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UNEXPECTED RESULT FROM THE INTERACTION OF 1,8-DIAMINO-NAPHTHALENE WITH AROMATIC NITRILES IN POLYPHOSPHORIC ACID

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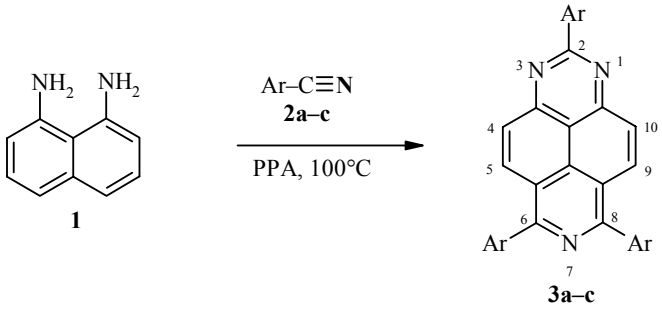
The reaction of 1,8-diaminonaphthalene dihydrochloride with acetonitrile and butyronitrile at high temperature gave 2-methyl- and 2-propylperimidine respectively [1]. We investigated the reaction of 1,8-diaminonaphthalene (**1**) with aromatic nitriles in polyphosphoric acid* (PPA) assuming that it would form only 2-Ar-perimidines, or (by analogy with carbonic acids [2]) products of their acylation. The reaction occurred on heating the reagents above 100°C, but the unexpected products were the previously unknown 2,6,8-triaryl-1,3,7-triazapyrenes **3a-c**.



1 **3a–c**

3 a Ar = Ph; **b** Ar = 4-BrC_6H_4; **c** Ar = 4-$O_2NC_6H_4$

The proposed mechanism for this conversion includes formation of a 2-Ar-perimidine **4**, electrophilic attack on **4** by the nitrile cation at position 6(7), and then at nitrogen atom of the ketimine **5** to give the intermediate **6** and its subsequent cyclization at the *peri* position. Subsequent aromatization occurs *via* elimination of ammonia.

So interaction of aromatic nitriles in PPA with the *peri* diamine **1** not only leads to closure of the perimidine ring but also to *peri*-annelation of the [*c,d*]pyridine ring leading to a *one-pot synthesis* of the previously unknown 1,3,7-triazapyrene. We intend to investigate some general characteristics of this reaction with respect to perimidine and other condensed aromatic and heteroaromatic compounds.

* PPA used contains 86% P_2O_5; was prepared as in [3].

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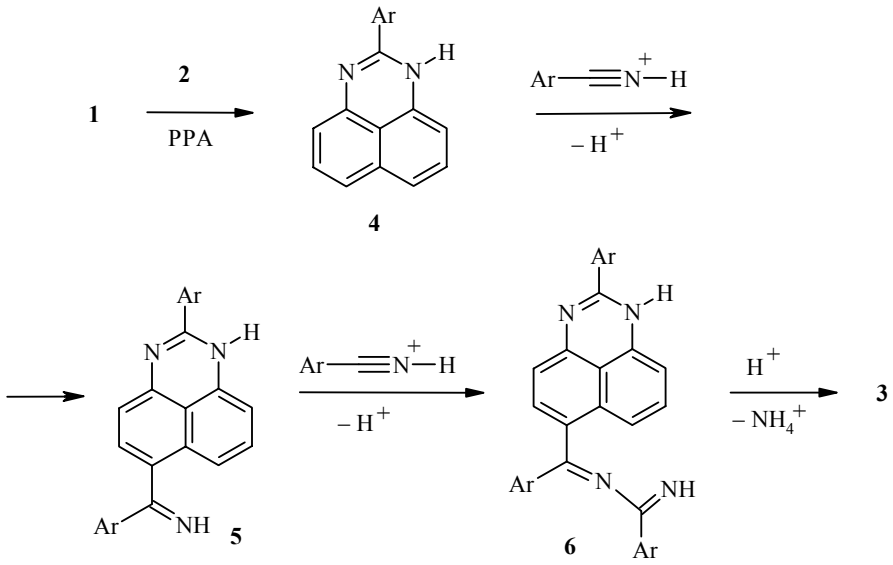
The ^{1}H NMR spectra of $CDCl_3$ solutions with TMS as internal standard were recorded on a Bruker-200 (200 MHz) instrument.



General Method. A mixture of 1,8-diaminonaphthalene (**1**) (0.158 g, 1 mmol), the corresponding nitrile (3.5 mmol), and PPA (3-4 g) was vigorously stirred for 3 h at 180°C. The reaction mixture was cooled to 80°C and poured with stirring into cold water (30 ml), basified with ammonia solution to pH ~ 8, the precipitate was filtered off and dried in the air. The dried substance was extracted with ethyl acetate for 1.5 h in a Soxhlet apparatus. The solution was evaporated and the precipitate filtered off.

2,6,8-Triphenyl-1,3,7-triazapyrene (3a, $C_{31}H_{19}N_3$). Yield 0.155 g (35%). Yellow crystals, mp 286-288°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61 (9H, m, H-*m* and –*p*, 2-, 6-, and 8-C_6H_5); 7.95 (4H, d, *J* = 7.5, 6- and 8-C_6H_5, H-*o*); 8.26 (2H, d, *J* = 9.5, H-5,9); 8.76 (2H, d, *J* = 9.5, H-4,10); 8.84 (2H, d, *J* = 7.5, *o*-H, 2-C_6H_5). 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.

2,6,8-Tri(4-bromophenyl)-1,3,7-triazapyrene (3b, $C_{31}H_{16}Br_3N_3$) Yield 0.168 g (24%). Yellow crystals, mp 193-195°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61 (4H, d, *J* = 8.8, 6 and 8-C_6H_5); 7.74 (2H, d, *J* = 8.1, H-*m* 2-C_6H_5); 7.94 (4H, d, *J* = 8.8, H-*o* 6- and 8-C_6H_5); 8.29 (2H, d, *J* = 9.5, H-5,9); 8.72 (2H, d, *J* =9.5, H-4,10); 8.75 (2H, d, *J* = 8.1, H-*o* 2-C_6H_5). Found, %: C 55.72; H 2.38; N 6.21. $C_{31}H_{16}Br_3N_3$. Calculated, %: C 55.56; H 2.41; N 6.27.

2,4,6-Tri(4-nitrophenyl)-1,3,7-triazapyrene (3c, $C_{31}H_{16}N_6O_6$). Yield 0.142 g (27%). Yellow crystals, mp 182-184°C (ethyl acetate). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.98 (4H, d, *J* = 8.7, H-*o*, 6-, 8-C_6H_5); 8.29 (2H, d, *J* = 9.5, H-5,9); 8.42 (4H, d, *J* = 8.7, 3,5-H-*m* 6-, 8-C_6H_5); 8.46 (2H, d, *J* = 8.5, H-*m* 2-C_6H_5); 8.76 (2H, d, *J* = 9.5, H-4,10); 8.79 (2H, d, *J* = 8.5, C-2, H-*o* 2-C_6H_5). Found, %: C 65.68; H 2.81; N 14.67. $C_{31}H_{16}N_6O_6$. Calculated, %: C 65.50; H 2.84; N 14.78.

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