NWC TP 6739

(12)

Synthetic Studies of Dinitrogen Pentoxide (N_2O_5)

by
John W. Fischer
Stephen P. York
and
Ronald L. Atkins

JANUARY 1987

NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001

Approved for public release; distribution is unlimited.

Naval Weapons Center

FOREWORD

There is a need for explosives and propellants which exceed the performance of RDX and HMX. Because both of these compounds are nitramines, the search for replacements has centered on this class of materials. Although methods exist for nitramine synthesis, many nitration reagents are incompatible with available energetic material precursors. With hopes of circumventing present problems, of gaining a better understanding of nitration and nitrolysis chemistry, and of developing new methods of synthesis, a study was conducted which investigated the synthetic utility of dinitrogen pentoxide in the formation of nitramines. The results are discussed in this report.

The work was performed with Naval Sea Systems Command funding, Task and Project Number SR02403, Work Unit Number 138509, Program Element Number 61153N under the sponsorship of H. G. Adolph. This report has been reviewed for technical accuracy by Richard A. Hollins and Arnold T. Nielsen.

Approved by
R. L. DERR, Head
Research Department
9 January 1987

Under authority of
J. A. BURT
Capt., USN
Commander

Released for publication by
G. R. SCHIEFER
Technical Director

NWC Technical Publication 6739

Published by . . . . . Technical Information Department
Collation . . . . . Cover, 11 leaves
First printing . . . . . 205 copies

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

AD-A178017

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Public release; unlimited distribution.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NWC TP 6739	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Naval Weapons Center 6b. OFFICE SYMBOL (*If applicable*)	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (*City, State, and ZIP Code*) China Lake, CA 93555-6001	7b. ADDRESS (*City, State, and ZIP Code*)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (*If applicable*)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (*City, State, and ZIP Code*)	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61153N	SR02403	SR02403	138509

11. TITLE (*Include Security Classification*)

SYNTHETIC STUDIES OF DINITROGEN PENTOXIDE (N_2O_5)

12. PERSONAL AUTHOR(S)
John W. Fischer, Stephen P. York, Ronald L. Atkins

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (*Year, Month, Day*)	15. PAGE COUNT
Final	FROM 84 May TO 86 May	1987, January	20

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
FIELD	GROUP	SUB-GROUP	Dinitrogen Pentoxide, Nitramines, Nitrosamines, Nitrolysis
07	03		

19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

(U) A series of nitrolysis reactions of nitrosamines to nitramines were investigated using dinitrogen pentoxide (N_2O_5) in various solvents. Reactions were found to be very solvent dependent. The best results were achieved using N_2O_5 in 100% nitric acid. The conversion of hexamine to RDX in one step employing N_2O_5 was also studied.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (*Include Area Code*)	22c. OFFICE SYMBOL
John W. Fischer	619-939-1641	3853

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

☆U.S. Government Printing Office: 1986-607-047

UNCLASSIFIED

CONTENTS

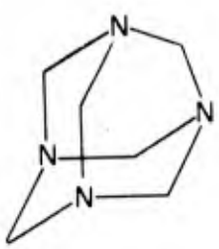
ACKNOWLEDGMENT

The authors would like to thank A. T. Nielsen for the R-salt samples.

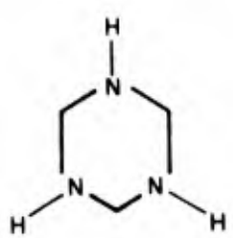
INTRODUCTION

Nitramines are important energetic materials with many ordnance applications. Among the most energetic materials used in explosive and propellant formulations which are currently in production are 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). New synthetic techniques which make the preparation of new energetic nitramine compounds possible in high yield and in high purity are extremely desirable. We are concerned with the development of a new process that realizes these two goals and also makes possible the preparation of many new polynitramino compounds that may have utility as explosives, propellant ingredients, gas generants, and other ordnance applications.

Most synthetic techniques that are currently employed to prepare nitramines involve the cleavage of a protective group from a suitable precursor. This heterolysis reaction, the critical step in nitramine synthesis, most often makes use of mixed acid solutions (various mixtures of sulfuric, acetic, and acetic anhydride, with nitric acid). HMX and RDX are both prepared from a common precursor, hexamine, and serve to illustrate this feature of nitramine synthesis. Hexamine can be



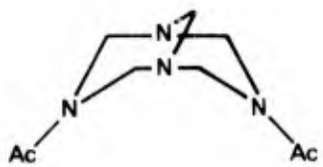
Hexamine



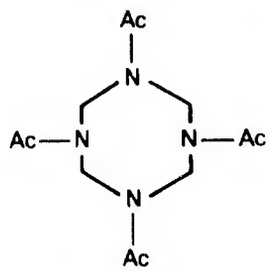
1,3,5-Hexahydrotriazine

looked upon as a protected 1,3,5-triazacyclohexane. This latter compound is unknown. Attempts to prepare it from formaldehyde and ammonia under a variety of conditions always lead to aqueous solutions of hexamine (Reference 1). Under specific conditions, hexamine can be converted in good yields to RDX and/or HMX. For example, the Bachmann process involves the conversion of hexamine to RDX (Reference 2) with a yield of 70-73%. The RDX obtained in this fashion is contaminated with HMX. By suitable adjustment of reaction conditions, RDX of sufficient purity for use in ordnance can be obtained.

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane is also obtained from hexamine via one of two intermediates (Reference 3). Treatment of



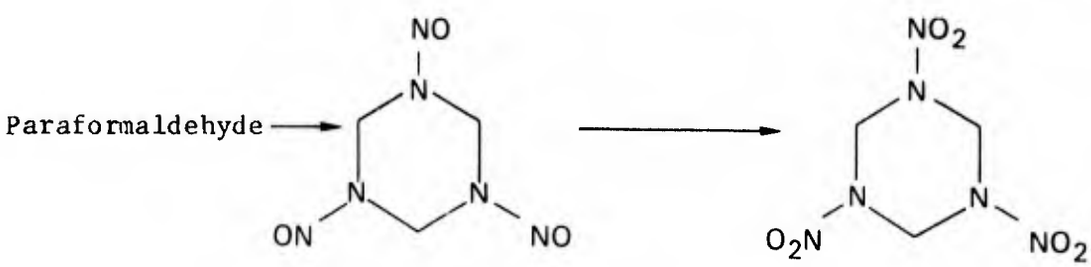
DAPT



TAT

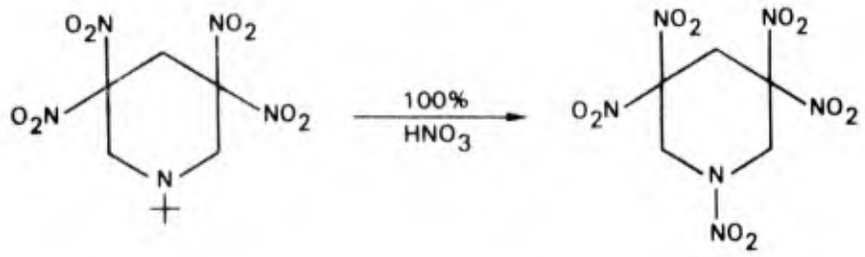
hexamine with acetic anhydride/water generates 3,7-diacetyl-1,3,5,7-tetraazabicyclo-[3.3.1]nonane (DAPT). 3,7-Diacetyl-1,3,5,7-tetraazabicyclo-[3.3.1]nonane reacts with mixed acid to give 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN), or with acetic anhydride/acetyl chloride to give 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (TAT). Both DADN and TAT are converted in high yield and in high purity to HMX upon nitrolysis with nitric acid/phosphoric acid.

1,3,5-Trinitro-1,3,5-triazacyclohexane prepared by the Bachmann process always contains some HMX impurity. Pure RDX can be prepared from 1,3,5-trinitroso-1,3,5-triazacyclohexane (R-salt) (Reference 1). Treatment of R-salt with mixed acid yields pure RDX in >95% yield (Reference 4).



R-Salt RDX

Similarly, amines protected by alkyl groups such as tert-butyl, isopropyl, or methyl can be nitrolyzed to yield nitramines (Reference 5). For example, the protected amine compound, 1-tert-butyl-3,3,5,5-tetranitropiperidine (TBP) can be converted to the corresponding nitro compound upon treatment with 100% nitric acid with 96% yield.



A recent report by Harrar and Pearson described the efficient electrochemical preparation of solutions of N_2O_5 in 100% nitric acid (Reference 6). Harrar and Pearson also reported that solutions of N_2O_5 in nitric acid prepared by this method were very efficient in conversions of TAT to give pure HMX in >85% yield. These results suggested to us that this reagent might be usable for the nitrolysis of other protected nitramino precursors as well.

RESULTS AND DISCUSSION

Recently the preparation of trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) was reported (Reference 7). This new energetic nitramine, prepared from trans-1,4,5,8-tetraazadecalin, has very good calculated detonation properties. The measured and calculated properties are given in Table 1.

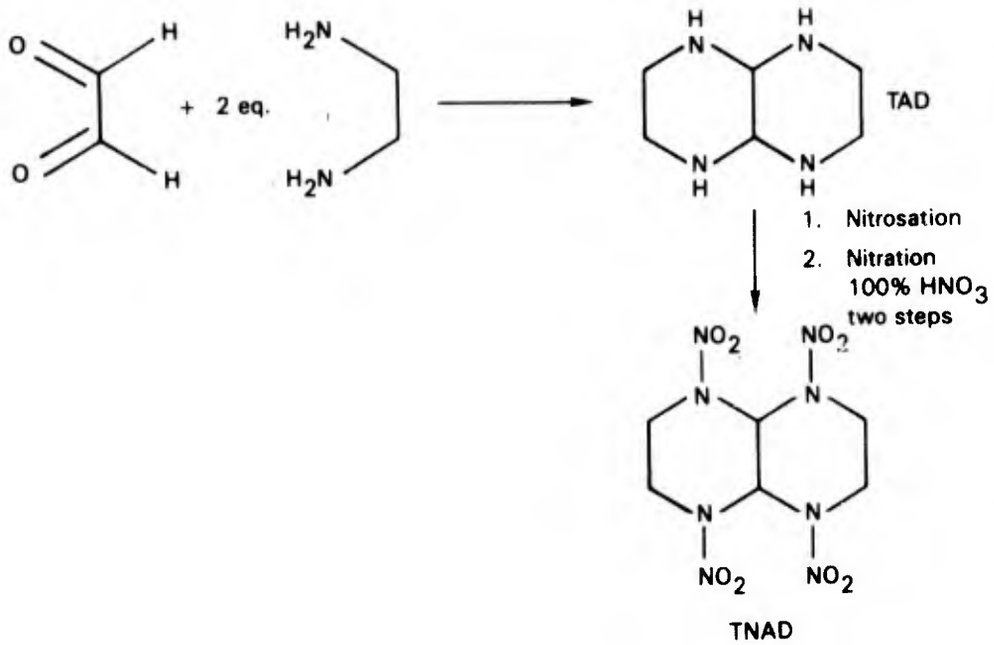
TABLE 1. Physical and Chemical Properties of TNAD.[a]

Property	Calculated	Measured
Density (g/cc)	1.77	1.80
Detonation velocity (mm/μs)	8.36	...
Detonation pressure (kbar)	310	...
Impact sensitivity (cm, 2.5 kg)	...	35
Melting point (°C)	...	232-234
Heat of formation (kcal/mol)	...	+17.5

[a] (Reference 8)

The synthesis of TNAD is shown in Scheme 1. Reaction of glyoxal with ethylene diamine gives trans-1,4,5,8-tetraazadecalin (TAD) in 85% yield. TAD cannot be nitrated directly, but must be converted to a precursor that can be readily nitrolyzed to the desired tetranitro derivative (Reference 9). Nitrosation of TAD with sodium nitrite in 1 N HCl results in the formation of 1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin in 91% yield. Nitrolysis of the tetranitrosodecalin precursor

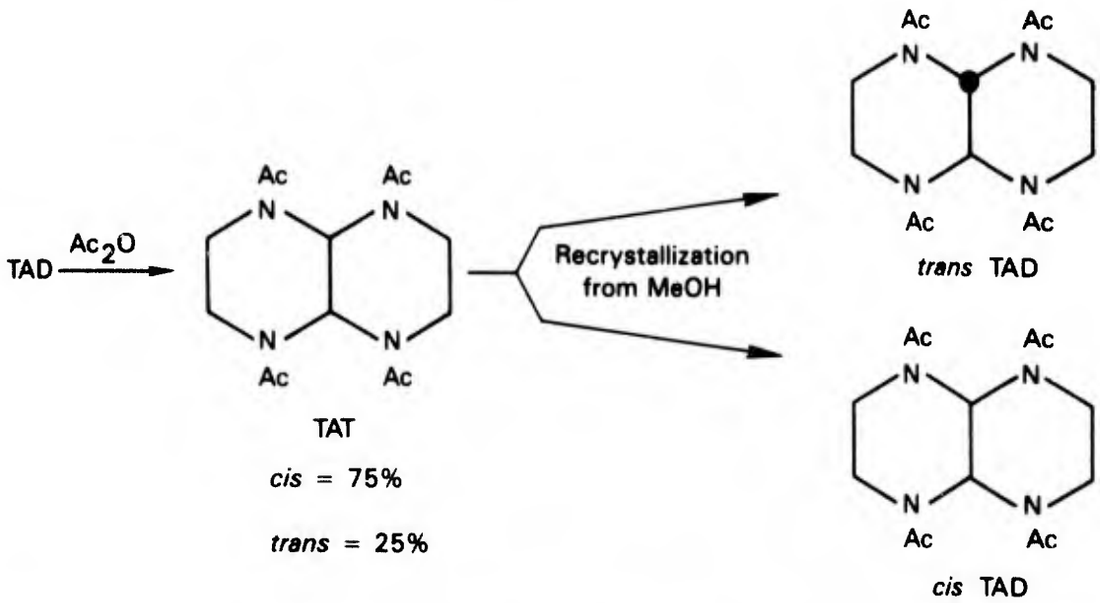
Scheme 1



in 100% nitric acid gives a 90% yield of trans-8-nitroso-1,4,5-trinitro-1,4,5,8-tetraazadecalin. A second nitrolysis in 100% nitric acid is required to convert the mixed nitroso-nitrodecalin into the desired TNAD. This second nitrolysis proceeds in moderate yield (68%). Attempts to scale-up the nitrolysis procedures for the formation of TNAD from the tetranitroso precursor failed because of thermal decomposition of starting material and the formation of intermediates during the nitrolysis. Therefore, if sufficient quantities were to be synthesized for further characterization and testing, an alternate synthesis of this interesting energetic nitramine would be required.

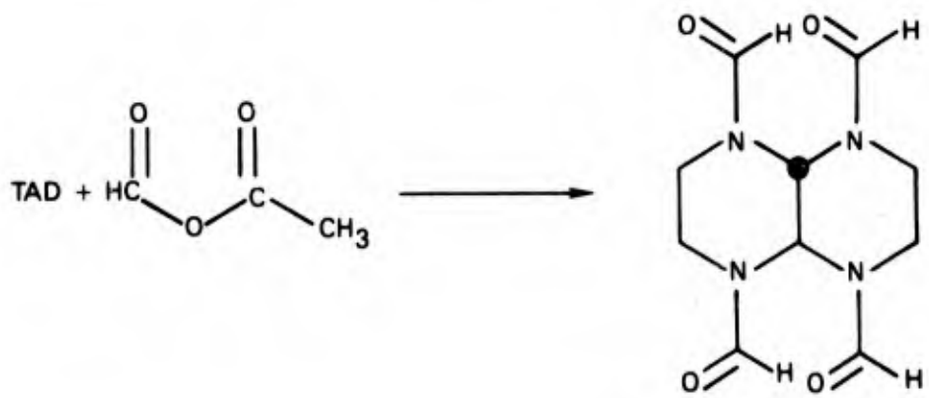
Treatment of TAD under a variety of conditions with acetic anhydride has been reported to give mixtures of cis- and trans-1,4,5,8-tetraaza-1,4,5,8-tetraacetyldecalins (Reference 10). In our hands, reaction of TAD with acetic anhydride in carbon tetrachloride, methylene chloride, or chloroform gave no acetyl derivatives, but resulted in the recovery of starting material. Similarly, treatment of TAD with acetyl chloride neat or in solution again resulted in the recovery of starting material. Reaction of TAD with acetic anhydride using the procedure of Baganz resulted in the formation of a 3:1 ratio of cis- to trans-TNAD (Reference 11). The separation of the cis and trans isomers was achieved by fractional crystallization from methanol and pure samples of each isomer had spectra identical to those reported by Fuchs (Reference 10) (Scheme 2).

Scheme 2



Similarly, reaction of TAD with excess neat formylacetate gave trans-1,4,5,8-tetraformyl-1,4,5,8-tetraazadecalin (Scheme 3).

Scheme 3



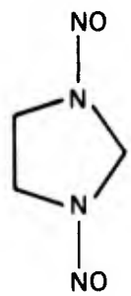
Under conditions which were similar to the successful nitrolysis of TAT as reported by Harrar and Pearson (Reference 6), the 3:1 mixture of cis- and trans-1,4,5,8-tetraacetyl-1,4,5,8-tetraazadecalin obtained from treatment of TAD with acetic anhydride was treated with a 24.5% N_2O_5 solution. Upon quenching the reaction over crushed ice, only a trace amount of product was isolated. Changes in the ratio of starting material to N_2O_5 (4:1 stoichiometric ratio) did not improve the yield. Evidently, the starting material, which is predominately the cis isomer, and/or the partially nitrolyzed products undergo hydrolysis under the reaction conditions. Likewise, the reaction of the model compound

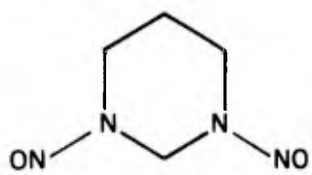
1,3-diacetyl-1,3-diazacyclopentane with N_2O_5 under a variety of conditions resulted in complete hydrolysis of the starting material.

Reaction of trans-1,4,5,8-tetraformyl-1,4,5,8-tetraazadecalin with N_2O_5 resulted in the production of a complex mixture of products from which no pure materials could be isolated.

Trans-1,4,5,8-tetraacetyl-1,4,5,8-tetraazadecalin however, upon treatment with N_2O_5 (8:1 stoichiometry, -10°C) gave a 42% yield of the desired TNAD. Apparently, the rate of hydrolysis of the trans tetraacetyl decalin is much less than that of the cis isomer, thus allowing for the desired nitrolysis to occur. In view of the difficulties in obtaining the appropriate trans isomer, the reaction of this isomer with N_2O_5 was not optimized.

Nitrolysis of nitroso protected amines utilizing 100% nitric acid or nitric acid in mixed acid media has proven effective for the preparation of nitramines. In order to test the efficiency of N_2O_5 as a nitrolysis reagent for nitrosamines, two model compounds were examined. The readily available 1,3-dinitroso-1,3-diazacyclopentane and cyclohexane were subjected to nitrolysis (Reference 12).



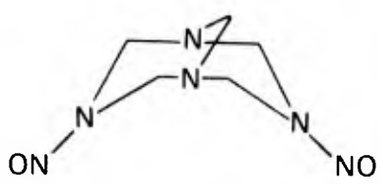


Reaction of the dinitrosocyclopentane with N_2O_5 resulted in the clean conversion to the desired dinitramine in 75-85% yield. Attempted nitrolysis of the compound using 100% nitric acid results in the formation of 1-nitroso-3-nitro-1,3-diazacyclopentane. Under more stringent reaction conditions (higher reaction temperatures and excess N_2O_5), the starting material decomposes, and none of the desired dinitramines can be isolated.

Treatment of the dinitrosocyclohexane with N_2O_5/HNO_3 resulted in the production of a mixture of the dinitramine and the intermediate 1-nitroso-3-nitro-1,3-diazacyclohexane.

Reaction of 1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin with N_2O_5 under a variety of conditions gave in excellent yields the desired TNAD. The reaction was successfully scaled up to 25 g batches and routinely resulted in yields of TNAD in excess of 95%.

Because N_2O_5 in nitric acid proved to be a useful reagent in the synthesis of TNAD, we decided to investigate the utility of this material with other systems. As previously stated, R-salt can be nitrolyzed to RDX with 100% nitric acid. When R-salt was treated with a 25% solution of N_2O_5 in nitric acid, RDX was formed albeit in much lower yields. Similar results were found with the attempted nitrolysis of 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT). The reaction is extremely vigorous and exothermic with generation of copious amounts of NO_x. If care was not taken when mixing the reagents, small fires and explosions occurred even though the reactions were run under CCl_4. Varying the amounts of N_2O_5/HNO_3 and decreasing the temperature did not improve the yields. In this example, the N_2O_5/HNO_3 reagent is such a powerful nitrating agent that it probably causes decomposition of the starting material or of the intermediate. This is an indication of the increased reactivity of N_2O_5/HNO_3 as a nitrolysis/nitration agent as compared to 100% nitric acid.



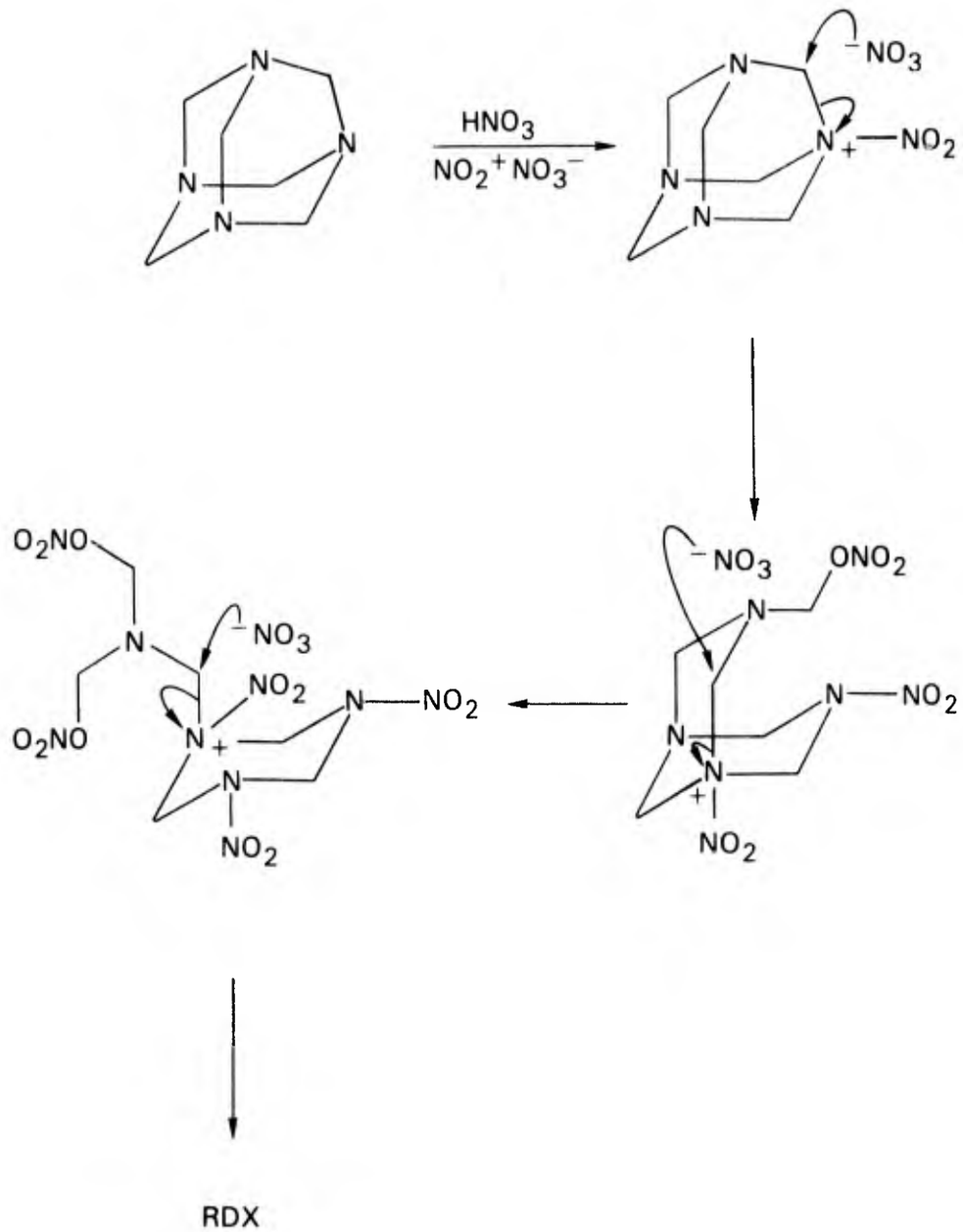
DNPT

The nitrolysis reaction of N_2O_5/HNO_3 and hexamine was examined. As stated in the introduction, hexamine is converted commercially to RDX via the Bachmann process in a number of steps and always contains significant amounts of HMX as a contaminant. In our examination, when hexamine was treated with N_2O_5/HNO_3, pure RDX (57% yield) was isolated. The important features of this reaction are the formation of a product free of HMX and, in contrast to the Bachmann process, RDX is formed in only one step from hexamine. A proposed possible mechanism for this transformation is shown in Scheme 4. Dinitrogen pentoxide ionizes in nitric acid to NO_2^+ and NO_3^- (Reference 13). The electrophilic nitronium ion then N-nitrates forming an electron deficient quaternary amine. Nucleophilic attack by nitrate on an adjacent methylene forms the first nitramine. Repeating this process eventually gives RDX. Attempts to follow the reaction by proton nuclear magnetic resonance (NMR) failed as the conversion of hexamine to RDX is essentially instantaneous on an NMR time scale.

We next decided to investigate the utility of dinitrogen pentoxide in inert solvents. In contrast to ionizing to nitronium and nitrate ions as seen in nitric acid, N_2O_5 in nonpolar solvents remains as the salt $NO_2^+NO_3^-$ (Reference 14). Because N_2O_5 in nitric acid was too harsh a reagent for the nitrolysis of R-salt, it was believed that N_2O_5 in dichloromethane may produce high yields of RDX. Much to our dismay

however, the reactivity decreased too much. All nitrolysis attempts using an inert, nonpolar, aprotic solvent failed. Only starting material was recovered. If prolonged reaction times and elevated temperatures were used, a decomposition of R-salt was seen. These decomposition products were complex in the proton NMR and could not be identified. Because N_2O_5 in nonpolar, aprotic solvents has been shown to possess weak diradical character (Reference 15), we believe this decomposition process to be a free radical induced process.

Scheme 4



Because N_2O_5 in nitric acid was too reactive as a solvent, and too unreactive in dichloromethane, we felt it worthwhile to investigate the effect of mild acid catalysis in dichloromethane. When p-toluenesulphonic acid (p-TSA) was used catalytically with ten equivalents of N_2O_5, a small amount of RDX was formed along with a large amount of unidentified side products. Due to the significant amount of decomposition still occurring, acid catalysis with R-salt was not examined further.

The nitrolysis of 1,4-dinitrosopiperazine was also investigated with N_2O_5 in inert solvents. The solvents studied were dichloromethane,

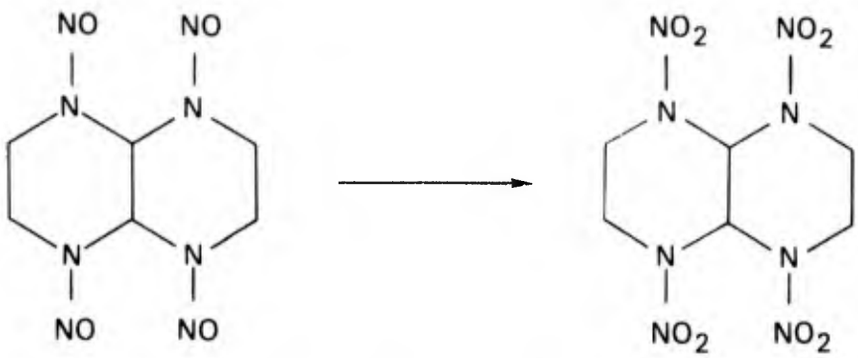
acetonitrile, dioxane, and dichloroethane. Using a variety of different reaction times, temperatures, and amounts of reagents, no nitrolysis occurred. Once again, we decided to determine the effects of trace amounts of acid. When a catalytic amount of p-TSA was used, no nitrolysis was detected. However, a catalytic amount of HCl did show signs of desired reaction in dichloromethane. Proton NMR revealed that a clean conversion of dinitrosopiperazine to dinitropiperazine was taking place. Even though this result appeared promising, it had to be approached with caution. Under proper conditions, N_2O_5 and anhydrous HCl will react to form NO_2Cl (Reference 16). Because we used concentrated 37% HCl instead of anhydrous HCl, we felt that NO_2Cl formation

$$N_2O_5 + HCl \text{ (anhydrous)} \rightarrow NO_2Cl + HNO_3 \qquad (1)$$

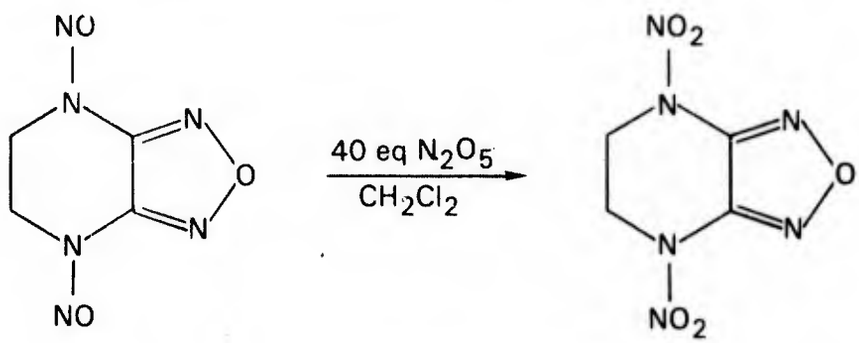
would be minimal and the H^+ would be available as a catalyst. This was not the situation. When dinitrosopiperazine was treated with N_2O_5/CH_2Cl_2 and two equivalents of HCl, dinitropiperazine was isolated in 67% yield. A large excess of N_2O_5 simply removed the water and NO_2Cl formed acting as the nitrolysis reagent. p-TSA or HNO_3 in catalytic amounts with N_2O_5/CH_2Cl_2 failed to undergo any reaction with dinitrosopiperazine.

When trans-1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin was treated with N_2O_5 in the previously mentioned inert solvents, no nitrolysis to TNAD was seen. Nitrolysis also failed when 2,4,8,10-tetranitroso-2,4,8,10-tetraaza[5.5]undecane was used as the nitrosamine (Reference 17). Each of these compounds was also treated with N_2O_5 in

dichloromethane and four equivalents of HCl (37% aqueous). The tetraazadecalin decomposed and the spirotetraazaundecane was recovered unreacted.



Next, we turned our attention to the nitrolysis of an electron-deficient nitrosamine, 1,4-dinitrosofurazano[3,4-b]piperazine. Reaction with 40 equiv. of N_2O_5 in dichloromethane gave a 68% yield of 1,4-dinitrofurazano[3,4-b]piperazine (CL-7.5) (Reference 18). This result



gave some useful insight into the reaction. Because of the strong electron withdrawing nature of the furazan moiety (Reference 19), the N-NO bond is weak. As mentioned above, N_2O_5 in organic, nonpolar, aprotic solvents may well nitrate/nitrolyze via a free radical mechanism. The electron deficient amine nitrogen and nitroso nitrogen can easily support free radicals upon homolytic bond cleavage. In a nonpolar solvent, free radicals would be favored thermodynamically over ion formation. This environment, which favors free radicals, would be predicted to give a good conversion to CL-7.5 from dinitrosofurazanopiperazine, the result found experimentally. We believe that this reaction may find future applications in the nitrolysis/nitration of electron-deficient amines and nitrosamines.

Finally, conversion of hexamine to RDX using N_2O_5 in dichloromethane was attempted. Results were disappointing. Employing a variety of conditions (time, temperature, and reactant ratios) we were not able to effect complete nitrolysis. When the solutions remained neutral, only R-salt was formed. This was, initially, an encouraging result

because partial nitrolysis had occurred. Unfortunately, as discussed previously, the R-salt could not be transformed into RDX. When small amounts of acid were added (p-TSA, HCl, HNO_3) only decomposition products were observed.

CONCLUSION

We have shown that N_2O_5 can be useful for the preparation of selected nitramines. Depending upon the solvent, the reaction proceeds via a free radical or ionic mechanism. It is hoped that these results may find future applications in the synthesis of new nitramines.

EXPERIMENTAL SECTION

WARNING! The nitrosamines described in this report may be carcinogenic and should be handled accordingly. The nitramines are high explosives, and the requisite precautions should be exercised when working with them. Satisfactory elemental analyses were obtained for all new compounds; all previously known compounds were spectrally identical with authentic materials prepared by established procedures. Melting points were determined in capillary tubes with a Buchi 510 melting point apparatus. Infrared spectra (IR) were recorded as potassium bromide disks with a Perkin-Elmer 137, 1330, or a Nicolet 7199 Fourier transform instrument. Proton magnetic resonance spectra were recorded with a Nicolet WB200 or IBM NR80 instrument. Solutions of N_2O_5 in 100% nitric acid were prepared as described by Harrar and Pearson (Reference 6). Concentration of N_2O_5 was determined by the NMR technique of Happe and Whittaker (Reference 20). Analysis of residual N_2O_4 was performed by Laser-Raman analysis (Reference 20). Dinitrogen pentoxide in inert solvents was made by mixing ozone and gaseous N_2O_4 and by trapping the N_2O_5 in a tared glass vessel at -78°C, then dissolving the white solid in the appropriate solvent.

PREPARATION OF TRANS-1,4,5,8-TETRAAZADECALIN (TAD)

A modification of the method of Fuchs was employed for the synthesis of TAD (Reference 21). Ethylenediamine (120 g; 2 mol) was cooled to 8°C with stirring, and 40% aqueous glyoxal (72.5 g; 0.5 mol) was slowly added (over a period of 2 h) while maintaining the reaction temperature below 10°C. The addition required 2 h. Upon completion of the addition, the reaction mixture was heated at 80°C for 5 h. The heating bath was removed, and the reaction suspension was allowed to slowly cool to room temperature (27°C). The suspension was then cooled to -10°C, and

the tan precipitate was collected by filtration. The filtrate was washed with 200 mL of 95% ethanol chilled to -10°C. The resulting white crystalline solid was dried in vacuo to give 57.1 g (0.405 mol; 81% yield) of the desired TAD (mp 160 to 200°C with decomposition). This material was used without further purification for derivitization.

PREPARATION OF TRANS-1,4,5,8-TETRAACETYL-1,4,5,8-TETRAAZADECALIN

Trans-1,4,5,8-tetraazadecalin (14.2 g; 0.1 mol) was slowly added to 300 mL of rapidly stirred acetic anhydride over a period of 45 min. The temperature was maintained at 22°C by means of an ice bath. Stirring was continued at room temperature for 4 h. The majority of the excess acetic anhydride was removed at reduced pressure (20 mm/25°C) on a roto-evaporator over a 72-h period. The resulting slurry was washed with 150 mL of acetone to give 14.5 g of crystalline solid. Nuclear magnetic resonance analysis proved this material to be predominately the cis isomer (3:1 ratio of cis to trans). The mixed product was dissolved in 100 mL of methanol. Concentration to 50 mL followed by slowly cooling to 25°C resulted in the deposition of a small amount of white crystalline material. The mother liquors were decanted, and the remaining solid was washed with cold methanol giving 1.1 g of white crystalline material (mp 287 to 292°C with decomposition). The IR spectrum shows the expected carbonyl stretch absorption band at 1650 cm^{-1}. The NMR spectrum in DMSO-d_6 taken at 70°C shows the expected pattern (Δ 5.39, 2 H, broad singlet, trans ring methine protons; δ 3.77, 8 H, broad singlet, ring methylene protons; δ 1.90, 12 H, acetyl methyl protons). The NMR spectrum is identical to that reported by Fuchs for the trans isomer.

PREPARATION OF TRANS-1,4,5,8-TETRAFORMYL-1,4,5,8-TETRAAZADECALIN

Formic acetic anhydride (10 mL) was cooled to 10°C, and trans-TAD (1.42 g; 10 mmol) was added in one portion with stirring. The reaction temperature rose to 35°C with concomitant deposition of a white precipitate. The resulting suspension was stirred for 45 min while the temperature of the reaction fell to room temperature. The reaction was quenched by pouring the suspension onto 70 mL of ice water. The white precipitate was filtered, washed with water (3 x 50 mL) and air dried to give 1.54 g of fine white solid which melted with decomposition above 275°C. The IR spectrum shows the expected strong carbonyl absorption band as a doublet at 1754 and 1733 cm^{-1}. The N-H absorption bands of the starting material are absent. The compound is extremely insoluble. An NMR spectrum was obtained of a dilute solution at 110°C in DMSO-d_6. The spectrum contained the expected three resonance signals in the appropriate ratio (δ 8.17, S, 4 H, formyl protons; δ 5.53, S, 2 H, methine protons; δ 3.77, bs, 8 H, methylene protons). Due to the dilute solution, the three resonances were somewhat broad. Based on the chemical shift of the ring methine protons of δ 5.53, the compound is tentatively assigned the trans stereochemistry. Compare the cis methine

chemical shift of δ 5.97 versus 5.33 for that of the trans stereoisomer of the closely related tetraacetyl derivatives. Analysis calculated for $C_{10}H_{14}N_4O_4$: C, 46.99; H, 5.59; N, 21.74. Found: C, 47.24; H, 5.55; N, 22.04.

PREPARATION OF 1,3-DINITROSO-1,3-DIAZACYCLOPENTANE (DNDCP) AND 1,3-DINITROSO-1,3-DIAZACYCLOHEXANE (DNDCH)

1,3-Dinitroso-1,3-diazacyclopentane and 1,3-dinitroso-1,3-diazacyclohexane were prepared in 90 and 95% yield as described in Reference 12 by the reaction of the requisite diamine with formaldehyde and by trapping the resulting aminal by nitrosation with HONO.

PREPARATION OF 1,3,5-TRINITROSO-1,3,5-TRIAZACYCLOHEXANE (R-SALT)

R-Salt was prepared in 29% yield by reaction of paraformaldehyde with ammonia and by trapping the incipient hexahydrotriazine by treatment with nitrous acid (Reference 1).

REACTION OF 1,3-DINITROSO-1,3-DIAZACYCLOPENTANE WITH N_2O_5

1,3-Dinitroso-1,3-diazacyclopentane (0.74 g; 5.6 mmol) was slowly added to 8 mL of a 30% solution of N_2O_5 in 100% nitric acid (32 mmol of N_2O_5) over a period of 3 min. Slight exotherm upon addition accompanied by the production of NO_x as evidenced by the generation of pink coloration upon addition of the DNDCP. The reaction temperature was maintained below 0°C throughout the addition. The reaction solution was stirred an additional 15 min at 0°C then quenched over 20 g of crushed ice giving a faint blue milky solution. The solution was extracted with methylene chloride (2 x 50 mL). Concentration on the rotoevaporator gave 0.50 g of white crystalline solid. Nuclear magnetic resonance analysis revealed the presence of some of the mixed nitrosonitro intermediate in this product. Crystallization from 95% ethanol gave 0.3 g (33% yield) of beautiful crystalline product (mp 131 to 133°C). The yield could be improved to 85% yield by carrying out the reaction at -35°C (Reference 7). Reaction of 1,3-diacetyl-1,3-diazacyclopentane under identical conditions resulted in complete hydrolysis of the starting material.

REACTION OF 1,3-DINITROSO-1,3-DIAZACYCLOHEXANE WITH N_2O_5

1,3-Dinitroso-1,3-diazacyclohexane (0.81 g; 5.6 mmol) was added to 8 mL of a 30% solution of N_2O_5 in 100% nitric acid in portions over 7 min. The reaction temperature was kept below 10°C. The reaction solution was stirred an additional 8 min and then quenched by pouring over 20 g of crushed ice giving a pale blue solution which paled to

yellow upon standing. The solution was extracted with methylene chloride (3 x 50 mL) and dried quickly over anhydrous magnesium sulfate. Filtration and evaporation of solvent gave 0.81 g of crude product. Nuclear magnetic resonance analysis showed this material to be a mixture of the desired dinitro compound and the intermediate nitroso-nitro derivative. There were no peaks remaining that corresponded to the starting material. Integration of the spectrum indicated the product to be 67% 1,3-dinitro-1,3-diazacyclohexane and 33% 1-nitroso-3-nitro-1,3-diazacyclohexane.

REACTION OF 1,4,5,8-TETRAFORMYL-1,4,5,8-TETRAAZADECALIN WITH N_2O_5

Trans-1,4,5,8-tetraformyl-1,4,5,8-tetraazadecalin (0.51 g; 2.0 mmol) was suspended in 25 mL of 1,2-dichloroethane. The suspension was cooled to 10°C and 2 1/2 mL of a 30% N_2O_5 solution was added dropwise over 2 min. The suspension was stirred an additional 30 min; at this time a 3 mL aliquot was withdrawn and quenched over 5 mL of ice water. Evaporation of the liquid phase left a small amount of yellow solid. The NMR spectrum of this material showed a multiplicity of resonances, none of which corresponded to the desired trans-TNAD. The reaction was stirred an additional 3 h, then quenched over 80 mL of ice water. Evaporation of the two liquid phases gave only a small amount of yellow mobile oil. The NMR of this oil again showed no resonance signals for the desired product, but only a multiplicity of signals from which no structural information could be deduced.

The reaction was repeated neat using an excess of N_2O_5 (10:1 mmol ratio). Quenching over ice water gave no precipitate. Removal of the aqueous phase gave a small amount of green oil from which no product could be induced to crystallize.

REACTION OF CIS-1,4,5,8-TETRAACETYL-1,4,5,8-TETRAAZADECALIN WITH N_2O_5

Cis-1,4,5,8-tetraacetyl-1,4,5,8-tetraazadecalin (3.54 g; 10 mmol; the NMR of shows only a trace of the trans isomer) was added with stirring to 24 mL of a 24.6% solution of N_2O_5 in nitric acid (8.64 g; 80 mmol) at 0°C over a 5-min period. The reaction solution was stirred an additional hour at 0°C, and then quenched over 50 g of crushed ice to give a yellow green aqueous phase. No precipitate was evident. Extraction of the aqueous phase with methylene chloride did not yield any product. Evidently, the cis isomer undergoes hydrolysis under these reaction conditions.

NITROLYSIS OF TRANS-1,4,5,8-TETRAACETYL-1,4,5,8-TETRAAZADECALIN

Trans-1,4,5,8-tetraacetyl-1,4,5,8-tetraazadecalin (0.5 g; 1.6 mmol; the NMR shows the absence of the cis isomer) was added in portions over 3 min to 4.8 mL of 24% N_2O_5 (1.74 g; 16 mmol). The reaction temperature was kept below -10°C. The starting material did not go into solution after 15 min, so the cooling bath was removed, and stirring was continued for an additional 30 min while the reaction mixture slowly warmed (red fumes of NO_x were evolved). The reaction was quenched over 10 g of crushed ice giving a white precipitate. Filtration and drying in the vacuum oven (50°C, 20 mm Hg) yielded 0.217 g of TNAD (42%). The NMR and IR spectra of this material were identical with those of an authentic sample.

NITROLYSIS OF TRANS-1,4,5,8-TETRANITROSO-1,4,5,8-TETRAAZADECALIN

Trans-1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin (5.16 g; 20 mmol) was added over 5 min in small portions to a solution of 50 mL methylene chloride and 46 mL of a 25% N_2O_5 solution (160 mmol). The temperature of the reaction was maintained below 0°C. The reaction mixture was stirred for an hour at 0°C. Red fumes were continuously evolved and were swept out of the reaction vessel by means of a slow dry nitrogen purge stream. The reaction was quenched over 150 g of crushed ice. Filtration gave a cream colored white solid. This was washed with water (2 x 50 mL) and then with methanol (2 x 75 mL). After drying in the vacuum oven overnight (65°C; 29 mm Hg), 6.54 g of white crystalline solid which melted at 233°C, with decomposition, remained. The NMR of this material is identical to that of an authentic sample of trans-TNAD. This constitutes a quantitative yield of the desired nitramine.

NITROLYSIS OF R-SALT TO RDX

R-salt (100 mg, 0.57 mmol) was added in portions over a period of 2 min to a stirred solution of 25% N_2O_5 in 100% HNO_3 (7.5 g, 17.2 mmol) under CCl_4 at 0°C. **ADD THE R-SALT CAREFULLY!** After 30 min at 0°C, the mixture was poured onto ice water (10 mL) and placed in a freezer for 20 h. A white solid (found to be RDX by comparison with an authentic sample) (40 mg, 32%) was collected by vacuum filtration.

NITROLYSIS OF HEXAMINE TO RDX

Hexamine (0.5 g, 3.6 mmol) was added in portions over 5 min to a stirred solution of 25% N_2O_5 in HNO_3 (36 mL, 142 mmol) under CCl_4 (20 mL) kept at -20°C. 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 solvent removal, a white solid was

isolated (0.46 g, 57%) which was shown to be RDX by comparison with an authentic sample (mp 202°C, decomposition, lit 204°C, decomposition).

NITROLYSIS OF DINITROSOPIPERAZINE TO DINITROPIPERAZINE

1,4-Dinitrosopiperazine (100 mg, 0.7 mmol) was dissolved in dichloromethane (5 mL) containing concentrated HCl (8 drops, approximately 1.4 mmol) and cooled to 5°C with stirring. Dinitrogen pentoxide in dichloromethane (46 mL, 1 M solution, 66 equiv.) was added dropwise and the reaction was allowed to stir for 3 days after slowly warming to ambient temperature. The mixture was poured into ice water (20 mL) and the layers separated. The organic layer was dried ($MgSO_4$) and solvent removed under reduced pressure to afford a white solid (800 mg, 67%) which was found to be dinitropiperazine by comparison with an authentic sample.

PREPARATION OF 1,4-DINITROSOFURAZANO[3,4-b]PIPERAZINE

Concentrated HCl (4 mL) was added dropwise to a stirred solution of furazano[3,4-b]piperazine (Reference 11) (1.0 g, 8 mmol) and sodium nitrite (1.24 g, 18 mmol) in water (50 mL) at 60°C. A thick, yellow solid formed, which was stirred at 60°C for 50 min and then cooled to 0°C for an additional 45 min, collected by suction filtration, and recrystallized from warm benzene to yield 1.0 g of 1,4-dinitrosofurazano[3,4-b]piperazine (mp 93 to 95°C, 68%) as yellow plates. ^1H NMR: broad singlet at 4.29 ppm (major conformer). Two minor conformers were seen as broad singlets at 5.20 and 4.49 ppm. ^{13}C NMR (major conformer): 39.28, 144.51 ppm. IR (KBr) cm^{-1}: 3000, 1630, 1560, 1500, 1400, 1350, 1075. Analysis calculated for $C_4H_4N_6O_3$: C, 26.09; H, 2.19; N, 45.65. Found: C, 26.08; H, 2.25; N, 45.72.

NITROLYSIS OF 1,4-DINITROSOFURAZANO[3,4-b]PIPERAZINE TO 1,4-DINITROFURAZANO[3,4-b]PIPERAZINE

1,4-Dinitrosofurazano[3,4-b]piperazine (0.25 g, 1.36 mmol) was dissolved in dichloromethane (5 mL) and cooled to 0°C. To this stirred solution was added dropwise N_2O_5 in dichloromethane (54.4 mL, 1 M solution, 40 equiv.). The mixture was stirred at 0°C for 45 min then poured into ice water (20 mL). The organic layer was separated, washed with water (10 mL), dried ($MgSO_4$), and solvent removed under reduced pressure to afford a light yellow solid (0.20 g, 68%), which by comparison with an authentic sample was shown to be CL-7.5.

REFERENCES

1. A. T. Nielsen, D. W. Moore, M. D. Ogan, and R. L. Atkins. "Structure and Chemistry of the Aldehyde Ammonia. 3. Formaldehyde-Ammonia Reaction. 1,3,5-Hexahydrotriazine," *J. Org. Chem.*, Vol. 44 (1979), pp. 1678-84.

2. W. E. Bachmann and J. C. Sheehan. "A New Method of Preparing the High Explosive RDX," *J. Am. Chem. Soc.*, Vol. 71 (1949), p. 1842.

3. E. E. Gilbert and V. I. Siele. "Alternative Procedures for Preparing HMX," *Prop. and Explo.*, Vol. 6 (1981), p. 67.

4. Pouderie Nationale de Sorgues. *Contribution a l'Etude de la Transformation de la Trimethylenetrinitrosamine en Hexogen,* by P. Abertein and H. Pascal. Service de Poudres, Pouderie Nationale de Sorgues, 16 January 1961. (Technical Note No. 430.)

5. D. A. Cichra and H. G. Adolph. "Nitrolysis of Dialkyl tert-Butylamines," *J. Org. Chem.*, Vol. 47 (1982), p. 2474-76.

6. J. E. Harrar and R. K. Pearson. "Electrosynthesis of N_2O_5 by Controlled-Potential Oxidation of N_2O_4 in Anhydrous HNO_3," *J. Electrochem. Soc.*, Vol. 130 (1983), p. 108-12.

7. R. L. Willer. "Synthesis and Characterization of High Energy Compounds. I. trans-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin (TNAD)," *Prop., Explo., and Pyrotech.*, Vol. 8 (1983), p. 65.

8. M. J. Kamlet and S. J. Jacobs. "Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C-H-N-O Explosives," *J. Chem. Phys.*, Vol. 48 (1968), p. 23.

9. R. F. Evans. "Hydropyrimidines. V. Hexahydropyrimidines. The Reaction of Aldehydes and Ketones with 1,3-Diaminpropanes," *Aust. J. Chem.*, Vol. 20 (1967), p. 1643.

10. B. Fuchs and others. "Structure and Conformation of Heterocycles. 12. 1,4,5,8-Tetraacyl-1,4,5,8-tetraazadecalins: Configurational and Conformational Analysis in the Crystal and in Solution," *Tetrahedron,* Vol. 40 (1984), p. 257.

11. H. Baganz, L. Domaschke, and G. Kirchner. "Ringschlussreaktionen des 1,2-Dichlor-1,2-diathoxy-athans mit Diaminen," *Chem. Ber.*, Vol. 94 (1961), p. 2676.

12. R. L. Willer and R. L. Atkins. "An Alternate Synthesis of Cyclic 1,3-Dinitramines," *J. Org. Chem.*, Vol. 49 (1984), pp. 5147-5150.

13. C. W. Tait, J. A. Happe, R. W. Sprague, and H. F. Cordes. "Kinetics and Thermal Decomposition of Liquid Nitric Acid," *J. Amer. Chem. Soc.*, Vol. 78 (1956), pp. 2670-73.

14. V. Gold, E. D. Hughes, C. K. Ingold, and G. H. Williams. "Nitration by Dinitrogen Pentoxide in Aprotic Solvents," *J. Chem. Soc.*, 1950, pp. 2452-66.

15. K. Okada, S. Yabushita, K. Yamaguchi, and T. Fuero. "Electronic Structure of Dinitrogen Pentoxide," *Chem. Lett.*, No. 10 (1977), pp. 1247-50.

16. J. Heubel. "Action of Liquid Hydrogen Chloride on Nitric Anhydride. Preparation of Nitryl Chloride," *Compt. Rend.*, Vol. 252 (1961), pp. 3268-70.

17. Naval Weapons Center. *Synthesis and Characterization of a New Insensitive High Energy Polynitramine Compound, 2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane (TNSU),* by R. L. Willer. China Lake, Calif., NWC, March 1982. 12 pp. (NWC TP 6353, publication UNCLASSIFIED.)

18. Naval Weapons Center. *Synthesis of 1,4-Dinitrofurazano[3,4-b]-piperazine (CL-7.5),* by R. L. Willer. China Lake, Calif., NWC, October 1983. 22 pp. (NWC TP 6461, publication UNCLASSIFIED.)

19. V. G. Andrianou and A. V. Eremeev. "Aminofurazans (Review)," *Chem. Het. Cpds (U.S.S.R.) (Eng),* 1984, pp. 937-51.

20. J. A. Happe and A. G. Whittaker. "Proton Resonance Shifts for the Systems HNO_3-H_2O and HNO_3-KNO_3," *J. Chem. Phys.*, Vol. 30 (1959), p. 417.

21. B. Fuchs and A. Ellencweig. "Structure and Conformation of Heterocycles. X. On 1,4,5,8-Tetraazadecalins," *Rec. Trav. Chem. Pays-Bas,* Vol. 98 (1979), p. 326.

INITIAL DISTRIBUTION

4 Naval Air Systems Command
- AIR-320G, B. Sobers (1)
- AIR-320R (1)
- AIR-723 (2)

12 Chief of Naval Research, Arlington
- ONCR-253, D. Siegel (1)
- ONCR-413, Dr. G. Neece (1)
- ONCR-432P, Dr. R. S. Miller (10)

6 Naval Sea Systems Command
- SEA-09B312 (2)
- SEA-62R2, C. M. Christensen (1)
- SEA-62R32, G. Edwards (1)
- SEA-64E (1)
- SEA-96R, Dr. J. Pastine (1)

1 Commander in Chief, U.S. Pacific Fleet (Code 325)

1 Headquarters, U.S. Marine Corps (Code RD-1, A. L. Slafkosky, Scientific Advisor)

1 Commander, Third Fleet, Pearl Harbor

1 Commander, Seventh Fleet, San Francisco

2 Naval Academy, Annapolis (Director of Research)

1 Naval Explosive Ordnance Disposal Technology Center, Indian Head (Code D, L. Dickinson)

2 Naval Ordnance Station, Indian Head
- Code 5253, W. G. Roger (1)
- Code 5253L, J. Moniz (1)

1 Naval Postgraduate School, Monterey (Code 012, Dr. J. Wall, Director, Research Administration)

8 Naval Research Laboratory
- Code 2627 (6)
- Code 6030, Dr. R. Gilardi (1)
- Code 6120, Dr. W. Moniz (1)

1 Naval Surface Weapons Center, Indian Head (Code R16, J. Consaga)

12 Naval Surface Weapons Center, White Oak Laboratory, Silver Spring
- Code R10, K. F. Mueller (1)
- Code R10B, M. J. Stosz (1)
- Code R10C, L. A. Roslund (1)
- Code R10D, H. G. Adolph (1)
- Code R10E, J. M. Kelley (1)
- Code R11
  - C. Gotzmer (1)
  - M. J. Kamlet (1)
  - J. M. Short (1)
- Code R13, C. Dickinson (1)
- Code R16, N. Seiden (1)
- Dr. J. Holden (1)
- Dr. R. Doherty (1)

1 Naval War College, Newport

1 Naval Weapons Support Center, Crane, IN (Code 5063, Dr. H. Webster III)

1 Naval Weapons Station, Yorktown (L. R. Rothstein, Assistant Director, Naval Explosives Development Engineering Department)

1 Office of Naval Technology, Arlington (DNL-071, Dr. E. Zimet)

4 Army Armament Research and Development Command, Dover
SMCAR-LCE-C
Dr. J. Alster (1)
Dr. E. Gilbert (1)
Dr. N. Slagg (1)
Dr. G. Sollott (1)
1 Army Missile Command, Redstone Arsenal (DRSMI-RKL, W. W. Wharton)
5 Army Ballistic Research Laboratory, Aberdeen Proving Ground
DRDAR-IBD, A. Junasz (1)
DRXBR-IBD
Director (1)
Dr. I. W. May (1)
DRXBR-TBD
Dr. P. Howe (1)
J. J. Rocchio (1)
3 Army Research Office, Research Triangle Park
Chemical & Biological Sciences Division
R. Ghirardelli (1)
G. Ronald Husk (1)
Engineering Division, Dr. D. Mann (1)
1 Ballistic Missile Defense Advanced Technology Center, Huntsville (D. C. Sayles)
1 Air Force Academy, Colorado Springs (FJSRL/NC, J. S. Wilkes, Jr.)
1 Air Force Armament Division, Eglin Air Force Base (AFATL/DLJG, O. K. Heiney)
1 Air Force Intelligence Service, Bolling Air Force Base (AFIS/INTAW, Maj. R. Lecklider)
3 Air Force Office of Scientific Research, Bolling Air Force Base
Directorate of Aerospace Sciences, L. H. Caveny (1)
Directorate of Chemical & Atmospheric Sciences
Dr. D. L. Ball (1)
Dr. A. J. Matuszko (1)
2 Air Force Rocket Propulsion Laboratory, Edwards Air Force Base
AFRPL/DY, R. Geisler, MS 24 (1)
AFRPL/LKLR, Dr. R. D. Champman (1)
12 Defense Technical Information Center