

Synthesis of Pure RDX

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As part of a project on the bioremediation of explosives there was a need for RDX which is uncontaminated by HMX. The usual procedure for the synthesis of RDX, the Bachmann process, always has residual amounts of HMX present as a side product of the synthesis. There are two reported procedures for the synthesis of pure RDX; one involving the oxidation of R-salt (1,3,5-trinitroso-1,3,5-triazacyclohexane) with a $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture¹, the other by the nitration of hexamine with 40 equivalents of a 25% $\text{N}_2\text{O}_5/\text{HNO}_3$ mixture at -20°C ². The absence of HMX in the RDX samples was confirmed by ^1H -nmr spectroscopy and by melting point determination.

Procedure

Synthesis of R-salt (1,3,5-trinitroso-1,3,5-triazacyclohexane)¹: To a stirred solution of 21g (0.15 mol) of hexamine in 280 mL of water and 120g of ice was added an ice-cold solution of 68 mL of cold conc. HCl and 200g of ice. The acid solution was stirred while a solution of 50g (0.72 mol) of NaNO_2 in 50 mL of water and 30g of ice were added. The reaction mixture turned blue and then green and foamed up with the precipitate rising to the surface. The mixture was allowed to stand 0.5h without stirring. The precipitate was collected by suction filtration, washed with water, and air-dried to give 10.5g (40%) of a light

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yellow powder. Recrystallization from EtOH (95 mL) yielded 9.5g (36%) of light yellow plates; m.p. 106-107 °C.

RDX Synthesis:

Method 1¹: To 293g (194 mL) (4.64 mol) of 100% HNO₃ cooled to -40 to -45 °C was added dropwise 4.7 mL (0.041 mol) of 30% aqueous H₂O₂. To this mixture was added in small portions 9.5g (0.055 mol) of R-salt with vigorous stirring at -40 °C over a 40 min period. After addition the reaction mixture was allowed to warm to room temperature and stir 2h. The mixture was poured onto 550g of ice and the resulting white solid was collected by suction filtration, washed with water and air-dried (7.2g). Recrystallization from 75 mL of acetic acid yielded 5.8g of white microcrystals; m.p. 204-205.5 °C.

Method 2²: Hexamethylenetetramine (1.0g) (72 mmol) was added portion-wise over a 5 min period to a stirred solution of 20-25% N₂O₅/ HNO₃ (72 mL) (284 mmol) under CCl₄ (40 mL) kept at -20 °C with a dry ice-CCl₄ cooling bath. After addition stirring was continued for 30 min at -20 °C and then poured carefully onto 100g of ice in an 800 mL beaker. The mixture was neutralized with NaHCO₃, extracted twice with 100 mL of EtOAc. The EtOAc solution was dried over anhydrous Magnesium sulfate and the solvent was removed under vacuum to yield 1.14g (67%) of a light yellow powder. Recrystallization from acetic acid (11 mL) (10% solution) yielded 0.80g (50%) of white microcrystals; m.p. 204.5-206.5 °C.

References

1. F.J. Brockman, D.C. Downing, G.F. Wright, *Can. J. Res.*, **1949**, *27B*, 1469.
2. J.W. Fischer, R.L. Atkins, *Org. Prep Proceed. Int.*, **1986**, *18*, 281.