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SHORT COMMUNICATIONS

Boger Synthesis of 2-Azolyl-Substituted Pyridines

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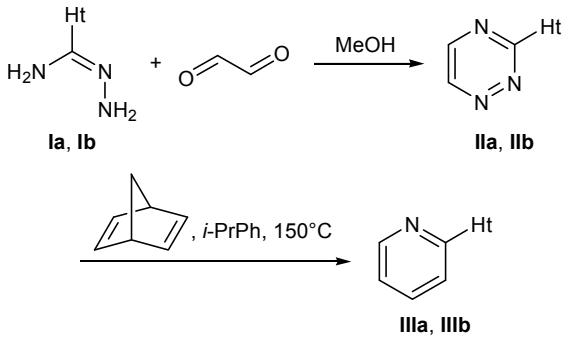
We previously demonstrated the possibility for synthesizing hitherto unknown 3-azolyl-1,2,4-triazines from readily accessible azole-1-carboxamidrazones and 1,2-diketones [1, 2]. In continuation of our studies on the synthetic potential of azole-1-carboxamidrazones, we have synthesized 2-azolylpyridines **IIIa** and **IIIb** by the Boger reaction [3, 4]. In the first step, amidrazones **Ia** and **Ib** reacted with a 40% solution of glyoxal in methanol at room temperature to produce 1,2,4-triazines **IIa** and **IIb** in 86 and 90% yield, respectively. Triazines **IIa** and **IIb** were then brought into the Boger reaction with norbornadiene, and we succeeded in isolating azolylpyridines **IIIa** and **IIIb** from the reaction mixtures. Although several synthetic approaches to azolylpyridines have been reported [5–7], they require the use of metal-containing catalysts, and the isolation procedure is relatively complex. The procedure described by us ensures preparation of azolylpyridines in two steps with good yields without chromatographic purification.

Amidrazones **Ia** and **Ib** were synthesized as described in [2, 8], and 1,2,4-triazines **IIa** and **IIb**, as described in [1].

A mixture of 10 mmol of 1,2,4-triazine **IIa** or **IIb** and 1 mL (10 mmol) of norbornadiene in 50 mL of cumene was heated for 15 h under reflux. The mixture was then evaporated on a rotary evaporator, the residue was dissolved in 70 mL of ethyl acetate–hexane (1 : 5), the solution was filtered through a layer of silica gel, the filtrate was evaporated, and the residue was recrystallized from a minimum volume of ethyl acetate–hexane (1 : 1).



Ht = 1*H*-imidazol-1-yl (**a**), 1*H*-benzimidazol-1-yl (**b**).

2-(1*H*-Imidazol-1-yl)pyridine (IIIa). Yield 1.03 g (71%), mp 38–39°C; published data [9]: mp 37–39°C. IR spectrum, ν, cm^{-1}: 2784–2738, 1617, 1528, 1326, 1177, 828. ^{1}H NMR spectrum, δ, ppm: 8.52 t (1H, Py, J = 1.2 Hz), 8.47 d.d.d (1H, Py, J = 4.9, 1.9, 0.8 Hz), 8.01–7.92 m (2H, Im, Py), 7.82–7.76 m (1H, Im), 7.35 d.d.d (1H, Py, J = 7.4, 4.9, 0.9 Hz), 7.13–7.09 m (1H, Im). ^{13}C NMR spectrum, δ_C, ppm: 148.9, 148.6, 139.7, 134.9, 130.0, 122.3, 116.5, 112.7. Found, %: C 66.23; H 4.90; N 28.91. $C_8H_7N_3$. Calculated, %: C 66.19; H 4.86; N 28.95.

1-(Pyridin-2-yl)-1*H*-benzimidazole (IIIb). Yield 1.43 g (73%), mp 60–61°C. IR spectrum, ν, cm^{-1}: 2866–2749, 1621, 1481, 1305, 1247, 1195, 811. ^{1}H NMR spectrum, δ, ppm: 8.64–8.61 m (1H, BIm), 8.61 s (1H, BIm), 8.10–8.06 m (1H, BIm), 7.94–7.86 m (2H, Py, BIm), 7.60 d (1H, Py, J = 8.2 Hz), 7.43–7.34 m (2H, Py, BIm), 7.31 d.d.d (1H, Py, J = 7.4, 4.9, 7.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 149.9, 149.5, 144.5, 141.3, 138.9, 131.1, 132.1, 124.2, 123.3, 121.8, 120.6, 114.4, 112.7. Found, %: C 73.88; H 4.69; N 21.57. $C_{12}H_9N_3$. Calculated, %: C 73.83; H 4.65; N 21.52.

The IR spectra were recorded in KBr on an FSM-1201 spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-400 instrument at 400 and 100 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The elemental analyses were obtained on a Vario El Cube analyzer.

The melting points were determined on a Boetius hot stage and are uncorrected.

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