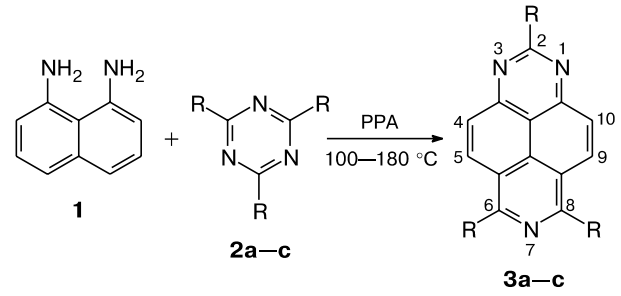
1,3,7-Triazapyrenes: the unexpected products of the reaction of 1,8-diaminonaphthalene with 1,3,5-triazines in polyphosphoric acid

I. V. Borovlev, A. V. Aksenov, I. V. Aksenova, and S. V. Pisarenko*

Stavropol State University,
1a ul. Pushkina, 355009 Stavropol, Russian Federation.
Fax: +7 (865) 235 4033. E-mail: nauka@stavsu.ru

Earlier,[1] it was reported that the catalyst-free reaction of 1,8-diaminonaphthalene (**1**) with 1,3,5-triazine (**2a**) leads to perimidine. Our efforts to carry out the similar reaction with 2,4,6-trimethyl- (**2b**) and 2,4,6-triphenyl-1,3,5-triazine (**2c**) under the same conditions were unsuccessful. We suggested that this transformation can be accomplished in polyphosphoric acid (PPA),* since the similar cyclization of aromatic *ortho*-diamines with carboxylic acids and their derivatives in PPA is known for

Scheme 1

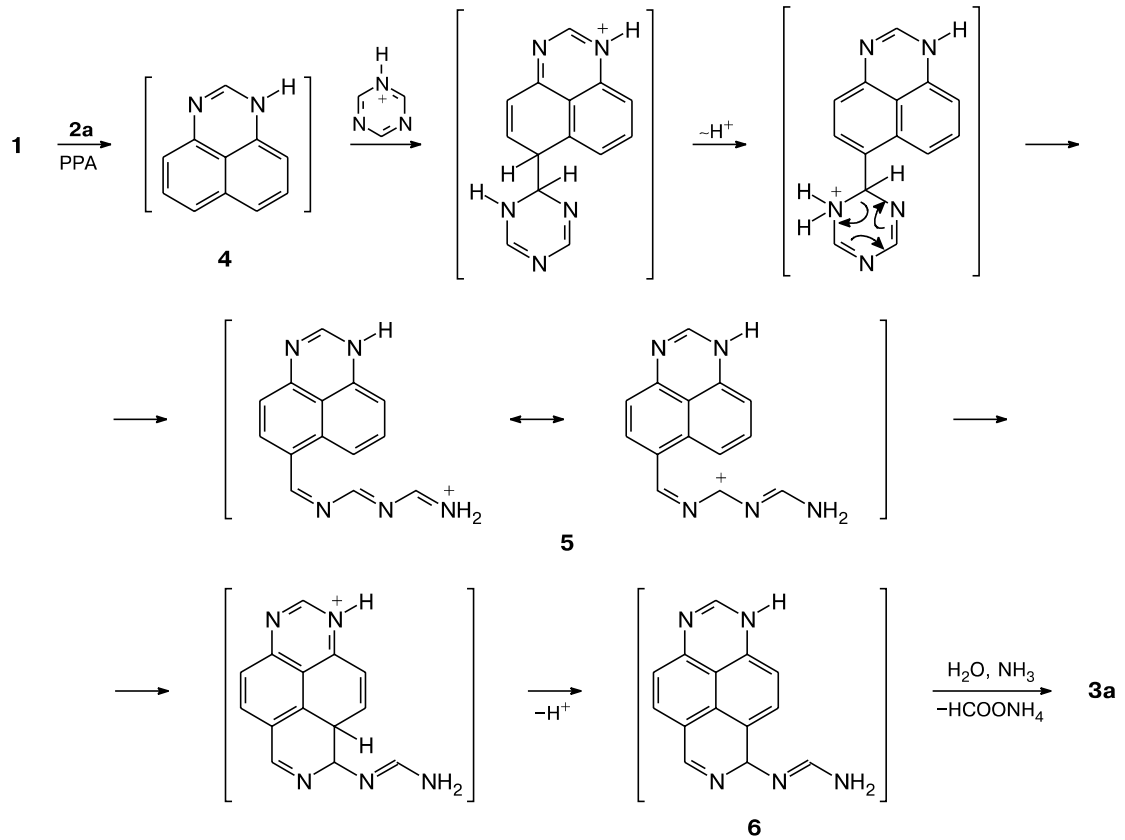


1 **2a—c** **3a—c**

R = H (**a**), Me (**b**), Ph (**c**)

* Polyphosphoric acid with 86% content of P_2O_5, obtained by the known procedure,[2] was used.

Scheme 2



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a long time.[3] The reaction proceeds under heating of reagents above 100 °C, however, the earlier unknown 1,3,7-triazapyrenes **3a—c** unexpectedly turned out to be the products of the reaction instead of the corresponding perimidines (Scheme 1).

A suggested mechanism of this transformation (with compound **3a** as the example) includes the formation of perimidine (**4**), the electrophilic attack of 1,3,5-triazinium cation at its position 6(7), the triazine ring opening with the formation of intermediate **5**, and the subsequent cyclization of **5** at *peri*-position. The aromatization of intermediate **6** proceeds through the elimination of amidine, which undergoes hydrolysis during isolation (Scheme 2).

In conclusion, a one-pot reaction of *sym*-triazines in PPA with *peri*-diamine **1** leads not only to the closure of the perimidine ring, but also to the *peri*-annulation of the [*c*,*d*]pyridine ring. Further, we are going to study the scope of the reaction, in particular, with respect to perimidines and other fused aromatic and heteroaromatic compounds.

^{1}H and ^{13}C spectra were recorded on a Bruker DRX-500 and Bruker AM-300 spectrometers. Melting points were determined in the sealed capillary tubes on a PTP instrument and were not corrected. 1,8-Diaminonaphthalene (Merck) was distilled *in vacuo* before use. 1,3,5-Triazine and 2,4,6-triphenyl-1,3,5-triazine were commercially available from Aldrich; 2,4,6-trimethyl-1,3,5-triazine was obtained according to the known procedure.[4]

Synthesis of compounds 3a—c (general procedure). A mixture of 1,8-diaminonaphthalene (**1**) (0.158 g, 1 mmol), the corresponding triazine (2.5 mmol), and PPA (3—4 g) was vigorously stirred for 1 h at 100—105 °C (**2a**), 2 h at 140—145 °C (**2b**), 3 h at 180—185 °C (**2c**). The reaction mixture was cooled to 80 °C, poured to cold water (30 mL) with stirring, and made basic to pH ~8 with aqueous ammonia. The precipitate was filtered off, dried in air, and recrystallized from octane (**3a,b**) or ethanol (**3c**).

1,3,7-Triazapyrene (3a). The yield was 0.09 g (44%), crystals yellow in color, m.p. 240—242 °C (from octane; with subl.). Found (%): C, 76.22; H, 3.01; N, 20.28. $C_{13}H_7N_3$. Calculated (%): C, 76.08; H, 3.44; N, 20.48. ^{1}H NMR (DMSO-d_6), δ: 9.76 (s, 1 H, H(2)); 9.72 (s, 2 H, H(6), H(8)); 8.26, 8.80 (both d, 2 H each, H(4), H(10), H(5), H(9), J = 9.22 Hz).

2,6,8-Trimethyl-1,3,7-triazapyrene (3b). The yield was 0.094 g (38%), crystals orange in color, m.p. 206—208 °C (from octane; with subl.). Found (%): C, 77.87; H, 5.18; N, 16.72. $C_{16}H_{13}N_3$. Calculated (%): C, 77.71; H, 5.30; N, 16.99. ^{1}H NMR (DMSO-d_6), δ: 2.98 (s, 3 H, C(2)Me); 3.08 (s, 6 H, C(6)Me, C(8)Me); 7.92, 8.67 (both d, 2 H each, H(4), H(10), H(5), H(9), J = 9.40 Hz). ^{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).

2,6,8-Triphenyl-1,3,7-triazapyrene (3c). The yield was 0.13 g (30%), crystals yellow-brownish in color, m.p. 286—288 °C (from ethanol). Found (%): C, 86.09; H, 4.21; N, 9.49. $C_{31}H_{19}N_3$. Calculated (%): C, 85.89; H, 4.42; N, 9.69. ^{1}H NMR ($CDCl_3$), δ: 7.61 (m, 9 H, C(2)Ph, C(6)Ph, C(8)Ph, *m*-H and *p*-H); 7.95 (br.d, 4 H, C(6)Ph, C(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, C(2)Ph, *o*-H).

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