SYNTHESIS OF CONDENSED MESOIONIC HETEROCYCLES. INTRAMOLECULAR CYCLIZATION OF 3-ACETONYL(PHENACYL)-1,2,3-TRIAZOLIUM-5-OLATES

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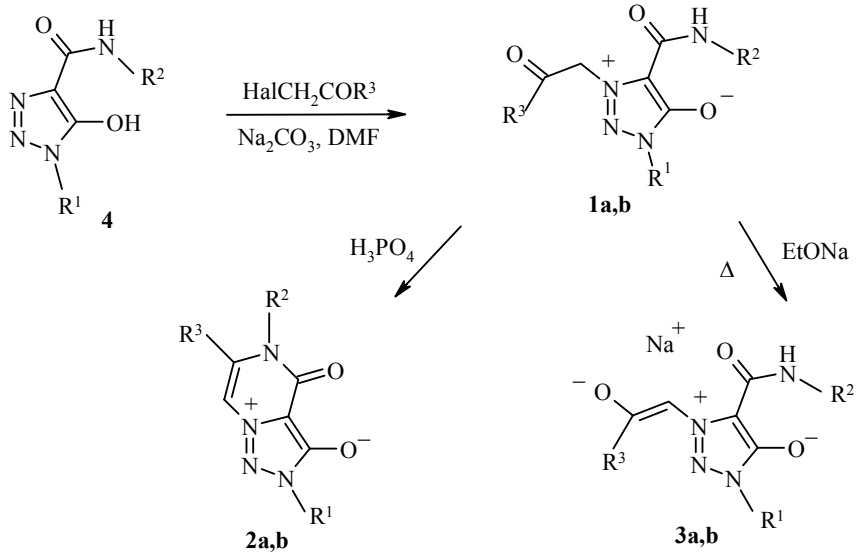
There are several known approaches to synthesis of monocyclic mesoionic heterocycles [1]. At the same time, the number of examples of mesoionic condensed zwitterionic heterocycles is quite limited [2]. Earlier we proposed a novel method for synthesis of zwitterionic 1,2,3-triazolopyrazines and -triazepines [3, 4]. In this work, we have shown that in contrast to 3-cyanomethyl-1,2,3-triazolium-5-olates [3], in the presence of basic reagents 3-acetonyl(phenacyl)-1,2,3-triazolium-5-olates **1a,b** do not undergo ring closure to form triazolopyrazines **2** but rather form the corresponding enolates **3a,b**. We have observed that upon treatment with polyphosphoric acid, intramolecular condensation of the carbonyl and amide moieties of the triazole molecule **1** occurs and [1,2,3]triazolo[1,5-*a*]pyrazines **2a,b** are formed. Under similar conditions, 3-cyanomethyl-1,2,3-triazolium-5-olates are converted to the starting 5-hydroxy-1,2,3-triazoles **4**. Thus we propose a novel method for synthesis of mesionic [1,2,3]triazolo[1,5-*a*]pyrazines.



1–3 a $R^1 = R^2 = C_6H_4OMe$-4, R^3 = Me, **b** $R^1 = N{=}CHC_6H_4Me$-4, R^2 = Me, $R^3 = C_6H_4Cl$-4

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The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 (400 MHz and 100 MHz) in DMSO-d_6, internal standard TMS. The mass spectra were recorded on a MAT11 (electron impact, 70 eV).

6-Methyl-2,5-di(4-methoxyphenyl)-4-oxo-2H-[1,2,3]triazolo[1,5-*a*]pyrazinium-3-olate (2a). Compound **1a** (0.20 g, 0.6 mmol) [5] in orthophosphoric acid (5 ml) was heated at 100°C in a glycerol bath until completely dissolved and then for another 3 h. The solution was cooled down and diluted with water (25 ml) at 0°C, the precipitate was filtered out and the reaction product was crystallized from alcohol. Yield 0.16 (80%); mp 287-288°C. Mass spectrum, *m*/*z* (I_{rel}, %): 378 $[M]^+$ (42). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.03 (2H, d, *J* = 7.9, ArH); 7.50 (4H, d, *J* = 7.9, ArH); 7.38 (4H, d, *J* = 7.7, ArH); 7.03 (1H, s, H-7); 6.82 (1H, d, *J* = 7.7, ArH); 3.98 (3H, s, OMe); 3.92 (3H, s, OMe); 2.42 (3H, s, Me). Found, %: N 14.59. $C_{20}H_{18}N_4O_4$. Calculated, %: N 14.81.

6-(4-Chlorophenyl)-5-methyl-2-(4-methylbenzylideneamino)-4-oxo-2H-[1,2,3]triazolo[1,5-*a*]-pyrazinium-3-olate (2b) was obtained analogously from compound **1b** [4]. Yield 88%; mp 226-230°C. Mass spectrum, *m*/*z* (I_{rel}, %): 395 (14), 393 $[M]^+$ (43). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 7.29 (2H, d, *J* = 8.1, ArH); 7.47 (1H, s, H-7); 7.57 (4H, t, *J* = 8.8, ArH); 7.78 (2H, d, *J* = 8.1, ArH); 9.35 (1H, s, N=CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 21.2 (q, *J* = 124.0, CH_3), 31.7 (q, *J* = 142.0, NCH_3), 105.4 (d, *J* = 201.6, $C_{(7)}$), 108.6 (d, *J* = 4.0, $C_{(3a)}$), 128.4 (d, *J* = 169.0, C_{arom}), 129.9 (d, *J* = 165.6, C_{arom}), 129.7 (m, C_{arom}), 129.9 (m, C_{arom}), 130.0 (d, *J* = 167.7, C_{arom}), 131.1 (d, *J* = 168.7, C_{arom}), 135.1 (m, C_{arom}), 140.2 (m, $C_{(6)}$), 142.4 (m, C_{arom}), 150.2 (s, $C_{(3)}$), 153.4 (d, *J* = 166.0, N=CH), 154.2 (s, $C_{(4)}$). Found, %: C 60.85; H 4.01; N 17.45. $C_{20}H_{16}ClN_5O_2$. Calculated, %: C 61.00; H 4.09; N 17.78.

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