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UNEXPECTED RESULT OF THE REACTION OF PERIMIDINES WITH 1,3,5-TRIAZINE IN THE PRESENCE OF SODIUM NITRITE

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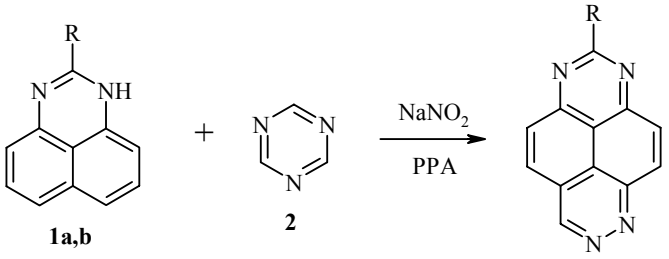
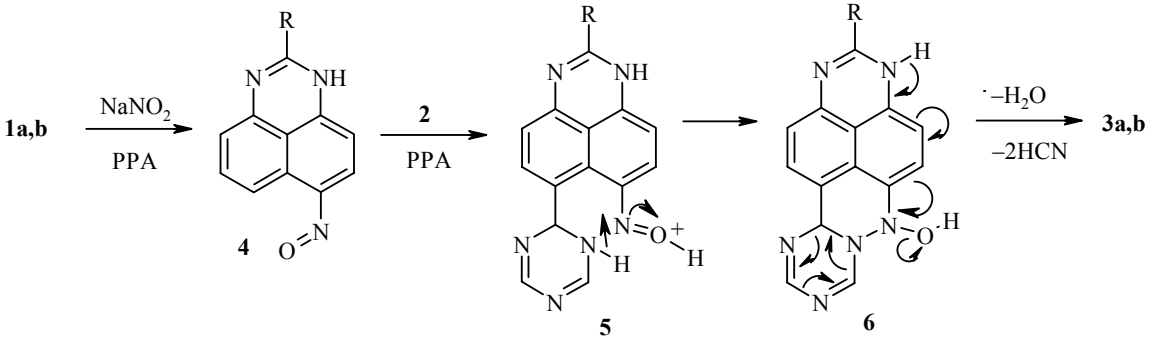
Keywords: perimidines, PPA (polyphosphoric acid), 1,2,6,8-tetraazapyrenes, 1,3,5-triazine, annelation.

The method of acylation (formylation) of perimidines, which we developed [1], is based on their reaction with 1,3,5-triazine in PPA (polyphosphoric acid). However, addition of sodium nitrite to the reaction mixture unexpectedly led to a change in the direction of the process. For example, on heating 1 mmol of compounds **1a,b** with 1.8 mmol of triazine **2** and 2 mmol of sodium nitrite in 3-4 g of PPA* at 60-70°C (isolation is common for similar reactions) gave the previously unknown 1,2,6,8-tetraazapyrenes **3a,b** in yields of 12 and 16% respectively.



1a,b **2** **1, 3 a** R = H, **b** R = Ph **3a,b**

It is probable that the reaction occurs *via* the following scheme:



* PPA containing 86% P_2O_5 made by method [2] was used.

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Nitrosation of perimidines **1a,b** occurs in the first stage. The nitroso compound **4** is then acylated with triazine **2** to give the nitroso compounds **5** which form the pentacyclic compounds **6,** which are converted to the tetraazapyrenes **3a,b**.

^{1}H NMR Spectra of DMSO-d_6 solutions with TMS as internal standard were recorded with a Bruker-200 (200 MHz) machine.

1,2,6,8-Tetrazapyrene (3a). Yield 0.034 g (16%); mp 142-144°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.11 (1H, d, *J* = 9.5, H-4); 8.34 (1H, d, *J* = 9.5, H-10); 8.62 (1H, d, *J* = 9.5, H-5); 8.91 (1H, d, *J* = 9.5, H-9), 9.71 (1H, s, H-3), 9.89 (1H, s, H-7). Found, %: C 70.04; H 2.87; N 27.09. $C_{12}H_6N_4$. Calculated, %: C 69.90; H 2.93; N 27.17.

7-Phenyl-1,2,6,8-tetraazapyrene (3b). Yield 0.033 g (12%); mp 244-246°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.62 (3H, m, 3,4,5-C_6H_5); 8.14 (1H, d, *J* = 9.5, H-10); 8.38 (1H, d, *J* = 9.5, H-4); 8.63 (1H, d, *J* = 9.5, H-5); 8.71 (2H, d, *J* = 7.5, 2,6-C_6H_5); 8.88 (1H, d, *J* = 9.5, H-9); 9.76 (1H, s, H-3). Found, %: C 76.67, H 3.52, N 19.81. $C_{18}H_{10}N_4$. Calculated, %: C 76.58; H 3.57; N 19.85.

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