

# Nitration of the 6-methyl-1,3,5-triazine derivatives, 6-methyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione and 2,4-dimethoxy-6-methyl-1,3,5-triazine

Anthony J. Bellamy<sup>a\*</sup>, Nikolaj V. Latypov<sup>b</sup> and Patrick Goede<sup>b</sup>

<sup>a</sup>Cranfield University, Royal Military College of Science, Shrivenham, Swindon SN6 8LA, UK

<sup>b</sup>Swedish Defence Research Agency (FOI), SE-147 25 Tumba, Sweden

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Nitration of 6-methyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione (**III**) gave 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid, **V**) and tetranitromethane, whilst nitration of 2,4-dimethoxy-6-methyl-1,3,5-triazine (**IV**) gave 2,4-dimethoxy-6-trinitromethyl-1,3,5-triazine (**VII**) or a furazan *N*-oxide derivative (**IX**), depending upon the nitration medium.

**Keywords.** 1,1-Diamino-2,2-dinitroethene, FOX-7, 6-methyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione, 2,4-dimethoxy-6-methyl-1,3,5-triazine, nitration.

1,1-Diamino-2,2-dinitroethene (**I**), also known as FOX-7, has generated considerable interest in recent years as an explosive with relatively high performance and low sensitivity to both friction and impact.<sup>1</sup> It was originally synthesised via nitration of 2-methylimidazole,<sup>2</sup> but more recently nitration of 2-methylpyrimidin-4,6(3*H*,5*H*)-dione (**II**) has been shown to be the method of choice.<sup>3–5</sup> However, nitration of **II** has a significant disadvantage. Nitration occurs not only on the desired methyl group, but also on the C-5 methylene group. Nitrating agent is thereby wasted and dinitromethane is an unwanted by-product.

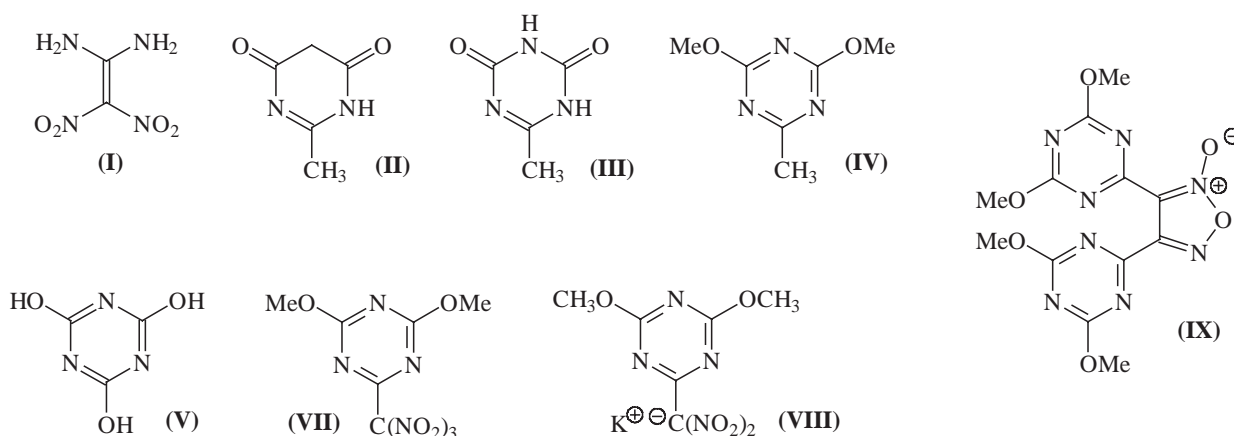
It was envisaged that the use of the analogous triazine system, 6-methyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione (**III**), instead of 2-methylpyrimidin-4,6(3*H*, 5*H*)-dione (**II**) might furnish 1,1-diamino-2,2-dinitroethene (**I**) via nitration of the methyl group without concomitant nitration in other parts of the molecule. The nitration of both **III** and the precursor of **III**, 2,4-dimethoxy-6-methyl-1,3,5-triazine (**IV**), were investigated as alternative routes to **I**.

It had been demonstrated,<sup>9</sup> via deuterium exchange, that under acidic conditions, the hydrogen atoms in the methyl group of **III** are labile, and a species with an exocyclic methylene group was suggested to be involved. It therefore seemed likely that this molecule would undergo nitration at the methyl group. This was indeed found to be the case, but the conditions required to effect any nitration were more severe than those used for **II** *viz.* HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> at 80°C/20h vs 25°C/1.25h, and the products formed, 2,4,6-trihydroxy-1,3,5-triazine (**V**, cyanuric acid; essentially quantitative yield) and tetranitromethane, were the result of more extensive nitration.

Treatment of **II** under these same conditions led to extensive degradation, the only product isolated being the ammonium salt of 5-nitrobarbituric acid (3.5%). Nitration of **III** with concentrated HNO<sub>3</sub> alone also gave **V**, even at room temperature (60% after 46h, and 84% after 166h).

The nitration of 2,4-dimethoxy-6-methyl-1,3,5-triazine (**IV**), a synthetic precursor of **III**, was also studied. HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> gave a clean conversion to 2,4-dimethoxy-6-trinitromethyl-1,3,5-triazine (**VII**) in moderate yield (57%). Although this was not the desired product, it was hoped that selective removal of one of the nitro groups followed by hydrolytic removal of the methoxy groups might furnish **I**. Treatment of **VII** with methanolic KI using the method of Glover and Kamlet<sup>11</sup> did produce the potassium salt of 2,4-dimethoxy-6-dinitromethyl-1,3,5-triazine (**VIII**). However hydrolysis under the conditions used<sup>7</sup> for the hydrolysis of **IV** to **III** (5M HCl) gave 2,4,6-trihydroxy-1,3,5-triazine (**V**).

When **IV** was nitrated with nitric acid alone, the product (~60%) was 3,4-bis(3',5'-dimethoxy-1,3,5-triazinyl)-1,2,5-oxadiazole 2-oxide (**IX**), a furazan *N*-oxide derivative, together with a small amount of the former trinitromethyl derivative **VII**. Neither product could be converted into the other by treatment with the alternative nitration conditions. Furazan *N*-oxides are commonly formed<sup>12</sup> by uncatalysed dimerisation of nitrile oxides. In this case it is probable that mono-nitration of the methyl group leads, via tautomerisation and loss of water, to a nitrile oxide which then dimerises. Under the more forcing conditions of mixed acid nitration, the mono-nitro derivative is further nitrated before it can be converted into the nitrile oxide and thence the dimer.



Schemes 1–5

\* To receive any correspondence. E-mail: a.j.bellamy@rmcs.cranfield.ac.uk

**Caution:** See the **caution** concerning the potential explosive nature of some of the compounds concerned: the Experimental Section of the full-text version: J Chem Res(M) 0946.

Scheme 1. Synthesis of 1,1-diamino-2,2-dinitroethene (I) from 2-methylpyrimidine-4,6(3*H*,5*H*)-dione (II).

Scheme 2. Possible synthesis of 1,1-diamino-2,2-dinitroethene (I) from 6-methyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione (III).

Scheme 3. Nitration of 6-methyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione (III).

Scheme 4. Nitration of 2,4-dimethoxy-6-methyl-1,3,5-triazine (IV)

Scheme 5. Further reactions of 2,4-dimethoxy-6-trinitromethyl-1,3,5-triazine (VII).

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