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Synthesis of 1,3,7-triazapyrene and 1,2,3,7-tetraazapyrene derivatives as a result of anomalous Hoesch reaction

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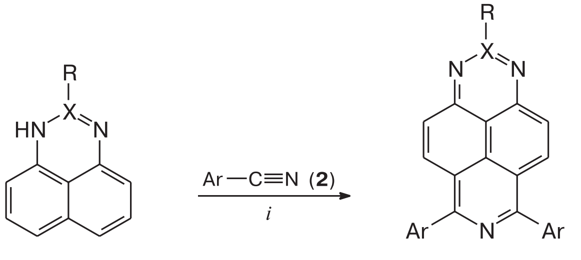
Method for the synthesis of 6,8-diaryl-1,3,7-triazapyrenes and 6,8-diaryl-1,2,3,7-tetraazapyrenes, based on the reaction of 2-R-1*H*-perimidines and 1*H*-naphtho[1,8-*de*][1,2,3]triazine with aromatic nitriles in polyphosphoric acid, has been elaborated.

Key words: perimidine, 1*H*-naphtho[1,8-*de*][1,2,3]triazine, 1,3,7-triazapyrene, 1,2,3,7-tetraazapyrene, nitriles, cyclization, the Hoesch reaction.

Special electronic structure of perimidines[1] **1** makes them a good target for electrophilic agents. For example, they can be easily acylated with carboxylic acids in polyphosphoric acid (PPA) medium.[2] In the present work, we have studied the possibility of their acylation under modified conditions of the Hoesch reaction: by the action of nitriles in PPA.*

The heating of perimidines **1a,b** with 2.4 molar excess of benzonitriles **2a—c** in polyphosphoric acid at 150 °C unexpectedly afforded 6,8-diaryl-1,3,7-triazapyrenes **3a—d** as the only reaction products (Scheme 1).

Scheme 1



1a,b, 4 **3a—d, 5a,b**

i. PPA, 150 °C

Compound	X	R	Ar	Compound	X	R	Ar
1a	C	H		**3a**	C	H	Ph
1b	C	Ph		**3b**	C	Ph	Ph
4	N	N		**3c**	C	H	4-BrPh
2a			Ph	**3d**	C	H	4-O_2NPh
2b			4-BrPh	**5a**	N	—	Ph
2c			4-O_2NPh	**5b**	N	—	4-O_2NPh

Similarly to 1*H*-perimidines **1a,b**, the reaction of 1*H*-naphtho[*de*][1,2,3]triazine (**4**) with benzonitriles **2a** and **2c** in polyphosphoric acid leads to the earlier unknown 6,8-diaryl-1,2,3,7-tetraazapyrenes **5a,b** (see Scheme 1).

A proposed mechanism of this transformation includes a regioselective attack of the nitrilium cation first at positions 6 or 7 of compounds **1a,b** or **4** and then at the nitrogen atom of ketimine **6** to form intermediate **7** with its subsequent cyclization at the *peri*-position. The aromatization of **8** occurs by elimination of the ammonium cation (Scheme 2).

In conclusion, a *one-pot* reaction of aromatic acid nitriles **2a—c** with 1*H*-perimidines **1a,b** and 1*H*-naphtho[*de*][1,2,3]triazine (**4**) in polyphosphoric acid leads to the *peri*-annulation of the [*c,d*]pyridine ring with the formation of 6,8-diaryl-1,3,7-triazapyrenes and 6,8-diaryl-1,2,3,7-tetraazapyrenes, respectively.

Experimental

NMR spectra were recorded on a Bruker DRX-500 and Bruker AV-300 spectrometers (500 MHz (^{1}H) and 75 MHz (^{13}C)) with the use of Me_4Si as the internal standard, the assignment of signals was made with the help of the double resonance spectra. Melting points were determined in the sealed capillary tubes on a PTP device and were not corrected.

1*H*-Perimidine (**1a**),[4] 2-phenylperimidine (**1b**),[4] and 1*H*-naphtho[1,8-*de*][1,2,3]triazine (**4**)[5] were obtained according to the known procedures.

Arylated 1,3,7-triazapyrenes (3a—d) and 1,2,3,7-tetraazapyrenes (5a,b) (general procedure). A mixture of the corresponding 1*H*-perimidine **1a,b** or 1*H*-naphtho[1,8-*de*][1,2,3]triazine (**4**) (1 mmol) and PPA (6 g) was heated at 60—70 °C until the complete homogeneity, then the corresponding nitrile **2a—c** (2.4 mmol) was added to it. The reaction mixture was kept for 6 h at 150 °C. The hot reaction mixture was poured into cold water (50 mL) under vigor-

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* PPA with 86% content of P_2O_5, obtained by known procedure,[3] was used

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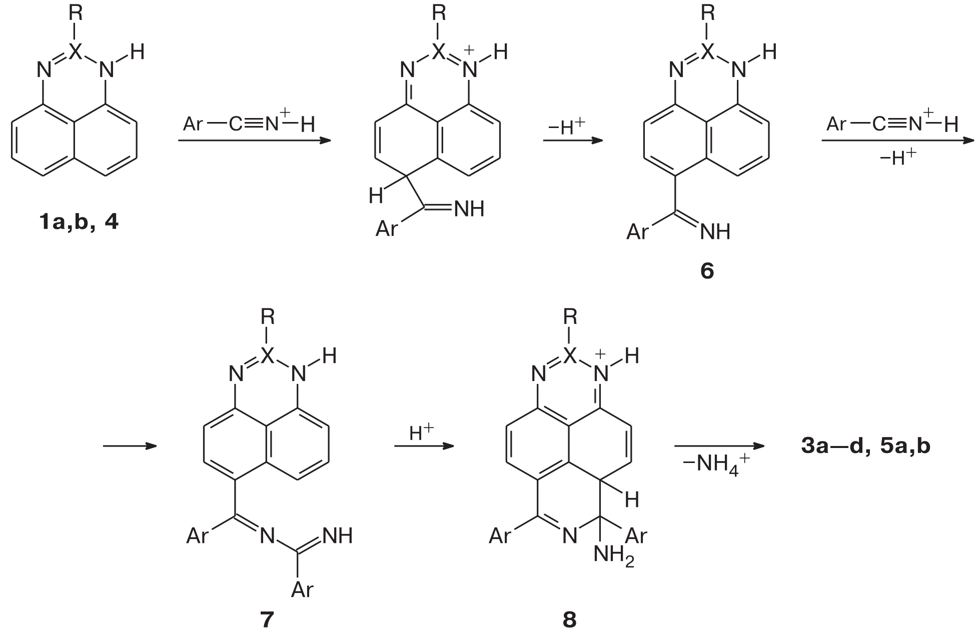
Scheme 2



ous stirring and neutralized with aqueous ammonia to the slightly basic pH of the reaction mixture. A precipitate was filtered off, washed with water, dried, and recrystallized from ethyl acetate.

6,8-Diphenyl-1,3,7-triazapyrene (3a). The yield was 0.24 g (68%), m.p. 257—259 °C (from ethyl acetate; with subl.). Found (%): C, 84.16; H, 4.18; N, 11.66. $C_{25}H_{15}N_3$. Calculated (%): C, 84.01; H, 4.23; N, 11.76. ^{1}H NMR (DMSO-d$_6$), δ: 7.69 (m, 6 H, *m*- and *p*-H 6-Ph and 8-Ph); 7.95 (br.d, 4 H, *o*-H 6-Ph and 8-Ph, *J* = 7.4 Hz); 8.31, 8.79 (both d, 2 H each, H(4), H(10), H(5), H(9), *J* = 9.5 Hz); 9.86 (s, 1 H, H(2)). ^{13}C NMR (50.3 MHz, $CDCl_3$), δ: 118.48 (2 C), 124.63 (2 C), 127.42 (4 C), 128.41 (2 C), 128.69 (4 C), 130.02 (2 C), 132.104 (2 C), 133.12 (1 C), 133.38 (1 C), 152.94 (2 C), 153.67 (2 C), 167.89 (1 C).

2,6,8-Triphenyl-1,3,7-triazapyrene (3b). The yield was 0.13 g (30%). Yellowish brown crystals, m.p. 286—288 °C (from ethyl acetate). Found (%): C, 58.37; H, 2.48; N, 8.23. $C_{25}H_{13}Br_2N_3$. Calculated (%):C, 58.28; H, 2.54; N, 8.16. ^{1}H NMR ($CDCl_3$), δ: 7.61 (m, 9 H, 2-Ph, 6-Ph, 8-Ph, *m*- and *p*-H); 7.95 (br.d, 4 H, 6-Ph, *o*-H, 8-Ph, *o*-H); 8.26, 8.76 (both d, 2 H each, H(4), H(10), H(5), H(9), *J* = 9.5 Hz); 8.84 (br.d, 2 H, 2-Ph, *o*-H).

6,8-Di(4-bromophenyl)-1,3,7-triazapyrene (3c). The yield was 0.4 g (77%), m.p. 188—189 °C (from ethyl acetate). Found (%): C, 86.06; H, 4.23; N, 9.71. $C_{31}H_{19}N_3$. Calculated (%): C, 85.89; H, 4.42; N, 9.69. ^{1}H NMR ($CDCl_3$), δ: 7.61 (d, 4 H, *m*-H 6-Ar and 8-Ar, *J* = 8.8 Hz); 7.95 (d, 4 H, *o*-H 6-Ar and 8-Ar, *J* = 8.8 Hz); 8.32, 8.78 (both d, 2 H each, H(4), H(10), H(5), H(9), *J* = 9.5 Hz); 9.87 (s, 1 H, H(2)).

6,8-Di(4-nitrophenyl)-1,3,7-triazapyrene (3d). The yield was 0.22 g (49%). Yellowish orange crystals, m.p. 203—204 °C (from ethyl acetate). Found (%): C, 86.06; H, 4.23; N, 9.71. $C_{25}H_{13}N_5O_4$. Calculated (%): C, 67.11; H, 2.93; N, 15.65. ^{1}H NMR ($CDCl_3$), δ: 7.97 (d, 4 H, *o*-H 6-Ar and 8-Ar, *J* = 8.7 Hz); 8.42 (d, 4 H, *m*-H 6-Ar and 8-Ar, *J* = 8.7 Hz); 8.29, 8.78 (both d, 2 H each, H(4), H(10), H(5), H(9), *J* = 9.5 Hz); 9.89 (s, 1 H, H(2)). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 20.64 (2 C), 25.80 (1 C), 111.27 (1 C), 118.48 (2 C), 124.41 (1 C), 124.63 (2 C), 131.14 (2 C), 152.96 (2 C), 153.78 (2 C), 165.46 (1 C).

6,8-Diphenyl-1,2,3,7-tetraazapyrene (5a). The yield was 0.22 g (61%), yellow crystals, m.p. 205—207 °C (decomp., from ethyl acetate). Found (%): C, 80.62; H, 3.88; N, 15.50. $C_{24}H_{14}N_4$. Calculated (%): C, 80.43; H, 3.94; N, 15.63. ^{1}H NMR ($CDCl_3$), δ: 7.61 (m, 6 H, *m*- and *p*-H 6-Ph and 8-Ph); 7.96 (br.d, 4 H, *o*-H 6-Ph and 8-Ph, *J* = 7.4 Hz); 8.33, 8.79 (both d, 2 H each, H(4), H(10), H(5), H(9), *J* = 9.5 Hz).

6,8-Di(4-nitrophenyl)-1,2,3,7-tetraazapyrene (5b). The yield was 0.103 g (23%). Yellowish orange crystals, m.p. 236—239 °C (decomp., from ethyl acetate). Found (%): C, 64.36; H, 2.65; N, 18.67. $C_{24}H_{12}N_6O_4$. Calculated (%): C, 64.29; H, 2.70; N, 18.74. ^{1}H NMR ($CDCl_3$), δ: 7.99 (d, 4 H, *o*-H 6-Ar and 8-Ar, *J* = 8.7 Hz); 8.43 (d, 4 H, *m*-H 6-Ar and 8-Ar, *J* = 8.7 Hz); 8.37, 8.79 (both d, 2 H each, H(4), H(10), H(5), H(9), *J* = 9.5 Hz).

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