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SYNTHESIS OF 1H-1,5,7-TRIAZACYCLOPENTA[*c,d*]PHENALENES, A NEW HETEROCYCLIC SYSTEM

A. V. Aksenov[1], A. S. Lyakhovnenko[1], and N. C. Karaivanov[1]**

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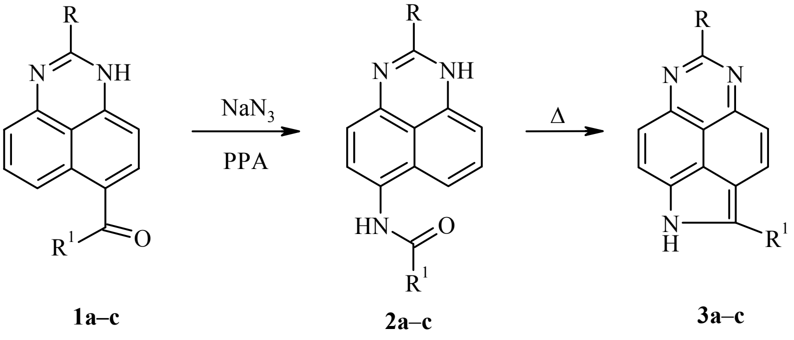
In previous work [1-4], we have developed a number of methods for the *peri* annelation of six-membered rings to give perimidines. In light of the high biological activity of a significant number of indole derivatives, we propose a method for the *peri* annelation of the pyrrole ring to perimidines. The reaction of ketones **1a-c** (1 mmol) and NaN_3 (0.07 g, 1.08 mmol) in PPA* (2-3 g) at 70-80°C for 1 h and then at 150-160°C for 4 h monitored by thin-layer chromatography leads to 1H-1,5,7-triazacyclopenta[*c,d*]phenalenes **3a-c** in 36-48% yield.

The reaction involves intermediante formation of amides **2a-c**, which cam be isolated, for example **2a**.

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



1a–c **2a–c** **3a–c**

1–3 a R = H, R^1 = Me, **b** R = R^1 = Me, **c** R = Me, R^1 = Ph

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*The PPA sample used containing 86% P_2O_5 was prepared according to Uhlig [5].

** To whom correspondence should be addressed, e-mail: k-biochem-org@stavsu.ru.

[1]Stavropol State University, Stavropol 355009, Russia.

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The reaction mixture was treated with 50 ml water and then brought to pH 8-9 by adding ammonium hydroxide. The precipitate formed was filtered off and the mother liquor was extracted with three 50-ml benzene portions. The solvent was distilled off and the residue was combined with the precipitate. The products obtained were purified by recrystallization.

6(7)-Acetaminoperimidine (2a) was obtained in 86% yield; mp 225-226°C (ethyl acetate). ^{1}H NMR, δ, ppm (*J*, Hz): 2.08 (3H, s, $COCH_3$); 6.43 (2H, m, H-4(9), H-9(4)); 7.03 (1H, d, *J* = 8.5, H-7(6)); 7.15 (1H, dd, *J* = 8.5, *J* = 7.3, H-8(5)); 7.24 (1H, d, *J* = 8.1, H-7(6)); 7.32 (1H, s, H-2); 9.21 (1H, br. s, NHCO); 10.61 (1H, br. s, NH). Found, %: C 69.45; H 4.86; N 18.61. $C_{13}H_{11}N_3O$. Calculated, %: C 69.32; H 4.92; N 18.65.

2-Methyl-1H-1,5,7-triazacyclopenta[*c,d*]phenalene (3a) was obtained in 44% yield (0.091 g); mp 259-260°C (benzene). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.98 (3H, s, CH_3); 7.58 (1H, d, *J* = 9.0, H-9); 7.78 (1H, d, *J* = 9.0, H-3); 8.31 (1H, d, *J* = 9.0, H-4); 8.47 (1H, d, *J* = 9.0, H-8); 9.36 (1H, s, H-6); 13.1 (1H, br. s, NH). Found, %: C 75.54; H 4.31; N 20.15. $C_{13}H_9N_3$. Calculated, %: C 75.35; H 4.38; N 20.28.

2,6-Dimethyl-1H-1,5,7-triazacyclopenta[*c,d*]phenalene (3b) was obtained in 48% yield (0.106 g); mp 271-272°C (benzene). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.87 (3H, s, 2-CH_3), 2.95 (3H, s, 6-CH_3), 7.50 (1H, d, *J* = 9.0, H-9); 7.67 (1H, d, *J* = 9.0, H-3); 8.24 (1H, d, *J* = 9.0, H-4); 8.41 (1H, d, *J* = 9.0, H-8); 12.8 (1H, br. s, NH). Found, %: C 76.18; H 4.95; N 18.87. $C_{14}H_{11}N_3$. Calculated, %: C 76.00; H 5.01; N 18.99.

6-Methyl-2-phenyl-1H-1,5,7-triazacyclopenta[*c,d*]phenalene (3c) was obtained in 36% yield (0.102 g); mp 291-292°C (benzene). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.92 (3H, s, CH_3); 7.49 (1H, t, *J* = 7.7, H-4 Ph); 7.49 (2H, t, *J* = 7.7, H-3, H-5 Ph); 7.68 (1H, d, *J* = 9.0, H-9); 7.81 (1H, d, *J* = 9.0, H-3); 8.19 (2H, d, *J* = 7.7, H-2, H-6 Ph); 8.34 (1H, d, *J* = 9.0, H-4); 8.73 (1H, d, *J* = 9.0, H-8); 12.9 (1H, br. s, NH). Found, %: C 80.69; H 4.55; N 14.76. $C_{19}H_{13}N_3$. Calculated, %: C 80.69; H 4.62; N 14.83.

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