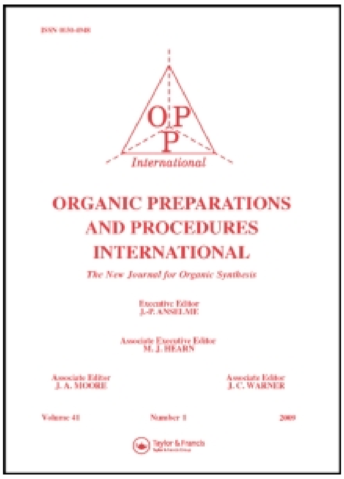

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DIRECT PREPARATION OF 1,3,5-TRIAZA-1,3,5-TRINITROCYCLOHEXANE FROM HEXAMETHYLENETETRAMINE

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DIRECT PREPARATION OF 1,3,5-TRIAZA-1,3,5-TRINITROCYCLOHEXANE FROM HEXAMETHYLENETETRAMINE

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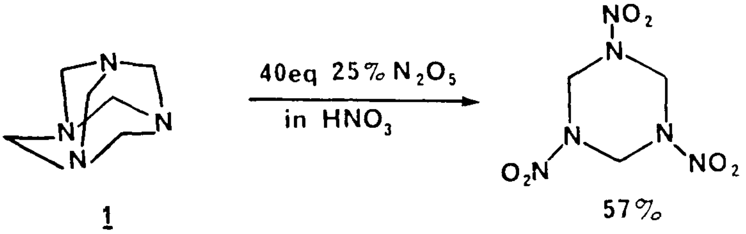
Recent synthetic efforts in our laboratory have involved the development of new methods for the preparation of nitramines,[1] which are usually obtained by nitrolysis of *a protected amine precursor.*[2] We have reported[1] the facile nitrolysis of a number of cyclic nitrosamines to the corresponding nitramines employing dinitrogen pentoxide in 100% HNO_3[3] and now describe the extension of the method to the preparation of 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX, 2), an important energetic material.

Pure RDX had previously been prepared by nitrolysis of 1,3,5-triaza-1,3,5-trinitrosocyclohexane (R-salt) with excess 100% nitric acid.[4]



1

Treatment of R-salt with an equivalent amount of dinitrogen pentoxide in nitric acid also gave RDX, albeit in only 32% yield. RDX is most often prepared by the Bachman process.[5] This multistep procedure involves hexamethylenetetramine (1) as precursor and the product always contains significant amounts of 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX) impurity. Hexamethylenetetramine in this instance can be viewed as a protected hexahydrotriazine and the formal amine precursor of RDX, which has never been isolated as the free base.[6] Treatment of 1 with 40 equivalents of 25% dinitrogen pentoxide in nitric acid gave pure RDX in 57% yield with no trace of HMX as determined by 200 MHz ^{1}H NMR.

EXPERIMENTAL SECTION

Preparation of 25% N_2O_5 in 100% HNO_3.- An electrochemical cell identical to the apparatus described by Harrar and Pearson[3] was constructed. A potential of 1.8 V/2 A was applied to 100% red fuming nitric acid (500 ml) and the temperature was maintained between 0 to 5° for 24 hrs; the potential decreased to zero. Dinitrogen tetroxide (180 ml) was then added and the electrolysis was continued beginning again with a potential of 1.8 V/2 A; the temperature must be maintained between 0 and 5° at all times. The applied potential slowly dropped to zero after 1 week. The initially red solution became a clear light yellow. An ^{1}H NMR analysis[3] (200 MHz) showed the mixture to be 25% N_2O_5 in HNO_3; this mixture may be stored at temperatures below 0° indefinitely.

1,3,5-Triaza-1,3,5-trinitrocyclohexane (2).- Hexamethylenetetramine (0.5 g, 3.6 mmol) was added in portions over 5 min. to a stirred solution of 25% N_2O_5/HNO_3 (36 ml, 142 mmol) under CCl_4 (20 ml) kept at -20°. After 30 min. the yellow mixture was carefully poured onto ice (50 g), neutralized with $NaHCO_3$ and extracted into EtOAc. After drying ($MgSO_4$) and removal of the solvent, 0.46 g. (57%) of a white solid was isolated, which is shown to be pure RDX, mp. 202° (dec.), lit.[7] 204° (dec.), by comparison with an authentic sample.

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A FACILE AND EFFICIENT SYNTHESIS OF PYRROLE-3-CARBOXYLIC ACID FROM PYRROLE

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Only a few procedures have been described for the synthesis of pyrrole-3-carboxylic acid (3),[1] and these procedures give very low overall yields and require special conditions and reagents. Pyrrole-3-carboxylic acids and derivatives are frequently obtained by ring syntheses which lead in most cases to polysubstituted pyrroles.[2] Recently, a method for the