DERIVATIVES OF 3,4,5,6-TETRAHYDRO-6a,10b-DIAZAINDENO[1,2,3-*c,d*]AZULENE

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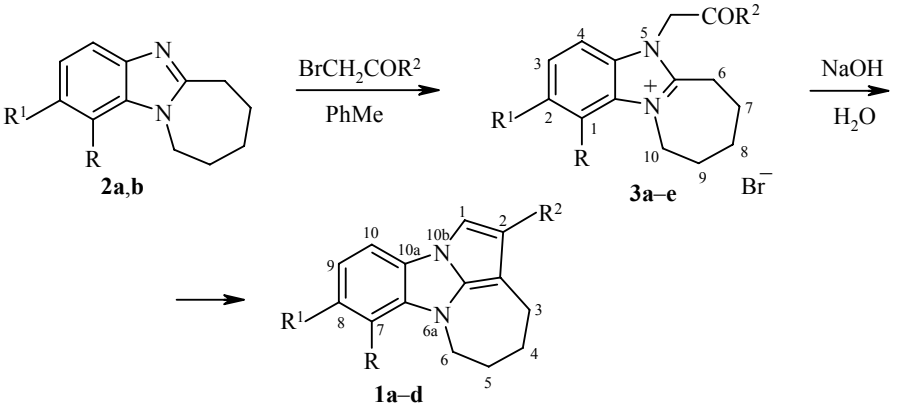
The heterocyclic system 3,4,5,6-tetrahydro-6a,10b-diazaindeno[1,2,3-*cd*]azulene (**1**) is unknown. Derivatives of the similar systems pyrrolo[1,2-*a*]benzimidazole [1-4] and 5,6,7,8-tetrahydro-2a,4a-diazacyclopenta[*c,d*]azulene [5, 6] have shown themselves to be physiologically active compounds and dyes. We have developed a method for obtaining derivatives of system **1** from 1,2-pentamethylenebenzimidazoles **2**, described previously in [7], using the Chichibabin reaction to form the annelated pyrrole ring.

The benzimidazoles **2a,b**, when heated briefly with bromo ketones in toluene, yield the quaternary salts **3a-e**; substituted 3,4,5,6-tetrahydro-6a,10b-diazaindeno[1,2,3-*cd*]azulenes **1a-d** are formed from the salts **3a-d** when they are boiled in dilute NaOH solution.

The structure of salts **2** and products **1** was confirmed by the ^{1}H NMR spectra.



1, **3 a**, **b** R = H, R^1 = F; **c**, **d**, **e** R = R^1 = F; **a**, **c** R^2 = Me;
b, **d** R^2 = C_6H_4OMe-*p*; **e** R^2 = C_6H_4F-*p*, **2 a** R = H, R^1 = F, **b** R = R^1 = F

2-Fluoro-5-(2-oxopropyl)-7,8,9,10-tetrahydro-6H-azepino[2,1-*b*]benzimidazolium bromide (3a). A mixture of compound **2a** (2.3 g, 11.27 mmol) and bromoacetone (1.54 g, 11.27 mmol) was refluxed in toluene for 2 h. The mixture was cooled down and the precipitate was filtered out and washed with acetone.

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Yield 2.65 g (69%); mp > 300°C (ethanol–DMF). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.73 (2H, m, 7-CH_2); 1.85 (2H, m, 8-CH_2); 1.93 (2H, m, 9-CH_2); 2.39 (3H, s, CH_3); 3.29 (2H, m, 6-CH_2); 4.65 (2H, m, 10-CH_2); 5.83 (2H, s, CH_2); 7.53 (1H, d, *J* = 9.0, 4-H); 8.10 (2H, d, 1-H and m, 3-H, overlapped). Found, %: F 5.71. $C_{15}H_{18}FBrN_2O$. Calculated, %: F 5.57.

Compounds **3b-d** were obtained as for **3a**.

2-Fluoro-5-[2-(4-methoxyphenyl)-2-oxoethyl]-7,8,9,10-tetrahydro-6H-azepino[2,1-*b*]benzimidazolium Bromide (3b). Yield 97%; mp 254°C (ethanol). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.78 (2H, m, 7-CH_2); 1.92 (4H, m, 8-, 9-CH_2); 3.27 (2H, m, 6-CH_2); 3.05 (3H, s, OCH_3); 4.71 (2H, m, 10-CH_2); 6.45 (2H, s, CH_2); 7.19 (2H, d, *J* = 9.0, 2'-, 6'-H); 7.52 (1H, dt, J_1 = 2.7, J_2 = 9.0, 4-H); 8.08 (1H, d, 1-H); 8.14 (2H, d, *J* = 9.3, 3'-, 5'-H); 8.14 (1H, m, 3-H). Found, %: Br 18.24. $C_{21}H_{22}FBrN_2O_2$. Calculated, %: Br 18.40.

1,2-Difluoro-5-(2-oxopropyl)-7,8,9,10-tetrahydro-6H-azepino[2,1-*b*]benzimidazolium Bromide (3c). Yield 78%; mp 264-266°C (*i*-PrOH). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.74 (2H, m, 7-CH_2); 1.96 (4H, m, 8-, 9-CH_2); 2.40 (3H, s, CH_3); 3.33 (2H, m, 6-CH_2); 4.73 (2H, m, 10-CH_2); 5.88 (2H, s, CH_2); 7.80 (1H, m, 3-H); 7.95 (1H, dd, J_1 = 0.9, J_2 = 9.0, 4-H). Found, %: F 10.41. $C_{15}H_{17}BrF_2N_2O$. Calculated, %: F 10.58.

1,2-Difluoro-5-[2-(4-methoxyphenyl)-2-oxoethyl]-7,8,9,10-tetrahydro-6H-azepino[2,1-*b*]benz-imidazolium Bromide (3d). Yield 98%; mp 176°C (ethanol–hexane). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.78 (2H, m, 7-CH_2); 1.99 (4H, m, 8-, 9-CH_2); 3.37 (2H, m, 6-CH_2); 3.93 (3H, s, OCH_3); 4.79 (2H, m, 10-CH_2); 6.48 (2H, s, CH_2); 7.19 (2H, d, *J* = 8.7, 2'-, 6'-H); 7.75 (1H, m, 3-H); 7.95 (1H, dd, *J* = 7.8, 4-H); 8.13 (2H, d, *J* = 8.7, 3', 5'-H). Found, %: Br 17.86. $C_{21}H_{21}F_2BrN_2O_2$. Calculated, %: Br 17.67.

8-Fluoro-2-methyl-3,4,5,6-tetrahydro-6a,10b-diazabenzo[*a*]cyclopenta[*c,d*]azulene (1a). Compound **3a** (1.5 g, 4.40 mmol) in a 10% NaOH solution (20 ml) was refluxed for 2 h. The mixture was cooled down and the precipitated solid oil was filtered out and washed with water and then dried. Yield 1 g (94%); mp 86-87°C (*i*-PrOH–hexane). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.91 (2H, m, 4-CH_2); 2.01 (2H, m, 5-CH_2); 2.07 (3H, s, CH_3; 2.50 (2H, m, 3-CH_2); 3.85 (2H, m, 6-CH_2); 6.77 (1H, t, *J* = 8.6, 10-H); 6.91 (1H, s, 1-H); 7.13 (1H, d, *J* = 10.5, 7-H); 7.47 (1H, m, 9-H). Found, %: F 7.92. $C_{15}H_{15}FN_2$. Calculated, %: F 7.84.

Compounds **1b-d** were obtained as for **1a**.

8-Fluoro-2-(4-methoxyphenyl)-3,4,5,6-tetrahydro-6a,10b-diazabenzo[*a*]cyclopenta[*c,d*]azulene (1b). Yield 91%; mp 126-127°C (ethanol). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.92 (2H, m, 4-CH_2); 2.08 (2H, m, 5-CH_2); 2.75 (2H, m, 3-CH_2); 3.77 (3H, s, OCH_3); 3.90 (2H, m, 6-CH_2); 6.84 (1H, dt, J_1 = 2.7, J_2 = 9.0, 10-H); 6.96 (2H, d, *J* = 8.4, 2'-, 6'-H); 7.21 (1H, d, 7-H); 7.31 (1H, s, 1-H); 7.39 (2H, d, *J* = 8.7, 3'-, 5'-H); 7.61 (1H, m, 9-H). Found, %: F 5.89. $C_{21}H_{19}FN_2O$. Calculated, %: F 5.68.

7,8-Difluoro-2-methyl-3,4,5,6-tetrahydro-6a,10b-diazabenzo[*a*]cyclopenta[*c,d*]azulene (1c). Yield 98%; mp 74-75°C (hexane). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.85 (2H, m, 4-CH_2); 1.97 (2H, m, 5-CH_2); 2.07 (3H, s, CH_3); 2.52 (2H, m, 3-CH_2); 4.02 (2H, m, 6-CH_2); 6.90 (1H, s, 1-H); 6.98 (1H, m, 9-H); 7.28 (1H, dd, J_1 = 3.8, J_2 = 8.8, 10-H). Found, %: F 14.45. $C_{15}H_{14}F_2N_2$. Calculated, %: F 14.60.

7,8-Difluoro-2-(4-methoxyphenyl)-3,4,5,6-tetrahydro-6a,10b-diazabenzo[*a*]cyclopenta[*c,d*]azulene (1d). Yield 86%; mp 152-154°C (ethyl acetate). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 1.86 (2H, m, 4-CH_2); 2.06 (2H, m, 5-CH_2); 2.70 (2H, m, 3-CH_2); 3.78 (3H, s, OCH_3); 4.07 (2H, m, 6-CH_2); 6.96 (2H, d, *J* = 12.9, 2'-, 6'-H); 7.04 (1H, m, 9-H); 7.30 (1H, s, 1-H); 7.37 (2H, d, *J* = 12.9, 3'-, 5'-H); 7.42 (1H, dd, *J* = 5.7, 10-H). Found, %: F 10.61. $C_{21}H_{18}F_2N_2O$. Calculated, %: F 10.78.

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