

The Nitration of 1,3,5-Triazine with Dinitrogen Pentoxide

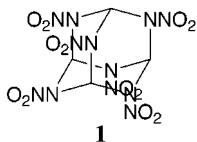
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Recently, Bakke and Riha reported the reaction of pyrimidine with dinitrogen pentoxide followed by an alcohol to give 1,3-dinitro-2,4-dialkoxy-1,2,3,4-tetrahydropyrimidines.¹ The high yields and ease of the reaction intrigued us, and we decided to try to extend the reaction to 1,3,5-triazine. The product would be a possible precursor to 2,4,6,8,9,10-hexaaza-2,4,6,8,9,10-hexanitroadamantane (**1**), a target of the energetic materials community for many years.²



When 1,3,5-triazine is allowed to react with dinitrogen pentoxide and quenched with methanol, the product is indeed 1,3,5-trinitro-2,4,6-trimethoxyhexahydrotriazine. Upon chromatography, it is possible to isolate two isomers, the *cis*- and *trans*-2,4,6-trimethoxy-1,3,5-trinitrohexahydrotriazine in about an equimolar ratio. The X-ray crystal structures of both are shown in Figures 1 and 2. Note that the methoxy substituents prefer an equatorial environment due to the strong anomeric effect.

Bakke and Riha mentioned a possible mechanism for this reaction, namely formation of the nitroazinium salt followed by attack of methanol on the carbonium ion. To get di- or trinitro compounds via this mechanism, either a di- or trication would be necessary or the second nitration would have to take place in the presence of methanol. Either scenario seemed to us unlikely. For one thing, nitropyridinium salts are known to nitrate methanol.³ If dinitrogen pentoxide were to add covalently across the imine bond the product would be an α -nitro nitramine. α -Nitro nitramines are known and can be displaced with nucleophiles.⁴ The reaction sequence shown in Scheme 1 is therefore more reasonable.

We decided, therefore, to look into the mechanism of this reaction. Upon addition of a solution of triazine in deuterated nitromethane to a solution of dinitrogen pentoxide in deuterated nitromethane at $-10\text{ }^{\circ}\text{C}$, no triazine could be detected by ^1H NMR. Three peaks were seen in a ratio of 1:0.46:0.87. The chemical shifts were 9.33, 9.20, and 9.08. This is somewhat upfield of where

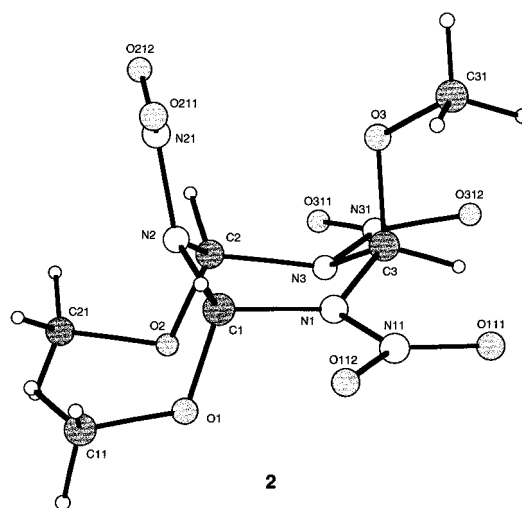


Figure 1. *trans*-2,4,6-Trimethoxy-1,3,5-trinitro hexahydro-1,3,5-triazine.

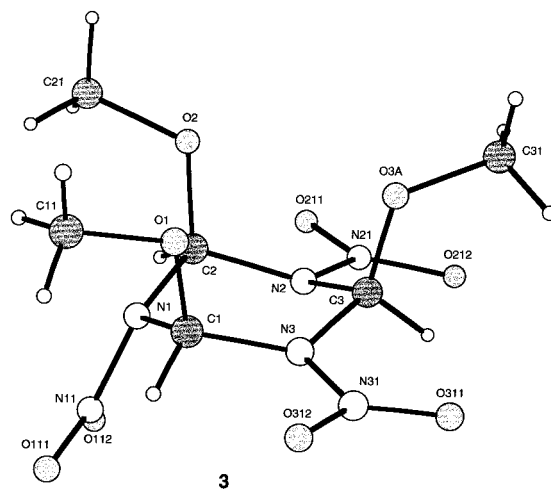
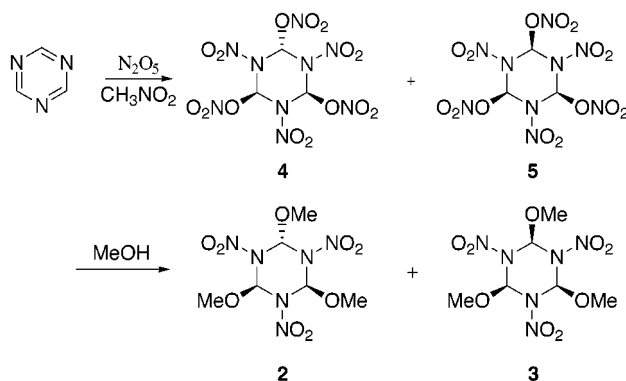


Figure 2. *cis*-2,4,6-Trimethoxy-1,3,5-trinitro hexahydro-1,3,5-triazine.

Scheme 1



the mono-, di-, or trinitrotriazinium salts would be expected (the ortho protons in *N*-nitropyridinium tetrafluoroborate resonate at 9.98 ppm⁵). This is where the

(5) Olah, G. A.; Subhash, C. N.; Olah, J. A.; Pearson, R. L.; Cupas, C. A. *J. Am. Chem. Soc.* **1980**, *102*(10), 3507.

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(1) Bakke, J. M.; Riha, J. *Synth. Commun.* **1999**, *29*(6), 959–963.

(2) See, for example: *Chemistry of Energetic Materials*; Olah, G., Squire, D., Eds.; Academic Press: San Diego, 1991.

(3) Olah, G. A.; Narang, S. C.; Pearson, R. L.; Cupas, C. A. *Synthesis* **1978**, 452.

(4) Chapman, B. F.; Owston, P. G.; Woodcock, D. *J. Chem. Soc.* **1949**, 1647.

