Transformation of 1-(Benzylideneamino)imidazolidinetrione to Methyl 5-Hydroxy-1,2,4-triazole-3-carboxylate (1)

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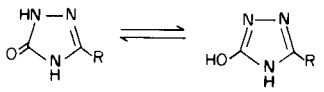
During the course of another investigation it was discovered that treatment of 1-(benzylideneamino)imidazolidinetrione (**1**) with methanol containing hydrochloric acid gave a product of empirical formula $C_4H_5N_3O_3$. The purpose of this communication is to report the identity of this product and to demonstrate the novel transformation of **1** into methyl 5-hydroxy-1,2,4-triazole-3-carboxylate (**2**).

The infrared spectrum of this product was characterized by a band at 5.73 μ while the nmr spectrum of the product exhibited a singlet at 3.87 ppm and a broad exchangeable singlet at 12.25 ppm in the relative ratio of 3:2. Since the 3.87 ppm signal appears in the region where the CH_3O function normally is evident and the 5.73 μ band in the infrared is attributable to an ester carbonyl, the product was tentatively assigned the 1,2,4-triazole-3-carboxylate structure **2**, the empirical formula of which is $C_4H_5N_3O_3$.



(a) (b)

This structural assignment was verified by independent synthesis of ester **2** from the known acid **3**. The acid was prepared by a slight modification of the literature method in a two step sequence originating with aminoguanidine bicarbonate (**4**) and oxalic acid (**5**) (2,3,4). Treatment of acid **3** with methanol and sulfuric acid gave the ester **2**, the infrared spectrum of which was identical to that of the product derived from **1**. Thus the product of empirical formula $C_4H_5N_3O_3$ was shown to be the 1,2,4-triazole **2**.

Subsequently it was shown that the imidazolidinetrione **1** could be converted in methanol-concentrated hydrochloric acid to the ester **2** in 79% yield.

Presumably in the transformation of **1** → **2**, trione **1** is hydrolyzed to the amine **6** which is converted to **7** with methanolic hydrochloric acid. Ring opening of **7** gives rise to **8** which recyclizes to the ester **2**.

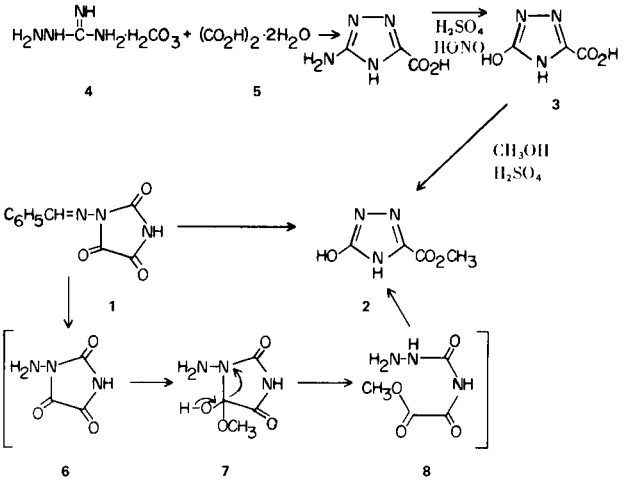
This is apparently the first reported instance of transformation of a 1-(benzylideneamino)imidazolidinetrione to an ester of a 1,2,4-triazole-3-carboxylic acid.

EXPERIMENTAL

Melting points were taken in a Mel-Temp apparatus in open capillary tubes and are uncorrected. The nuclear magnetic resonance spectra were taken on a Varian A-60A instrument and were compared with TMS as an internal standard. Infrared spectra were determined as Nujol Mulls on a Perkin-Elmer 137B spectrophotometer.

Methyl 5-Hydroxy-1,2,4-triazole-3-carboxylate (**2**) from **1**.

A mixture of 100 g. (0.461 mole) of **1**, 1000 ml. of methanol, and 100 ml. of concentrated hydrochloric acid was stirred and refluxed for 5.0 hours. The mixture was cooled in an ice bath and filtered to give 52.0 g. (79%) of the product, m.p. 238-240° (eff.). Recrystallization from water gave the analytical sample, m.p. 235-237° (eff.); nmr (DMSO-d_6) δ: 3.87 (s, 3, CH_3O); 12.25 (broad s, 2, N-H); infrared μ: 5.73 (C=O, ester); 5.84-5.98 (C=O, amide); 6.42 (C=N); 8.30 (C-O-C ester).



Anal. Calcd. for $C_4H_5N_3O_3$: C, 33.57; H, 3.52; N, 29.37. Found: C, 33.55; H, 3.60; N, 29.49.

The infrared spectrum of the product was identical to that of the material obtained by the esterification of acid **3**.

5-Hydroxy-1,2,4-triazole-3-carboxylic Acid (**3**).

Diazotization of 5-amino-1,2,4-triazole-3-carboxylic acid (**3**) and treatment of the resulting filtered diazonium salt with 25% sulfuric acid by the previously described method (2,4) gave a 54%

yield of **3**. The analytical sample, m.p. 208-210° (eff.), was obtained by recrystallization from water; literature (2) m.p. 205° (dec).

Anal. Calcd. for $C_3H_3N_3O_3$: C, 27.91; H, 2.34; N, 32.56. Found: C, 28.18; H, 2.43; N, 32.97.

Methyl 5-Hydroxy-1,2,4-triazole-3-carboxylate (**2**) from **3**.

To a suspension of 1.0 g. (0.0077 mole) of **3** in 50 ml. of methanol was added cautiously 3.0 ml. of concentrated sulfuric acid. The mixture was stirred and refluxed for 15 hours, cooled in an ice bath, and filtered to give 0.87 g. (79%) of the product. Recrystallization from water gave a sample which melted at 235.5-237° (eff.).

Acknowledgment.

Thanks are expressed to Mr. Fred Abbott and Mr. Alexander Winterstein for synthesis of chemical intermediates, Miss Daria Stiles and Mr. Warren Smith for the microanalysis, and Mrs. Patricia Curtis and Mrs. Connie Lloyd for the nmr spectra.

REFERENCES

(1) Although infrared spectral evidence indicates the 1,2,4-triazoles described herein exist in the 5-oxo (lactam) form (a), these compounds will be referred to as the tautomeric 5-hydroxy-1,2,4-triazoles (b) for the sake of convenience.

(2) W. Manchot, *Ber.*, 31, 2445 (1898).

(3) G. Cipens, *Metody Poluch. Khim. Reaktivov Prep.*, 14, 9 (1966); thru *Chem. Abstr.*, 67: 64306^{v} (1967).

(4) G. Cipens, *Metody Poluch. Khim. Reaktivov Prep.*, 14, 119 (1966); thru *Chem. Abstr.*, 67, 64307^{w} (1967).