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REDUCTIVE CYCLIZATION OF N-(2,4-DINITROPHENYL)PYRIDINIUM CHLORIDE BY TIN(II) CHLORIDE

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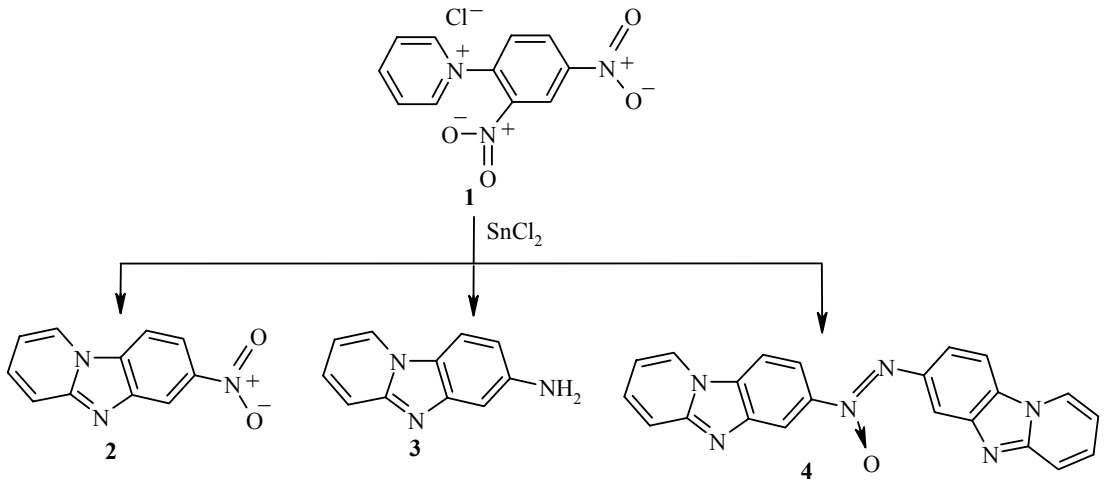
Reactions of N-(2,4-dinitrophenyl)pyridinium chloride with various nucleophilic agents are widely used in organic synthesis [1, 2].

We propose to use the reductive cyclization of N-(2,4-dinitrophenyl)pyridinium chloride (**1**) by treatment with $SnCl_2$ for synthesis of pyrido[1,2-*a*][1,3]benzimidazoles, which are potential biologically active drugs [3, 4]. The reaction was conducted at a temperature of 20°C. Different end products are formed depending on the process conditions, which is explained by the higher reactivity of the *ortho* nitro group compared with the *para* nitro group in compound **1**.



When the reaction is conducted in a homogeneous medium with mole ratio **1**:$SnCl_2$ 1:3, reduction of only the *ortho* nitro group and formation of 7-nitropyrido[1,2-*a*][1,3]benzimidazole (**2**) occur. Reduction of the *para* nitro group was also observed when the amount of $SnCl_2$ was doubled. As a result, we obtained 7-aminopyrido[1,2-*a*][1,3]benzimidazole (**3**). Carrying out the cyclization in a heterogeneous medium with a

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ratio **1**:$SnCl_2$ of 1:6 leads to accumulation in the reaction mass of products of incomplete reduction of the *para* nitro group (nitroso- and hydroxylamino derivatives) and condensation of the latter to form 1,2-dipyrido[1,2-*a*]-[1,3]benzimidazol-7-yldiazene oxide (**4**).

Thus, by changing the reaction conditions for reaction of N-(2,4-dinitrophenyl)pyridinium chloride with $SnCl_2$, we can obtain different pyrido[1,2-*a*][1,3]benzimidazoles.

7-Nitropyrido[1,2-*a*][1,3]benzimidazole (2). Solutions of N-(2,4-dinitrophenyl)pyridinium chloride (5 g, 0.0178 mol) in ethyl alcohol (20 ml) and $SnCl_2 \cdot 2H_2O$ (12 g, 0.0533 mol) in 3% hydrochloric acid (20 ml) were added simultaneously to a three-necked flask with rapid stirring. After 10 min, the reaction mixture was alkalinized with 25% aqueous solution of ammonia to pH 7-8 and extracted with several portions of chloroform (Σ = 200 ml). After distilling off chloroform, we obtained 3.44 g (91% yield) of 7-nitropyrido-[1,2-*a*][1,3]benzimidazole; mp 290-292°C. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz), δ, ppm (*J*, Hz): 9.13 (1H, d, *J* = 7, H-1); 8.64 (1H, d, *J* = 1.5, H-6); 8.50 (1H, d, *J* = 8.5, H-9); 8.20 (1H, dd, *J* = 8.5, *J* = 2, H-8); 7.78 (1H, d, *J* = 9, H-4); 7.67 (1H, t, *J* = 7.5, H-3); 7.11 (1H, t, *J* = 7, H-2). Mass spectrum, *m*/*z* (I_{rel}, %): 213 $[M]^+$ (100), 183 (4), 167 (91), 155 (14), 140 (28), 78 (12). Found, %: C 61.6; H 3.1; N 20.0. $C_{11}H_7N_3O_2$. Calculated, %: C 62.0; H 3.3; N 19.7.

7-Aminopyrido[1,2-*a*[[1,3]benzimidazole (3). Solution of N-(2,4-dinitrophenyl)pyridinium chloride (5 g, 0.0178 mol) in ethyl alcohol (20 ml) was added to solution of $SnCl_2 \cdot 2H_2O$ (24 g, 0.107 mol) in 3% hydrochloric acid (20 ml). After 10 min, the reaction mixture was alkalinized with 25% aqueous solution of ammonia to pH 7-8 and extracted with several portions of chloroform (Σ = 200 ml). After distilling off chloroform, we obtained 3.16 g (97% yield) of 7-aminopyrido[1,2-*a*][1,3]benzimidazole; mp 180-182°C. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz), δ, ppm (*J*, Hz): 8.82 (1H, d, *J* = 7, H-1); 7.9 (1H, d, *J* = 9.5, H-9); 7.47 (1H, d, *J* = 10, H-4); 7.38 (1H, t, *J* = 7.5, H-3); 6.85 (1H, t, *J* = 7, H-2); 6.82 (1H, d, *J* = 1.5, H-6); 6.7 (1H, dd, *J* = 10, *J* = 2, H-8); 5.1 (2H, s, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 183 $[M]^+$ (100), 166 (4), 155 (15), 78 (12). Found, %: C 71.9; H 4.5; N 23.3. $C_{11}H_9N_3$. Calculated, %: C 72.1; H 4.9; N 23.0.

1,2-Dipyrido[1,2-*a*][1,3]benzimidazol-7-yldiazene Oxide (4). Solution of $SnCl_2 \cdot 2H_2O$ (24 g, 0.107 mol) in 3% hydrochloric acid (20 ml) was added to emulsion of N-(2,4-dinitrophenyl)pyridinium chloride (5 g, 0.0178 mol) in ethyl alcohol (10 ml). After 10 min, the reaction mixture was alkalinized with 25% aqueous solution of ammonia to pH 7-8 and was extracted with several portions of chloroform (Σ = 200 ml). After distilling off chloroform, we obtained 2.32 g (69% yield) of 1,2-dipyrido[1,2-*a*][1,3]-benzimidazol-7-yldiazene oxide; mp >300°C. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz), δ, ppm (*J*, Hz): 9.13 (1H, d, *J* = 6.8, H-1); 9.05 (1H, d, *J* = 6.8, H-1'); 8.88 (1H, d, *J* = 1.5, H-6); 8.73 (1H, d, *J* = 1.5, H-6'); 8.49 (1H, dd, *J* = 8.8, *J* = 1.5, H-8); 8.42 (1H, dd, *J* = 8.8, *J* = 1.5, H-8'); 8.36 (1H, d, *J* = 8.8, H-9); 8.05 (1H, d, *J* = 8.8, H-9'); 7.75 (1H, d, *J* = 9.3, H-4); 7.70 (1H, d, *J* = 9.5, H-4'); 7.65 (1H, t, *J* = 8, H-3); 7.56 (1H, t, *J* = 8.3, H-3'); 7.08 (1H, t, *J* = 7.5, H-2); 7.04 (1H, t, *J* = 7.8, H-2'). Mass spectrum, *m*/*z* (I_{rel}, %): 378 $[M]^+$ (30), 197 (5), 181 (87), 167 (100), 155 (38), 78 (39), 44 (57). Found, %: C 70.6; H 3.6; N 22.7. $C_{22}H_{14}N_6O$. Calculated, %: C 69.84; H 3.7; N 22.2.

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