

SYNTHESIS OF 1,3,5-TRI(NITRO-<sup>15</sup>N)-1,3,5-HEXAHYDROTRIAZINE, RDX-(<sup>15</sup>NO<sub>2</sub>)<sub>3</sub>

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SUMMARY

The synthesis of 1,3,5-tri(nitro-<sup>15</sup>N)-1,3,5-hexahydrotriazine, RDX-(<sup>15</sup>NO<sub>2</sub>)<sub>3</sub>, by nitrolysis of 1,3,5-triacetyl-1,3,5-hexahydrotriazine is described. A method for recovery of the nitrogen-15 labelled nitric acid not consumed in the nitrolysis is also provided.

Key Words: Nitramines, RDX, Nitrogen-15, Nitrolysis

INTRODUCTION AND DISCUSSION

A need for RDX-(<sup>15</sup>NO<sub>2</sub>)<sub>3</sub>, 1, prompted us to investigate existing literature methods for labelled or unlabelled RDX which could be adapted to provide the target compound. The only literature method for <sup>15</sup>N-labelled RDX was one that gave the fully labelled material (<sup>15</sup>N in all nitro groups and ring positions) as a minor product (15%) via a rather complicated procedure (1). Therefore, no attempt was made to adapt this procedure to give 1. However, we did modify a literature method for unlabelled RDX (nitrolysis of 1,3,5-triacetyl-1,3,5-hexahydrotriazine with 100% nitric acid and phosphorus pentoxide) (2) to provide excellent yields of 1 (Scheme I) as well as easy recovery of the labelled nitric acid not consumed in the reaction. A major modification to the literature procedure was a substantial increase (over fourfold) in the ratio of 1,3,5-triacetyl-1,3,5-hexahydrotriazine to 100% nitric acid in order to obtain maximum product from the labelled nitric acid. This large deviation from the published procedure required some



100% Nitric Acid-<sup>15</sup>N

To 42g (0.312 mole) of a 9.6 N solution of nitric acid-<sup>15</sup>N (47% H<sup>15</sup>NO<sub>3</sub> W/W) stirred in an ice bath was slowly added 20.6g (0.312 mole) of 85% potassium hydroxide in 20 ml of water. The precipitate of potassium nitrate-<sup>15</sup>N was removed by filtration and combined with additional material obtained by removal of the water from the filtrate on a rotary evaporator. The dried salt (32.0g) was added with cooling to 54 ml of conc. sulfuric acid after which a vacuum (water aspirator) was adjusted so that 100% nitric acid-<sup>15</sup>N distilled at 45°C to give 19.0g (95%) of product. (Distillation began when the pot temperature approached 100°C but a slow increase to 150°C was required to complete the distillation).

RDX-(<sup>15</sup>NO<sub>2</sub>)<sub>3</sub> (1)

A 50 ml three-necked flask containing 8.0g (0.056 mole) of phosphorus pentoxide was equipped with a magnetic stirrer and a reflux condenser (drierite tube) and immersed in a cold (10°C) water bath. 100% Nitric acid-<sup>15</sup>N (17.9g, 0.28 mole) was added all at once with stirring and a vigorous exothermic reaction ensued. After the reaction subsided, the cold water bath was replaced with a water bath at 30°C and the mixture was stirred until the phosphorus pentoxide was evenly dispersed. The reaction flask was then quickly immersed in a cold (10°C) water bath and immediately 2.5g (0.0117 mole) of 1,3,5-triacetyl-1,3,5-hexahydrotriazine (3) was added all at once. (Caution !! Efficient stirring to provide good heat exchange is essential at this point. A thermometer should not be in the flask because solids will tend to dam up behind it and become charred). After the vigorous exothermic reaction subsided the cold water bath was replaced with a water bath at 35-40°C. The reaction mixture was held at this temperature until foaming subsided (about 1 hr.) and then was stirred in an oil bath at 65°C for 1 hr.

(Slow reflux at 55°C occurs during the latter heating period). The mixture was cooled to 35°C and poured onto ice and the solid precipitate was removed by filtration and washed well with water to give 2.38g (91%) of 1, mp 202-204°C (dec.). Crystallization from acetone-water gave 2.29g, mp 203-204°C (dec.). <sup>1</sup>H-NMR [(CD<sub>3</sub>)<sub>2</sub>C=O] 6.30 (t).

Aqueous potassium hydroxide was added with cooling to the filtrate from which 1 was removed until the pH reached 11. Most of the water was then removed on a rotary evaporator to give a viscous mixture which was cooled to -5°C and filtered to give 13.4g of potassium nitrate-<sup>15</sup>N. This recovered material was converted to 7.4g of 100% nitric acid-<sup>15</sup>N which was used as above to give an additional 0.96g of 1.

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