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Synthesis and reactions of 5,5-dinitrobarbituric acid

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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^{1,4} 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.^{2,3,5} 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, $\epsilon=8600$ l* mol^{-1}). 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

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

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