Synthesis of 1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalenes involving electrophilic amination of 1*H*-perimidines with sodium azide in polyphosphoric acid

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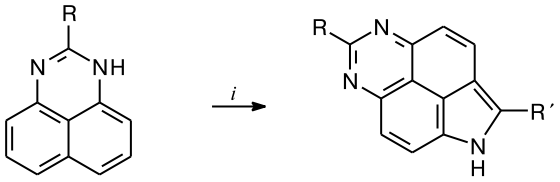
Earlier, we have developed several methods of *peri*-annulation of 6-membered rings to perimidines.[1—4] Taking into account high biological activity of many indole derivatives, in the present work we proposed a method of *peri*-annulation of the pyrrole ring to perimidines, which is based on the recently found reagent combination NaN_3/polyphosphoric acid (PPA*).[6] We showed that the reaction of perimidines **1a—c** with a threefold molar excess of NaN_3 in PPA at 80—90 °C for 4 h followed by addition of a carboxylic acid and heating for 5 h at 110—120 °C results in the earlier unknown 1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalenes **2a—e** in yields of 48—67% (Scheme 1).

Scheme 1



1a—c **2a—e**

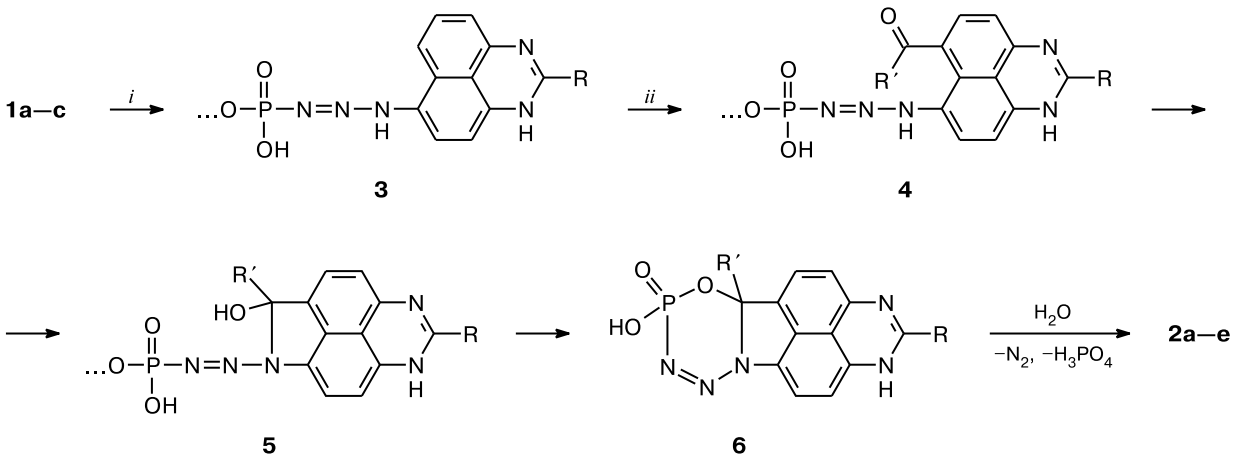
i. 1) NaN_3/PPA; 2) R´CO_2H

	R	R´		R	R´
1a	H	—	**2b**	Me	Me
1b	Me	—	**2c**	Ph	Me
1c	Ph	—	**2d**	Me	Ph
2a	H	Me	**2e**	Ph	Ph

The proposed mechanism of this transformation includes the formation of triazenes **3** according to the mechanism given in Ref. 6, their acylation and cyclization followed by the successive formation of intermediates **4**, **5**, and **6**, which results in 1*H*-1,5,7-triazacyclopenta[*c*,*d*]-phenalenes **2a—e** (Scheme 2).

Thus, the consecutive reaction of sodium azide and carboxylic acids with 1*H*-perimidines in PPA affords the hitherto unknown 1*H*-1,5,7-triazacyclopenta[*c*,*d*]phen-

Scheme 2



i. NaN_3, PPA; *ii*. R´CO_2H, PPA.

* PPA containing 86% of P_2O_5, which has been prepared according to the previously described procedure,[5] was used.

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alenes through the *one-pot* reaction. In future, we intend to study to what extent this reaction is general with respect to other azaphenalenes.

NMR spectra were recorded on a Bruker WP-200 (200 MHz) instrument in DMSO-d_6 using $SiMe_4$ as the internal standard. The course of the reaction and the purity of the compounds synthesized were monitored by TLC on Silufol UV-254 plates using chloroform as a solvent. Perimidine, 2-methyl-, and 2-phenylperimidine **1a—c** were prepared according to known procedures.[7]

Synthesis of compounds 2a—e (general procedure). A mixture of the corresponding 1*H*-perimidine **1a—c** (1 mmol) and NaN_3 (0.195 g, 3 mmol) in PPA (2—3 g) were thoroughly stirred at 80—90 °C for 4 h (TLC control). Then, a carboxylic acid (4 mmol) was added, the temperature was raised to 110—120 °C, and the mixture was stirred for additional 5 h. The reaction mixture was cooled to 80 °C, poured into cold water (30 mL), and alkalified with aqueous ammonia to pH ~8. The precipitate that formed was filtered off, the mother liquor was extracted with benzene (3×50 mL), and the precipitate was dried and extracted in a Soxhlet apparatus with benzene (100 mL) for 3 h. The benzene extracts were combined and the solvent was removed. The compounds were purified by recrystallization.

2-Methyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (2a) was obtained in a yield of 0.128 g (62%), m.p. 259—260 °C (from benzene). ^{1}H NMR, δ: 2.98 (s, 3 H, Me); 7.58 (d, 1 H, H(9), J = 9.0 Hz); 7.78 (d, 1 H, H(3), J = 9.0 Hz); 8.31 (d, 1 H, H(4), J = 9.0 Hz); 8.47 (d, 1 H, H(8), J = 9.0 Hz); 9.36 (s, 1 H, H(6)); 13.1 (br.s, 1 H, 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-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (2b) was obtained in a yield of 0.148 g (67%), m.p. 271—272 °C (from benzene). ^{1}H NMR, δ: 2.87 (s, 3 H, Me(2)); 2.95 (s, 3 H, Me(6)); 7.50 (d, 1 H, H(9), J = 9.0 Hz); 7.67 (d, 1 H, H(3), J = 9.0 Hz); 8.24 (d, 1 H, H(4), J = 9.0 Hz); 8.41 (d, 1 H, H(8), J = 9.0 Hz); 12.8 (br.s, 1 H, 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.

2-Methyl-6-phenyl-1*H*-1,5,7-triazacylcopenta[*c*,*d*]phenalene (2c) was obtained in a yield of 0.184 g (65%), m.p. 245—246 °C (from benzene with hexane). ^{1}H NMR, δ: 2.98 (s, 3 H, Me); 7.53 (m, 3 H, Ph, H(3), H(4), H(5)); 7.66 (d, 1 H, H(9), J = 9.1 Hz); 7.85 (d, 1 H, H(3), J = 8.8 Hz); 8.32 (d, 1 H, H(4), J = 8.8 Hz); 8.50 (d, 1 H, H(8), J = 9.1 Hz); 8.70 (d, 2 H, Ph, H(2), H(6), J = 7.3 Hz); 13.1 (br.s, 1 H, NH). Found (%): C, 80.66; H, 4.56; N, 14.78. $C_{19}H_{13}N_3$. Calculated (%): C, 80.55; H, 4.62; N, 14.83.

6-Methyl-2-phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (2d) was obtained in a yield of 0.15 g (53%), m.p. 291—292 °C (from benzene). ^{1}H NMR, δ: 2.92 (s, 3 H, Me); 7.49 (t, 1 H, Ph, H(4), J = 7.7 Hz); 7.49 (t, 2 H, Ph, H(3), H(5), J = 7.7 Hz); 7.68 (d, 1 H, H(9), J = 9.0 Hz); 7.81 (d, 1 H, H(3), J = 9.0 Hz); 8.19 (d, 2 H, Ph, H(2), H(6), J = 7.7 Hz); 8.34 (d, 1 H, H(4), J = 9.0 Hz); 8.73 (d, 1 H, H(8), J = 9.0 Hz); 12.9 (br.s, 1 H, NH). Found (%): C, 80.69; H, 4.55; N, 14.76. $C_{19}H_{13}N_3$. Calculated (%): C, 80.55; H, 4.62; N, 14.83.

2,6-Diphenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (2e) was obtained in a yield of 0.166 g (48%), m.p. 169—170 °C (from benzene with hexane). ^{1}H NMR, δ: 7.5—7.7 (m, 6 H, 2-Ph, 6-Ph, H(3), H(4), H(5)); 7.85 (d, 1 H, H(9), J = 9.0 Hz); 7.98 (d, 1 H, H(3), J = 9.0 Hz); 8.21 (d, 2 H, 2-Ph, H(2), H(6), J = 7.7 Hz); 8.41 (d, 1 H, H(4), J = 9.0 Hz); 8.73 (d, 2 H, 6-Ph, H(2), H(6), J = 8.1 Hz); 8.81 (d, 1 H, H(8), J = 9.0 Hz); 13.0 (br.s, 1 H, NH). Found (%): C, 83.62; H, 4.29; N, 12.09. $C_{24}H_{15}N_3$. Calculated (%): C, 83.46; H, 4.38; N, 12.17.

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