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SYNTHESIS OF BENZIMIDAZO-[1,2-*a*]PYRIDO[2,1-*c*]PYRAZINIUM SYSTEMS

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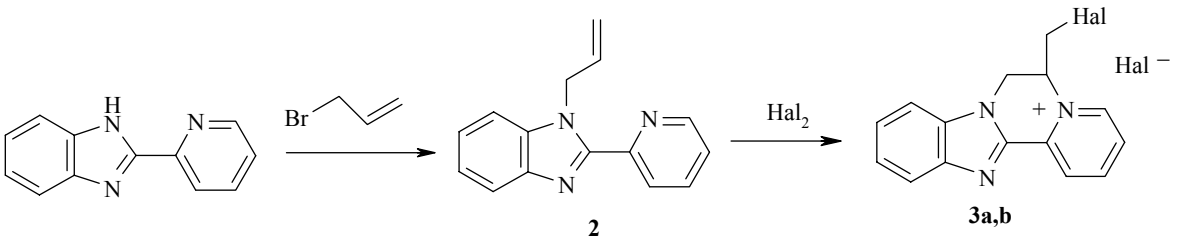
Benzimidazo[1,2-*a*]pyrido[2,1-*c*]pyrazinium systems have hardly been studied. In previous work [1], we developed a synthesis for 6,7-dihydrobenzimidazo[1,2-*a*]pyrido[2,1-*c*]pyrazinium bromide (alternative name, 6H,7H-pyrido[2',1':3,4]pyrazino[1,2-*a*]benzimidazolium bromide) by the reaction of 1-(2-hydroxyethyl-2-(2-pyridyl)benzimidazole with hydrobromic acid. The composition and structure of this compound were confirmed by elemental analysis and UV spectroscopy but no NMR data were given.



2 **3a,b**

3 a Hal = Br, **b** Hal = I

In the present work, 6-halomethyl-6,7-dihydrobenzimidazo[1,2-*a*]pyrido[2,1-*c*]pyrazinium halides **3a**,**b** were synthesized for the first time by the halocyclization of 1-allyl-2-(2-pyridyl)benzimidazole (**2**), which, in turn, was obtained by the alkylation of 2-(2-pyridyl)benzimidazole (**1**) using allyl bromide. The pyridine ring proton signals in the ^{1}H NMR spectra of compounds **3a**,**b** are shifted downfield by 0.5-1.0 ppm in comparison with the spectrum of starting compound **2**, indicating a quaternized pyridine nitrogen atom.

The ^{1}H NMR spectra were taken on a Bruker DRX-400 spectrometer at 400 MHz in DMSO-d_6 with TMS as the internal standard.

1-Alkyl-2-(2-pyridyl)benzimidazole (2). Benzimidazole **1** (0.975 g, 5 mmol) was added to a solution of KOH (5 g) in water (10 ml) followed by a solution of allyl bromide (0.43 ml, 5 mmol) in dichloromethane (5 ml) and tetrabutylammonium bromide (0.04 g). The mixture was stirred for 2.5 h. The organic layer was separated and dried over calcium chloride. Dichloromethane was distilled off. The residue

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was recrystallized from hexane to give 0.538 g (46%) **2**; mp 35°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.96 (1H, dd, *J* = 17.2, *J* = 1.5, =CH_2); 5.09 (1H, dd, *J* = 10.3, *J* = 1.5, =CH_2); 5.54 (2H, d, *J* = 5.3, NCH_2); 6.04 (1H, m, CH=); 7.29 (1H, t, *J* = 7.4, H-5); 7.32 (1H, t, *J* = 7.3, H-6); 7.52 (1H, d, *J* = 8.2, H-4); 7.61 (1H, d, *J* = 8.2, H-7); 7.74 (1H, t, *J* = 6.9, H-5'); 8.00 (1H, t, *J* = 7.4, H-4'); 8.33 (1H, d, *J* = 8.0, H-3'); 8.73 (1H, d, *J* = 4.8, H-6'). Found, %: C 76.32; H 5.43; N 17.97. $C_{15}H_{13}N_3$. Calculated, %: C 76.57; H 5.57; N 17.86.

6-Bromomethyl-6,7-dihydrobenzimidazo[1,2-*a*]pyrido[2,1-*c*]pyrazinium Bromide (3a). A solution of bromine (0.16 g, 1 mmol) in dichloromethane (4 ml) was added to a solution of benzimidazole **2** (0.141 g, 0.6 mmol) in dichloromethane (3 ml). The precipitate formed was filtered off, washed with acetone, and dried to give 0.230 g of compound **3a** (98%); mp 175°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.08 (2H, m, CH_2Br); 4.97 (1H, dd, *J* = 14.0, *J* = 4.7, NCHH); 5.30 (1H, d, *J* = 14.0, NCHH); 5.98 (1H, m, H-6); 7.45 (1H, t, *J* = 7.1, H-11); 7.53 (1H, t, *J* = 7.2, H-10); 7.84 (1H, d, *J* = 8.2, H-9); 7.91 (1H, d, *J* = 8.2, H-12); 8.29 (1H, t, *J* = 6.3, H-2); 8.82 (1H, t, *J* = 7.8, H-3); 8.88 (1H, d, *J* = 8.0, H-1); 9.29 (1H, d, *J* = 6.0, H-4). Found, %: C 45.36; H 3.36; Br 40.87; N 10.73. $C_{15}H_{13}Br_2N_2$. Calculated, %: C 45.60; H 3.32; Br 40.45; N 10.64.

6-Iodomethyl-6,7-dihydrobenzimidazo[1,2-*a*]pyrido[2,1-*c*]pyrazinium Iodide (3b). A solution of iodine (0.305 g, 1.2 mmol) in 2-propanol (3 ml) was added to a solution of benzimidazole **2** (0.141 g, 0.6 mmol) in 2-propanol (3 ml). The precipitate formed was filtered off and dissolved in acetone. Then, NaI was added. The yellow precipitate was filtered off, washed with acetone, and dried to give 0.121 g (41%) **3b**; mp 150°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.77 (2H, m, CH_2I); 4.95 (1H, dd, *J* = 14.0, *J* = 4.5, NCHH); 5.27 (1H, d, *J* = 8.2, NCHH); 5.84 (1H, m, H-6); 7.45 (1H, t, *J* = 7.4, H-11); 7.54 (1H, t, *J* = 7.3, H-10); 7.86 (1H, d, *J* = 8.2, H-9); 7.92 (1H, d, *J* = 8.2, H-12); 8.28 (1H, t, *J* = 6.9, H-2); 8.79 (1H, t, *J* = 7.4, H-3); 8.87 (1H, d, *J* = 8.0, H-1); 9.27 (1H, d, *J* = 6.1, H-4). Found, %: C 36.57; H 2.48; I 52.01; N 8.41. $C_{15}H_{13}I_2N_2$. Calculated, %: C 36.84; H 2.68; I 51.89; N 8.59.

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