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SYNTHESIS OF NOVEL 1,2,3,6-TETRAAZAPYRENE HETEROCYCLIC SYSTEM REPRESENTATIVES – 3,8-DIHYDROPYRIDO[2',3',4':4,5]NAPHTHO-[1,8-*de*][1,2,3]TRIAZIN-7(6*H*)-ONES

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Amongst the few azapyrenes synthesized to this time, a series of compounds have been found having useful properties as organic luminophores, dyes, and effective medicines [1-3].

The poor availability of azapyrenes probably is mostly due to the absence of efficient methods for the *peri*-annelation of heterocyclic rings. In this work, we propose a method for the *peri*-annelation of an [*ab*]pyridine ring to the 1*H*-naphtho[1,8-*de*][1,2,3]triazine (**1**) through its reaction with β-nitrostyrenes.

We have shown that reaction of naphthotriazine **1** with a 1.05-fold molar excess of β-nitrostyrenes **2a-c** for 3 h in PPA at 65-70ºC gives the previously unknown 8-aryl-3,8-dihydropyrido[2',3',4':4,5']naphtho[1,8-*de*]-[1,2,3]triazin-7(6*H*)-ones **6a-c** in 23-37% yields.

The reaction mechanism probably includes successive alkylation of the naphthotriazine **1** by the β-nitrostyrenes **2a-c** to form the nitro compounds **3a-c** and an intramolecular variant of our recently discovered acetamidation reaction of aromatic compounds by nitroalkanes in PPA [4, 5]. The oximes **5a-c** are formed as intermediates and subsequently undergo a Beckmann rearrangement.

Hence the methodology reported in this work has allowed us to develop a synthetic method for previously unknown representatives of the 1,2,3,6-tetraazapyrene system.

^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument (500 MHz) using DMSO-d_6 with TMS as internal standard. Elemental analysis was carried out on a KOVO CHN-1 CHN analyzer. Melting points were determined on a PTP-M apparatus (Khimlaborpribor). Monitoring of the reaction course and the purity of the synthesized compounds was carried out on Silufol UV-254 plates with EtOAc as eluent. Commercial PPA with an 80% P_2O_5 content was used.

8-Aryl-3,8-dihydropyrido[2',3',4':4,5]naphtho[1,8-*de*][1,2,3]triazin-7(6*H*)-ones 6a-c (General Method). A mixture of 1*H*-naphtho[1,8-*de*][1,2,3]triazine (**1**) (0.169 g, 1 mmol) and the corresponding β-nitrostyrene **2a-c** (1.05 mmol) in 80% PPA (2-3 g) was heated for 3 h at 65-70ºC with vigorous stirring. The reaction

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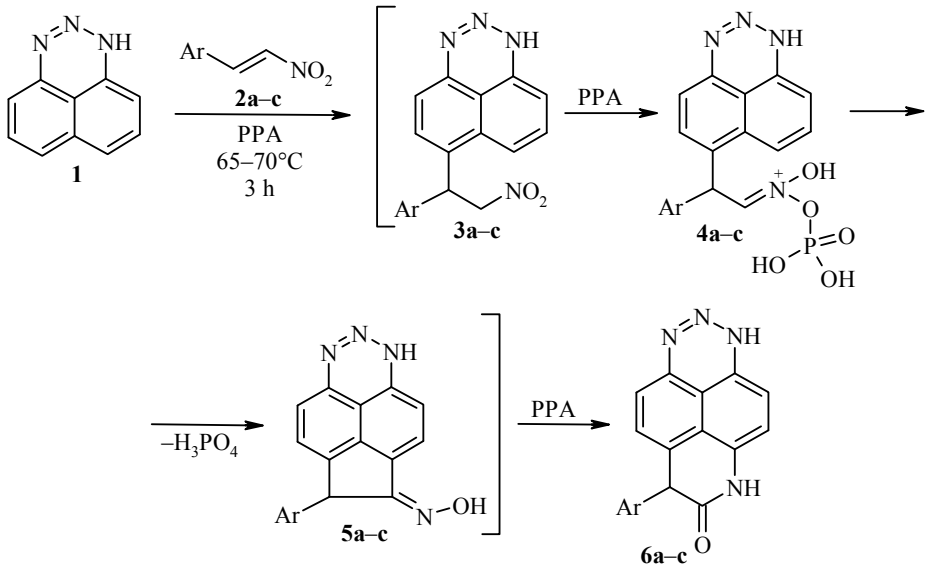
mixture was poured into water (30 ml), neutralized with ammonia solution, and extracted with butanol (3×50 ml). The extract was filtered through an L40/100 silica gel layer (*d* = 50 mm, *l* = 30 mm) and most of the butanol was evaporated. The virtually pure compound **6a-c** precipitated upon cooling.



2–6 a Ar = Ph, **b** Ar = 4-BrC_6H_4, **c** Ar = 4-$O_2NC_6H_4$

8-Phenyl-3,8-dihydropyrido[2',3',4':4,5]naphtho[1,8-*de*][1,2,3]triazin-7(6*H*)-one (6a). Yield 0.111 g (37%); mp > 295ºC (decomp., BuOH). ^{1}H NMR spectrum, δ, ppm (*J* , Hz): 5.02 (1H, s, H-8); 6.49 (1H, br. d, *J* = 7.7, H-10); 6.53 (1H, br. d, *J* = 8.1, H-4); 7.04-7.32 (6H, m, H-5, H Ph); 7.38 (1H, d, *J* = 7.7, H-9); 9.88 (1H, br. s, NHCO); 11.04 (1H, br. s, NH). Found, %: C 72.18; H 3.92; N 18.69. $C_{18}H_{12}N_4O$. Calculated, %: C 71.99; H 4.03; N 18.66.

8-(4-Bromophenyl)-3,8-dihydropyrido[2',3',4':4,5]naphtho[1,8-*de*][1,2,3]triazin-7(6*H*)-one (6b). Yield 0.121 g (32%); mp > 300ºC (decomp., BuOH). ^{1}H NMR spectrum, δ, ppm (*J* , Hz): 5.02 (1H, s, H-8); 6.46 (1H, br. d, *J* = 7.7, H-10); 6.51 (1H, br. d, *J* = 8.1, H-4); 7.09 (2H, d, *J* = 8.1, H-2',6'); 7.23 (1H, d, *J* = 8.1, H-5); 7.34 (1H, d, *J* = 7.7, H-9); 7.44 (2H, d, *J* = 8.1, H-3',5'); 9.86 (1H, br. s, NHCO); 11.02 (1H, br. s, NH). Found, %: C 57.18; H 2.83; N 14.69. $C_{18}H_{11}BrN_4O$. Calculated, %: C 57.01; H 2.92; N 14.77.

8-(4-Nitrophenyl)-3,8-dihydropyrido[2',3',4':4,5]naphtho[1,8-*de*][1,2,3]triazin-7(6*H*)-one (6c). Yield 0.079 g (23%); mp > 300ºC (decomp., BuOH). ^{1}H NMR spectrum, δ, ppm (*J* , Hz): 5.07 (1H, s, H-8); 6.48 (1H, br. d, *J* = 7.7, H-10); 6.58 (1H, br. d, *J* = 8.1, H-4); 7.28 (1H, d, *J* = 8.1, H-5); 7.41 (1H, d, *J* = 7.7, H-9); 7.47 (2H, d, *J* = 8.4, H-2',6'); 8.15 (2H, d, *J* = 8.4, H-3',5'); 9.88 (1H, br. s, NHCO); 11.04 (1H, br. s, NH). Found, %: C 62.77; H 3.17; N 20.22. $C_{18}H_{11}N_5O_3$. Calculated, %: C 62.61; H 3.21; N 20.28.

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