

1,3,5-TRINITROSO- AND 1,3,5-TRINITROHEXAHYDRO-1,3,5-TRIAZINE-²H₆

Joseph H. Boyer and G. Kumar
Department of Chemistry, University of Illinois at Chicago,
Chicago, Illinois 60680

SUMMARY

Perdeuteration of 1,3,5-trinitrosohexahydro-1,3,5-triazine was brought about by treatment with potassium alkoxide in CH₃O²H(99.5%). The important high energy compound, 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX), was obtained in its perdeuterated modification (>99% ²H) by oxidation of the perdeuterated trinitrosamine with a mixture of nitric acid (100%) and hydrogen peroxide (30%).

Key words: 1,3,5-trinitrosohexahydro-1,3,5-triazine, 1,3,5-trinitrohexahydro-1,3,5-triazine, RDX, deuterium exchange, oxidation.

DISCUSSION

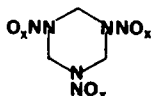
We wish to report a preparation of 1,3,5-trinitrosohexahydro-1,3,5-triazine-²H₆ (1) by deuterium exchange and its subsequent oxidation to 1,3,5-trinitrohexahydro-1,3,5-triazine-²H₆ (RDX-²H₆, 2) (>99% ²H). This preparation of the nitramine 2 offers several advantages over an alternative preparation from O=C²H₂, N²H₃, N²H₄NO₃, CH₃CO₂²H, and ²HNO₃.¹ It removes the possibility of contamination by 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane-²H₈ (HMX-²H₈) an expected by-product since HMX formation can accompany RDX formation in the nitrolysis of hexamethylenetetramine.² Also it is more economical in the consumption of deuterium; its efficiency is greater (74% vs 58%), and it is a convenient operation.

The base catalyzed α -deuteration of simple nitrosamines was first reported in 1970³ and reviews of the reaction have appear-

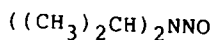
ed.^{4,5} Monofunctional nitrosamines generally resist alkaline degradation, have been distilled from 3N sodium hydroxide⁶ and have undergone α -deuteration in $\text{NaO}^2\text{H}/^2\text{H}_2\text{O}$ at 100° .³⁻⁵

Attempts to deuterate 1,3,5-trinitrosohexahydro-1,3,5-triazine (3) in the presence of either aqueous alkali or lithium diisopropylamide were unsuccessful and resulted, instead, in ring degradation. As the nitrosamine was consumed on treatment with sodium hydroxide (40%) at 25° an ammoniacal odor was noted (a similar degradation of 1-nitroso-3,5-dinitrohexahydro-1,3,5-triazine when heated in sodium hydroxide (10%) was reported).² Extensive transnitrosation to the lithium amide gave diisopropyl nitrosamine (5), isolated in good yield. Similar reactions were known to be competitive with α -deuteration when certain simple nitrosamines were treated with lithium amides.⁴

Potassium tert-butoxide or methoxide catalyzed deuterium exchange at 25° between $\text{CH}_3\text{O}^2\text{H}$ (99.5% ^2H) and 1,3,5-trinitrosohexahydro-1,3,5-triazine (3) to give quantitatively the perdeutero modification 1. Progress of the reaction was monitored by the disappearance, complete in 15 minutes, of ^1H nmr signals at δ 5.66, 6.28, and 6.92 characteristic of the nitrosamine 3.⁷ Recyclization insured the quantitative formation of analytically pure product 1, $\text{C}_3^2\text{H}_6\text{N}_6\text{O}_3$.



- 1, X = 1, H = ^2H
2, X = 2, H = ^2H (RDX- $^2\text{H}_6$)
3, X = 1, H = ^1H
4 X = 2, H = ^1H (RDX)



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Oxidation of the trinitrosamine 1 by a mixture of nitric acid (100%) in hydrogen peroxide (30%) gave RDX-²H₆ 2 (70%). A similar oxidation 3 + 4 (74%) was reported.² The FD mass spectrum showed the molecular ion M⁺ at 228 (100%) and contained no evidence for the presence of contamination with partial deuteration products with masses 222-227.

EXPERIMENTAL

Melting points were determined from a Thomas-Hoover mp apparatus and are uncorrected. NMR spectra were recorded on a Varian EM 360A spectrometer using TMS as an internal standard. Mass spectra were obtained from a Field Ionization and from a Field Desorption mass spectrometer (see Acknowledgment).

The 1,3,5-trinitrosohexahydro-1,3,5-triazine (3) was prepared from the condensation of formaldehyde and ammonia followed by the nitrosolysis of hexamethylenetetramine.^{7a} Methanol-O-²H (99.5% ²H) was obtained from Aldrich Chemical Company.

1,3,5-Trinitrosohexahydrohexahydro-1,3,5-triazine-²H₆ (1). A solution of the nitrosamine 3 (0.174 g, 1.0 mmol) and potassium methoxide (1.0 ml of a 0.001 M solution of potassium methoxide in CH₃O²H) in CH₃O²H (5.0 ml) at 25° completed deuterium exchange within 15 minutes as shown by ¹H nmr monitoring. After the solvent was removed by evaporation, the residue, dissolved in methylene chloride, was washed with ²H₂O and dried. Removal of methylene chloride by evaporation left perdeuterated 1,3,5-trinitrosohexahydro-1,3,5-triazine (1) as a colorless solid, 0.16 g (90%) mp 102-103° after recrystallization from ethanol.

Anal. Calcd for C₃²H₆N₆O₃: C, 20.00; ²H, 6.71; N, 46.65. Found: C, 20.03; ²H, 6.50; N, 46.29. Ir(KBr): 2280 (C-²H) and 1475 cm⁻¹ (N=O). FIMS m/e: 180 M⁺ (100%), 179 (15%) To insure complete deuteration the product was recycled under the same conditions.

1,3,5-Trinitrohexahydro-1,3,5-triazine-²H₆ (2). To a mixture of hydrogen peroxide (30%, 0.71 g, 6.3 mmol) and nitric acid (100%,

9.2 g, 142 mmole) the deuterated nitrosamine 1 (0.31 g, 1.7 mmol) was added slowly at -40° . The reaction mixture was warmed and held at 20° for 5 minutes, and poured onto crushed ice (20 g) to precipitate 1,3,5-trinitrohexahydro-1,3,5-triazine- $^2\text{H}_6$ 2 as a colorless solid (0.27 g, 71%), mp $201-202^{\circ}$ after recrystallization from acetic acid.

Anal. Calcd for $\text{C}_3^2\text{H}_6\text{N}_6\text{O}_6$: C, 15.79; ^2H , 5.30; N, 36.83. Found: C, 15.76; ^2H , 5.25; N, 36.55. Ir (KBr): 2300 ($\text{C}-^2\text{H}$), 1525 and 1340 cm^{-1} (NO_2). FDMS m/e 228 M^+ (100%).

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