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LETTERS TO THE EDITOR

NEW THREE-COMPONENT REACTION OF PERIMIDINES WITH SODIUM AZIDE AND SODIUM NITRITE IN POLYPHOSPHORIC ACID

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Polynuclear aromatic and heteroaromatic compounds, including compounds with *peri*-annelated penta- and hexa-membered rings, have considerable practical value. Effective medications [1, 2] and luminescent intercalators [3, 4] have been created based on them.

We have previously developed a series of methods for *peri*-annelation of pyrrole [1, 5-7] and furan [5] rings to naphthalene derivatives. At the same time, there are only a few examples of the *peri*-annelation of the pyrazole nucleus [5, 8]. In the present work, we have developed a method for the synthesis of compounds with such fragments based on the electrophilic amination of arenes with sodium azide in polyphosphoric acid (PPA) [9-11] and nitrosation of the heterocyclic intermediates with sodium nitrite.

We have established that heating of the perimidines **1a-c** with a threefold excess of sodium azide and a twofold molar excess of $NaNO_2$ in PPA (86% content of P_2O_5) gave 1,2,5,7-tetraazacyclopenta[*cd*]phenalenes **2a-c** in 46-52% yields.

The reaction can be carried with a simultaneous mixture of all components, but in this case the yields are somewhat lower (37-41%).

The mechanism of the reaction probably includes the formation of the intermediate compounds **3a-c** from the perimidines **1a-c** and sodium azide [9-11]. Subsequent nitrosation of these compounds at the nitrogen atom leads to the intermediates **4a-c**, which by loss of PPA and a molecule of nitrogen, are converted into the *N*-nitroso derivatives **5a-c**. Cyclization of the latter gives the required compounds **2a-c**.

^{1}H NMR spectra were recorded with a Bruker WP-200 (200 MHz) spectrometer with TMS as internal standard. IR spectra were recorded with a UR-20 spectrophotometer using KBr pellets. The course of the reactions and the purity of the products were monitored by TLC on Silufol UV-254 plates in ethyl acetate. PPA with 86% P_2O_5 content was prepared by a known method [12].

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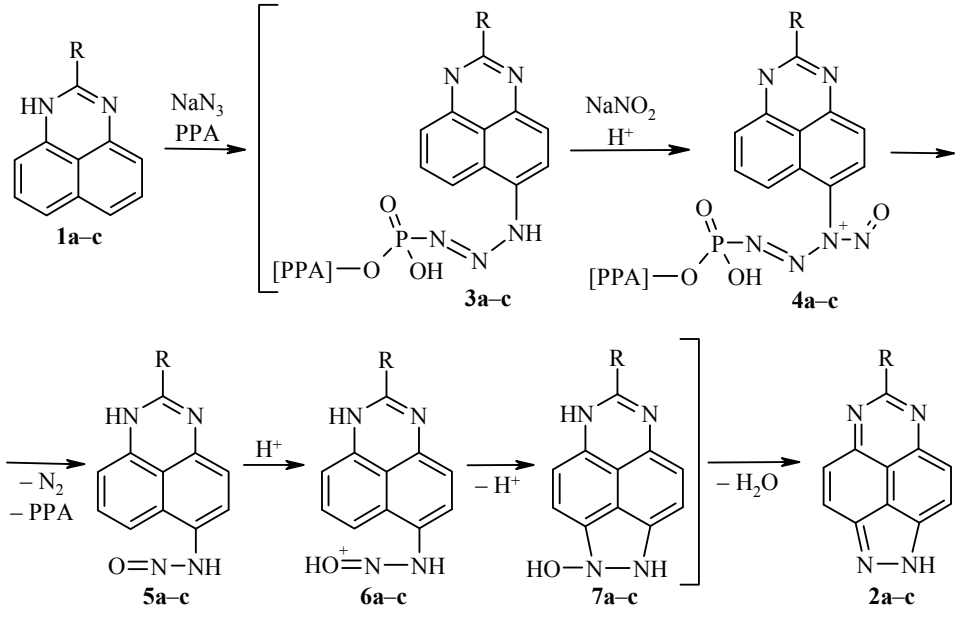
1,2,5,7-Tetraazacyclopenta[*cd*]phenalenes 2a-c (General Method). A. A mixture of perimidine **1a-c** (1.00 mmol), NaN_3 (0.07 g, 1.07 mmol) in 86% PPA (2-3 g) was heated with vigorous stirring for 4 h at 80-90°C and for 1 h at 110°C. $NaNO_2$ (0.14 g, 2.00 mmol) was then added, and stirring continued for 2 h at 110°C. The reaction mixture was poured into water (30 ml), neutralized with ammonia solution, and extracted with benzene (6×30 ml), the solvent was evaporated, and the residue was recrystallized from benzene.

B. The same components in the same quantities as in method A were mixed simultaneously and heated for 4 h at 80-90°C and for 3 h at 110°C. The products were isolated as in method A.



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

1*H*-1,2,5,7-Tetraazacyclopenta[*cd*]phenalene (2a). Yield 0.101 g (52%) (method A), 0.080 g (41%) (method B); mp 233-235°C (decomp., benzene) (mp 233°C (decomp., benzene) [8]). IR spectrum, ν, cm^{-1}: 3410 (NH). ^{1}H NMR spectrum was identical to the published one [8].

6-Methyl-1*H*-1,2,5,7-tetraazacyclopenta[*cd*]phenalene (2b). Yield 0.108 g (52%) (method A), 0.085 g (41%) (method B); mp 231-233°C (decomp., benzene) (mp 231°C (decomp., benzene) [8]). IR spectrum, ν, cm^{-1}: 3488 (NH). ^{1}H NMR spectrum was identical to the published one [8].

6-Phenyl-1*H*-1,2,5,7-tetraazacyclopenta[*cd*]phenalene (2c). Yield 0.124 g (46%) (method A), 0.100 g (37%) (method B); mp 258-260°C (decomp., benzene). IR spectrum, ν, cm^{-1}: 3407 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.18 (1H, d, *J* = 9.9, H-9); 7.49-7.55 (3H, m, H-3,4,5 Ph); 7.94 (1H, d, *J* = 9.9, H-8); 8.33 (1H, d, *J* = 9.5, H-4); 8.49-8.51 (2H, m, H-2,6 Ph); 9.22 (1H, d, *J* = 9.5, H-3); 12.70 (1H, br. s, NH). Found, %: C 75.62; H 3.68; N 20.70. $C_{17}H_{10}N_4$. Calculated, %: C 75.54; H 3.73; N 20.73.

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