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LETTERS TO THE EDITOR

Transformation of 2-Acylamino-3,3-dichloroacrylonitriles into Substituted 4-Amino[1,3]oxazolo[4,5-*e*]pyrazolo-[1,5-*a*]pyrimidines

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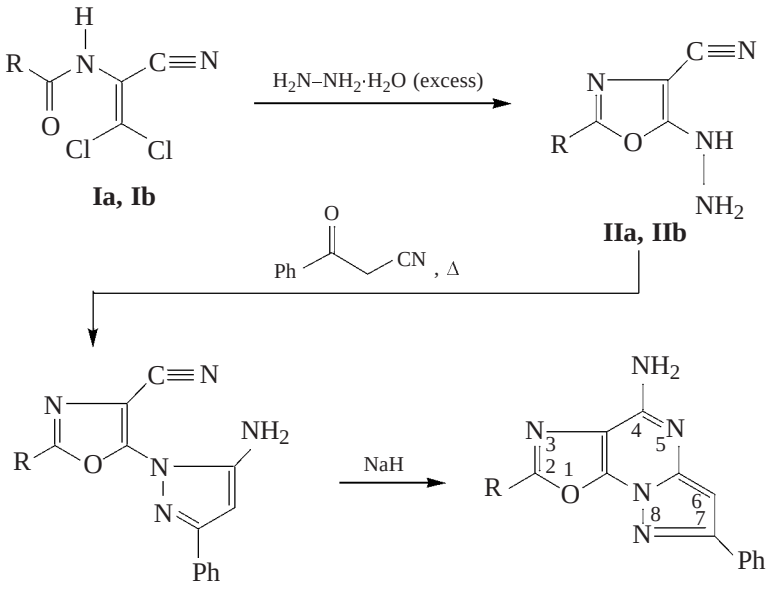
As shown previously, accessible 2-acylamino-3,3-dichloroacrylonitriles **I** can be readily converted into oxazole [1], imidazole [2], pyrazole [3], 1,3,4-oxadiazole [4], 1,3,4-thiadiazole [5], pyrazolo[1,5-a]-pyrimidine [6], and oxazolo[4,5-*d*]pyrimidine derivatives [7] via simple transformations. Here we report on a facile route to representatives of a new fused heterocyclic system, [1,3]oxazolo[4,5-*e*]pyrazolo[1,5-*a*]pyrimidines, on the basis of compounds **I**. The procedure involves initial treatment of acrylonitriles **I** with hydrazine hydrate, followed by reactions with benzoylacetonitrile and sodium hydride. The transformation sequence **I** → **II** → **III** → **IV** is shown in the scheme given below.



Ia, Ib **IIa, IIb** **IIIa, IIIb** **IVa, IVb**

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

The first step of the process was studied in [8], and cyclocondensation **II** → **III** is a particular case of numerous cyclizations of N-substituted hydrazines with acylacetonitriles [9]. The occurrence of intramolecular cycloaddition **III** → **IV** catalyzed by sodium hydride was confirmed not only by IR and ^{1}H NMR spectroscopy but also by X-ray analysis of final product **IVa**. The results of the X-ray diffraction study, as well as further modifications of compounds **IVa** and **IVb** and their analogs, will be reported elsewhere.

5-(5-Amino-3-phenyl-1*H*-pyrazol-1-yl)-2-methyl-(phenyl)-1,3-oxazole-4-carbonitriles IIIa and IIIb *(general procedure).* Concentrated hydrochloric acid, 0.85 ml, and benzoylacetonitrile, 0.01 mol, were added to a suspension of 0.01 mol of compound **IIa** or **IIb** in 40 ml of ethanol, and the mixture was heated for 4 h under reflux with stirring. It was then cooled to 20–25°C, and the precipitate was filtered off, washed with a 1% solution of sodium hydrogen carbonate and with water, dried, and recrystallized. Yield of **IIIa** 71%, mp 210–211°C (from ethanol). IR spectrum: ν 2245 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 5.83 s (1H, 4-H), 6.11 br.s (2H, NH_2), 7.38–7.77 m (5H, H_{arom}). Found, %: C 63.10; H 4.34; N.26. $C_{14}H_{11}N_5O$. Calculated, %: C 63.39; H 4.18; N 26.40.

Yield of **IIIb** 87%, mp 259–260°C (from ethanol–DMF, 3 : 1). IR spectrum: ν 2250 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 5.93 s (1H, 4-H), 6.23 br.s (2H, NH_2), 7.43–8.12 m (10H, H_{arom}). Found, %: C 69.92; H 3.81; N 21.09. $C_{19}H_{13}N_5O$. Calculated, %: C 69.71; H 4.00; N 21.39.

4-Amino-2-methyl(phenyl)-7-phenyl-7,8-dihydro[1,3]oxazolo[4,5-*e*]pyrazolo[1,5-*a*]pyrimidines IVa and IVb *(general procedure).* Sodium hydride, 0.005 mol, was added under stirring to a suspension of 0.01 mol of compound **IIIa** or **IIIb** in 40 ml of tetrahydrofuran, the mixture was stirred for 0.5 h at 20–25°C, a solution of 0.005 mol of acetic acid in 40 ml of water was added, and the precipitate was filtered off and recrystallized from dimethylformamide. Yield of **IVa** 78%, mp >300°C. ^{1}H NMR spectrum, δ, ppm: 2.69 s (3H, CH_3), 6.49 s (1H, 6-H), 7.25 br.s (2H, NH_2), 7.43–7.95 m (5H, H_{arom}). Found, %: C 63.25; H 4.26; N 26.28. $C_{14}H_{11}N_5O$. Calculated, %: C 63.39; H 4.18; N 26.40.

Yield of **IVb** 95%, mp >300°C. ^{1}H NMR spectrum, δ, ppm: 6.66 s (1H, 6-H), 7.43–8.16 m (10H, H_{arom}), 7.52 br.s (2H, NH_2). Found, %: C 69.92; H 3.93; N 21.18. $C_{19}H_{13}N_5O$. Calculated, %: C 69.71; H 4.00; N 21.39.

The IR spectra were recorded in KBr on a UR-20 spectrometer. The ^{1}H NMR spectra were measured on a Varian VXR-300 instrument from solutions in DMSO-d_6 using tetramethylsilane as internal reference.

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