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NOVEL ROUTE FOR THE SYNTHESIS OF PARTIALLY HYDROGENATED 1,2a,5a,8a-TETRAAZAACENAPHTHYLENES AND 1,4a,5,9,8a-PENTAAZAFLUORENES

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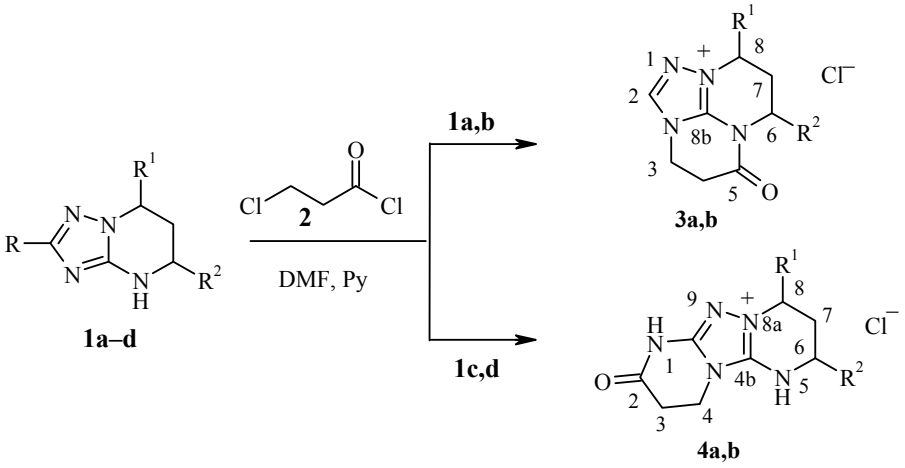
Partially hydrogenated [1,2,4]triazolo[1,5-*a*]pyrimidines are polyfunctional compounds which can react readily with electrophilic reagents [1-3]. Using this feature we now propose a one-pot method for the synthesis of 5-oxo-4,5,7,8-tetrahydro-3H,6H-1,2a,5a-triaza-8a-azoniumacenaphthylene **3a**,**b** and 2-oxo-1,2,3,4,5,6,7,8-octahydro-1,4a,5,9-tetraaza-8a-azoniumfluorene chlorides **4a**,**b** by treating the readily available 4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-*a*]pyrimidines **1a-d** [1, 2] with 3-chloropropionic acid chloride (**2**).



1 a, **b** R = H, **c**, **d** R = NH_2; **1a**,**c**, **3a, 4a**, R^1 = Ph, **1b**, **3b** R^1 = 4-ClC_6H_4, **1d**, **4b** R^1 = 4-$MeOC_6H_4$; **1a**,**b**,**d**, **3a**,**b**, **4b** R^2 = Ph, **1c**, **4a** R^2 = Me

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The composition and structure of compounds **3** and **4** were confirmed by elemental analysis and from spectroscopic data which included the NOESY spectrum of compound **3a** (correlation of H-2 and NCH_2 protons) and the ^1H–^{13}C HMBC spectra of compounds **3a**,**4a** (correlation of the NCH_2 group protons and both carbon nuclei of the triazole ring) as well as through an X-ray structural analysis of compound **4a**. The crystallographic data was deposited in the Cambridge structural database, reference CCDC 811047. A detailed report of the structure will be published separately.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 600 instrument (600 and 150 MHz respectively) using DMSO-d_6 with TMS as internal standard. Mass spectra (EI) were obtained on a Finnigan MAT Incos 50 spectrometer with direct introduction of the sample into the ion source and ionization energy of 70 eV. Elemental analysis was carried out on a Perkin-Elmer 2400 analyzer.

5-Oxo-6,8-diphenyl-4,5,7,8-tetrahydro-3H,6H-1,2a,5a-triaza-8a-azoniaacenaphthylene Chloride (3a). A solution of the acid chloride **2** (0.41 g, 3.3 mmol) in acetonitrile (2 ml) was added dropwise with stirring to a mixture of amine **1a** (0.83 g, 3.0 mmol), anhydrous DMF (5 ml), and pyridine (0.26 g, 3.3 mmol), stirred for 20 min at room temperature and then for 6 h at 80-90ºC. The precipitate formed on cooling was filtered off, washed with acetone, and dried to give 0.68 g (62%) of the product with mp 212-213ºC (MeOH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.65-2.85 (2H, m, H-7); 3.09 (2H, m, H-4); 4.52 (1H, m, H-3); 4.65 (1H, m, H-3); 5.39 (1H, m, H-6); 5.63 (1H, m, H-8); 7.13-7.36 (10H, m, 2Ph); 8.99 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 331 $[M\text{-}Cl]^+$ (4), 330 $[M\text{-}HCl]^+$ (17), 275 (13), 197 (24), 193 (16), 171 (100), 115 (24), 104 (77). Found, %: C 65.15; H 5.40; N 14.94. $C_{20}H_{19}ClN_4O$. Calculated, %: C 65.48; H 5.22; N 15.27.

8-(4-Chlorophenyl)-5-oxo-6-phenyl-4,5,7,8-tetrahydro-3H,6H-1,2a,5a-triaza-8a-azoniaacenaphthylene Chloride (3b) was prepared similarly to compound **3a** from amine **1b** and the acid chloride **2**. Yield 0.78 g (65%); mp 229-231ºC (MeOH). ^1H NMR spectrum, δ, ppm: 2.73-2.78 (1H, m, H-7); 2.84-2.88 (1H, m, H-7); 3.16 (2H, m, H-4); 4.57 (1H, m, H-3); 4.70 (1H, m, H-3); 5.45 (1H, m, H-6); 5.74 (1H, m, H-8); 7.13-7.37 (9H, m, Ar); 9.13 (1H, s H-2). ^{13}C NMR spectrum, δ, ppm: 29.47 C(4), 37.41 C(7), 39.68 C(3), 54.24 C(6), 57.47 C(8), 125.61, 126.91, 127.83, 127.89, 128.86, 132.67, 134.46, 137.84, 140.29 C(2), 146.22 C(8b), 164.30 C(5). Mass spectrum, *m/z* ($I_{rel,}$ %): 365 $[M\text{-}Cl]^+$ (7), 364 $[M\text{-}HCl]^+$ (19), 309 (27), 197 (17), 171 (67), 138 (34), 104 (33). Found, %: C 60.01; H 4.39; N 14.25. $C_{20}H_{18}Cl_2N_4O$. Calculated, %: C 59.86; H 4.52; N 13.96.

` **6-Methyl-2-oxo-8-phenyl-1,2,3,4,5,6,7,8-octahydro-1,4a,5,9-tetraaza-8a-azoniafluorene Chloride (4a)** was prepared similarly to compound **3a** from amine **1c** and the acid chloride **2**. Yield 0.62 g (65%); mp 289-290ºC (MeOH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (3H, d, *J* = 6.3, CH_3); 1.88 (1H, m, H-7); 2.42 (1H, m, H-7); 2.83 (2H, m, H-3); 3.84 (1H, m, H-6); 4.24 (1H, m, H-4); 4.43 (1H, m, H-4); 5.25 (1H, dd, *J* = 4.8, *J* = 11.0, H-8); 7.33-7.40 (5H, m, Ph); 10.40 (1H, s, NH); 11.71 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 19.40 (CH_3); 28.80 C(3); 38.12 C(4); 38.68 C(7); 46.10 C(6); 58.82 C(8); 127.26, 128.31, 128.47, 137.59, 144.27 (C-9a); 146.05 (C-4b); 166.53 (C-2). Mass spectrum, *m/z* (I_{rel}, %): 284 $[M\text{-}Cl]^+$ (7), 283 $[M\text{-}HCl]^+$ (58), 269 (13), 268 (100), 179 (23). Found, %: C 56.48; H 5.78; N 21.62. $C_{15}H_{18}ClN_5O$. Calculated, %: C 56.34; H 5.67; N 21.90.

8-(4-Methoxyphenyl)-2-oxo-6-phenyl-1,2,3,4,5,6,7,8-octahydro-1,4a,5,9-tetraaza-8a-azoniafluorene Chloride (4b) was prepared similarly to compound **3a** from the amine **1d** and acid chloride **2**. Yield 0.73 g; (59%); mp 292-294ºC (MeOH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (1H, m, H-7); 2.55 (1H, m, H-7); 2.83 (2H, m, H-3); 3.74 (3H, s, CH_3O); 4.16 (1H, m, H-4); 4.32 (1H, m, H-4); 4.95 (1H, m, H-6); 5.36 (1H, dd, *J* = 3.7, *J* = 10.3, H-8); 6.92 (2H, d, *J* = 8.5, Ar); 7.19 (2H, d, *J* = 8.5, Ar); 7.40-7.54 (5H, m, Ph); 9.95 (1H, br. s, NH); 11.80 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 28.90, 37.96, 54.03, 55.27, 58.86, 113.97, 127.14, 128.51, 128.74, 128.77, 129.28, 139.10, 144.45, 146.48, 159.46, 166.62. Mass spectrum, *m/z* (I_{rel}, %): 376 $[M\text{-}Cl]^+$ (3), 375 $[M\text{-}HCl]^+$ (8), 315 (26), 272 (18), 240 (100), 134 (90), 119 (14). Found, %: C 61.51; H 5.22; N 16.73. $C_{21}H_{22}ClN_5O_2$. Calculated, %: C 61.24; H 5.38; N 17.00.

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