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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.

Keywords: nitration; nitro compounds; nitrogen heterocycles.

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 (λ_{max}=320 nm, ε=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 (λ_{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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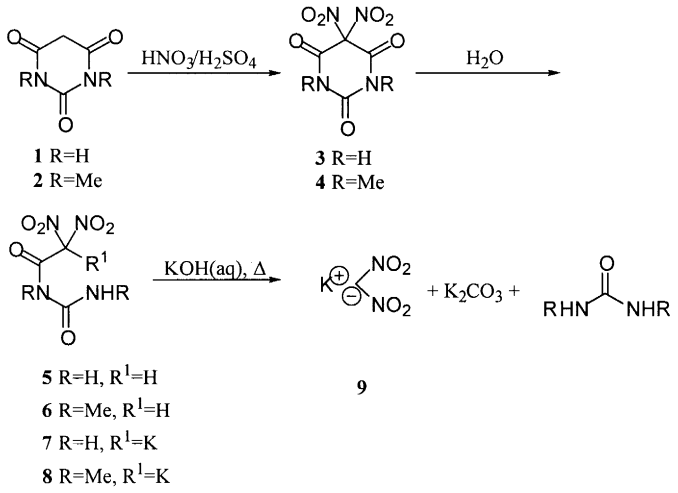
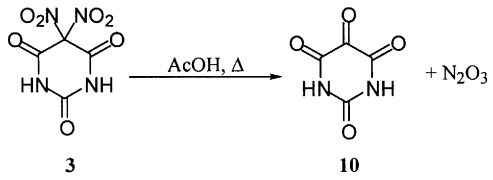


Scheme 1.

of 5-chloro-5-nitrobarbituric acid as described by Ziegler and Kappe[6]. 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-5,5-dinitroacetylurea (**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[1,4] 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[6] (Scheme 2).



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 $C(NO_2)_2$, 1378 $C(NO_2)_2$; ^{1}H NMR (DMSO-d_6) δ 11.03 broad; ^{13}C NMR (DMSO-d_6) δ 113.5, 149.0, 155.1. Anal. calcd for $C_4H_2N_4O_7$*1/2 H_2O: 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.

References

1. Bergman, J.; Bergman, S. *Tetrahedron Lett.* **1996**, *37*, 9263–9266.
2. Hartman, W. W.; Sheppard, O. E. *Organic Synthesis* **1932**, 58–61 and references cited therein.
3. Kaupp, G.; Schmeyers, J. *J. Org. Chem.* **1995**, *60*, 5494–5503 and references cited therein.
4. Latypov, N. V.; Bergman, J.; Langlet, A.; Wellmar, U.; Bemm, U. *Tetrahedron* **1998**, *54*, 11525–11536.
5. Nutiu, R.; Sebe, I. *Rev. Roum. Chim.* **1971**, *16*, 919–923 and references cited therein.
6. Ziegler, E.; Kappe, T. *Monatshefte* **1964**, *95*, 1057–1060.