## 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.<sup>1</sup> 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.<sup>2</sup>



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 equitorial 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.<sup>3</sup> If dinitrogen pentoxide were to add covalently across the imine bond the product would be an  $\alpha$ -nitrato nitramine. α-Nitrato nitramines are known and can be displaced with nucleophiles.<sup>4</sup> 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 °C, no triazine could be detected by <sup>1</sup>H 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

\* To whom correspondence should be addressed. (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.



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-1,3,5triazine.



the mono-, di-, or trinitrotriazinium salts would be expected (the ortho protons in N-nitropyridinium tetrafluoroborate resonate at 9.98 ppm<sup>5</sup>). This is where the

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<sup>(3)</sup> Olah, G. A.; Narang, S. C.; Pearson, R. L.; Cupas, C. A. Synthesis 1978. 452.

<sup>(4)</sup> Chapman, B. F.; Owston, P. G.; Woodcock, D. J. Chem. Soc. 1949, 1647

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



Figure 3. 3 equiv of  $N_2O_5/1$  equiv of 1,3,5-triazine in  $CD_3NO_2$  at 27 °C.



shifts for the corresponding nitrate esters should be based on the shifts of the trimethoxy compounds and the difference in shift found for the  $\alpha$  protons between aliphatic nitrate esters and methyl ethers.<sup>6</sup> The peak at 9.20 is a triplet (J = 0.51 Hz) and the peak at 9.08 is a doublet (J = 0.51 Hz); therefore, we assign 9.33 ppm to *cis*-2,4,6-trinitrato-1,3,5-trinitrohexahydrotriazine (**5**) and 9.20 along with 9.08 ppm to *trans*-2,4,6-trinitrato-1,3,5trinitrohexahydrotriazine (**4**).

Whether the addition of O2N-O-NO2 across the double bond is truly concerted or not is difficult to ascertain. However, nitrogen pentoxide is known to exist in its covalent (O<sub>2</sub>N-O-NO<sub>2</sub>) form in nitromethane.<sup>7</sup> The nitrate ester intermediates were found to be moderately stable. There was very little change if the solution was kept below 0 °C. On warming to approximately room temperature, both intermediates disappeared at about the same rate (see Figure 3). One possible decomposition mode is a retro [2 + 2 + 2] cycloaddition (see Scheme 2). There is a short-lived peak at 9.45 ppm that is seen early on and that never rises above about 0.05 mole fraction before falling to zero about the same time as the nitrato nitramine intermediates. This is tentively identified as the nitrato nitrimine 6. The peak at 9.25 ppm is assigned to N,N-dinitroformamide (7). This slowly is converted into a final product (the lines cross at about 225 min) containing a single very acidic proton (which gives a peak at 13.11 ppm) that may be dinitramide (**8**). The addition of methanol at the point where the mix is nearly all **7** (around 1 h at room temperature) produces methyl formate (by comparison with the <sup>1</sup>H NMR of an authentic sample) slowly, being complete in about 8 h. Imidoyl nitrates such as **6** have been synthesized in the past from imidoyl chlorides and silver nitrate.<sup>8</sup> These authors were not able to observe the imidoyl nitrate itself due to a quick rearrangement to the nitroamide.

## **Experimental Section**

cis- and trans-1,3,5-Trinitro-2,4,6-trimethoxyhexahydrotriazine. A solution of 3.10 g of dinitrogen pentoxide (29 mmol) in 20 mL of CH<sub>3</sub>NO<sub>2</sub> was cooled to 0 °C while a solution of 0.665 g of 1,3,5-triazine (8.2 mmol) in 15 mL of CH<sub>3</sub>NO<sub>2</sub> was added. The solution was stirred at 0 °C for 15 min, and then 2 mL of methanol was added. After 30 min at 0 °C, the solution was poured into 30 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed with H<sub>2</sub>O followed by saturated aqueous NaHCO3. The solution was then dried with MgSO<sub>4</sub> and concentrated in a vacuum to give 1.41 g of an oily solid (55%). This was chromatographed on silica gel using 20% ethyl acetate/hexanes to give 0.36 g of pure 2 ( $R_f = 0.36, 14\%$ ) and 0.25 g of pure **3** ( $R_f = 0.28$ , 10%) along with 0.60 g of a white solid that was a mixture of 2 and 3 (23%): <sup>1</sup>H NMR 2 (CD<sub>3</sub>CN) 3.52 (3H), 3.65 (6H), 7.25 (2H), 7.64 (1H); <sup>13</sup>C NMR 2 (CD<sub>3</sub>CN) 57.34, 59.69, 91.67, 92.70; <sup>1</sup>H NMR 3 (CD<sub>3</sub>CN) 3.63 (9H), 7.68 (3H); <sup>13</sup>C NMR **3** (CD<sub>3</sub>CN) 59.05, 90.72.

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**Supporting Information Available:** Crystal data, refinement details, atomic coordinates, thermal parameters, distances, and angles for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(6)</sup> For example, the  $\alpha$  protons in 1-nitrato-2,3-propanediol resonate at 4.7 ppm and in 1-methoxy-2,3-propanediol at 3.7 ppm for a change of 1.0 ppm.

<sup>(7)</sup> Witanowski, M. J. J. Am. Chem. Soc. 1968, 90, 5683.

<sup>(8)</sup> De Carvalho, E.; Norberto, F.; Rosa, E.; Iley, J.; Patel, P. *J. Chem. Res., Synop.* **1985**, 132.