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AMMONIUM NITRATE IN ACETIC ACID, AN EFFICIENT REAGENT FOR THE NITRATION OF PERIMIDINES AND THE ONE-POT SYNTHESIS OF 6(7)-AMINOPERIMIDINES

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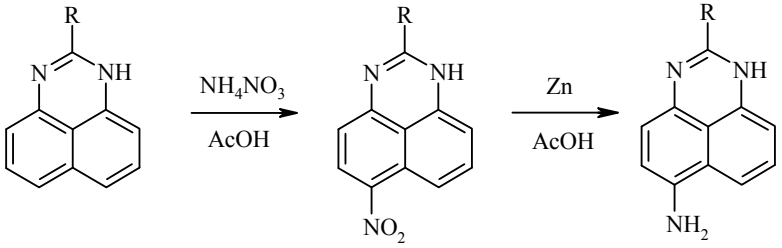
Nitro compounds are important intermediates in the synthesis of differently functionalized arenes. We have previously proposed a method for the nitration of perimidines using nitric acid (d 1.5) in acetic acid [1]. The product yields for mononitration at a *peri* position (the 6(7)-nitroperimidines **2** are 8% for perimidine **1a** and 46% for the 2-methylperimidine (**1b**). We have proposed that the low yield is linked to an incorrect choice of nitrating conditions. It was found that refluxing the perimidines **1a-c** (1 mmol) with NH_4NO_3 (0.12 g, 1.5 mmol), and glacial acetic acid (25 g) for 5-10 min (TLC monitoring), cooling, neutralization of the reaction mixture to pH ~ 8 with sodium carbonate solution, and filtration of the precipitate obtained gave the 6(7)-nitroperimidines **2a-c** in 76-83% yields.



1a–c **2a–c** **3a–c**

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

Treatment of the reaction mixture before neutralization with zinc powder (0.32 g, 5 mmol), refluxing for 30 min (TLC monitoring), filtration to remove the excess zinc, neutralization of the mother liquor, and filtration gave the corresponding 6(7)-aminoperimidines **3a-c** in 62-69% yields.

Dedicated to the anniversary of L. I. Belen'kii.

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Finally, it should be noted that only traces of 4(9)-nitroperimidines are formed in the course of the nitration using the proposed system of reagents.

^{1}H NMR spectra were taken on a Bruker WP-200 instrument (200 MHz) using DMSO-d_6 with TMS as internal standard. Monitoring of the reaction course and the purity of the synthesized compounds was carried out on Silufol UV-254 plates in the solvent system ethyl acetate and ethyl acetate–alcohol (1:1).

6(7)-Nitroperimidine (2a). Yield 0.177 g (83%); mp 240-242ºC (water) (mp 240-241°C [1]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.45 (1H, d, *J* = 8.2, H-9(4)); 6.72 (1H, d, *J* = 8.2, H-4(9)); 7.27 (1H, dd, *J* = 8.5, *J* = 8.2, H-8(5)); 7.62 (1H, s H-2); 8.03 (1H, d, *J* = 8.3, H-5(8)); 8.08 (1H, d, *J* = 8.5, H-7(6)); 10.58 (1H, br. s, NH). Found, %: C 62.15; H 3.26; N 19.66. $C_{11}H_7N_3O_2$. Calculated, %: C 61.97; H 3.31; N 19.71.

2-Methyl-6(7)-nitroperimidine (2b). Yield 0.184 g (81%); mp 233-235ºC (aqueous alcohol) (230-235ºC [1]); The ^{1}H NMR spectrum was similar to that given in [1].

2-Phenyl-6(7)-nitroperimidine (2c). Yield 0.220 g (76%); mp 207-209ºC (aqueous alcohol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.47 (1H, d, *J* = 8.2, H-9(4)); 6.74 (1H, d, *J* = 8.3, H-4(9)); 7.55 (4H, m, H-8(5), 3,4,5-Ph); 8.02 (1H, d, *J* = 8.3, H-5(8)); 8.07 (1H, d, *J* = 8.5, H-7(6)); 8.93 (2H, d, *J* = 7.3, 2,6-Ph); 10.55 (1H, br. s, NH). Found, %: C 70.71; H 3.78; N 14.54. $C_{17}H_{11}N_3O_2$. Calculated, %: C 70.58; H 3.83; N 14.52.

6(7)-Aminoperimidine (3a). Yield 0.126 g (69%); mp 261-262ºC (ethyl acetate) (mp 261-262ºC [2]). The ^{1}H NMR spectrum was similar to that given in [2].

6(7)-Amino-2-methylperimidine (3b). Yield 0.132 g (67%); mp 274-275ºC (ethyl acetate) (mp 274-275ºC [2]). Dihydrochloride mp > 310ºC (mp > 310ºC [3]). The ^{1}H NMR spectrum was similar to that given in [2].

6(7)-Amino-2-phenylperimidine (3c). Yield 0.161 g (62%); mp 288-289ºC (ethyl acetate) (mp 288-289ºC [4]). The ^{1}H NMR spectrum is similar to that given in [4].

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