

SHORT
COMMUNICATIONS

Formylation of Perimidine Derivatives in a System 1,3,5-Triazine–Polyphosphoric Acid

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Formerly [1] formylation of perimidines **I** was reported to be performed by Vilsmeier reaction, but the yield of the corresponding perimidine-6(7)-carbaldehydes **IV** was from 1 to 7%. We developed a new method of compounds **I** formylation based on their reaction with 1,3,5-triazine (**II**) (see Scheme).

The application of compound **II** in the role of formylating agent is well known [2]. In the classical version the reaction is carried out without catalyst or in the presence of Lewis acids. We demonstrated that under these conditions the perimidine formylation did not occur. Therefore another combination of reagents was used as formylating agent: 3-fold excess of 1,3,5-triazazine **II** in 80% polyphosphoric acid (PPA) at 55–60°C. The yield of aldehydes **IV** under these conditions was 83–91%.

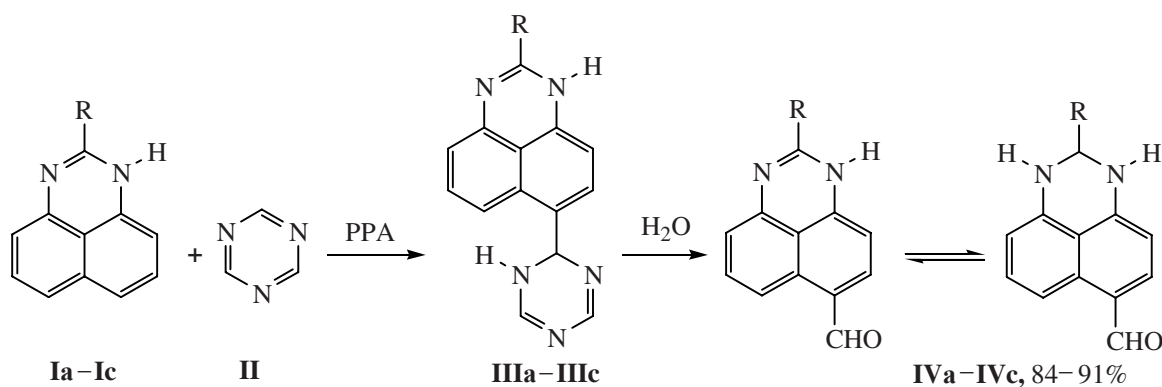
Formylation of perimidines in a system 1,3,5-triazazine–PPA. General procedure. A mixture of 1 mmol of perimidine **I**, 0.243 g (3 mmol) of 1,3,5-triazazine, and

4. g of PPA was stirred at 55–60°C for 1 h. Then the reaction mixture was poured into 50 ml of water, alkalinized with ammonia solution, and extracted with ethyl acetate (3 × 80 ml), and the extract was evaporated.

Perimidine-6(7)-carbaldehyde (IVa). Yield 0.178 g (91%), mp 212–214°C (from acetic acid) (212–214°C [1]). ¹H NMR spectrum (CDCl₃), δ, ppm: 6.57 br.s (1H, H⁹), 6.91 br.s (1H, H⁴), 7.50 s (1H, H²), 7.54 d.d (1H, H⁸, J₈₇ 8.9, J₈₉ 8.3 Hz), 7.68 d (1H, H⁵, J₅₄ 8.1 Hz), 8.77 d.d (1H, H⁷, J₇₈ 8.9 Hz), 9.97 s (1H, CHO). Found, %: C 73.31; H 4.01; N 14.03. C₁₂H₈N₂O. Calculated, %: C 73.45; H 4.11; N 14.28.

2-Methylperimidine-6(7)-carbaldehyde (IVb). Yield 0.187 g (89%), mp 196–198°C (from octane). (196–198°C [1]). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.28 s (3H, CH₃), 6.57 br.d (1H, H⁴, J₄₅ 7.7 Hz), 6.84 br.d (1H, H⁹, J₉₈ 7.9 Hz), 7.51 d.d (1H, H⁸, J₈₇ 8.7,

Scheme.



R = H (a), Me (b), Ph (c).

J_{89} 7.9 Hz), 7.67 d (1H, H⁵, J_{54} 7.7 Hz), 8.72 d (1H, H⁷, J_{78} 8.7 Hz), 9.95 s (1H, CHO). Found, %: C 74.05; H 4.50; N 13.19. C₁₃H₂₀N₂O. Calculated, %: C 74.26; H 4.80; N 13.33.

2-Phenylperimidine-6(7)-carbaldehyde (IVc).

Yield 0.226 g (83%), mp 238–239°C (from benzene). ¹H NMR spectrum (CDCl₃), δ, ppm: 6.52 br.s (1H, H⁹), 6.82 br.s (1H, H⁴), 7.50 s (1H, H²), 7.55 m (4H, H⁸, H^{mp}_{Ph}), 7.72 d (1H, H⁵, J_{54} 8.1 Hz), 8.93 d (2H, H^o_{Ph}, J_{54} 7.2 Hz), 8.78 d.d (1H, H⁷, J_{78} 8.9 Hz), 10.03 s (1H, 6-CHO). Found, %: C 79.22; H 4.49; N 10.34. C₁₈H₁₂N₂O. Calculated, %: C 79.40; H 4.44; N 10.29.

NMR spectra were registered on a spectrometer Bruker WP-200 (200 MHz) using TMS as internal reference. The reaction progress was monitored and the homogeneity of compounds synthesized was checked by TLC on Silufol UV-254 plates, eluent ethyl acetate.

REFERENCES

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