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AN UNEXPECTED RESULT OF THE REACTION OF PERIMIDINES WITH AN EXCESS OF 1,3,5-TRIAZINES IN POLYPHOSPHORIC ACID

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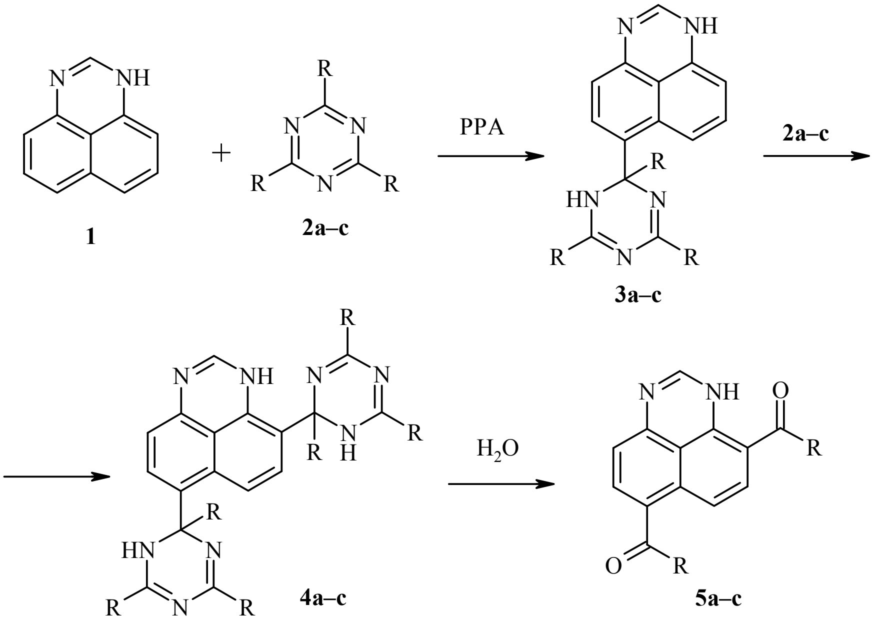
We have reported previously [1] that on reaction of perimidines **1** with a 2.5 times excess of 1,3,5-triazines in 80% PPA at 80°C in the case of triazines **2a,b** and at 60°C in the case of triazine **2c** products of monoacylation (formylation) are formed. 1,3,7-Triazapyrenes were formed when 1,3,5-triazines in 86% PPA and an increased temperature of 100-110°C were used [2]. When a threefold excess of 1,3,5-triazines was used in 86% PPA at 70-75°C and the reaction time was increased to 2-2.5 h we unexpectedly obtained products of 4,9-diacylation (formylation) in 41-82% yield. The reaction probably occurs by the following mechanism.



2–5 **a** R = Me, **b** R = Ph, **c** R = H

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As in the case of monoacylation, compounds **3** are formed in the first stage, which react, because of steric hindrance in the *peri* position, with the triazines to form compounds **4,** hydrolysis of which leads to compounds **5**.

^{1}H NMR spectra were recorded on a Bruker AS-200 (200 MHz) with TMS as internal standard. The progress of reactions and purity of the synthesized compounds were monitored on Silufol UV-254 plates with ethyl acetate as solvent. Preparative TLC was carried out on L5-17 silica gel with 3:1 petroleum ether- ethyl acetate as eluent.

General Method for the Preparation of Aldehydes and Ketones 5. A mixture of 1 mmol of compound **1** with 3 mmol of the corresponding 1,3,5-triazine **2** was heated with stirring in PPA* for 2-2.5 h at 70-75°C. At the end of the reaction the mixture was poured into water and extracted with ethyl acetate. A precipitate, which formed on evaporation of the solvent, was filtered of and dried. The dried material was dissolved in ethyl acetate and separated by preparative TLC, collecting the corresponding fractions with R_f 0.6 (**5a**), 0.62 (**5b**), and 0.58 (**5c**).

6,9-Diacetylperimidine (5a). Yield 74%; mp 168-170°C (ethyl acetate). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 2.66 (3H, s, CH_3); 2.67 (3H, s, CH_3); 7.03 (1H, d, *J* = 8.25, H-4); 7.92 (1H, d, *J* = 9.9, H-8); 8.08 (1H, s, H-2); 8.26 (1H, d, *J* = 8.25, H-5); 8.38 (1H, d, *J* = 9.9, H-7). Found, %: C 71.59; H 4.67; N 11.05. $C_{15}H_{12}N_2O_2$. Calculated, %: C 71.42; H 4.79; N 11.10.

6,9-Dibenzoylperimidine (5b). Yield 82%; mp 146-148°C (ethyl acetate), ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.04 (1H, s, H-4); 7.45 (1H, d, *J* = 8.8, H-5); 7.45-7.6 (9H, m, H-8, COPh(6), 3,4,5-COPh(9)); 7.75 (1H, d, *J* = 9.2, H-7 Ph); 7.82 (2H, br. d, *J* = 7.7, 2,6-COPh); 12.6 (1H, br. s, NH). Found, %: C 79.93; H 4.19; N 7.37. $C_{25}H_{16}N_2O_2$. Calculated, %: C 79.77; H 4.28; N 7.44).

Perimidine-2,6-dicarbaldehyde (5c). Yield 41%; mp 220-222°C (ethyl acetate). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.31 (1H, d, *J* = 8.1, H-4); 7.75 (1H, d, *J* = 9.1, H-8); 7.96 (1H, s, H-2); 8.10 (1H, d, *J* = 8.1, H-5); 8.79 (1H, d, *J* = 9.1, H-7); 9.92 (1H, s, 6-CHO); 10.02 (1H, s, 9-CHO); 12.5 (1H, br. s, NH). Found, %: C 69.83; H 3.53; N 12.37. $C_{13}H_8N_2O_2$. Calculated, %: C 69.64; H 3.60; N 12.49.

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* We used PPA containing 86% P_2O_5 prepared by method [3].

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