**) was ascribed.

Scheme 4



This difference in the direction of the reaction of diaminopyridine **1** with dimethylformamide or dimethylacetamide acetal can be explained by the sterical factors. Thus, as it follows from the experimental data, bisamidine **11** is a key compound in the synthesis of imidazole derivative **12**, and the process of cyclization is determined by the correlation of the rates of formation of this bisamidine and the closure of annulated five-membered ring. When amidine **7** (containing methyl group in the amidine *meso*-position) is formed, the steric hindrance for the attack of the amino group in position 4 of the pyridine ring by the ambident cation of dimethylacetamide acetal arises, and the reaction changes its direction to the cyclization at the oxo group of pyridine with the oxazole ring closure. Obviously, the presence of free amino group in position 4 of the pyridine ring makes the attack of carbonyl group of pyridone fragment easier (below we

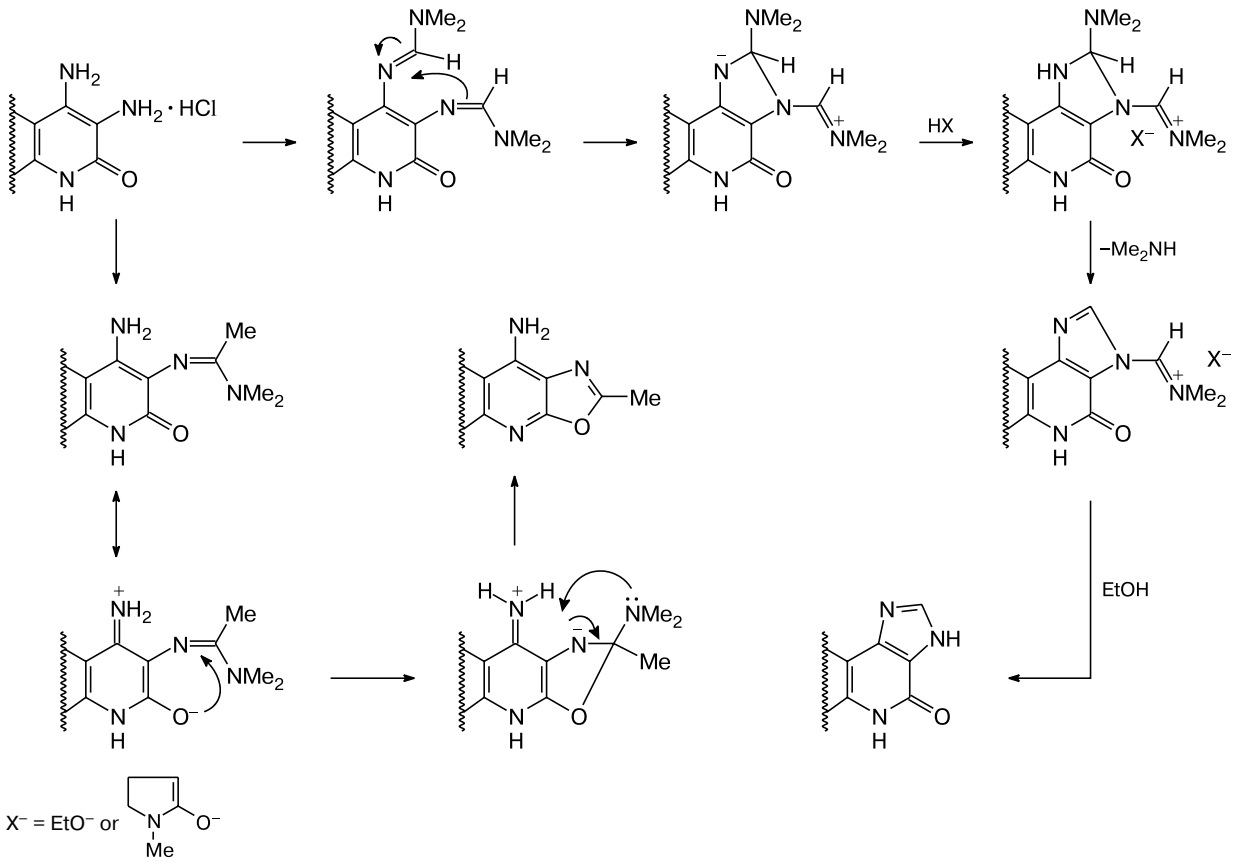
show the resonance hybrid, in which a significant partial negative charge is located on the oxygen atom, resulting in acceleration of the oxazole cyclization). When dimethylformamide acetal is used, the situation changes: the second amidine group in position 4 is considerably less effective donor of electrons than unsubstituted amino group, and the attack at the carbonyl group does not occur. It seems likely that there is no need in the preliminary hydrolysis of one of the amidine fragments in bisamidine **11** for the imidazole cyclization to take place, since, if the 4-amino group (in the pyridine ring) would have occurred during the hydrolysis, then the formation of oxazole ring became possible for the reasons mentioned above. However, this was not observed in the experiment and the formation of compound **12** proceeded in quite satisfactory yield. For the additional evidence, imidazole **12** was also obtained in 71% yield by the reflux of bisamidine **11** in minimum *N*-methylpyrrolidone.

The kinetics of the oxazole and imidazole cyclization, without which it is hardly possible to reliably establish their mechanism, was not studied in the frame of this work. Nevertheless, the nontrivial results that obtained are supposedly given in Scheme 5.

The structure of imidazole **12** was also confirmed by its reaction with dimethylformamide diethyl acetal, resulting in isolation from the reaction mixture of 6-phenyl-3-ethyl-4-ethoxy-3,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridine (**13**) in 39% yield. It is known that alkylation of 2-pyridones can occur both at the oxygen[21] and at the nitrogen atoms of the pyridone ring of the molecule.[22] The HMBC spectrum unambiguously proves that the process of alkylation of compound **12** proceeds toward formation of 4-ethoxyimidazopyrazolopyridine **13**: the methylene group in position 3 (δ 4.45) has the correlation peaks with C(2) and C(3a) atoms, whereas the methylene group in position 4 (δ 4.60), with C(4) atom. The full assignment of signals of carbon atoms, made on the basis of HMBC and HSQC spectra, is given in the Experimental.

A reflux of imidazole **12** in acetic anhydride for 2 h leads to 4-acetoxy-3-acetyl-6-phenyl-3,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridine (**14**), which is described[23–25] for the similar compounds, containing a pyridin-2-one fragment. The structure of compound **14** was established on the basis of NOEDIFF spectrum: during saturation of the signal of the acetyl group (δ 2.86), a response in only one singlet at δ 8.87 was observed; an increase of the intensity of the signal due to the NOE was 18%. This result is in agreement with the selective *N*-acetylation at position 3 (if the acetylation occurs at

Scheme 5



position 1, a response should be expected in the singlet of the proton at δ 8.66, too).

In the IR spectrum of this compound, a strong absorption band at 1759 cm^{-1} is observed, characteristic of the ester group (acetoxy group), which excludes the versions of the second acetylation at position 5.

In conclusion, we successfully accomplished a number of transformations of 4,5-diamino-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6(7*H*)-one hydrochloride to obtain a series of tricyclic systems, *viz.*, the derivatives of pyrazolo[3,4-*b*][1,2,5]thiadiazolo[3,4-*d*]pyridine, pyrazolo[3,4-*b*][1,2,3]triazolo[4,5-*d*]pyridine, [1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridine, and imidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridine, and found out the unusual distinction in the direction of cyclizations of 4,5-diaminopyrazolo[3,4-*b*]pyridine when dimethylformamide and dimethylacetamide acetal were used.

Experimental

IR spectra of the compounds were recorded on a Perkin—Elmer 457 spectrometer in Nujol, mass spectra (EI) were recorded on a Finnigan SSQ-710 mass-spectrometer with the direct inlet of the sample into the source of ions. NMR spectra were recorded on a Bruker AC-300 and DRX-500 spectrometers. Monitoring of the products purity and the reaction course was carried out by TLC on Merck TLC Silicagel 60 F_{254} plates (eluents: hexane—acetone, 3 : 1; chloroform—methanol, 10 : 1; visualization, by the UV light). Melting points were determined on a Electrothermal 9100 instrument.

Physical and chemical characteristics and elemental analysis data of the synthesized substances are given in Table 1.

2,4-Dimethyl-8-phenyl-7,8-dihydropyrazolo[4′,3′:5,6]pyrido[3,4-*b*]diazepin-6(5*H*)-one (2). A solution of sodium methoxide (0.097 g, 1.8 mmol) in methanol (10 mL) was slowly added dropwise to a vigorously stirred suspension of hydrochloride **1** (0.5 g, 1.8 mmol) to pH ~7. Pentan-2,4-dione (1.46 g, 14.6 mmol) was added to the reaction mixture obtained and this was refluxed with stirring and simultaneous distillation off of water for 4 days. The precipitate of compound **2** was filtered off and washed with methanol.

2-Methyl-6-phenyl-5,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridin-4(3*H*)-one hydrochloride (3). Pentan-2,4-dione (1.46 g, 14.6 mmol) was added to a suspension of hydrochloride **1** (1.0 g, 3.61 mmol) in ethanol (30 mL). The reaction mixture was heated under stirring for 2 h, cooled, the precipitate of compounds **3** formed was filtered off, washed with propan-2-ol, and recrystallized from EtOH. IR (Nujol), ν/cm^{-1}: 3363 (N—H); 1660 (C=O). ^{1}H NMR (DMSO-d_6), δ: 2.79 (s, 3 H, Me); 7.41 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.55 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 7.88 (d, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 8.27 (s, 1 H, H(8)); 12.80 (br.s, 2 NH).

2-Methyl-6-phenyl-5,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridin-4(3*H*)-one (4). Sodium hydroxide (0.13 g, 3.3 mmol) was added to a solution of imidazole hydrochloride **3** (1.0 g, 3.31 mmol) in water (30 mL). After 2 h, the precipitate of compound **4** formed was filtered off, washed with cold methanol, and recrystallized from EtOH.

Table 1. Yields, melting points, elemental analysis data, and mass spectrometry data for compounds **3—6** and **9—14**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula	MS, m/z (I_{rel} (%))
			C	H	N		
3	69	>290	55.72 55.73	4.15 4.01	23.32 23.21	$C_{14}H_{12}ClN_5O$	265 $[M]^+$ (98)
4	33	275—278	63.44 63.39	4.11 4.18	26.51 26.40	$C_{14}H_{11}N_5O$	265 $[M]^+$ (98)
5	78	286—288	53.59 53.52	2.70 2.62	25.94 26.01	$C_{12}H_7N_5OS$	269 $[M]^+$ (80)
6	67	>300	57.26 57.14	3.15 3.20	33.22 33.32	$C_{12}H_8N_6O$	252 $[M]^+$ (45)
9	36	235—237	62.21 63.39	4.29 4.18	26.33 26.40	$C_{14}H_{13}N_5O$	265 $[M]^+$ (100)
10	80	225—6	63.62 63.74	4.98 5.03	26.14 26.23	$C_{17}H_{16}N_6O$	320 $[M]^+$ (100)
11	84	202—203	61.47 61.52	6.17 6.02	27.89 27.90	$C_{18}H_{21}N_7O$	351 $[M]^+$ (55)
12	69	>300	57.95 57.99	4.26 4.12	26.00 26.01	$C_{13}H_9N_5O \cdot H_2O$	251 $[M]^+$ (100)
13	39	135—137	66.50 66.43	5.50 5.58	22.68 22.79	$C_{17}H_{17}N_5O$	307 $[M]^+$ (70)
14	85	238—240	60.78 60.89	3.87 3.91	20.76 20.89	$C_{17}H_{13}N_5O_3$	251 $[M]^+$ (45)

6-Phenyl-5,6-dihydro-4*H*-pyrazolo[3,4-*b*][1,2,5]thiadiazolo[3,4-*d*]pyridin-4(3*H*)-one (5). Sulfuric acid (3 drops) was added to a suspension of hydrochloride **1** (1.0 g, 3.61 mmol) in thionyl chloride (10 mL) and this was refluxed with stirring for 24 h. The reaction mixture was cooled and concentrated dry *in vacuo*. The precipitate was treated with water, filtered off, and after separation by column chromatography (SiO_2, eluent: chloroform—methanol, 10 : 1), pure product **5** was obtained. ^{1}H NMR (DMSO-d_6), δ: 7.47 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.59 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.36 (s, 1 H, H(8)); 12.70 (br.s, 1 H, N(5)H).

6-Phenyl-5,6-dihydropyrazolo[3,4-*b*][1,2,3]triazolo[4,5-*d*]pyridin-4(3*H*)-one (6). Aqueous sodium nitrite (0.25 g, 3.62 mmol) was slowly added dropwise to a solution of diamine hydrochloride **1** (1.0 g, 3.61 mmol) in water (20 mL) at 15 °C. After 10 min, the precipitate yellow in color was formed. The reaction mixture was stirred for 1 h at 20 °C. The precipitate of compound **6** obtained was filtered off, washed with water, and recrystallized twice from DMF. IR (Nujol), ν/cm^{-1}: 3105 (N—H); 1638 (C=O). ^{1}H NMR (DMSO-d_6), δ: 7.47 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.58 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.19 (s, 1 H, H(8)); 12.30 (br.s, 1 H, N(5)H).

6-Methyl-1-phenyl-1*H*-[1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridine-4-amine (9). A solution of diamine hydrochloride **1** (1.0 g, 3.61 mmol) and dimethylacetamide dimethyl acetal (1.82 g, 13.67 mmol) in methanol (10 mL) was refluxed with stirring for 6 h. After cooling in 30 min, a precipitate was formed. Acetone was added to the suspension, and the solution obtained was concentrated dry *in vacuo*. The precipitate was treated with water, filtered off, and pure oxazole **9** was isolated by crystallization from hexane—ethyl acetate. IR (Nujol), ν/cm^{-1}: 3342, 3205 (NH_2). ^{1}H NMR (DMSO-d_6), δ: 2.56 (s, 3 H, Me); 7.29 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.53 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 7.70 (br.s, 2 H, NH_2); 8.24 (m, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 8.49 (s, 1 H, H(3)).

4-[(Dimethylamino)methylidenamino]-6-methyl-1-phenyl-1*H*-[1,3]oxazolo[5,4-*b*]pyrazolo[4,3-*e*]pyridine (10). A suspension of oxazole **9** (1.0 g, 3.77 mmol) in dimethylformamide diethyl acetal (2.4 g, 16.33 mmol) was refluxed with stirring for 1 h. The reaction mixture was cooled, water (10 mL) was added, and this was triturated. The precipitate of compounds **10** was filtered off, washed with water, and recrystallized from acetonitrile. ^{1}H NMR (DMSO-d_6), δ: 2.62 (s, 3 H, Me); 3.22, 3.26 (both s, 3 H each, NMe_2); 7.27 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.52 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.28 (d, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 8.31 (s, 1 H, H(3)); 9.05 (s, 1 H, H(1″)).

4,5-Bis[(dimethylamino)methylidenamino]-1-phenyl-1,7-dihydro-1*H*-pyrazolo[3,4-*b*]pyridin-6-one (11). ***A.*** A solution of sodium metal (0.083 g, 3.61 mmol) in methanol was added to a stirred suspension of diamine hydrochloride **1** (1.0 g, 3.61 mmol) in methanol (30 mL). After 15 min, the precipitate was dissolved. Dimethylformamide dimethyl acetal (2.97 g, 24.83 mmol) was added to the solution obtained, and this was refluxed with stirring for 1 h. The reaction mixture was cooled, water (20 mL) was added, this was triturated and kept for 24 h at +5 °C. The precipitate of bisamidine **11** was filtered off, washed with water, and recrystallized from propan-2-ol.

B. A solution of diamine hydrochloride **1** (1.0 g, 3.61 mmol) in methanol (20 mL) and dimethylformamide dimethyl acetal (2.97 g, 24.83 mmol) was refluxed with stirring for 6 h. Water was added to the solution, this was triturated and kept for 24 h at +5 °C. The precipitate was filtered off, washed with water, and recrystallized from aq. acetone.

C. A suspension of diamine hydrochloride **1** (1.5 g, 5.42 mmol) in dimethylformamide dimethyl acetal (5.4 g, 36.73 mmol) was refluxed with stirring for 4 h. The reaction mixture was cooled and water (15 mL) was added. The precipitate formed was filtered off, washed with water, and recrystallized from aq. acetone. ^{1}H NMR (DMSO-d_6), δ: 3.01—3.14 (br.s and s, 12 H, 2 NMe_2); 7.19 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.46 (m, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.20 (s, 1 H, H(3)); 8.26 (d, 2 H, H(2″), H(5″), J_o = 8.4 Hz); 7.97, 8.62 (both s, 1 H each, N=C<u>H</u>NMe_2).

6-Phenyl-5,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridin-4(3*H*)-one monohydrate (12). ***A.*** A suspension of bisamidine **11** (1.0 g, 2.85 mmol) in ethanol (5 mL) was refluxed with stirring for 1 h. Water (10 mL) was added to the solution obtained and this was triturated. The precipitate of monohydrate of compound **12** was filtered off, washed, and recrystallized from aq. ethanol.

B. A suspension of bisamidine **11** (1.0 g, 2.85 mmol) in *N*-methylpyrrolidone (5 mL) was refluxed with stirring for 4 h. Water (10 mL) was added to the solution obtained and this was triturated. The precipitate of monohydrate of compound **12** was filtered off, washed, and recrystallized from propan-2-ol. IR (Nujol), ν/cm^{-1}: 3105 (N—H); 1664 (C=O). ^{1}H NMR (DMSO-d_6), δ: 7.37 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.53 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 7.90 (br.s, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 8.11 (s, 2 H, H(2), H(8)). ^{1}H NMR (pyridine-d_5), δ: 7.07 (d, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 7.18 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.32 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.47, 8.49 (both s, 1 H each, H(2), H(8)).

4-Ethoxy-3-ethyl-6-phenyl-5,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridine (13). A suspension of monohydrate of imidazole **12**(1.0 g, 3.98 mmol) in dimethylformamide diethyl acetal (4.3 g, 29.25 mmol) was refluxed with stirring for 4 h. The solution obtained was cooled, water (10 mL) was added, and this was triturated. The precipitate was filtered off and washed with water. After separation by column chromatography (SiO_2, eluent: chloroform—methanol, 10 : 1), product **13** (0.42 g) was obtained. ^{1}H NMR (DMSO-d_6), δ: 1.45, 1.47 (both t, 3 H each, $CH_2C\underline{H}_3$, J = 7.0 Hz); 4.45, 4.60 (both d, 2 H each, $C\underline{H}_2CH_3$, J = 7.0 Hz); 7.32 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.55 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.30 (d, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 8.37, 8.39 (both s, 1 H each, H(8), H(2)). ^{13}C NMR (DMSO-d_6), δ: 14.1, 16.8, 41.8, 62.5 (3-Et, 4-EtO); 105.5 (C(8a)); 114.8 (C(3a)); 120.2, 125.5, 129.0, 139.6 (C_{Ph}); 131.3 (C(8)); 144.1 (C(8b)); 144.8 (C(5a)); 145.4 (C(2)); 151.3 (C(4)).

4-Acetoxy-3-acetyl-6-phenyl-3,6-dihydroimidazo[4,5-*d*]pyrazolo[3,4-*b*]pyridine (14). A suspension of imidazole **12** (1.0 g, 3.98 mmol) in acetic anhydride (5 mL) was refluxed with stirring for 2 h. The precipitate was filtered off, washed with methanol, refluxed in water (10 mL), and filtered off to obtain pure product **14**. IR (Nujol), ν/cm^{-1}: 1759 (O—COMe); 1751 (COMe). ^{1}H NMR (DMSO-d_6—CD_3OD), δ: 2.45 (s, 3 H, OCOMe); 2.86 (s, 3 H, NCOMe); 7.33 (t, 1 H, H(4′), J_o = 8.4 Hz); 7.53 (t, 2 H, H(3′), H(5′), J_o = 8.4 Hz); 8.16 (d, 2 H, H(2′), H(6′), J_o = 8.4 Hz); 8.66, 8.87 (both s, 1 H each, H(8), H(2)).

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