

Thomas J. Schwan (1) and Timothy J. Sanford (2)

Scientific Affairs Department, Norwich Pharmacal Company Division of Morton-Norwich Products, Inc., Norwich, New York 13815

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The dehydrogenation of the alleged hexahydro-1,2,4-triazine-3,6-dione, recently reassigned the 3-amino-2,4-imidazolidinedione structure, gives upon reaction with bromine water or sodium hypobromite bis[3-(2,4-dioxoimidazolidinyl)]diazene instead of tetrahydro-1,2,4-triazine-3,6-dione as reported previously in the literature.

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The alleged hexahydro-1,2,4-triazine-3,6-dione (**1**) was first reported by Hoffman, *et al.*, (3) in 1952 and subsequently by Gante and Lautsch (4) twelve years later.

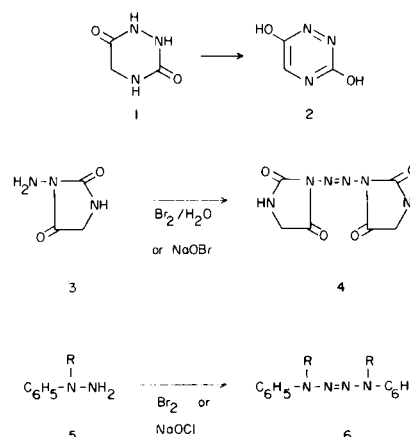
Following Hoffman's original publication, two reports of the dehydrogenation of **1** to **2** appeared. Grundmann, *et al.*, (5) reacted **1** with bromine water and obtained a compound that melted at 266° and gave an elemental analysis corresponding to a molecular formula of C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>2</sub>. Gante (6) reported that the transformation of **1** to **2** was effected with sodium hypobromite and reported a melting point of 241-243° for the product.

Recently, the structural assignment of **1** as a triazine-3,6-dione has come under question. Gut, *et al.*, (7) and Dain (8), relying mainly on infrared spectral evidence, have shown that the alleged triazine **1** prepared by Hoffman (3) as well as Gante and Lautsch (4) is in reality 3-amino-2,4-imidazolidinedione (**3**). Infrared spectral evidence accumulated on this product which was prepared in these laboratories by another method (9) corroborates these findings. This structural assignment raises the question as to the nature of the dehydrogenation product(s) of **3** reported previously (5,6).

We have repeated the procedures of Grundmann, *et al.*, (5) and Gante (6) in these laboratories and found that the same product is formed in each case. The nmr spectrum of this product is characterized by a singlet at 3.95 δ and a broad exchangeable multiplet centered at 7.97 δ in a relative ratio of 2:1. The former signal is attributable to the 5-CH<sub>2</sub> of the imidazolidine ring as this function in the nmr spectrum of **3** appears at 3.70 δ. The 7.97 δ signal in the dehydrogenation product of **3** is ascribed to the imidazolidine 1-NH function.

The infrared spectrum of the product is characterized by absorption in the 5.55 to 5.85 μ region, indicating the imidazolidinedione ring had remained intact during the transformation.

This information, along with the absence of a HC = signal in the nmr spectrum of the dehydrogenation product of **3**, prompts us to assign the previously unreported diazene structure **4** to this material. This structure of molecular formula C<sub>6</sub>H<sub>6</sub>N<sub>6</sub>O<sub>4</sub> is consistent with the



analytical data obtained in the aforementioned dehydrogenations of the alleged triazine **1**. Furthermore, the mass spectrum of the product is characterized by a molecular ion of 226 which is consistent with the assigned structure of **4**.

The transformation of **3** to **4** has precedent in the literature. For example, the conversion of **5** to **6** has been effected with, among other oxidizing agents, hypochlorous acid or bromine (10).

#### 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. The mass spectrum was run on a Finnegan 3300 mass spectrometer at Cornell University, Ithaca, New York.

Dehydrogenation of **3** to Bis[3-(2,4-dioxoimidazolidinyl)]diazene (**4**) Using the Procedure of Grundmann *et al.* (5).

To a solution of 1.0 g. (0.0087 mole) of **3** (9) in 40 ml. of water was added 2.0 g. (0.025 mole) of bromine in 40 ml. of water. The mixture was stirred vigorously for 30 minutes and the solid was filtered, washed with ethanol, and dried at 100° to give 0.31 g. (32%) of the product, m.p. 245-247°; lit (5) m.p. 266°; nmr (DMSO-*d*<sub>6</sub>) δ: 3.95 (s, 2, imidazolidinedione CH<sub>2</sub>); 7.91-8.03 (broad exchangeable multiplet, 1, imidazolidinedione 1-N-H); infrared (μ): 3.05 (N-H); 5.55-5.85 (imidazolidinedione C=O); ms M<sup>+</sup>: m/e 226.

Anal. Calcd. for C<sub>6</sub>H<sub>6</sub>N<sub>6</sub>O<sub>4</sub>: C, 31.87; H, 2.67; N, 37.16. Found: C, 31.69; H, 2.64; N, 36.84.

Dehydrogenation of **3** to **4** Using the Procedure of Gante (6).

To 1.0 g. (0.0087 mole) of **3** was added 24.4 ml. of sodium hypobromite solution (prepared from 1.6 g. of bromine and 23 ml. of 1*N* sodium hydroxide). The mixture was stirred vigorously for 30 minutes and 2.0 ml. of 2.7*M* hydrochloric acid was added. The solid was filtered, washed with water, and dried at 100° to give 0.35 g. (36%) of the product, m.p. 243-245°; lit. (6) m.p. 241-243°. The infrared spectrum of the product was identical to that of the dehydrogenation product of **3** obtained when Grundmann's procedure was employed.

*Anal.* Calcd. for C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>O<sub>4</sub>: C, 31.87; H, 2.76; N, 37.16. Found: C, 31.98; H, 2.76; N, 37.00.

NMR Spectrum of 3-Amino-2,4-imidazolidinedione (**3**).

This compound had spectral data as follows: (DMSO-*d*<sub>6</sub>) δ: 3.70 (s, 2, imidazolidinedione CH<sub>2</sub>); 4.43 (exchangeable singlet, 2, imidazolidinedione 3-NH<sub>2</sub>); 7.42-7.46 (exchangeable multiplet, 1, imidazolidinedione 1-N-H).

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## REFERENCES AND NOTES

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