SYNTHESIS OF 2,4,5,6-TETRAHYDRO-PYRROLO[1,2-*c*][1,2,3]TRIAZOLIO-5-OLATE

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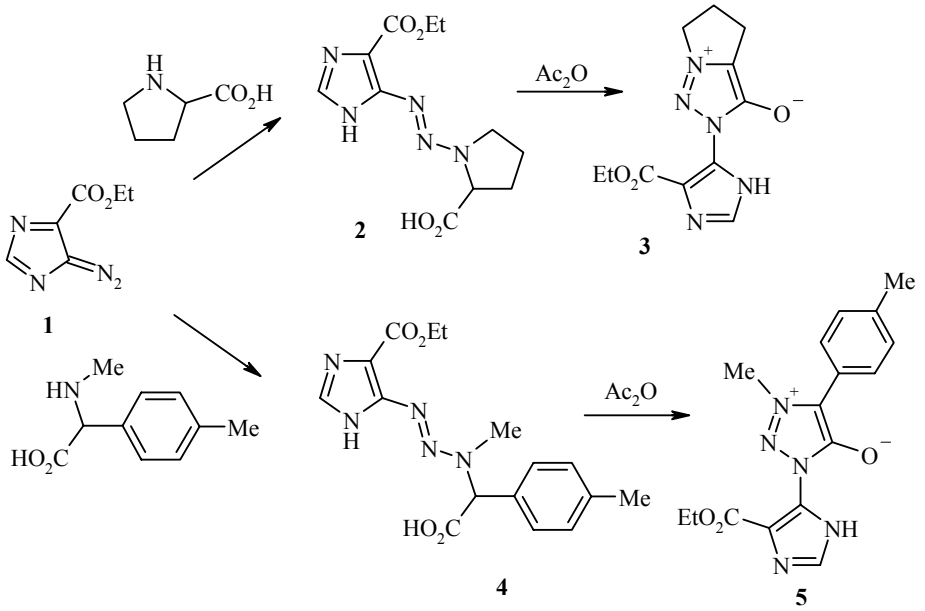
In continuing studies on condensed zwitterionic derivatives of 1,2,3-triazole [1-2], we proposed a simple and convenient method for synthesis of 1-imidazolylpyrrolo[1,2-*c*][1,2,3]triazolio-5-olate. By means of azo coupling of 5-diazoimidazole **1** with proline, we obtained triazene **2** [3], isolated as two isomers relative to the N=N bond.



The reaction of intramolecular acylation in acetic anhydride leads to formation of pyrrolo[1,2-*c*][1,2,3]triazolio-5-olate **3**. Cyclization of triazene **4**, obtained from *p*-tolyl-N-methylglycine and imidazole **1**, leads to the zwitterionic triazole **5**.

The ^{1}H NMR spectra were taken in DMSO-d6, internal standard TMS.

1-(4-Ethoxycarbonylimidazol-1-yl)-2,4,5,6-tetrahydropyrrolo[1,2-*c*][1,2,3]triazolio-5-olate (3). A solution of sodium nitrite (0.186 g, 2.7 mmol) in water (10 ml) was added dropwise at 0-5°C with stirring to a solution of the ethyl ester of 5-aminoimidazole-4-carboxylic acid (0.21 g, 1.1 mmol) in 0.1 N HCl (27 ml). The end of the reaction was monitored using iodine/starch paper. The yellow solution of diazo compound **1** obtained

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was added to a solution of proline (0.287 g, 1.1 mmol) in 1 N NaOH (10 ml), with cooling down to 0-5°C. The solution became dark red; it was acidified down to pH 4 with concentrated HCl, and the precipitate formed was filtered out. The triazene **2** obtained was dissolved in pyridine (5 ml) and Ac_2O (5 ml), stirred for 15 h at ~20°C, and then poured over ice. The precipitate formed was filtered out and recrystallized from alcohol, obtaining compound **3**. Yield 0.225 g (78%); mp 132°C. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 13.5 (1H, br. s, NH); 7.95 (1H, s, CH); 4.37 (2H, t, *J* = 7.5, CH_2); 4.15 (2H, q, *J* = 7.1, OCH_2); 2.78 (2H, t, *J* = 7.2, CH_2); 2.59 (2H, tt, *J* = 7.5, *J* = 7.2, CH_2); 1.15 (3H, t, *J* = 7.1 CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 263 (57), 218 (10), 191 (23), 167 (100). Found, %: N 26.8. $C_{11}H_{13}N_5O_3$. Calculated, %: N 26.60.

1-(4-Ethoxycarbonylimidazol-1-yl)-3-methyl-4-*p*-tolyl[1,2,3]triazolio-5-olate (5) was obtained similarly from *p*-tolyl-N-methylglycine. Yield 0.295 g (82%); mp 168°C. ^{1}H NMR spectrum (250 MHz), δ, ppm (*J*, Hz): 13.8 (1H, br. s, NH); 7.79 (1H, s, CH); 7.60 (2H, d, *J* = 7.9, ArH); 7.25 (2H, d, *J* = 7.9, ArH); 4.20 (2H, q, *J* = 6.7, OCH_2); 4.13 (3H, s, CH_3); 2.39 (3H, s, CH_3); 1.17 (3H, t, *J* = 6.7, CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 327 (26), 281 (4), 255 (7), 217 (2), 167 (4), 155 (9). Found, %: N 21.6. $C_{16}H_{17}N_5O_3$. Calculated, %: N 21.39.

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