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## Synthesis and reactions of 5,5-dinitrobarbituric acid

Abraham Langlet,<sup>a</sup> Nikolaj V. Latypov,<sup>a,\*</sup> Ulf Wellmar,<sup>a</sup> Patrick Goede<sup>a</sup> and Jan Bergman<sup>b,\*,†</sup>

<sup>a</sup>FOA, Defence Research Establishment, Department of Energetic Materials, S-147 25 Tumba, Sweden <sup>b</sup>Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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## Abstract

Nitration of barbituric acid at 40°C gave the previously unknown 5,5-dinitrobarbituric acid (3), which readily underwent hydrolysis to dinitroacetylurea (5), which in turn could be hydrolysed in basic media to the potassium salt of dinitromethane. Alloxane was prepared in a one step procedure by thermal decomposition of 5,5-dinitrobarbituric acid in hot acetic acid. © 2000 Elsevier Science Ltd. All rights reserved.

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Our interest in the formation of *gem*-dinitrocompounds prepared by nitration of various azolones<sup>1,4</sup> lead us to investigate the nitration of barbituric acid (1), a typical example of such molecules. Mononitration of barbituric acid (1) in concentrated nitric acid with the formation of 5-nitro barbituric acid has long been known.<sup>2,3,5</sup> We have studied the nitration of barbituric acid (1) with nitric acid in concentrated sulfuric acid and under these conditions the formation of *gem*-dinitrated products was found to be favourable. Thus the addition of 1 equivalent of nitric acid to a solution of barbituric acid (1) in sulfuric acid at room temperature lead to quick formation of 5-nitrobarbituric acid in quantitative yield, which was shown by comparing the UV spectrum of the quenched reaction solution with the corresponding spectrum of an authentic sample ( $\lambda_{max}=320$  nm,  $\varepsilon=8600$  1\*mol<sup>-1</sup>). Addition of another equivalent of nitric acid and increasing the temperature to 40°C lead to the appearance of a new maximum in the UV spectrum ( $\lambda_{max}=358$  nm). This maximum slowly increased in intensity and was accompanied by precipitation of a white solid from the reaction medium.

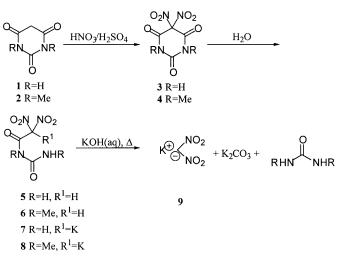
Analysis of the product showed it to be the previously unknown 5,5-dinitrobarbituric acid (3). 1,3-Dimethylbarbituric acid (2) behaved in the same way, forming 1,3-dimethyl-5,5-dinitrobarbituric acid (4) (Scheme 1).

The *gem*-dinitrated products were found to be extremely sensitive to several nucleophiles: e.g. reaction with water at room temperature for both compounds lead to a quick hydrolysis with loss of carbon dioxide and formation of the corresponding dinitroacetylureas (5 and 6). This behaviour is reminiscent to that

<sup>\*</sup> Corresponding authors.

<sup>&</sup>lt;sup>†</sup> Also at the Department of Organic Chemistry, CNT, NOVUM Research Park, S-141 57 Huddinge, Sweden.

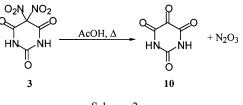
<sup>0040-4039/00/\$ -</sup> see front matter  $\, \odot$  2000 Elsevier Science Ltd. All rights reserved. PII: S0040-4039(00)00086-1



## Scheme 1.

of 5-chloro-5-nitrobarbituric acid as described by Ziegler and Kappe<sup>6</sup>. The dinitroacetylureas formed in the hydrolysis are strong acids which are rather soluble in water. In contrast many of their metal salts have a relatively low solubility. Potassium salts of both dinitroacetylurea (**7**) and 1,3-dimethyl-5,5dinitroacetylurea (**8**) were prepared and characterised. We also found that dinitroacetylurea (**7** and **8**) can be further hydrolysed in basic media at elevated temperature (80–90°C) leading to the formation of salts of dinitromethane (**9**), which provides a new efficient and safe method for making these compounds. The overall yield of potassium dinitromethanide (**9**) obtained by this method is 80% from barbituric acid.

Unlike other *gem*-dinitroazolones<sup>1,4</sup> 5,5-dinitrobarbituric acid (**3**) is thermally relatively stable with a decomposition temperature of around 150°C. Nonetheless, prolonged heating of (**3**) in boiling acetic acid lead to the formation of alloxan (**10**) in 27% yield, in the presence of 5% acetic anhydride the yield was increased to 38%. This thermal behaviour is analogous to that of 5-chloro-5-nitrobarbituric acid<sup>6</sup> (Scheme 2).





All aspects of these reactions are under active investigation and will be published in due course.

Representative experimental procedure. Caution: All nitro compounds are explosives and should be handled with appropriate precautions. Employ all standard energetic materials safety procedures in experimental operations involving such substances.

Nitration of barbituric acid (1). To a mixture of barbituric acid (1) (12.8 g, 0.1 mol) dissolved in 95% sulfuric acid (60 ml) was added fuming nitric acid (10 ml) while the temperature was kept below 25°C. The reaction mixture was then heated to 45°C for 4 h. The resulting precipitate, was filtered, washed with trifluoroacetic acid and dried, yielding 5,5-dinitrobarbituric acid (3) as a hemi hydrate (21.3 g, 0.094 mol, 94%), dec. temp. 150°C; IR (KBr): 3252 (NH), 1745 (C=O), 1611 (C=O), 1580 C(NO<sub>2</sub>)<sub>2</sub>, 1378 C(NO<sub>2</sub>)<sub>2</sub>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  11.03 broad; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  113.5, 149.0, 155.1. Anal. calcd for C<sub>4</sub>H<sub>2</sub>N<sub>4</sub>O<sub>7</sub>\*1/2 H<sub>2</sub>O: C, 21.16; H, 1.33; N, 24.67. Found: C, 21.11; H, 1.23; N, 24.89.

All compounds prepared had spectroscopic properties consistent with the proposed structures.

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