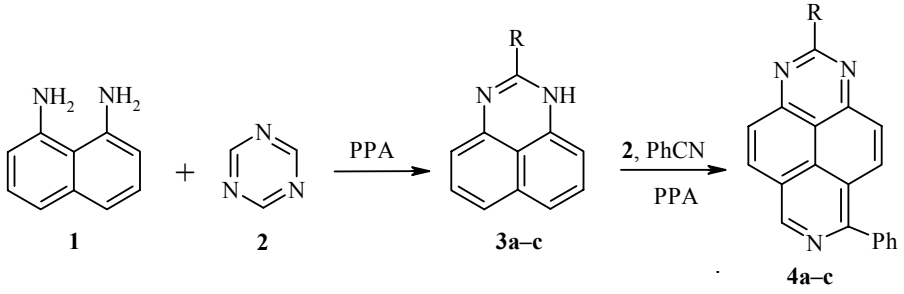
Chemistry of Heterocyclic Compounds, Vol. 44, No. 7, 2008

UNEXPECTED REACTION OF 1,8-NAPHTHYLENEDIAMINE AND PERIMIDINES WITH 1,3,5-TRIAZINE IN THE PRESENCE OF BENZONITRILE IN POLYPHOSPHORIC ACID

I. V. Aksenova, A. V. Aksenov, A. S. Lyakhovnenko, and I. V. Borovlev

Keywords: benzonitrile, 1,8-naphthylenediamine, perimidines, PPA, 1,3,7-triazapyrenes, 1,3,5-triazine, annelation.

We have developed a method for the acylation (formylation) of perimidines based on their reaction with 1,3,5-triazines **2** [1], and 1,3,7-triazapyrenes, based on the reaction of 1,8-naphthalenediamine (**1**) with nitriles in PPA [2]. In the reaction of diamine **1** (1 mmol) with 1,3,5-triazine **2** (3 mmol) and benzonitrile (5 mmol) in 3-4 g PPA* at 70-80°C for 8 h (separation is normal for similar reactions) 6-phenyl-1,3,7-triazapyrene (**4a**) (72%) was isolated from an unexpected mixture of products. It is probable that the reaction went *via* the intermediate formation of the perimidine **3a**, because when the compounds **3a-c** were used in this reaction (with 2 mmol of compound **2**), the triazapyrenes **4a-c** were isolated in 71-75% yield.



1 **2** **3a–c** **4a–c**

3, 4 a R = H, **b** R = Me, **c** R = Ph

^{1}H NMR spectra were recorded with a Bruker WP-200 (200 MHz) spectrometer with TMS as internal standard. Mass spectra were recorded with a MAT-311A instrument. The reactions and the purity of the synthesized products were controlled on Silufol UV-254 plates with ethyl acetate as solvent. Column chromatography was carried out on L 40/100 silica gel, with ethyl acetate as eluent.

* The PPA used, made by a standard method [3], contained 86% P_2O_5.

Stavropol State University, Stavropol 355009, Russia; e-mail: k-biochem-org@stavsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, 1106-1107, July, 2008. Original article submitted October 14, 2007.

6-Phenyl-1,3,7-triazapyrene (4a). Yield from perimidine was 0.211 g (75%), from 1,8-naphthalenediamine 0.2 g (71%); mp 174-176°C (nonane). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.68 (3H, m, 3,4,5-C_6H_5); 7.91 (2H, br. d, J = 8.0, 2,6-C_6H_5); 8.29 (1H, d, $J_{9,10}$ = 9.5, H-10); 8.33 (1H, d, $J_{4,5}$ = 9.1, H-4); 8.75 (1H, d, $J_{9,10}$ = 9.5, H-9); 8.91 (1H, d, $J_{4,5}$ = 9.1, H-5); 9.86 (1H, s, H-8); 9.89 (1H, s, H-2). Mass spectrum (70 eV), *m/z* (I_{rel}, %): 281 $[M]^+$ (100). Found, %: C 81.27; H 3.87; N 14.86. $C_{19}H_{11}N_3$. Calculated, %: C 81.12; H 3.94; N 14.94.

2-Methyl-6-phenyl-1,3,7-triazapyrene (4b). Yield 0.21 g (71%); mp 246-248°C (nonane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.19 (3H, s, CH_3); 7.63 (3H, m, 3,4,5-C_6H_5); 7.88 (2H, dd, J = 8.1, J = 1.3, 2,6-C_6H_5); 8.18 (1H, d, $J_{9,10}$ = 9.5, H-10); 8.24 (1H, d, $J_{4,5}$ = 9.2, H-4); 8.60 (1H, d, $J_{4,5}$ = 9.2, H-5); 8.76 (1H, d, $J_{9,10}$ = 9.5, H-9); 9.69 (1H, s, H-8). Found, %: C 81.44; H 4.38; N 14.18. $C_{20}H_{13}N_3$. Calculated, %: C 81.34; H 4.44; N 14.23.

2,6-Diphenyl-1,3,7-triazapyrene (4c). Yield 0.264 g (74%); mp 197-199°C (nonane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.63 (6H, m, 3,4,5-(2)C_6H_5, 3,4,5-(6)C_6H_5); 7.90 (2H, dd, J = 8.1, J = 1.6, 2,6-(6)C_6H_5); 8.30 (1H, d, $J_{9,10}$ = 9.5, H-10); 8.35 (1H, d, $J_{4,5}$ = 9.2, H-4); 8.63 (1H, d, $J_{4,5}$ = 9.2, H-5); 8.76 (1H, d, $J_{9,10}$ = 9.5, H-9); 8.84 (2H, dd, J = 8.1, J = 1.6, 2,6-(2)C_6H_5); 9.68 (1H, s, H-8). Found, %: C 84.14; H 4.19; N 11.67. $C_{25}H_{15}N_3$. Calculated, %: C 84.01; H 4.23; N 11.76.

REFERENCES

1. A. V. Aksenov, I. V. Borovlev, A. S. Lyakhovnenko, and I. V. Aksenova, *Khim. Geterotsikl. Soedin.* 629 (2007). [*Chem. Heterocycl. Comp*., **43**, 527 (2007)].
2. I. V. Aksenova, I. V. Borovlev, A. S. Lyakhovnenko, S. I. Pisarenko, and A. V. Aksenov, *Khim. Geterotsikl. Soedin.* 788 (2007). [*Chem. Heterocycl. Comp*., **43**, 665 (2007)].
3. F. Uhlig, *Angew. Chem.,* **66**, 435 (1954).