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UNEXPECTED RESULT IN THE REACTION OF 1,8-NAPHTHALENEDIAMINE WITH TRIAZINE AND CARBONYL COMPOUNDS IN POLYPHOSPHORIC ACID

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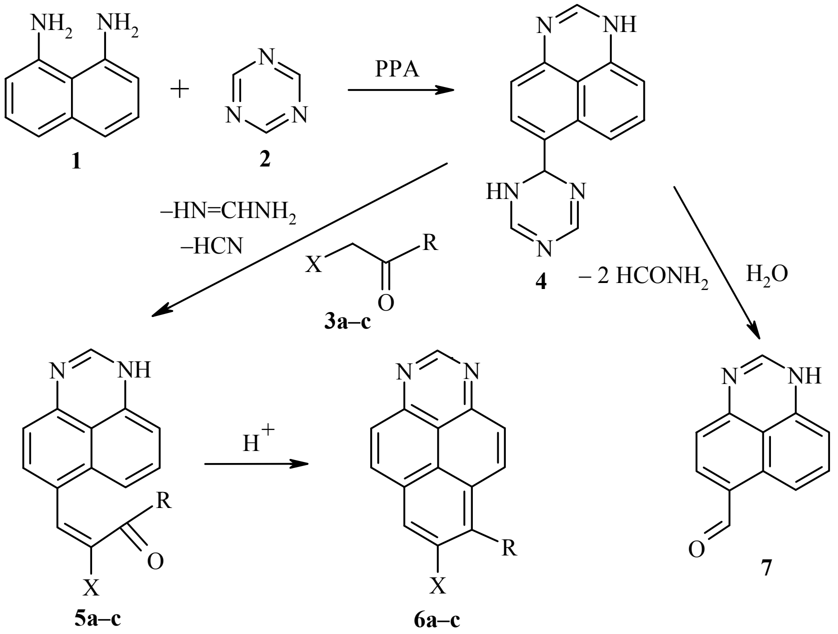
We have previously developed a method of acylation (formylation) of perimidines based on their reaction with 1,3,5-triazines **2** in PPA. The direction of the reaction was unexpectedly changed when trying to carry out this reaction in the presence of carbonyl compounds when the substrate is the 1,8-naphthalenediamine **1**. We have found that heating 1 mmol of compound **1** with 3 mmol of 1,3,5-triazine and 2 mmol of the carbonyl compound **3** in PPA* at 60-70°C for 9 h (general conditions for similar reactions) gave the 1,3-diazapyrene **6** in 57-68% yield. It is likely that the reaction occurs *via* the following stages:



3, **5**, **6** **a** R = Ph, X = H; **b** R = Me, X = COOEt; **c** R = Me, X = COMe

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* The PPA used was obtained by [2] and contained 86% P_2O_5.

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This scheme is confirmed by the fact that we could separate a quantitative yield of the perimidine-6(7)-carbaldehyde (**7**) in the absence of the carbonyl compound with shortening of the reaction time to 1 h and treatment of the reaction mixture with water.

^{1}H NMR spectra were recorded on a Bruker AS-200 (200 MHz) instrument using $CDCl_3$ solvent and TMS internal standard. Monitoring of the reaction course and the purity of the compounds prepared was carried out on Silufol UV-254 plates with ethyl acetate as solvent. Column chromatography was performed on L 40/100 silica gel with ethyl acetate eluent.

6-Phenyl-1,3-diazapyrene (6a). Yield 0.16 g (57%); mp 193-195°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.59-7.64 (5H, m, C_6H_5); 8.15 (1H, d, $J_{7,8}$ = 7.72, H-7); 8.32 (1H, d, $J_{4,5}$ = 9.4, H-5); 8.41 (1H, d, $J_{7,8}$ = 7.7, H-8); 8.48 (1H, d, $J_{9,10}$ = 9.4, H-9); 8.76 (1H, d, $J_{4,5}$ = 9.4, H-4); 8.98 (1H, d, $J_{9,10}$ = 9.4, H-10); 9.76 (1H, s, H-2). Found, %: C 85.82; H 4.25; N 8.93. $C_{20}H_{12}N_2$. Calculated, %: C 85.69; H 4.32; N 9.99.

Ethyl 6-Methyl-1,3-diazapyrene-7-carboxylate (6b). Yield 0.197 g (68%); mp 153-154°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.52 (3H, t, *J* = 6.8, $C\underline{H}_3CH_2$); 3.26 (3H, s, CH_3); 4.55 (2H, q, *J* = 6.8, $CH_3C\underline{H}_2$); 8.22 (1H, d, $J_{9,10}$ = 9.5, H-9); 8.31 (1H, d, $J_{4,5}$ = 9.5, H-5); 8.55 (1H, d, $J_{9,10}$ = 9.5, H-10); 8.85 (1H, d, H-8); 8.93 (1H, d, $J_{4,5}$ = 9.5, H-4); 9.80 (1H, s, H-2). Found, %: C 74.58; H 4.81; N 9.58. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

7-Acetyl-6-methyl-1,3-diazapyrene (6c). Yield 0.266 g (64%); mp 161-163°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.86 (3H, s, $COCH_3$); 3.14 (3H, s, CH_3); 8.23 (1H, d, $J_{9,10}$ = 9.5, H-9); 8.31 (1H, d, $J_{4,5}$ = 9.5, H-5); 8.54 (1H, d, $J_{9,10}$ = 9.5, H-10); 8.55 (1H, s, H-8); 8.90 (1H, d, $J_{4,5}$ = 9.5; H-4); 9.83 (1H, s, H-2). Found, %: C 78.58; H 4.59; N 10.71. $C_{17}H_{12}N_2O$. Calculated, %: C 78.44; H 4.65; N 10.76.

Perimidine-6(7)-carbaldehyde (7). Yield 91%; mp 212-214ºC (acetic acid), mp 212-214ºC [3]. A sample mixed with a known sample did not give a depression of melting point. The ^{1}H NMR spectrum agreed with that given in [3].

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