Letter

Three syntheses of 1,1-diamino-2,2-dinitroethene (FOX-7)– a comparison

Stefan Ek*, Martin Johansson*, and Nikolaj Latypov*

*The Swedish Defence Research Agency (FOI), Grindsjön Research Centre
SE-147 25 Tumba, SWEDEN
Phone : +46−855 50 60 00
Corresponding address : stefan.ek@foi.se

Received : November 26, 2011 Accepted : March 15, 2012

Keywords : synthesis and characterisation

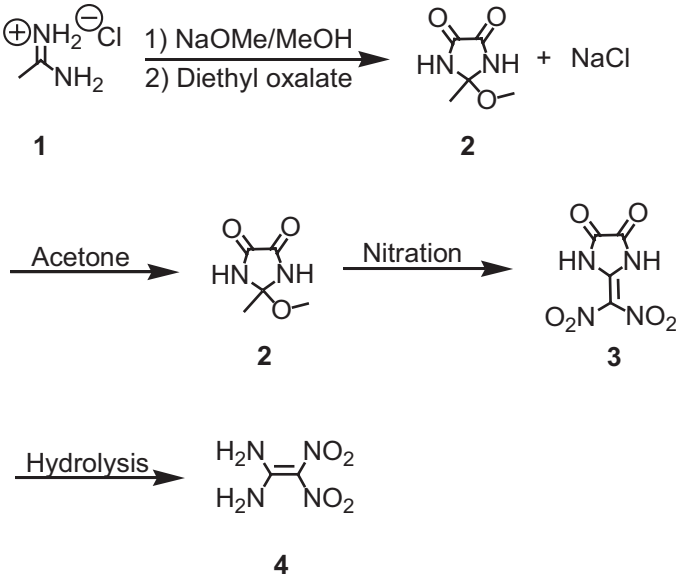
1. Introduction

Three different syntheses of 1,1-diamino-2,2-dinitroethylene (FOX-7, DADNE) are described and compared. The newest one of them could be suitable for scale-up, since it does not yield any hazardous or sensitive intermediates such as dinitromethane or 2-(dinitro-methylidene)-5,5-dinitrodihydropyrimidine-4,6 (1*H*, 5*H*)-dione. Thus, the process safety was enhanced in comparison with the commercial production process starting from 2-methylpyrimidine-4,6-dione.

2. Discussion

1,1-diamino-2,2-dinitroethene (FOX-7, DADNE), an insensitive energetic material, was first synthesised by Latypov *et al*.[1] in 1998, cf. Scheme 1. It has ever since attracted the interest of the research society for its high potential in diverse applications. Its performance as an explosive is comparable to 1,3,5-trinitro-1,3,5-triazinane (RDX), but its sensitivity to mechanical stimuli, and thus to involuntary detonation, is markedly lower.[2)−3)] This makes it attractive, since the low sensitivity of energetic materials will reduce the risk of serious and fatal accidents in connection with explosives.

Latypov's synthesis[1] of FOX-7(**4**) works excellently on the laboratory scale. Though, some of its features are unfavourable for scale-up. One such is that the starting material, 2-methoxy-2-methylimidazolidine-4,5-dione (**2**) is not commercially available. After the conden-sation of acetamidinium chloride **1** with diethyl oxalate and evaporation of methanol, **2** was contaminated with sodium chloride, which is partly soluble in methanol. Thus, the use of Soxhlet extraction to remove sodium chloride from **2** was required prior to nitration. The use of this technique is another disadvantage, not only in terms of the time required for the production. It also requires specialised equipment, lowers the yield and uses the highly flammable solvent acetone. Once pure **2** was obtained, it was nitrated in mixed acids to yield 2(dinitro-methyl-idene)-imidazolidine-4,5-dione **3**, which in turn was hydrolysed into **4**.

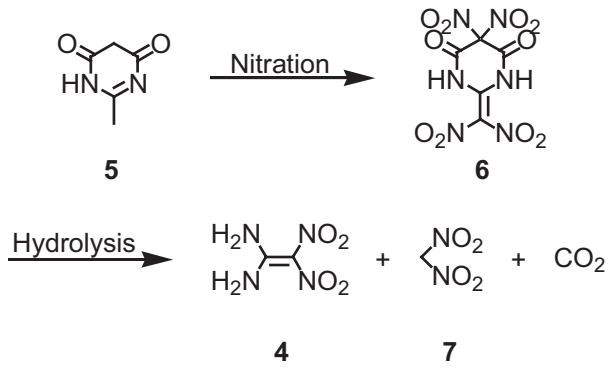


1 **2** **2** **3** **4**

Scheme 1 Latypov's synthesis of FOX-7

Another process, starting from 2-methylpyrimidine-4,6-dione 5, was presented by Astratev *et al*.[4] and optimised by Latypov *et al*.,[5] which is currently used in pilot scale production in batches up to 600 kg. cf. Scheme 2.[6]

The starting material **5** is commercially available. Nitration in mixed acid yields 2-(dinitro-methyl-idene)-5,5-dinitrodihydropyrimidine-4,6(1*H*, 5*H*)-dione (**6**), whose



Scheme 2 Astratev's synthesis of FOX-7

hydrolysis yields FOX-7 (**4**), dinitromethane (**7**) and carbon dioxide. The main disadvantage of this procedure is the handling of the intermediate **6**, which is sensitive to mechanical stimuli and furthermore chemically unstable.[5] One way to circumvent the handling of this risky intermediate is to dilute the nitration mixture with water, which will induce hydrolysis into FOX-7. However, such dilution produces 25% sulfuric acid, which is difficult to recycle. Regardless of the choice of hydrolysis method, **7** is formed as a by-product (0.7 kg for each kg of FOX-7). This substance is very unstable and it can decompose spontaneously even at ambient temperature.[7–8] This unpredictable decomposition can cause problems, such as runaway reactions, due to rapid heat evolution, during the hydrolysis step.[5] Moreover, the removal of **7** further complicates the recycling of the spent acids from the nitration.

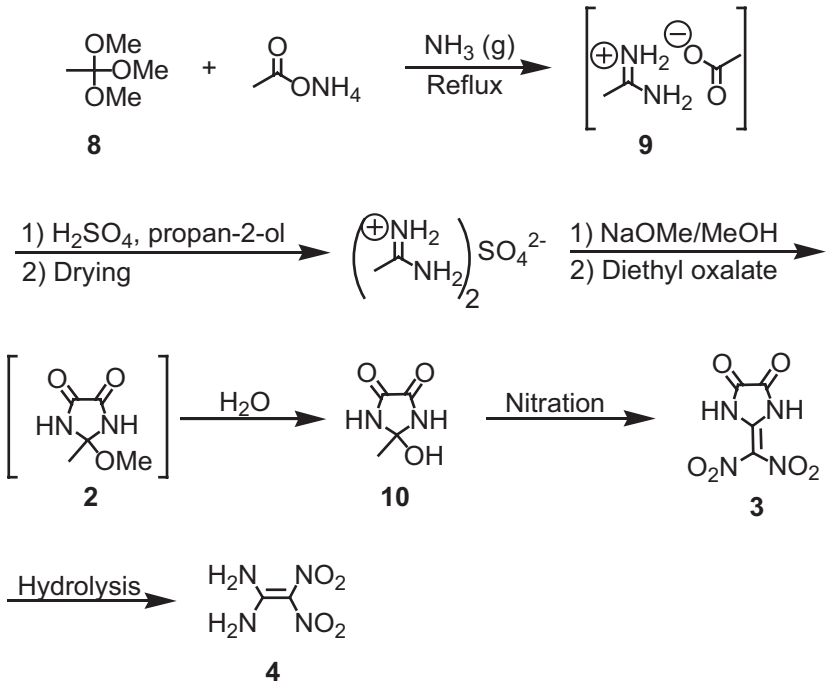
Numerous ways to circumvent the formation of **7** were attempted, *e. g.* the use 5,5-disubstituted-2-methylpyrimidine-4,6-diols or 2-methyl-1,3,5-triazine-4,6-diol as starting materials. It lead to rupture of C(methyl)-C (2) bond and formation of trinitromethane. The reason was probably higher solubility of the corresponding 2,2-dinitromethylidene[9] intermediates, in the reaction medium, which allowed them to undergo further nitration instead of precipitation. The failure of these attempts led Jalový *et al.*[10] back to the basics and prompted a reinvestigation and further development of the Latypov's procedure.[1]

Their first development steps were to use other counter ions than chloride to avoid the problems associated with the latter. The use of acetamidine acetate and sulphuric acid in the neutralisation step allowed the formed sodium sulphate to be removed by filtration. This is better from a production point of view. However, Celite had to be used as a filtering aid, which is unfavourable for large scale production, even if it can be used in the pilot plant.

Throughout the years, the authors had noted that **2** was stable for an extended period of time only when stored in a desiccator with a drying agent. When **2** was stored in a humid atmosphere (90% humidity), it was found that it changed into a number of undefined products and 2-hydroxy-2-methylimidazolidine-4,5-dione **10**, whose structure elucidation was described. A new procedure involving this intermediate was developed, cf. Scheme 3. Just as Latypov's procedure, it had **3** as it's nitrated intermediate, which is considerably less sensitive than **6**. Hydrolysis of **3** produces no **7**, so the risk associated with the compounds are avoided. Since the methoxy group in **2** was replaced by a hydroxyl group in **10**, the risk of formation of methyl nitrate in the nitrating mixture was eliminated.

3. Conclusions

The only procedure currently used in production, to the best of our knowledge, is the one developed by Astrat'ev



Scheme 3 Jalový's synthesis of FOX-7

and optimised by Latypov and many others. It has the benefits of using a commercially available starting material and having gone through the scrutiny of many scientists during scale-up at different sites. Its two main disadvantages are the sensitive intermediate **2** and the hazardous by-product **4**. Thus, this is the best synthesis of FOX-7 at present.

Jalový's procedure is very promising. In difference to Latypov's procedure, it does not include any unstable intermediates and it eliminates the risk of formation of methyl nitrate. Much work is left before Jalový's procedure can be used in large scale production. If this work is performed, this could be the best synthesis of FOX -7 in the future.

References

1) Latypov, N. V., Bergman, J., Langlet, A., Wellmar, U., Bemm, U. Tetrahedron, 54, 11525−11536 (1998).
2) Bellamy, A. In Structure and Bonding, Mingos, D.M.P., Klapötke, T.M, Eds., Springer-Verlag, Berlin, 1-33 (2007) and references cited therein.
3) Trzcinski, W. A., Cudzilo, S., Chylek, Z., Szymanczyk, L. J. Hazard. Mater., 157, 605−612 (2008).
4) Astrat'ev, A. A., Dasko, D. V., Mershin, A. Y., Stepanov, A. I., Urazgil'deev, N. A. Russ. J. Org. Chem. 37, 729−733 (2001).
5) Latypov, N. V., Johansson, M., Holmgren, E., Sizova, E. V., Sizov, V. V., Bellamy, A. J. Org. Process Res. Dev. 11, 56 (2006).
6) Östmark, H., Bergman, H., Bemm, U., Goede, P., Holmgren, E., Johansson, M., Langlet, A., Latypov, N. V., Pettersson, A., Pettersson, M.-L., Wingborg, N., Vörde, C., Stenmark, H., Karlsson, L., Hihkiö, M. Proc. 32nd International Annual Conference of ICT, Karlsruhe, 26/1−26/21 (2001).
7) Bedford, C. D., Nielsen, A. T. J. Org. Chem. 44, 633−636 (1979).
8) Legin, G. Y., Okhlobystina, L. V., Fainzilberg, A. A. Izv. Akad. Nauk, SSSR Ser. Khim., 12, 2220−2221 (1965).
9) Bellamy, A., Latypov, N. V., Goede, P. Proc. New Trends in Research of Energetic Materials, 7, 75−82 (2004).
10) Jalový, Z., Ek, S., Ottis, J., Dudek, K., Růžicka, A., Lyčka, A., Latypov, N. V., J. Energ. Mater. In print, DOI 07370652.2011.633964.