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## SHORT COMMUNICATIONS

# Synthesis of 5-Amino-4-imino-3,4-dihydropyrido[3,4-*d*]-pyridazin-1(2*H*)-one Derivatives

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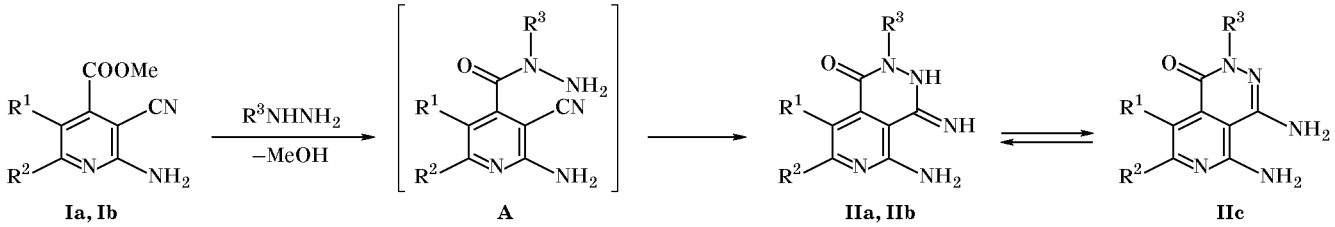
We previously reported on the synthesis of alkyl 5,6-dialkyl-2-amino-3-cyanopyridine-4-carboxylates **Ia** and **Ib**. These compounds were shown to react with oxygen-centered nucleophiles and amines to give pyrrolo[3,4-*c*]pyridines [1]. In continuation of these studies, we examined the reaction of substituted pyridines **I** with hydrazines. The reaction was carried out using the corresponding hydrazine as solvent, on heating for 1 h under reflux. The products were 2,7,8-trisubstituted 5-amino-4-imino-3,4-dihydropyrido-[3,4-*d*]pyridazin-1(2*H*)-ones **IIa**–**IIc** (Scheme 1). As shown in Scheme 1, the initial reaction stage is likely to be nucleophilic attack by the most substituted nitrogen atom of the hydrazine on the ester carbonyl carbon atom in **I**. Intermediate hydrazide **A** undergoes intramolecular heterocyclization to 5-amino-4-imino-3,4-dihydropyrido[3,4-*d*]pyridazin-1(2*H*)-one **II**. The structure of the products was proved by the IR, $^1$H NMR, and mass spectra. Compounds **IIa** and **IIb** in solution give rise to imine–enamine tautomerism, and the tautomeric equilibrium is displaced toward more stable 4-aminopyrido[3,4-*d*]pyridazine **IIc**. According to the $^1$H NMR data, the fraction of the imino tautomer is 2–3%.

**5-Amino-4-imino-7-methyl-3,4-dihydropyrido-[3,4-*d*]pyridazin-1(2*H*)-one (IIa).** Pyridine **Ia**, 0.191 g (0.001 mol), was dispersed in 10 ml of hydrazine hydrate at room temperature. The suspension was heated for 1 h under reflux and cooled to room temperature, and the yellow precipitate was filtered off and washed with 10 ml of 1,4-dioxane. The product was recrystallized from DMF and dried under reduced pressure over $P_2O_5$. Yield 0.164 g (86%), mp 243°C. IR spectrum, ν, cm$^{-1}$: 3190, 3295, 3354, 3435 (NH, $NH_2$); 1695 (C=O). $^1$H NMR spectrum, δ, ppm: 2.38 s (3H, $CH_3$), 5.17 s (2H, $NH_2$), 6.39 s (1H, NH), 6.8 s (1H, NH), 7.07 s (1H, CH), 11.62 s (1H, =NH). Found, %: C 50.24; H 4.70; N 36.65. $C_8H_9N_5O$. Calculated, %: C 50.26; H 4.74; N 36.63.

**5-Amino-4-imino-2,7-dimethyl-3,4-dihydropyrido[3,4-*d*]pyridazin-1(2*H*)-one (IIb).** Following the above procedure, from 0.191 g (0.001 mol) of **Ib** and 5 ml of methylhydrazine we obtained 0.189 g (92%) of product **IIb**. mp 254°C. IR spectrum, ν, cm$^{-1}$: 3150, 3285, 3320, 3443 (NH, $NH_2$); 1685 (C=O). Mass spectrum, *m*/*z* ($I_{rel}$, %): $M^+$ 205, 42 (21), 52 (7), 65 (25), 91 (13), 107 (16), 133 (58), 145 (7), 160 (17), 176 (21) (9 most abundant fragment ion peaks are given). Found, %: C 52.64; H 5.47; N 34.15. $C_9H_{11}N_5O$. Calculated, %: C 52.67; H 5.40; N 34.13.

**4,5-Diamino-7,8-dimethylpyrido[3,4-*d*]pyridazin-1(2*H*)-one (IIc).** Following the above procedure,

**Scheme 1.**




$R^1 = R^3 = H$, $R^2 = Me$ (**a**); $R^1 = H$, $R^2 = R^3 = Me$ (**b**); $R^1 = R^2 = Me$, $R^3 = H$ (**c**).

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from 0.205 g (0.001 mol) of compound **Ic** and 10 ml of hydrazine hydrate we obtained 0.192 g (84%) of product **IIc**. mp 257°C. IR spectrum, ν, $cm^{-1}$: 3190, 3340, 3430 (NH, $NH_2$); 1695 (C=O). $^1H$ NMR spectrum, δ, ppm: 2.37 s (3H, $CH_3$), 2.41 s (3H, $CH_3$), 6.05 s (2H, $NH_2$), 6.15 s (2H, $NH_2$), 10.56 s (1H, NH). Mass spectrum: *m*/*z* 205 $M^+$. Found, %: C 52.63; H 5.45; N 34.12. $C_9H_{11}N_5O$. Calculated, %: C 52.67; H 5.40; N 34.13.

The IR spectra were measured on a UR-20 instrument in mineral oil. The $^1H$ NMR spectra were recorded on Bruker WM-250, Bruker AM-300, and Bruker DRX-500 spectrometers operating at 250.13, 300.13, and 500.13 MHz, respectively; DMSO-$d_6$ was used as solvent, and tetramethylsilane, as internal reference. The low- and high-resolution mass spectra (70 eV) were obtained on a Varian MAT-212 instrument. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates; spots were visualized with UV light and iodine vapor.

## REFERENCES

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