Chemistry of Heterocyclic Compounds, Vol. 46, No. 9, 2010

AN ORIGINAL APPROACH TO THE SYNTHESIS OF 1,3,6,8-TETRAAZAPYRENES

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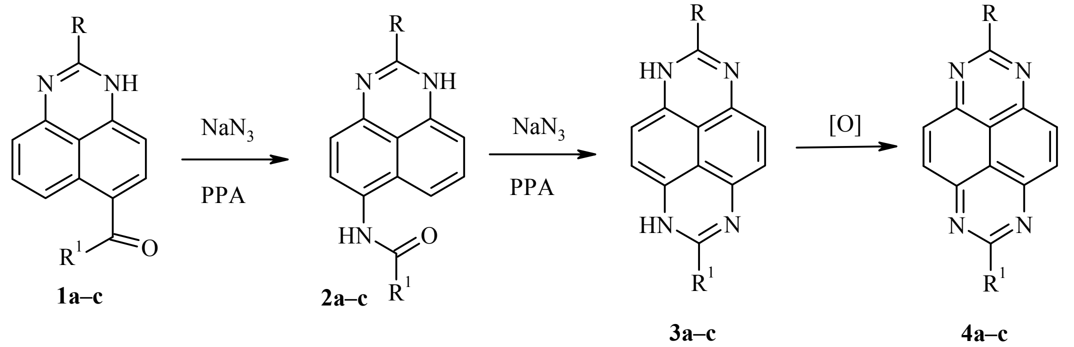
Keywords: sodium azide, perimidines, PPA, 1,3,6,8-tetraazapyrenes, amination, *peri* annelation, Schmidt reaction.

Methods have been developed for the synthesis of 1,3,6,8-tetraazapyrene based on the reaction of 1,4,5,8-tetraaminonaphthalene with formic acid [1] and the synthesis of 2,7-dimethyl-1,3,6,8-tetraazapyrene based on the reaction of 6,7-diamino-2-methylperimidine with acetic anhydride [2]. These methods involve the use of not readily available starting reagents and are not general. In the present work, we propose a method for the synthesis of such compounds from available perimidine ketones **1a-c**. Heating ketone **1a-c** (1 mmol) and NaN_3 (0.26 g, 4 mmol) in PPA (2-3 g) at 70-80°C for 1 h and then at 100-110°C for 4 h with monitoring by thin-layer chromatography leads to 1,3,6,8-tetraazapyrenes **4a-c** in 31-44% yield. The PPA sample containing 87% P_2O_5 was prepared according to Uhlig [3].

This reaction involves the intermediate formation of amides **2a-c**, whose amination using sodium azide in PPA, as previously described for perimidines [4, 5], leads to dihydro derivatives **3a-c**, which are oxidized by atmospheric oxygen to give tetraazapyrenes **4a-c**.



1–4 a R = R^1 = Me, **b** R = R^1 = Ph, **c** R = Ph, R^1 = Me

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1418-1420, September, 2010. Original article submitted June 3, 2010.

The ^1H NMR spectra were taken on a WP-200 spectrometer at 200 MHz in DMSO-d_6 with TMS as the internal standard. The course of the reactions and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates using 1:1 ethyl acetate–ethanol as the eluent.

The reaction mixture was treated with 50 ml water, brought to pH 8-9 by adding ammonium hydroxide. The precipitate formed was filtered off. The mother liquor was extracted with three 50-ml portions of butanol. The solvent was evaporated. The residue was combined with the precipitate. The compounds obtained were purified by recrystallization.

2,7-Dimethyl-1,3,6,8-tetraazapyrene (4a) was obtained in 36% yield (0.084 g); mp >300°C (butanol) (mp >300°C [2]). ^1H NMR spectrum, δ, ppm: 3.12 (6H, s, CH_3); 8.62 (4H, s, H-4, H-5, H-9, H-10). Found, %: C 71.94; H 4.23; N 23.83. $C_{14}H_{10}N_4$. Calculated, %: C 71.78; H 4.30; N 23.92.

2,7-Diphenyl-1,3,6,8-tetraazapyrene (4b) was obtained in 31% yield (0.111 g); mp >300°C (butanol). ^1H NMR spectrum, δ, ppm: 7.55 (6H, m, H-3, H-4, H-5 Ph); 8.58 (4H, s, H-4, H-5, H-9, H-10); 8.62 (4H, m, H-2, H-6 Ph). Found, %: C 80.54; H 3.88; N 15.58. $C_{24}H_{14}N_4$. Calculated, %: C 80.43; H 3.94; N 15.63.

2-Methyl-7-phenyl-1,3,6,8-tetraazapyrene (4c) was obtained in 44% yield (0.13 g); mp >300°C (butanol). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.89 (3H, s, CH_3); 7.49 (3H, m, H-3, H-4, H-5 Ph); 8.40 (2H, d, $J = 9.4$, H-5, H-9); 8.49 (2H, d, $J = 9.4$, H-4, H-10); 8.89 (2H, m, H-2, H-6 Ph). Found, %: C 77.12; H 4.02; N 18.86. $C_{19}H_{12}N_4$. Calculated, %: C 77.01; H 4.08; N 18.91.

This work was carried out with the financial support of the Russian Basic Research Fund (Grant 10-03-00193a).

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