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SYNTHESIS OF DERIVATIVES OF 4,5-DIHYDRO-IMIDAZO[1,2-*a*]PHENANTHROLINE

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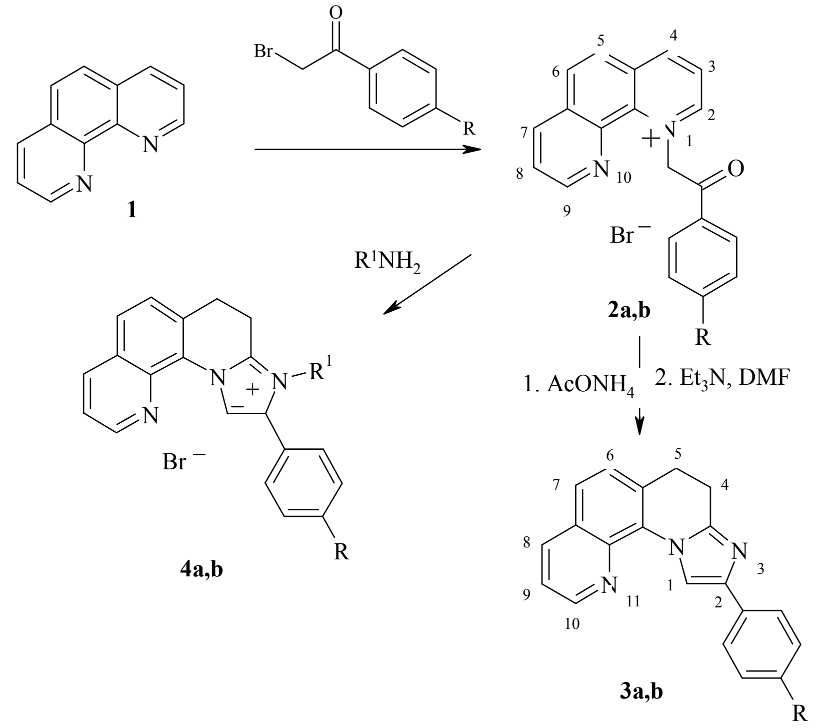
A simple and effective method for the synthesis of derivatives of a new heterocyclic system – 4,5-dihydroimidazo[1,2-*a*][1,10]phenanthroline – is proposed, based on the use of phenacyl-1,10-phenanthrolinium salts (**2**), obtained by the alkylation of 1,10-phenathroline (**1**) with ω-bromoacetophenone [1-3]. It was found that boiling these salts in the presence of excess ammonium acetate with subsequent treatment of the reaction mixture with hydrobromic acid led to the closing of the imidazole ring to give 2-aryl-4,5-dihydroimidazo[1,2-*a*][1,10]phenanthroline hydrobromides. The latter were converted into the



2, **3** **a** R = H, **b** R = Br; **4** **a** R = H, R^1 = *p*-MeC$_6$H$_4$, **b** R = Br, R^1 = *p*-MeC$_6$H$_4$

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corresponding bases **3a,b** on treatment with excess triethylamine in DMF. Treatment of compounds **2** with a two-fold excess of an aromatic amine gave quaternary salts of 2-aryl-4,5-dihydroimidazo[1,2-*a*][1,10]-phenanthroline **4a,b**.

All compounds were obtained in high yields (85-97%).

^{1}H NMR spectra of DMSO-d$_6$ with TMS as internal standard were recorded with a Varian VXR-300 (300 MHz) instrument.

2-Phenyl-4,5-dihydro-3,11,11c-triazacyclopenta[*c*]phenanthrene (3a). Compound **2a** (7 g, 18 mmol) and anhydrous ammonium acetate (2.8 g, 36 mmol) were boiled in glacial acetic acid (4.2 ml) for 3 h and cooled. The precipitate was triturated with conc. HBr (10 ml) and diluted with water (200 ml). The precipitate was filtered off, washed with water and dried. Triethylamine (20 ml) was added to a suspension of the hydrobromide in DMF (4 ml), shaken energetically, and diluted with water (200 ml), the precipitated crystals were filtered off, washed with water, dried, and recrystallized from benzene. Yield 3.8 g (95%); mp 156-157°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.13 (2H, t, *J* = 6.0, 4-CH$_2$); 3.20 (2H, t, *J* = 6.0, 5-CH$_2$); 7.24 (1H, m, C$_6$H$_5$); 7.41 (2H, m, C$_6$H$_5$); 7.60 (1H, q, *J* = 6.0, H-9); 7.64 (1H, d, *J* = 7.8, H-6); 7.84 (1H, d, *J* = 7.8, H-7); 7.86 (2H, m, C$_6$H$_5$); 8.43 (1H, d, *J* = 8.1, H-8); 9.06 (1H, d, *J* = 3.9, H-10); 9.28 (1H, s, H-1). Found: C 80.92; H 5.14; N 14.04. $C_{20}H_{15}N_3$. Calculated, %: C 80.78; H 5.08; N 14.13.

2-(4-Bromophenyl)-4,5-dihydro-3,11,11c-triazacyclopenta[*c*]phenanthrene (3b) was obtained analogously to compound **3a**. Yield 85%; mp 128-129°C (benzene). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.10 (2H, t, *J* = 6.0, 4-CH$_2$); 3.20 (2H, t, *J* = 6.0, 5-CH$_2$); 7.57 (2H, d, *J* = 8.1, C$_6$H$_4$); 7.60 (1H, q, *J* = 6.0, H-9), 7.65 (1H, d, *J* = 7.8, H-6); 7.81 (2H, d, *J* = 8.1, C$_6$H$_4$); 7.85 (1H, d, *J* = 7.8, H-7); 8.44 (1H, d, *J* = 8.1, H-8); 9.06 (1H, d, *J* = 3.9, H-10); 9.31 (1H, s, H-1). Found: C 63.78, Br 21.36; N 11.08. $C_{20}H_{14}BrN_3$. Calculated, %: C 63.85; Br 21.24; N 11.17.

2-Phenyl-3-*p*-tolyl-4,5-dihydro-3,11,11c-triazacyclopenta[*c*]phenanthrenium Bromide (4a). Compound **2a** (3g, 8 mmol) and *p*-toluidine (1.71 g, 16 mmol) in glacial acetic acid (1.8 ml) were boiled for 3 h and cooled. The mixture was triturated with conc. HBr (4 ml) and then diluted with water (100 ml). The precipitated crystals were filtered off, washed with water, dried and recrystallized from a 2-propanol – ethyl acetate mixture. Yield 3.63 g (97%); mp 283-284°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH$_3$); 3.22 (2H, t, *J* = 6.0, 5-CH$_2$); 3.43 (2H, t, *J* = 6.0, 4-CH$_2$); 7.06 (2H, d, *J* = 8.1, C$_6$H$_5$); 7.37 (2H, m, C$_6$H$_5$); 7.43 (3H, m, C$_6$H$_5$); 7.53 (2H, d, *J* = 8.1, C$_6$H$_5$); 7.74 (1H, q, *J* = 4.5, H-9); 7.81 (1H, d, *J* = 8.1, H-6); 8.17 (1H, d, *J* = 8.1, H-7); 8.63 (1H, d, *J* = 8.1, H-8); 9.14 (1H, d, *J* = 3.9, H-10); 9.68 (1H, s, H-1). Found, %: C 69.35; Br 17.17; N 8.84. $C_{27}H_{22}BrN_3$. Calculated, %: C 69.24; Br 17.06; N 8.97.

2-(4-Bromophenyl)-3-*p*-tolyl-4,5-dihydro-3,11,11c-triazacyclopenta[*c*]phenanthrenium Bromide (4b) was obtained analogously to compound **4a.** Yield 95%, mp 255-256°C (a mixture of 2-propanol and ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.42 (3H, s, CH$_3$); 3.22 (2H, t, *J* = 6.0, 5-CH$_2$); 3.41 (2H, t, *J* = 6.0, 4-CH$_2$); 7.30 (2H, d, *J* = 8.1, C$_6$H$_4$); 7.45 (2H, d, *J* = 8.1, C$_6$H$_4$); 7.52 (2H, d, *J* = 8.1, C$_6$H$_4$); 7.66 (2H, d, *J* = 8.1, C$_6$H$_4$); 7.74 (1H, q, *J* = 4.5, H-9); 7.81 (1H, d, *J* = 8.1, H-6); 8.17 (1H, d, *J* = 8.1, H-7); 8.62 (1H, d, *J* = 8.1, H-8); 9.13 (1H, d, *J* = 3.9, H-10); 9.72 (1H, s, H-1). Found,%: C 59.16; Br 29.19; N 7.52. $C_{27}H_{21}Br_2N_3$. Calculated, %: C 59.23; Br 29.25; N 7.68.

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