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REARRANGEMENT OF 1-AMINOIMIDAZOLIDINE-4,5-TRIONES TO 5-OXO-4,5-DIHYDRO-1,2,4-TRIAZOLE-3-CARBOXYLIC ACID

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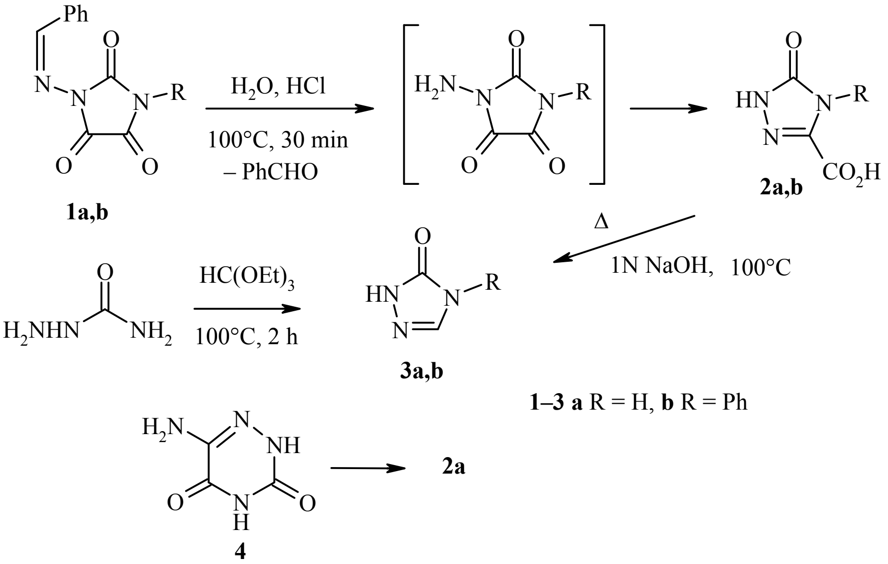
We have found that refluxing an aqueous suspension of compound **1a** in the presence of hydrochloric acid and steam distillation of the aldehyde evolved gave 5-oxo-1,2,4-triazole-3-carboxylic acid **2a** in 70% yield. Acid **2a** was also prepared by us from 6-amino-2,3,4,5-tetrahydro-1,2,4-triazine-3,5-dione (**4**) by the method reported in the literature [1].



Reaction of compound **1a** to **2a** includes a previously unreported rearrangement of 1-aminoimidazolidine-2,4,5-trione to 5-oxo-4,5-dihydro-1,2,4-triazole-3-carboxylic acid. Acid **2a** can be efficiently used in the synthesis of novel 1,2,4-triazole derivatives which include substances with a broad spectrum of biological activity [2, 3].

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When acid **2a** is heated to its melting point decarboxylation occurs to give 1,2,4-triazol-5-one **3a**. It was interesting to note that refluxing the N-phenylimidazolone **1b** in dilute hydrochloric acid gave the 4-phenyl-1,2,4-triazole **3b** as the decarboxylation product of the intermediate acid **2b**. Its structure was confirmed by the known reaction of semicarbazide with orthoformate [4].

^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX-400 instrument (400 and 100 MHz respectively) using DMSO-d$_6$ with TMS as internal standard. Mass spectra for the compound prepared were taken on a Varian MAT 311A spectrometer with an accelerating voltage of 3 kV and ionization energy of 70 eV and with direct introduction of the sample into the ion source.

The synthesis of the 3-(R-benzylideneamino)imidazolidine-2,4,5-triones **1a,b** was carried out by the method reported in [3].

5-Oxo-4,5-dihydro-1,2,4-triazole-3-carboxylic Acid (2a). A suspension of compound **1a** (0.088 mg, 0.4 mmol) in water (10 ml) and conc. HCl (1 ml) were refluxed with distillation of water and benzaldehyde as an azeotrope to full solution of the precipitate (25-30 min). The reaction product was concentrated *in vacuo*. The residue was filtered off. Yield 0.035 mg (67%); mp 234-235ºC (decomp.) (mp 235-237ºC [1]). ^{1}H NMR spectrum, δ, ppm: 13.50 (1H, br. s, OH); 11.92 (2H, s, $(NH)_2$). ^{13}C NMR spectrum, δ, ppm: 158.1 (COOH); 155.0 (C-3); 138.9 (C-5). Mass spectrum, *m/z* (I_{rel}, %): 129 $[M]^+$ (21), 85 $[M-CO_2]^+$ (100). Found, %: C 27.5; H 2.5; N 32.9. $C_3H_3N_3O_3$. Calculated, %: C 27.9; H 2.3; N 32.5.

Compound 2b was prepared from compound **1b**.

2,4-Dihydro-1,2,4-triazol-3-one (3a). Compound **2a** (0.129 g, 1.0 mmol) was heated at 235-240ºC for 3-5 min. Cooling gave compound **3a** (0.052 g, 63%); mp 234-235ºC. ^{1}H NMR spectrum, δ, ppm: 11.18 (1H, br. s, NH); 7.50 (1H, s, H-5). Mass spectrum, *m/z* (I_{rel}, %): 85 $[M]^+$ (52). Found, %: C 28.0; H 3.6; N 49.3. $C_2H_3N_3O$. Calculated, %: C 28.2; H 3.5; N 49.4

Phenyl-1H-1,2,4-triazol-5-one (3b) was prepared from compound **1b**. Yield 35%; mp 179-181ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.88 (1H, s, NH); 8.28 (1H, d, *J* = 1.5, H-5); 7.68 (2H, d, *J* = 8.3, H Ar); 7.46 (2H, t, *J* = 7.9, H Ar); 7.31 (1H, t, *J* = 7.5, ArH). Mass spectrum (EI), *m/z* (I_{rel}, %): 119 $[M]^+$ (21), 119 $[M-OCN]^+$ (21). Found, %: C 59.2; H 4.2; N 25.8. $C_8H_7N_3O$. Calculated, %: C 59.6; H 4.3; N 26.0.

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