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ABSTRACT

This work is focused on a continued, escalating effort to develop new energetic functional groups which offer enhanced energy, oxygen balance, and density in that order of priority.

A continuation of the study of addition of nitrene precursors to N,N-dialkyl nitrosamines is decribed; the nitrene derived from 1-amino-3,5-dinitro-1,2,4-triazole has been approached by oxidation of the parent amine. Initial results were not successful; aminodinitrotriazole in the presence of lead tetra-acetate does not produce detectable yields of dinitrotriazolyl azoxy dimethyl amine when aminodinitrotriazole and lead tetra-acetate are reacted in the presence of N,N-dimethylnitrosamine.

The synthesis of the 5-nitrotetrazole-2-N-oxide anion has been realized and optimized; it is carried out in water/potassium acetate buffer, and proceeds in 90% yield; due to the small enthalpy of this oxidation, scale up and heat dissipation do not present a problem. The density of hydroxyl ammonium 5-nitrotetrazole-2-oxide is 1.82 g/cc; its enthalpy of formation is +40 kcal/mole.

A number of new high energy ring systems were explored; 5,5'-bis-tetrazolyl-tert.butylamine was prominent among these. Amination and oxidation of this system produced multiple products; for the present, this target was abandoned, pending new developments.

Amination of the anionic forms of nitrotetrazole-N-oxides as well as nitrotriazole-N-oxides resulted in deoxygenation of the N-oxide.

Cycloadditions of diazenium diolates and other two-nitrogen species with trimethylsilyl azide in an effort to synthesize pentazole-N-oxides were not successful; catalysts and conditions will be modified extensively in the continuation of this effort.

Attempts to cyclize dinitrourea and carbamyl azide to unprecedented energetic heterocycles were not successful; catalysts and conditions will be varied in future attempts. An industrial scale of carbamyl azide has been developed in the process of conducting these studies.

Finally, a practical pathway to 1-alkoxy-5-amino tetrazoles has been developed; it is hoped that this will enable the synthesis of 5-nitrotetrazole-1,3-bis-N-oxides, a family of unprecedented materials with excellent heats of formation and oxygen balance that rivals ammonium perchlorate and ammonium dinitramide.

CONTENTS

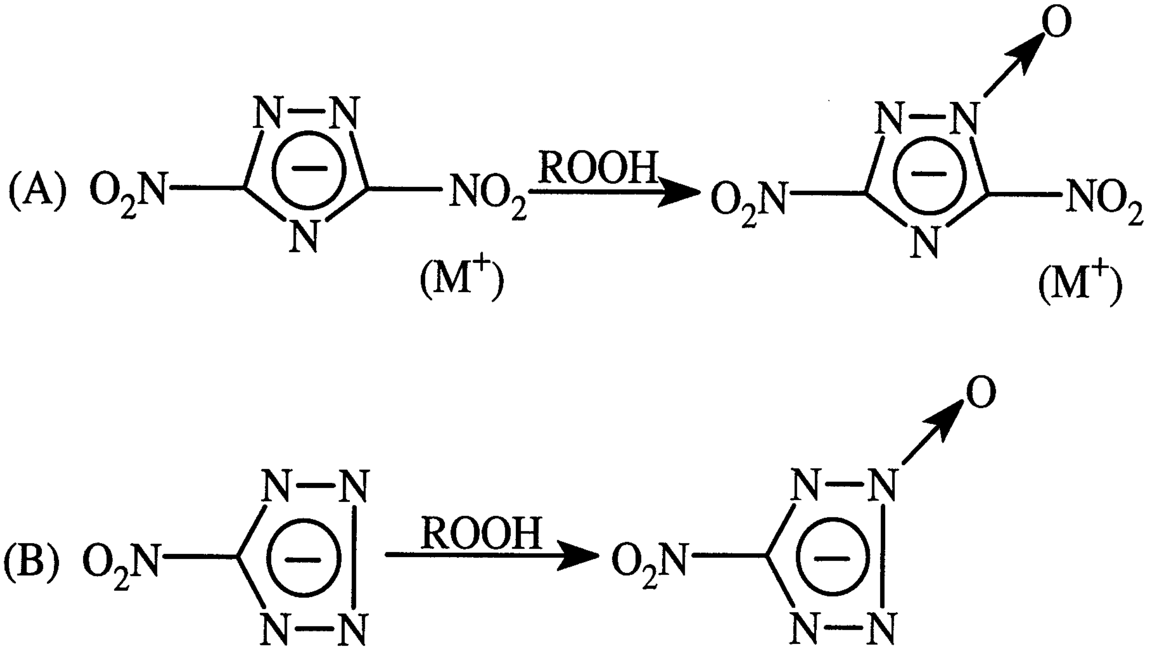
BACKGROUND

The validity of further investment in the basic research on high performance energetic materials is being tested as we enter the second phase of this program. New functional groups are being sought and demonstrated and their empirical densities and enthalpies of formation are being determined as molecules bearing these new functional groups are synthesized and characterized by x-ray crystallography, differential scanning calorimetry, and impact testing. While the first phase of the program bore hydroxynitrourea and its salts, which show promise as ingredients in formulations, the realization of even more dense, oxidizing, and energetic functional groups remains an urgent and largely unsatisfied mandate. Achievements in this second phase of the Nano/HEDM program are beginning to show greater promise as propellants and explosives whose performance exceeds that of CL-20 (hexanitro hexaza isowurtzitane) while retaining the safety of HMX and RDX. In addition, some of the targets realized in this second phase of the Nano/HEDM program display preparative facility and safety lacking in CL-20.

While some of the original proposed functional groups remain elusive, new ones are being conceived at a rate exceeding the rate of failure, justifying continuation of the core agenda: to create unprecedented families of energetic compounds based on new functional groups and to assemble them combinatorically into molecules whose whole exceeds the sum of its parts due to complimentarity of the attributes of these newly discovered functional groups. The 5-nitrotetrazole-2-N-oxide is an excellent example of this: it is easy to prepare in bulk, is stable, and can be used as the counterion in a wide array of energetic salts.

SYNTHESIS OF THE 5-NITROTETRAZOLE-2-0XIDE ANION AND ITS SALTS

Our most practical technological advance in this year's endeavors was the synthesis of the 5-nitrotetrazole-2-oxide anion and its salts. Based on our considerable difficulty in oxidizing the anion of 3,5-dinitro-1,2,4-triazole to its N-oxide (Final Report on Project 2489, Bottaro et al., September 2001), we anticipated considerable difficulty (Figures 1A and B) in the oxidation of the 5-nitrotetrazole to either of its two possible N-oxides. To our surprise, the oxidation of 5-nitrotetrazole to its 2-N-oxide (the regioselectivity was, fortunately, excellent; none of the 1-N-oxide could be detected by TLC or ion chromatography; we will discuss this later) was readily optimized in aqueous media using peroxymonosulfate ("OXONE") reagent. Not only was the regioselectivity good; the overall yield was consistently in excess of 90% and isolation was facile, involving addition of either tributyl ammonium sulfate or tetrabutyl ammonium bisulfate to the reaction mixture, followed by extraction of the product into ethyl acetate. The crude tetrabutyl ammonium nitrotetrazole 2-oxide can then be converted to any of its desired salts by simple ion exchange chromatography using AMBERLYST® polystyrene sulfonate resin charged with the NH_4^+, NH_3OH^+ Li^+, or any other desired cation. The efficiency of this chromatography is excellent because the end result of the chromatography is a set of products whose ionic counterparts are matched with respect to size and polarizability, the hallmark of a thermodynamically driven ion exchange.



Figures 1A and B. Oxidation of 3,5-dinitro-1,2,4-triazole anion and 5-nitrotetrazole anion to their respective N-oxides.

The absence of the 1-N-oxide as an impurity in the oxidation reaction mixtures is probably the result of the ability of the tetrazole-1-oxide to ring-open to its corresponding hydroximinoyl azide, which would be expected to be destroyed under the strongly oxidizing conditions of the reaction (Figure 2). The heat of formation of 5-nitrotetrazole-2-oxide hydroxyl ammonium salt was measured to be +40 kcal/mole at Morton Thiokol.

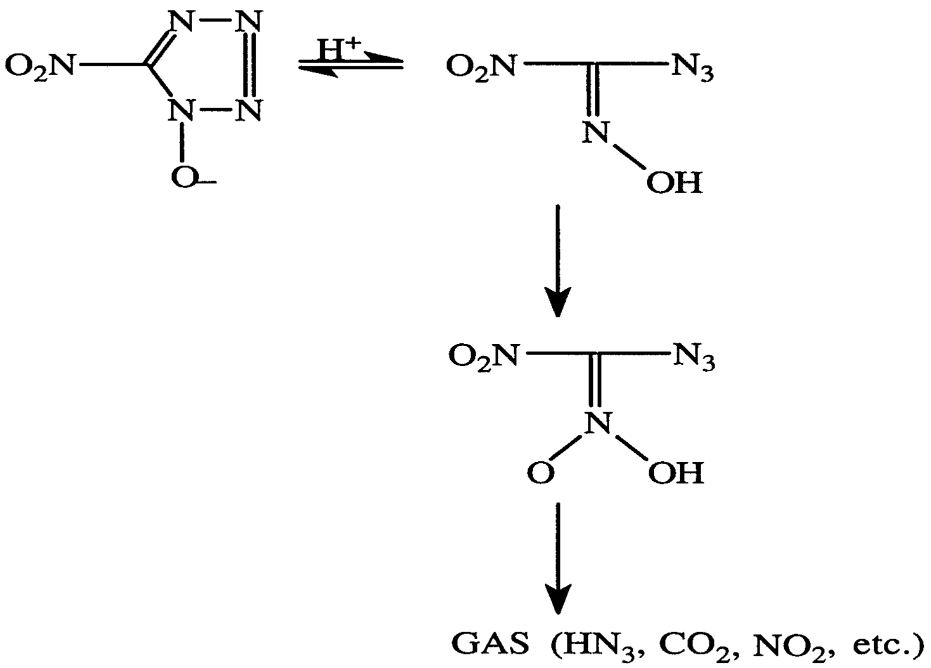


Figure 2. Expected fate of 5-nitrotetrazole-1-N-oxide.

FURTHER STUDIES ON THE REACTION OF NITRENE PRECURSORS WITH DIALKYL NITROSAMINES

The addition of nitrene and carbene equivalents to nitrosamines, which would yield precursors to nitroazoxyamines (diazanitrates) and other energetic groups as well, was pursued in our second year of study as well as our first. In our second series of efforts toward the addition of nitrenes to nitrosamines, N-nitroso-3,3-dinitroazetidine (Figure 3) was used as a model substrate along with the more inexpensive N,N-dimethyl nitrosamine.

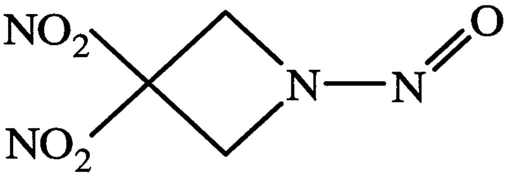


Figure 3. 1-Nitroso-3,3-dinitroazetidine.

The panel of nitrene and carbene precursors studied in this series is shown in Table 1. Unfortunately, none of these materials produced the desired addition analogous to the addition of oxygen enabled by peroxycarboxylic acids.

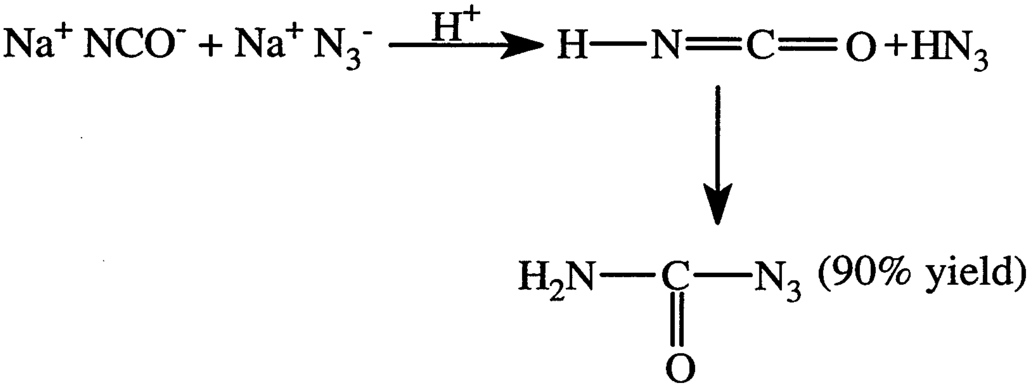
Table 1. Nitrene and carbene precursors reacted with 1-Nitroso-3,3-dinitroazetidine.

1. Potassium fluoronitramide
2. N,N-dibromonitramine
3. Potassium chlorocyanamide
4. Cyanamide + phenyliodine diacetate
5. Silver nitroformate
6. Cyanogen azide

In our final year, more reactive reagents will be sought, such as the O-(trifluoromethanesulfonyl) hydroxylamides and related structures. Photochemical degradation of nitryl azide in the presence of the target nitrosamine will also be examined.

SYNTHESIS OF AMMONIUM NITROCARBAMYL AZIDE

Due to the simultaneous presence of numerous energetic molecular targets involving carbamyl azide as starting material, we developed a convenient, large scale synthesis for carbamyl azide, which simply involves reacting sodium azide, potassium cyanate, and sulfuric acid in water, with vigorous stirring in ethyl acetate to extract the product as it forms to minimize hydrolysis (Figure 4).



$$Na^+\,NCO^- + Na^+\,N_3^- \xrightarrow{H^+} H{-}N{=}C{=}O + HN_3 \longrightarrow H_2N{-}C({=}O){-}N_3 \text{ (90\% yield)}$$

Figure 4. Bulk synthesis of carbamyl azide.

The first enticing target involving carbamyl azide was simply the ammonium salt of its N-nitro derivative. By analogy to the exceedingly smooth synthesis of nitrourethane from urethane using acetyl nitrate as the nitrating agent, acetyl nitrate was examined first in the development of a nitrating system for carbamyl azide. It was expected that the orbital energies, bond length, and redox potential for the amide nitrogen of carbamyl azide would strongly resemble those of urethane, making acetyl nitrate an attractive prospect. When the compatibility of acetyl nitrate with various azides was established by a cursory study of the reaction of acetyl nitrate with t-butyl azide and toluene sulfonyl azide, the synthesis of ammonium nitrocarbamyl azide was attempted. To our immense satisfaction, the reaction of acetyl nitrate with carbamyl azide at 0° proceeded easily (TLC assay, ethyl acetate eluting over silica gel). Addition of ammonium acetate formed the salt of the markedly acidic N-nitroamide, isolation was completed by addition of ethyl acetate to the salt solution followed by filtration (Figure 5). Infrared spectroscopy bore out the presence of azide and nitramine alike. Unfortunately, the ammonium nitrocarbamyl azide was very hygroscopic and had poor crystal morphology. In addition, it had nitroglycerine-like impact and friction sensitivity. When the hydroxylamine salt was synthesized, it decomposed on standing even at –15°C in solution. These unfavorable observations precluded our pursuit of x-ray crystallographic structure analyses as well as the synthesis of other salts of nitrocarbamyl azide, an energetic synthesis platform which would otherwise have enjoyed wide application.

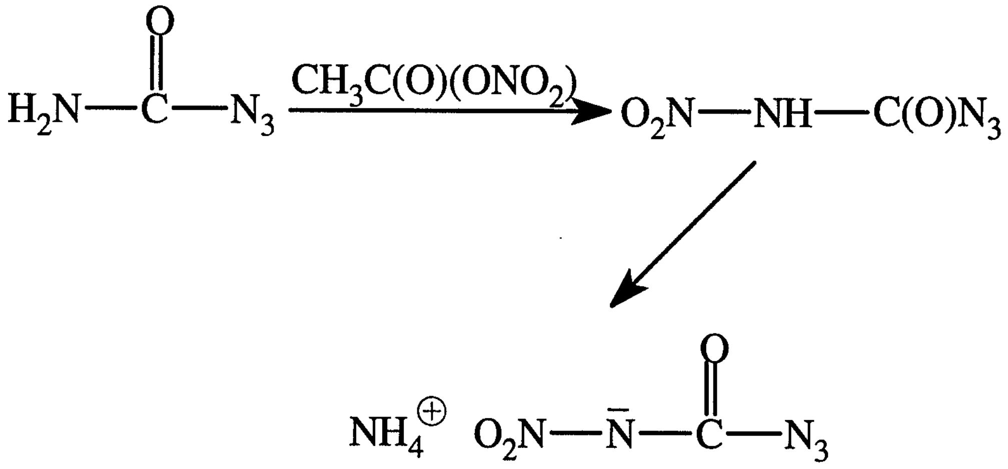


Figure 5. Synthesis of ammonium nitrocarbamyl azide.

EXPLORATION OF THE CHEMISTRY OF BIS-(5-TETRAZOLYL)-TERT-BUTYLAMINE

The compound bis-(5-tetrazolyl)-tert-butylamine was perceived to be a very useful platform for the synthesis of a vast array of energetic materials (Figure 6). Its synthesis was straightforward once the conditions for the reaction were optimized. Of interest was the selectivity of the second cyanation whose outcome was contrary to the mandates of steric hindrance (Figure 7).

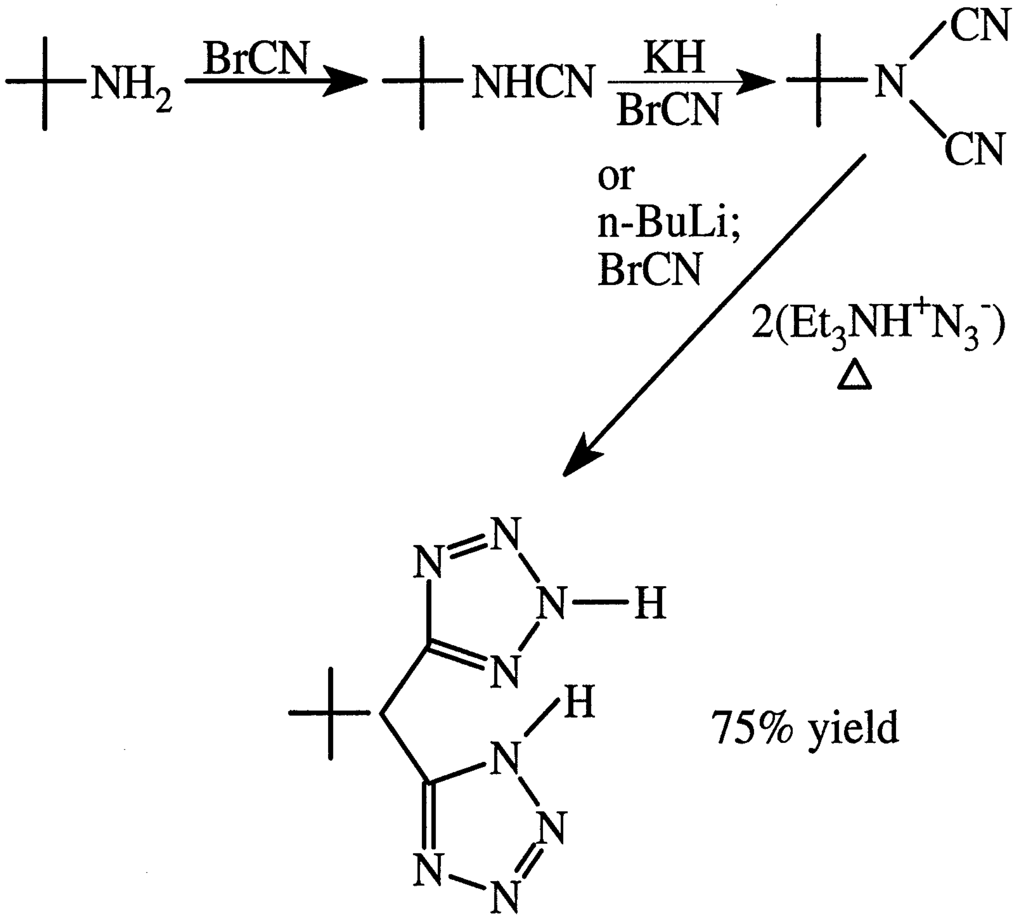


Figure 6. Synthesis of Bis-(5-tetrazolyl)-tert-butylamine)

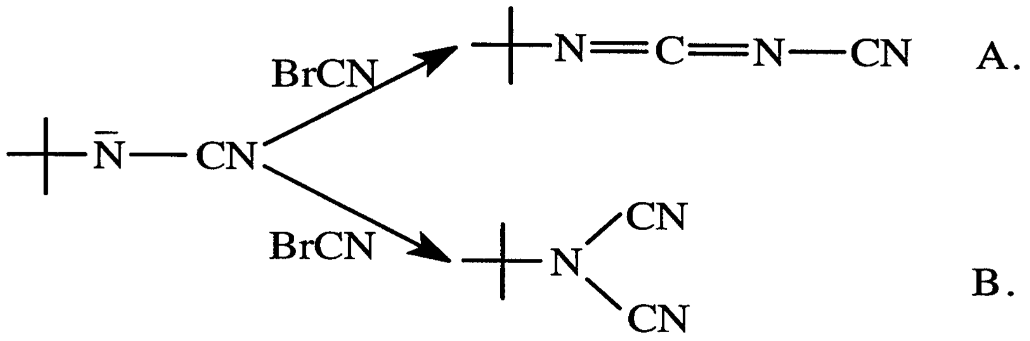


Figure 7. Cyanation of tert.butyl cyanamide.

In fact, when tert-butyl cyanamide (whose synthesis is trivial, and proceeds in 100% yield by reacting cyanogen bromide with tert-butyl amine in buffered media) is deprotonated with either potassium hydride or tert-butyllithium and treated with cyanogen bromide, almost half of the reaction mixture consists of the undesirable product A, which had to be destroyed during the workup by passing it through a short column of silica gel, followed by careful distillation.

The cycloaddition of tert.butyl dicyanamide with triethylammonium azide to give the desired bis-(5-tetrazolyl)-tert.butylamine had one interesting attribute: the reaction of the second mole of azide was much slower than the reaction of the first. This was attributed to the fact that the addition of the first mole of azide produces an anion (Figure 8) rendering the second reaction electrostatically encumbered by virtue of the fact that an anion is being made to react with an anion, a scenario which is almost always kinetically and thermodynamically disfavored.

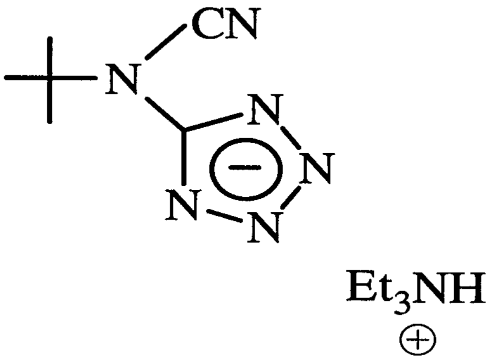


Figure 8. Anionic intermediate in the reaction of two moles of azide ion (as its triethylammonium salt) with tert-butyl dicyanamide.

Once the bis-(5-tetrazolyl)-tert-butylamine was synthesized in bulk and characterized by x-ray crystallography (see Appendix), attempts were made to cyclize it with bifunctional electrophiles such as methylene dibromide and methylene diiodide. Cyclic products were indeed derived; in fact, a large macrocycle was isolated from the reaction of the dianion of 5,5'-bis-(tetrazolyl)-tert-butyl amine with methylene diiodide (Figure 9).

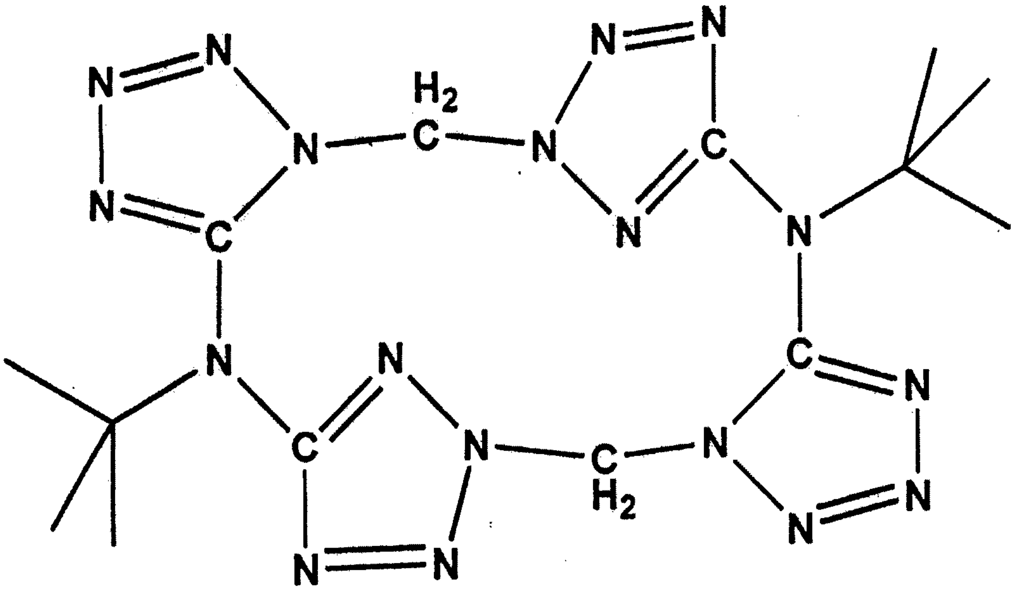


Figure 9. Macrocycle from dianion of 5,5'-bis-(tetrazolyl) amine reacting with methylene diiodide.

The amination of the dianion of 5,5'-bis-(tetrazolyl)-tert-butyl amine with electrophillic aminating agents such as hydroxylamine O-sulfonic acid or hydroxylamine-O-toluene-sulfonate similarly suffered from a lack of regioselectivity; such reactions gave complex mixtures containing one tetrazole ring aminated on the #2 nitrogen atom and the other aminated on the #1 nitrogen atom. It was hoped that a high yield of material aminated twice on the (#1 and 1') nitrogen atom could be oxidatively cyclized to give a fused ring system containing a central ring possessing two carbon atoms and five nitrogen atoms; oxidation of this ring would, hopefully, give some extremely energetic materials (Figures 10 and 11).

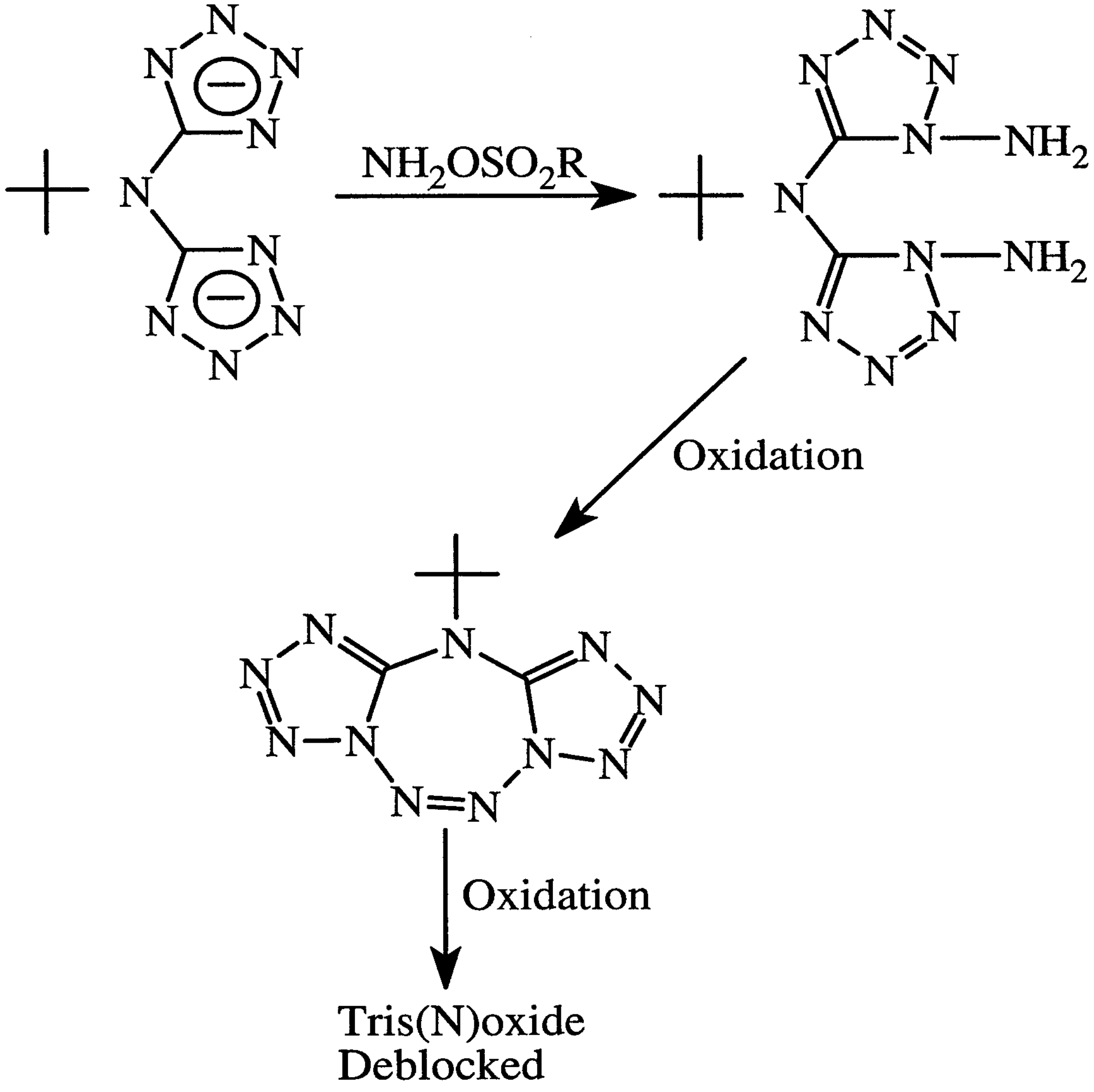


Figure 10. Hoped for amination pathway for bis-(5'-tetrazolyl)-tert-butyl amine.

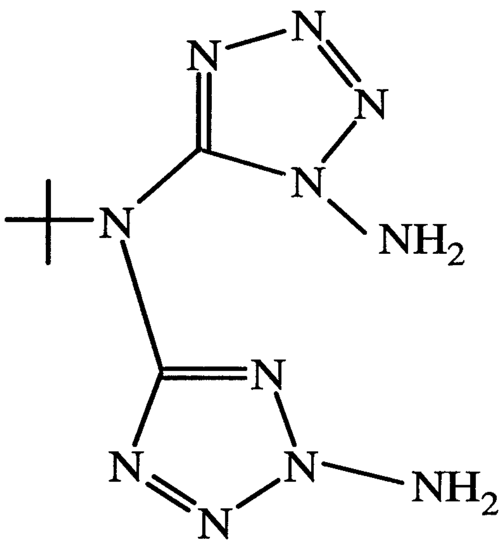


Figure 11. Actual product of amination of dianion of Bis-(5'-tetrazolyl)tert-butylamine.

Without any protocol for forcing the synthesis of the 1,1'-diamino-bis(5,5'-tetrazolyl)-tert-butylamine, this pathway and target were tentatively abandoned.

REACTION OF 1-AMINO-3,5-DINITRO-1,2,4-TRIAZOLE WITH N,N-DIMETHYL NITROSAMINE UNDER OXIDIZING CONDITIONS: ATTEMPTED SYNTHESIS OF THE DINITROTRIAZOLE AZOXY AMINE

A brief study was made of the utility of 1-amino-3,5-dinitro-1,2,4-triazole as a nitrene source under oxidizing conditions. The amino dinitro triazole was reacted with N,N-dimethyl nitrosamine under a variety of oxidizing conditions in order to effect the addition of the nitrene derived from the oxidation of the amino triazole to the nitrosamine, giving the dinitro triazolyl azoxy amine (Figure 12).

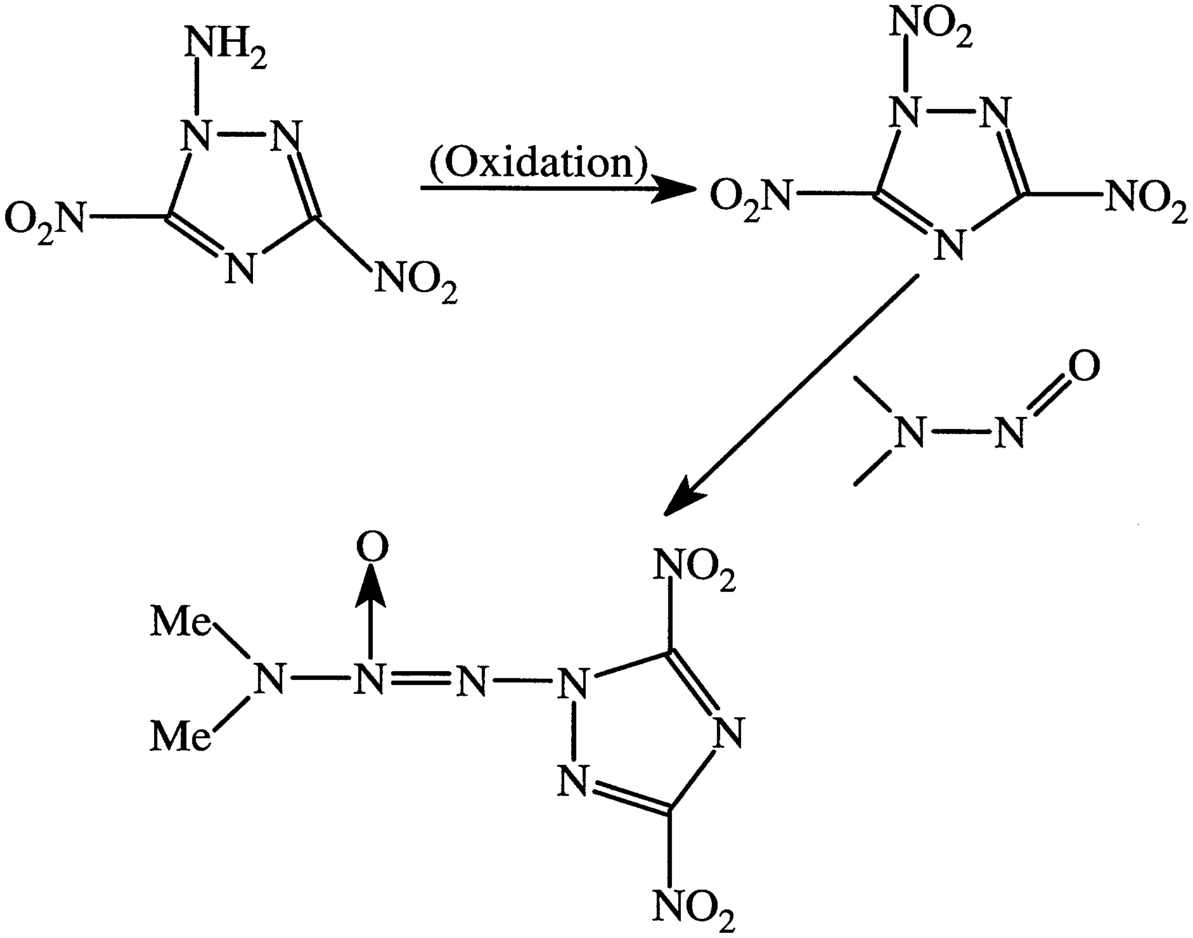


Figure 12. Synthesis of dinitro triazolyl azoxy dimethylamine.

With lead tetraacetate, phenyl iodine diacetate, and tert-butyl hypochlorite, only traces of unstable products were formed and this strategy was tentatively abandoned.

ATTEMPTED AMINATION OF 3,5-DINITRO-1,2,4-TRIAZOLE-1-N-OXIDE

It was hoped that the N-oxide of 3,5-dinitro-1,2,4-triazole anion could be aminated in the N-4 position to give the neutral, highly energetic, highly oxidized 4-amino-3,5-dinitro-1,2,4-triazole-1-N-oxide (Figure 13).

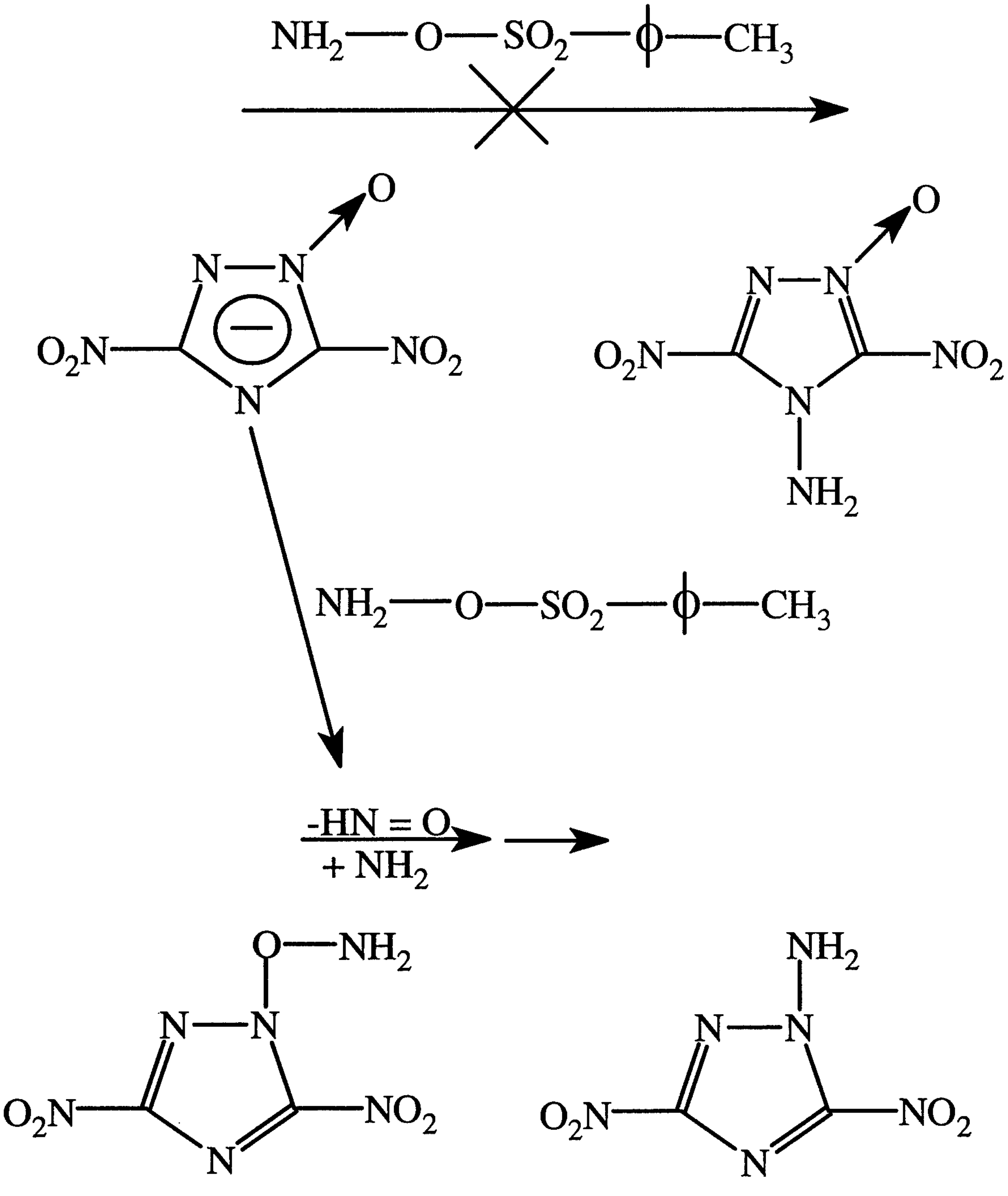


Figure 13. Attempted amination of 3,5-dinitro-1,2,4-triazole-1-N-oxide-anion.

When this amination was attempted, however, the only product observed was the 1-amino-3,5-dinitro-triazole derived by deoxygenation followed by amination. This strategy was tentatively abandoned, pending the development of a more enabling polyfunctionalization strategy.

ATTEMPTED REACTION OF THE DIANION OF BIS-5-TETRAZOLYL-TERT-BUTYLAMINE WITH TETRACHLOROPYRAZINE BIS-N-OXIDE

The dianion of bis-5-tetrazolyl-tert-butylamine with tetrachloropyrazine-bis-N-oxide was attempted (Figure 14) with and without copper (1) catalyst under an argon atmosphere; both reactions were unsuccessful.

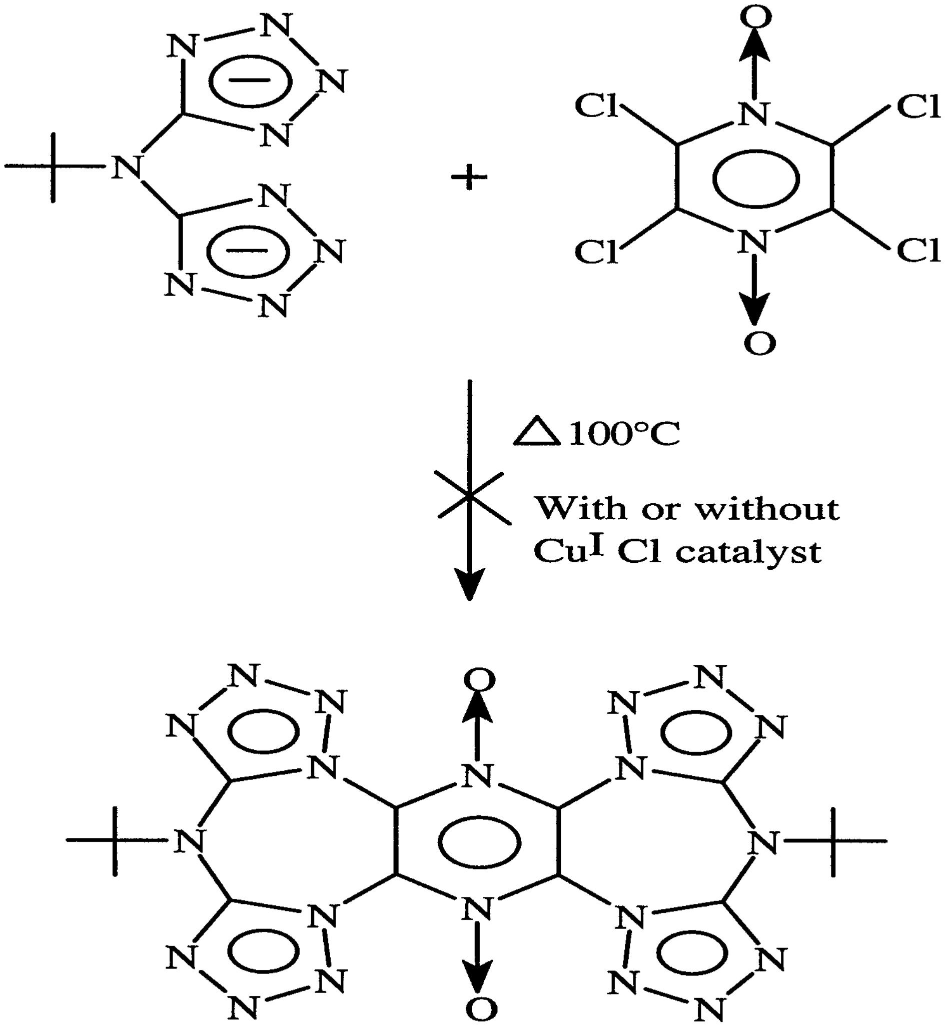


Figure 14. Attempted Reaction of bis-(5-tetrazolyl)-tert-butylamine dianion with tetrachloropyrazine bis-N-oxide.

ATTEMPTS TO OXIDIZE CYANURIC AZIDE TO ITS MONO-N-OXIDE

Cyanuric azide is a long-known high-nitrogen energetic material (Figure 15), which suffers from unacceptable volatility. Although, its heat of formation is tremendous (approximately +250 kcal per mole), it is underoxidized. Finally, its density falls short of the benchmark (1.90 g/cc) of present state-of-the-art materials.

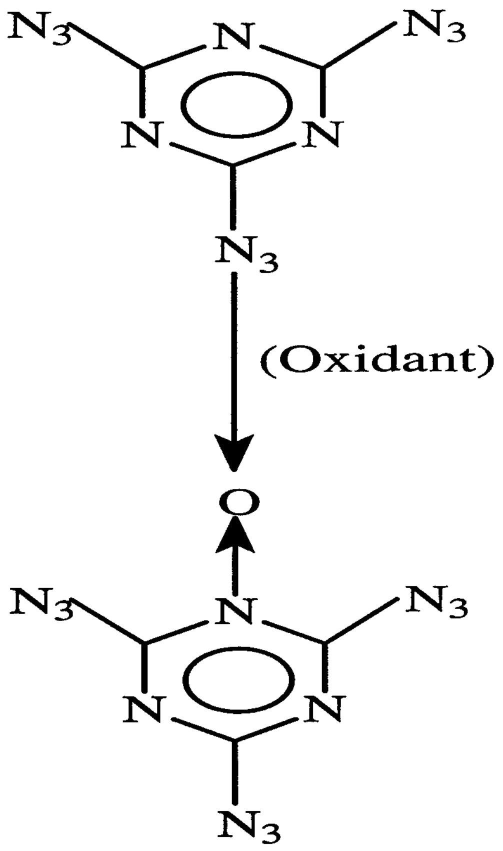


Figure 15. Cyanuric azide and its mono-oxide.

Oxidation of cyanuric azide to its mono-, di-, or tri-N-oxides could potentially solve all of these problems. Per acetic acid, peroxytrifluoro acetic acid, aqueous peroxy sulfate ("OXONE") and ozone all failed to effect the desired oxidation at room temperature. When heat was applied to these reactions, decomposition rather than clean oxidation to one or two characterizable products occurred. As a result, this target was abandoned, pending discovery of stronger oxidants compatable with the azide function.

ATTEMPTED ACID-CATALYZED CYLICZATION OF N-NITROSO-N-METHOXY BENZYLAMINE WITH TRIMETHYLSILYL AZIDE UNDER ACID CATALYSIS TO GIVE 5-BENZYL PENTAZOLE-1-OXIDE

By analogy to the benzo-1,2,3,4-tetrazene and its oxides discovered by the Russians (Figure 16), it was assumed that pentazole had a similar relationship with its N-oxides. The N-oxides were more stable in every case that could be investigated. As a result, a number of schemes were devised for the synthesis of pentazole N-oxide, pentazole 1,3-bis-N-oxide, and their alkylated or blocked derivatives.

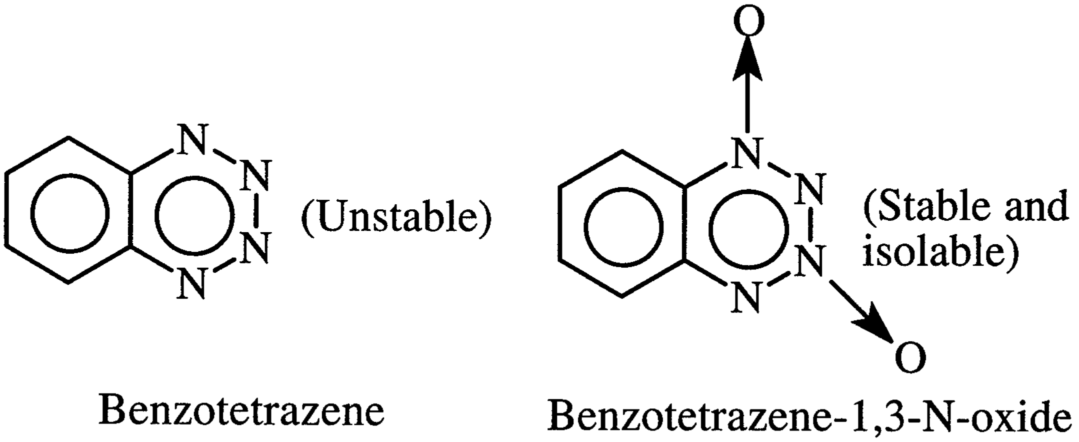


Figure 16. Benzotetrazene and its N-oxides.

Given our prior experience with N,N dialkyl nitrosamines undergoing clean silylation with trimethylsilyl triflate to give the dialkyl silyloxy diazenium cation (Figure 17), we assumed that the corresponding N-methoxy nitrosamines could undergo cycloaddition with trimethylsilyl azide to give 5-benzyl pentazole-1-oxide (Figure 18).

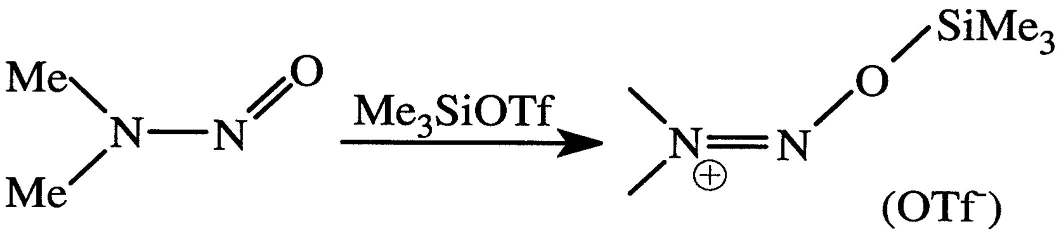


Figure 17. Silylation of dimethyl nitrosamine to give dimethyl silyloxy diazenium triflate.

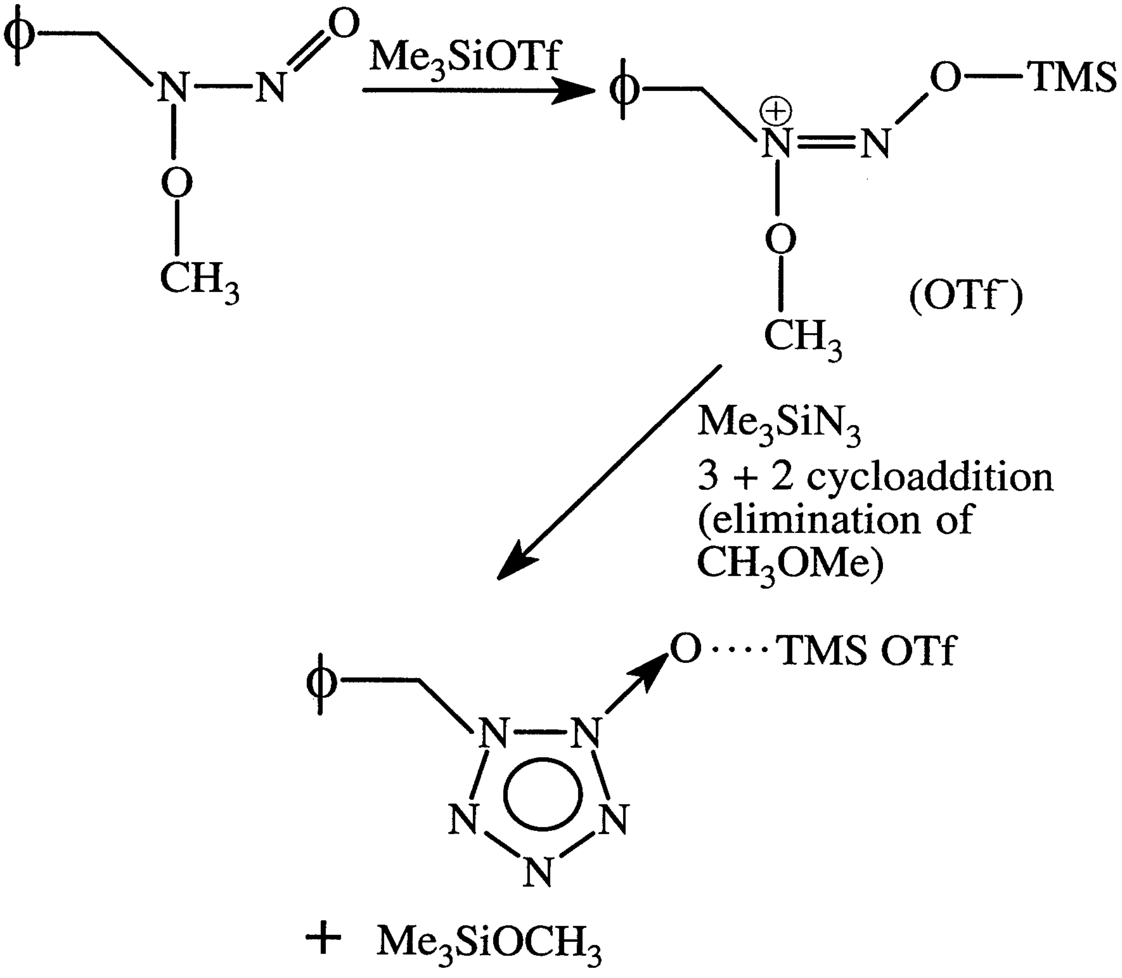


Figure 18. Synthetic scheme to 5-benzyl-pentazole-1-N-oxide.

Unfortunately, preliminary attempts at this synthesis at room temperature and at 70°C gave no reaction and decomposition correspondingly. Further attempts will be made using lanthanum triflate catalyst; if these fail, this scheme will be abandoned.

ATTEMPT TO EFFECT ACID CATALYZED CYCLOADDITION OF PHENYL DIAZENIUM DIOLATE TO AZIDOTRIMETHYLSILANE UNDER ACID CATALYSIS TO GIVE 5-PHENYL-PENTAZOLE-1-OXIDE

A tautomerically related functional group to the previously discussed N-methoxy-N-nitroso amine is the diazenium diolate. It can reasonably be expected to undergo cycloaddition to trimethylsilyl azide to give the pentazole-N-oxide group, given the correct choice of catalyst and reaction conditions (Figure 19).

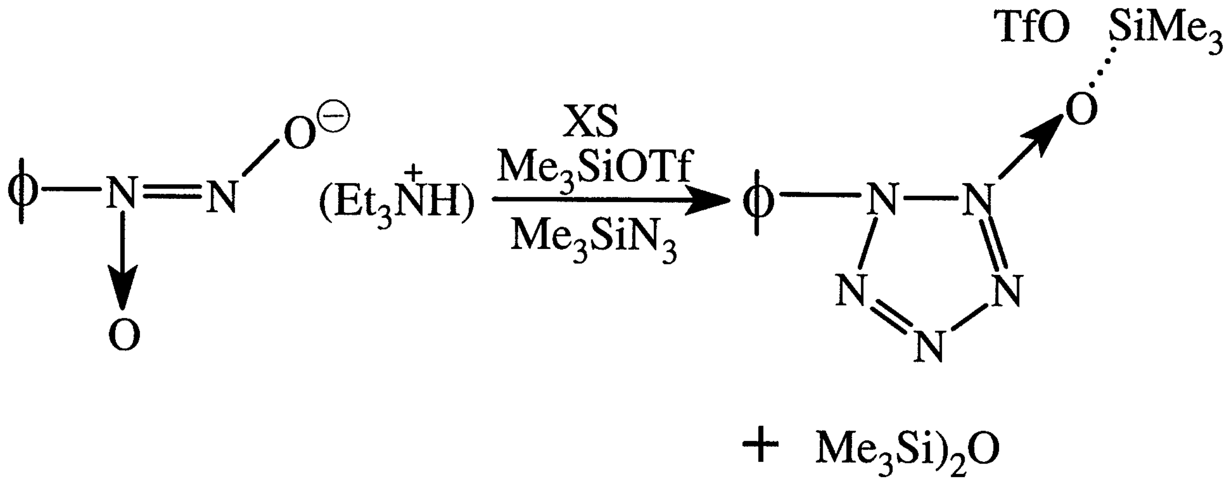


Figure 19. Pentazole N-oxide synthesis from cycloaddition of azide to diazenium diolate.

The commercial reagent “cupferron” is a readily available source of ammonium phenyl diazenium diolate. In our hands, the ammonium ion was readily displaced with the more basic triethylamine, giving the much more soluble triethyl ammonium diazenium diolate, which was reacted with excess trimethylsilyl triflate and excess trimethylsilyl azide at 0° under argon. Unfortunately, the crude product gassed and decomposed on warming to room temperature. It was never determined whether the desired product had formed or if the acidic medium destroyed it as opposed to its being inherently unstable. A more thorough investigation of this reaction will be undertaken using longer reaction times at 0° and a careful base work up. At present, the success of this scheme is inconclusive.

AMINATION OF THE DIANION OF DINITRO BITRIAZOLE

A sample of dinitrobitriazole was converted to its organic solvent-soluble dianion by reaction of one millimole of the bitriazole with two millimoles of the commercially available base DBU (diazabicycloundecane) in acetonitrile. This was treated with two millimoles of hydroxylamine-O-toluenesulfonate. Almost immediately, the desired product was formed in over 75% yield; this was isolated by simple aqueous extraction followed by a short column chromatography. The correct structure was demonstrated by x-ray crystallography (Appendix A) (Figure 20).

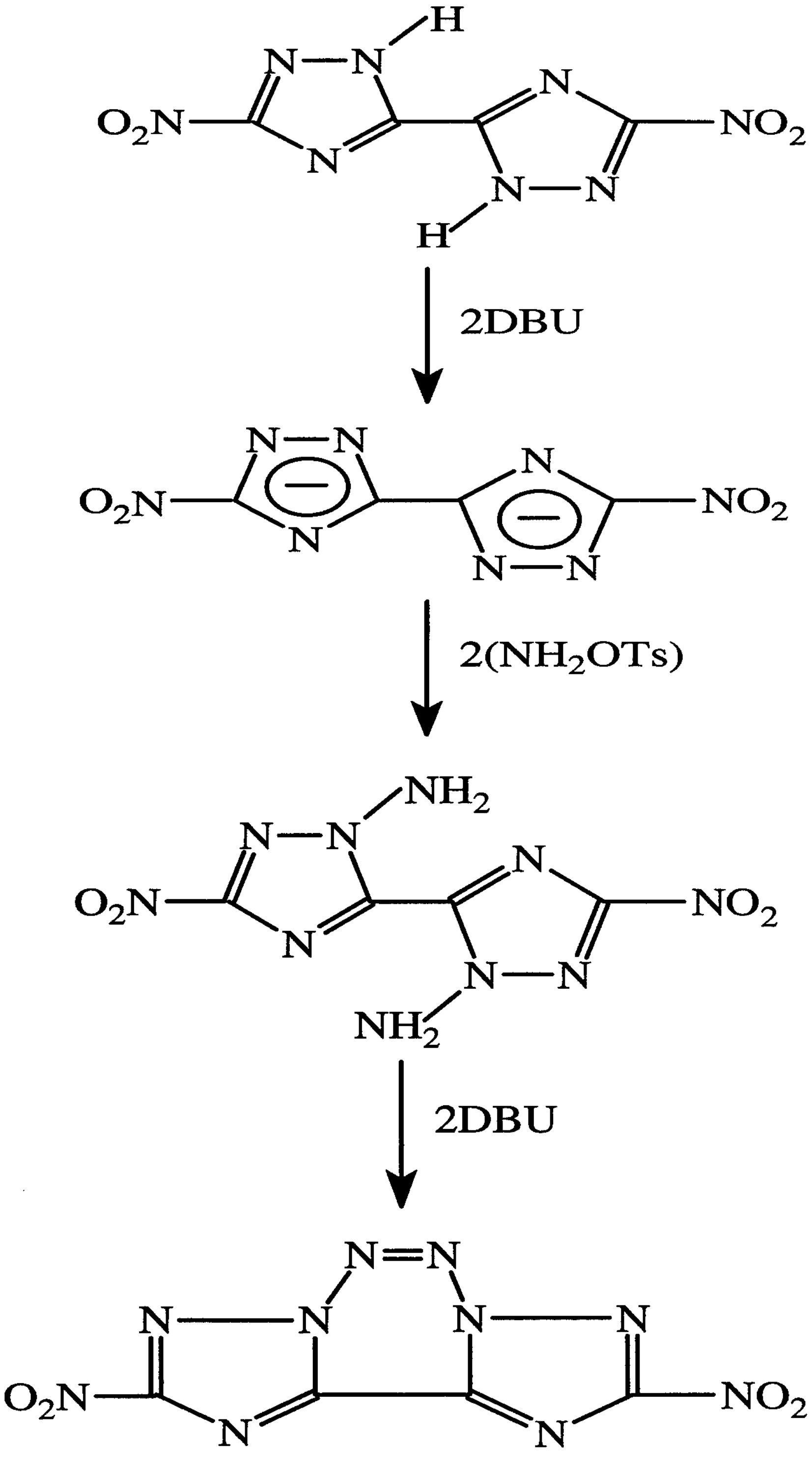


Figure 20. Chemistry of dinitrobitriazole.

It is hoped that the N,N' diamino derivative can be cyclized oxidatively to the long sought-after bi-triazolo-tetrazene, a material anticipated to be very dense (≥2.0 g/cc) and very energetic (ΔH ≥150 kcal/mole).

PRELIMINARY EXPLORATION OF THE N-NITRO IMINE YLIDE FUNCTIONAL GROUP

Throughout this program, we have sought the N-oxides of various heterocycles as materials which possess equivalent enthalpy and superior density (due to the enhanced dipole moment) and oxygen balance due to the extra oxygen atom; in every case investigated so far, this has been true. However, an even greater opportunity exists for each heterocycle that can be oxidized to an N-oxide: the N-nitro imine ylide (Figure 21).

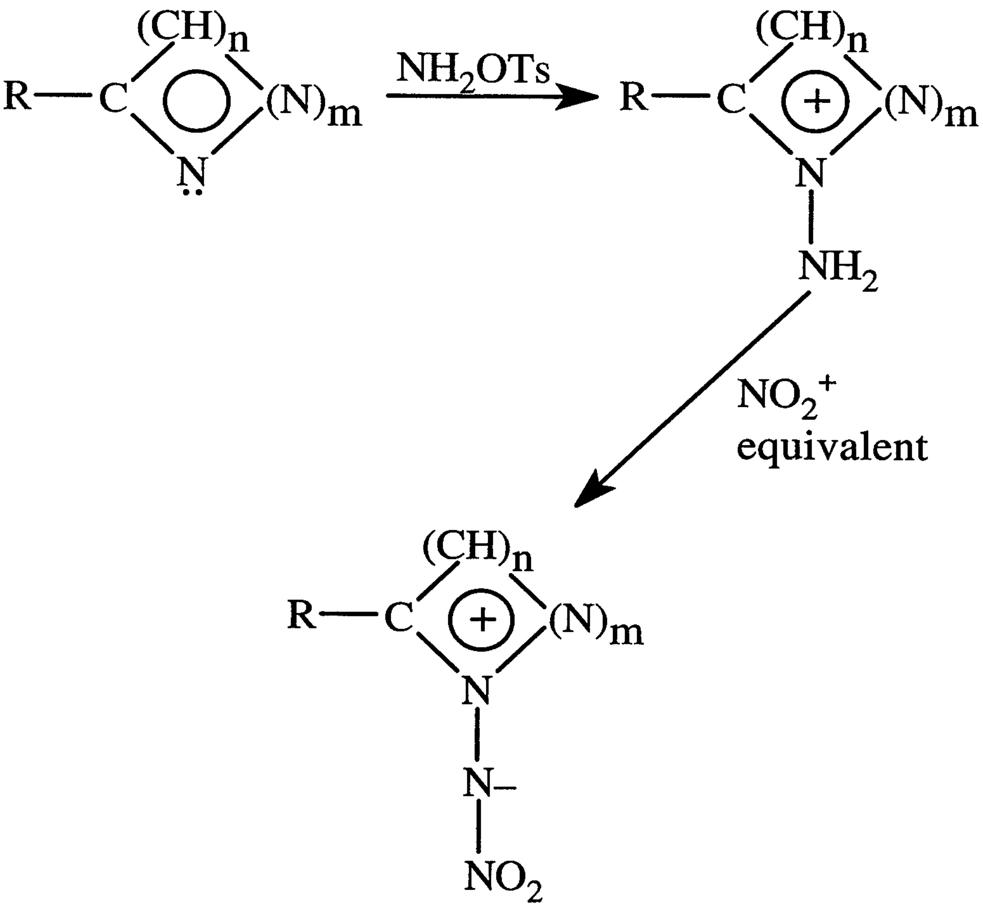


Figure 21. Synthesis of the N-nitro imine ylide.

In general, it is possible to aminate and then nitrate any aromatic heterocycle to its corresponding N-nitro imine ylide; some of this work has been demonstrated in the Russian literature (Tartakouskii work), and the generality of this synthesis as well as the functional group created by it remains to be exploited. As long as one can aminate a heterocycle to its N-amino cationic salt, it should be possible to nitrate the same material to an ylide, giving a neutral material with a great deal more energy and two more oxygen atoms than its purely nitrogenous precursor. To date, we have successfully aminated the tetrazole derived by cyclization of pyridyl-2-azide, 4-amino-1,2,4-triazole, and 1,5-diamino tetrazole to their corresponding N-amino cationic salts; preliminary nitration efforts appear to be successful by TLC and are awaiting x-ray crystal analysis. If successful, this methodology could create an entirely new family of overoxidized energetic materials, which due to their immense dipole moments, should be dense also.

ATTEMPT TO OXIDATIVELY COUPLE 1-AMINO-3,5-DINITRO-1,2,4-TRIAZOLE TO GIVE AZO BIS DINITROTRIAZOLE

Our success in oxidizing 1-amino-3-nitro-1,2,4-triazole to the highly energetic detonator 1,1' azo bis (3-nitro-1,2,4-triazole), U.S. Patent No. 5,889,161, dated March 30, 1999 (Figure 22) gave us the basis to expect that the same could be done with 1-amino-3,5-dinitro-1,2,4-triazole. Unfortunately, when this was attempted, coupling did indeed occur, but one of the nitro groups on each ring was displaced by chloride ion generated in the oxidation (Figure 23). Success in this endeavor awaits the successful use of an oxidizing system which does not release nucleophiles in the process of oxidation.

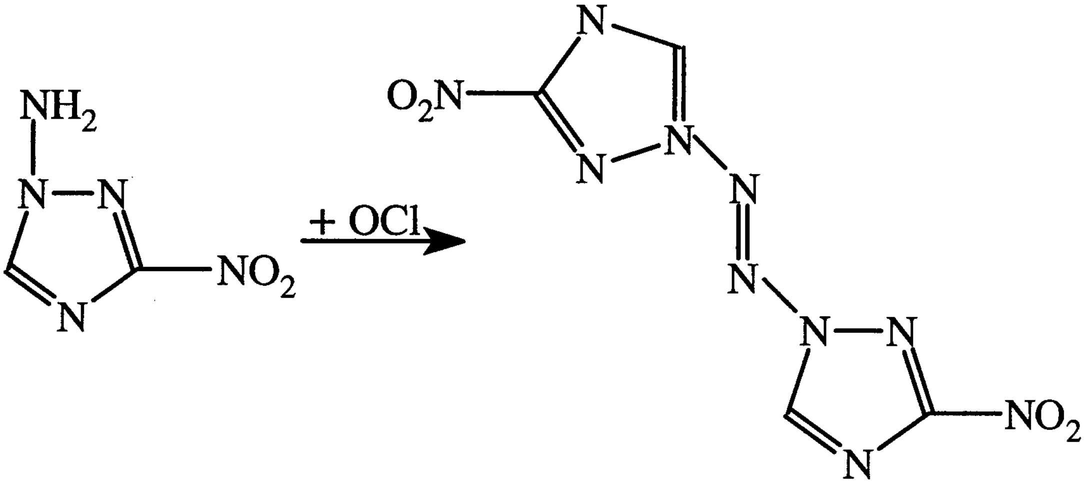


Figure 22. Synthesis of 1,1' azo-bis-(3-nitro-1,2,4-triazole).

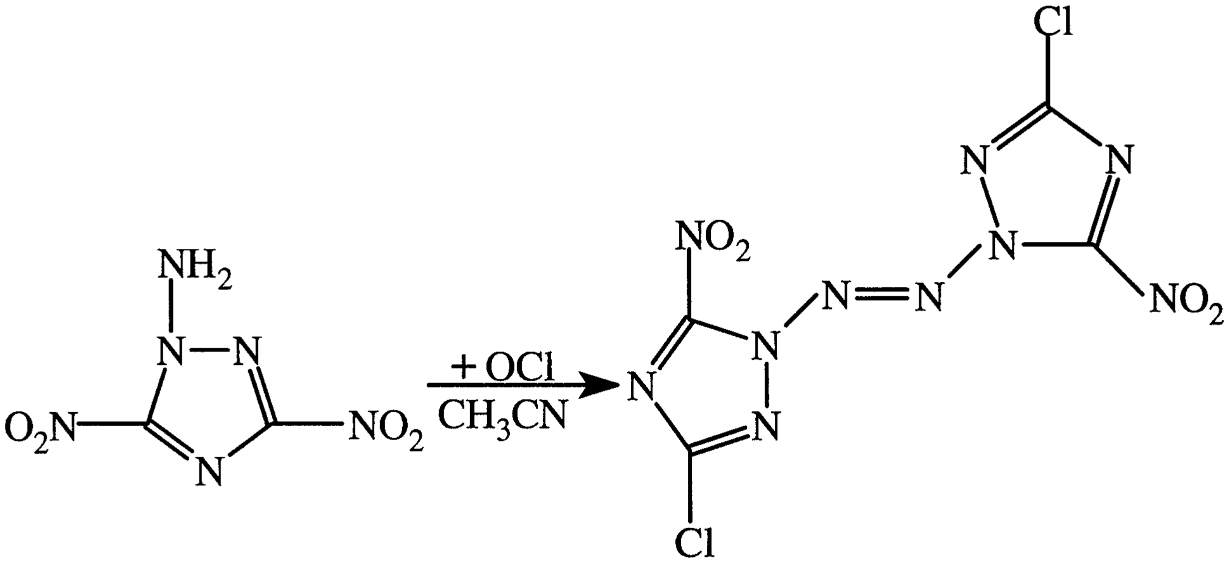
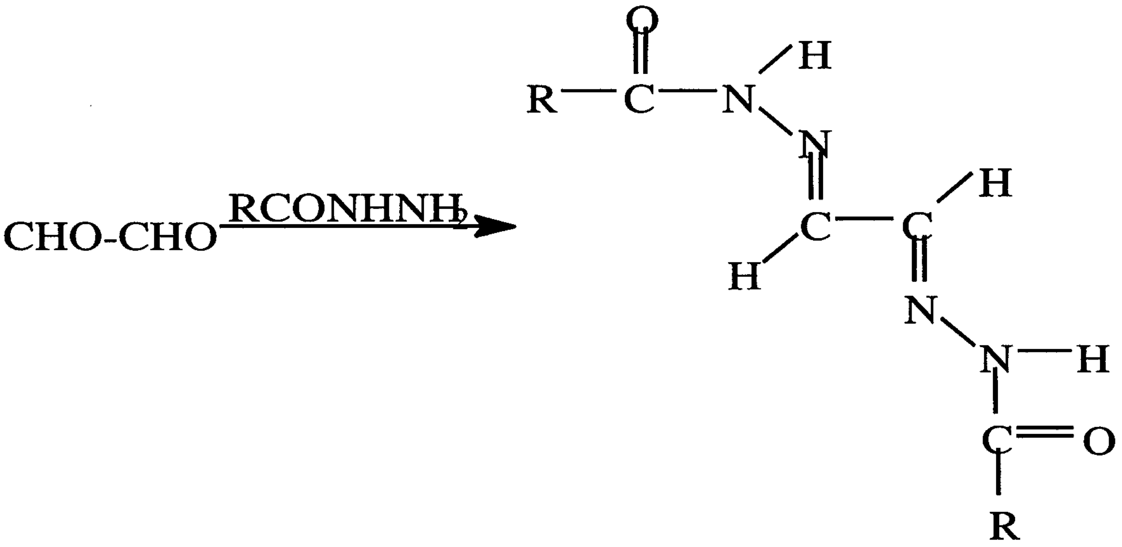


Figure 23. The hypochlorite oxidation of 1-amino-3,5-dinitro-1,2,4-triazole.

CHLORINATION OF THE HYDRAZONES OF GLYOXAL: THE FIRST STEP TO BIS (TETRAZOLO) TETRAZENES

One category of energetic molecules sought after in this program is the bis (tetrazolo) tetrazenes, which should be accessible by displacement of chlorine by azide in the glyoxal bis (hydrazonyl) chlorides (Figure 24). To date, we have succeeded as far as the chlorination step in the case of glyoxal bis (formyl hydrazone) and glyoxal bis (ethoxycarbonyl hydrazone). The rest of this synthesis is yet to be explored.



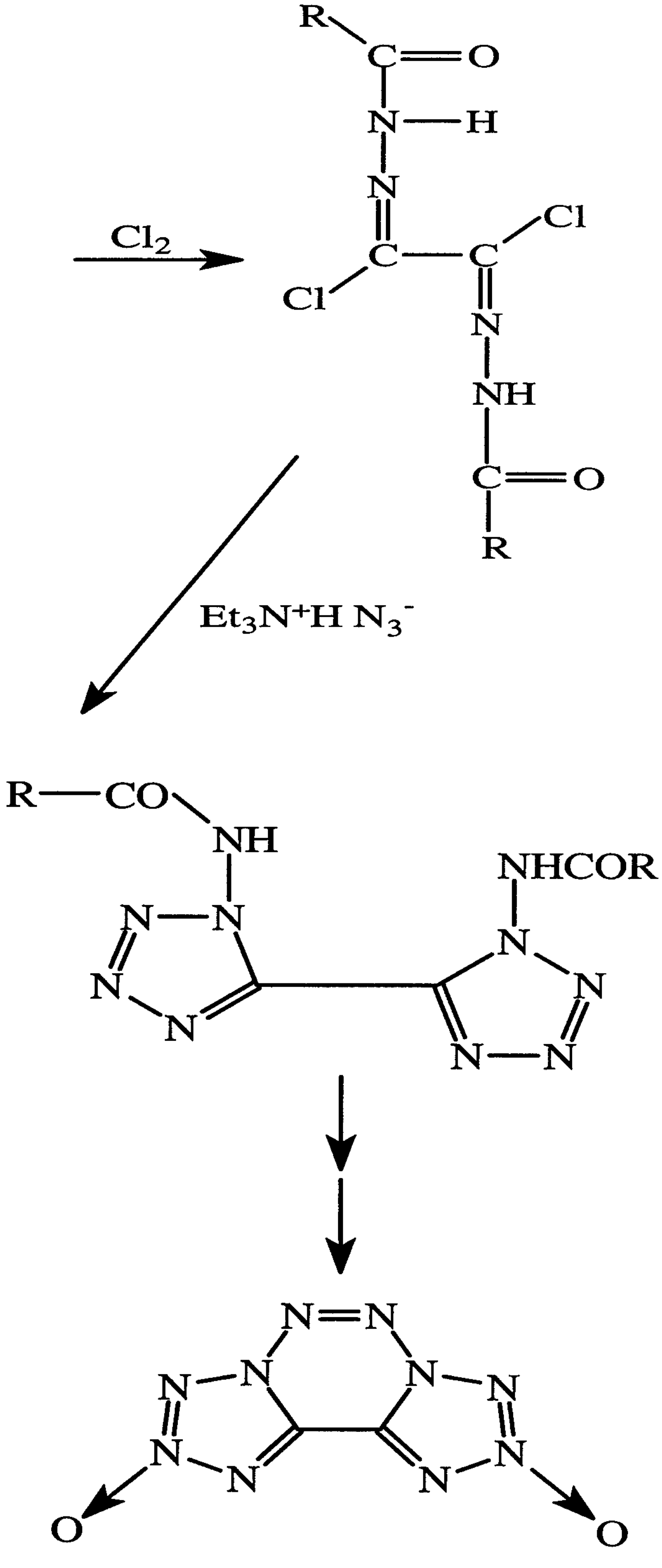


Figure 24. Chemistry of bis tetrazolo-tetrazenes.

ATTEMPTED AMINATION OF 5-NITROTETRAZOLE-2-N-OXIDE ANION

It was hoped that the amination of 5-nitrotetrazole-2-N-oxide anion would result in a neutral N-aminated N-oxide such as 1-amino-5-nitrotetrazole-3-N-oxide (Figure 25).

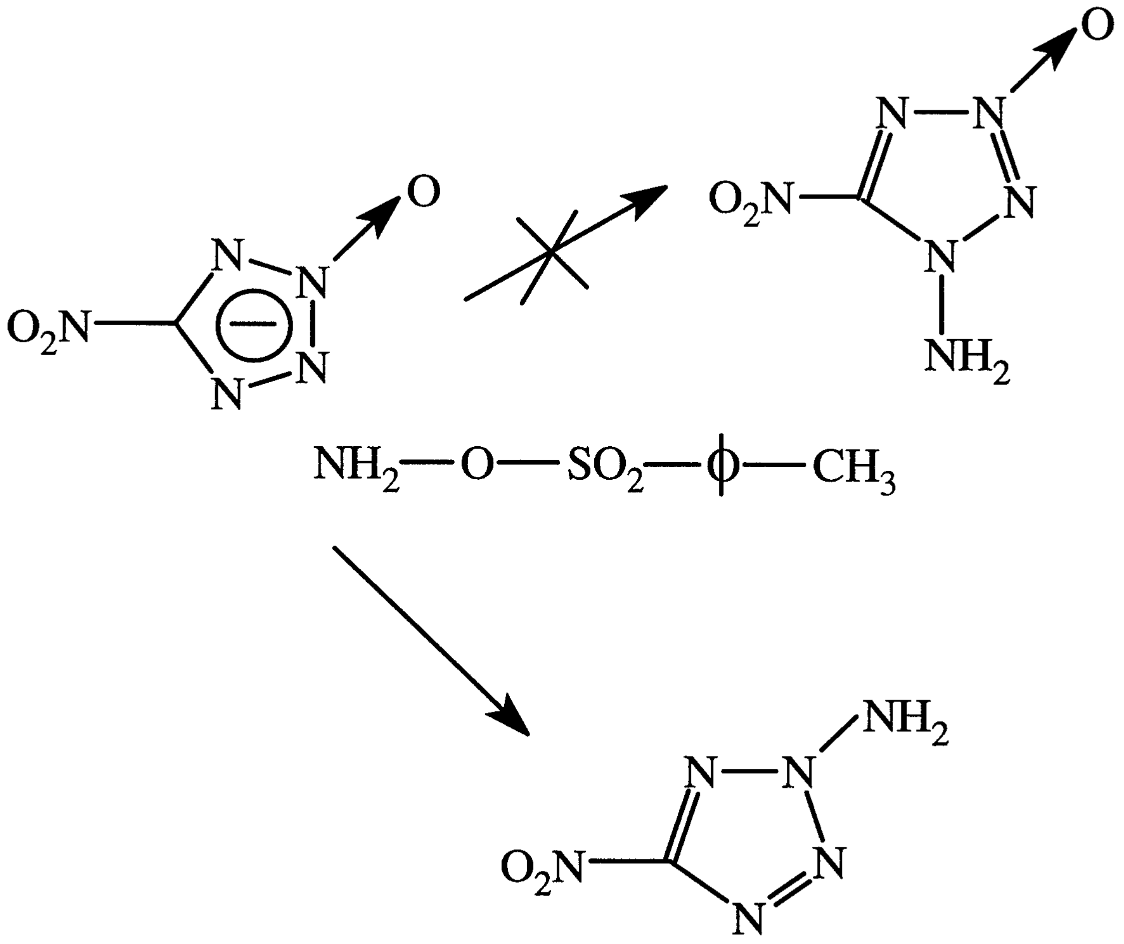


Figure 25. Amination reaction of 5-nitrotetrazole-2-N-oxide anion.

Unfortunately, this reaction resulted in the same product as was derived by direct amination of 5-nitrotetrazole anion with hydroxylamine-O-toluene sulfonate. This unexpected result can be attributed to amination on oxygen, followed by elimination of HNO, producing the 5-nitro-tetrazole anion, which is then aminated by excess available hydroxylamine-O-toluene sulfonate (Figure 26).

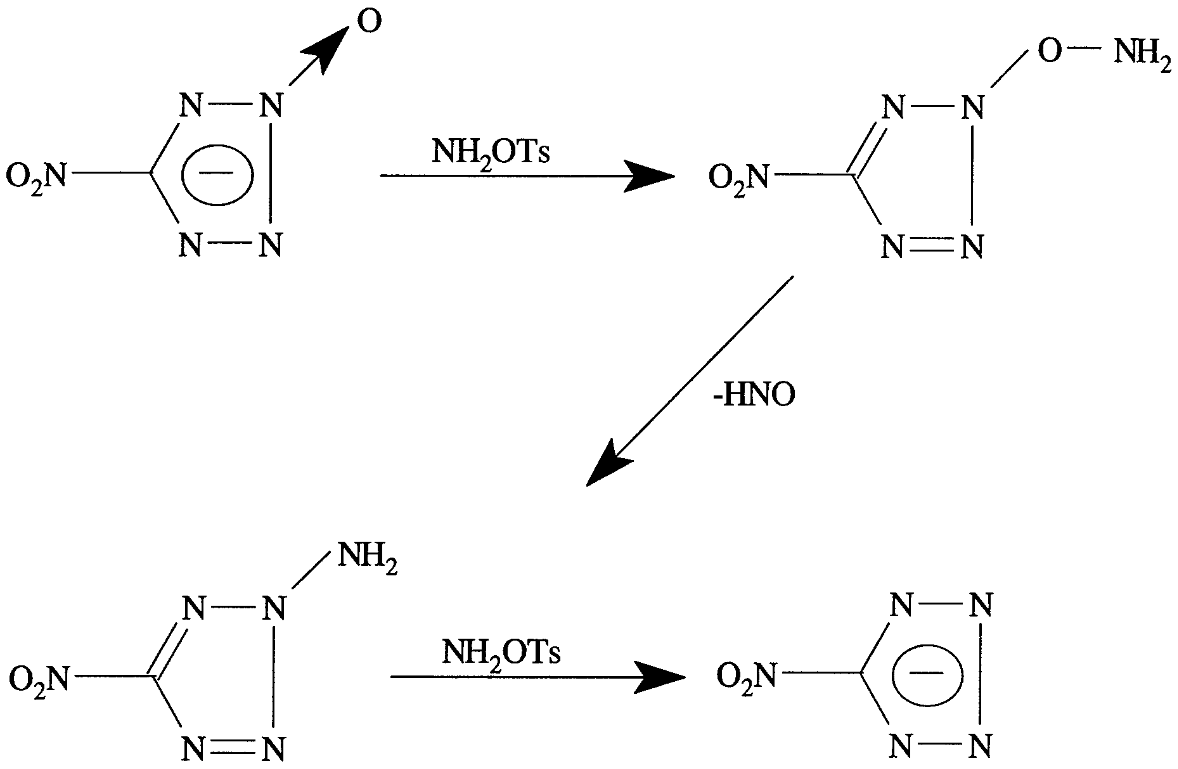


Figure 26. Deoxygenation of 5-nitrotetrazole-N-oxide.

An identical sequence of events was observed with the 1-N-oxide of 3,5-dinitro-1,2,4-triazole. Reaction of this material with hydroxylamine-O-toluene sulfonate resulted in the generation of 1-amino-3,5-dinitro-1,2,4-triazole.

ATTEMPTED DEHYDRATIVE CYCLIZATION OF N,N'-DINITROUREA

The dehydrative cyclization of N,N'-dinitrourea should, in concept, lead to an unprecedented aromatic (6-π-electron) heterocycle (Figure 27). Unfortunately, all attempts to do this using conventional dehydrating systems (e.g., $\phi SO_2Cl/Et_3N$) gave only gassing and decomposition.

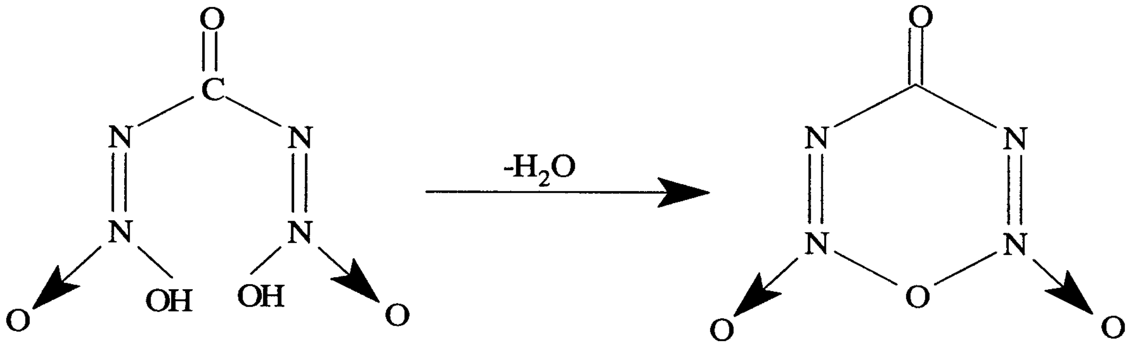


Figure 27. Dehydration of N,N'-dinitrourea.

ATTEMPTED NITROSATION OF CARBAMYL AZIDE TO GIVE 6-HYDROXY-PENTAZENE-2-OXIDE

Motivated by the exploratory possibilities of carbamyl azide, SRI developed a bulk industrial aqueous synthesis of this material, which consists of simply dissolving NaN_3 and NaNCO in water at approximately 2 M concentration, cooling to 0°C, and adding H_2SO_4 to achieve neutrality. The product can then be extracted with ethyl acetate and flash-chromatographed over SiO_2 to give, after crystallization from ethyl acetate/toluene, a 90% yield of pure carbamyl azide.

Our first investigation involving this material was to nitrosate it under basic conditions to achieve the synthesis of azido carbonyl diazotate, an unprecedented nitrogenous chain, which we anticipated would cyclize to 1,2,3,4,5-pentazene-2-oxide-6-one (Figure 28).

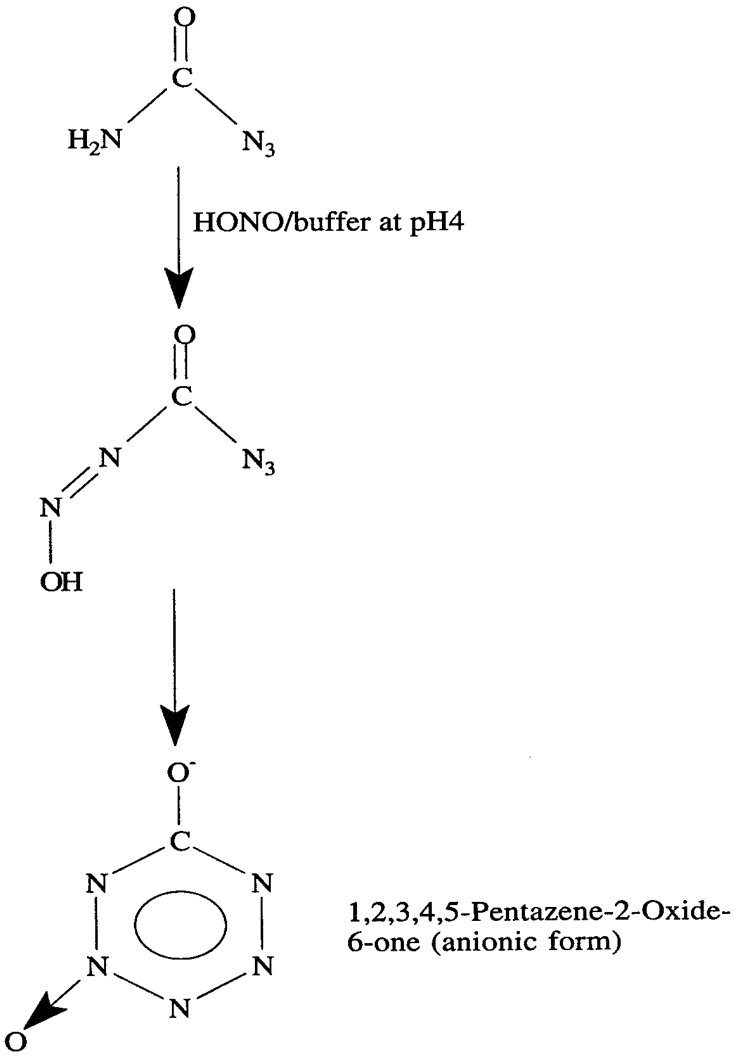


Figure 28. Proposed synthesis of 1,2,3,4,5-pentazene-2-oxide-6-one.

Unfortunately, our preliminary efforts in this direction failed to achieve the synthesis of this heterocycle; reaction of carbamyl azide in pyridine with a variety of nitrosating agents gave only gas and decomposition.

SYNTHESIS OF β-TRIMETHYLSILYL ETHOXY HYDROXYLAMINE, CYANATION OF HYDROXYLAMINES WITH BrCN AND SYNTHESIS OF 1-ALKOXY-5-AMINO TETRAZOLES

It was of interest to synthesize the tetrazole 1,3-N-oxide anions in order to achieve higher oxidation states of 5-nitrotetrazole (as well as its amino precursor). It was found that the commercially available t-butoxy amine could be cyanated on nitrogen with cyanogen bromide and cyclized to the tetrazole with triethyl ammonium azide (Figure 29).

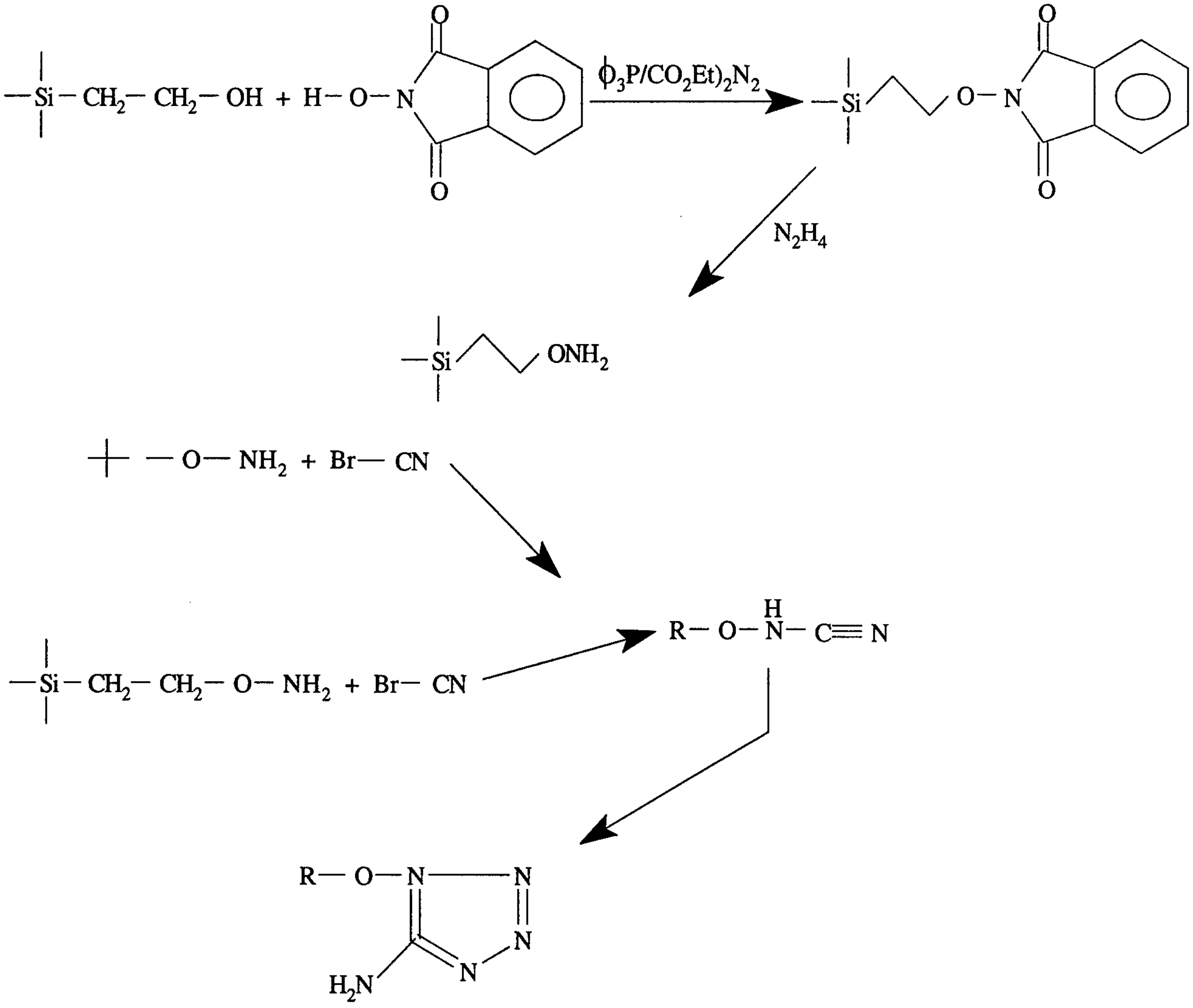


Figure 29. Synthesis of 1-alkoxy-5-amino-tetrazole.

The ultimate aim in this instance was to oxidize the 1-alkoxy-5-amino tetrazole to its 5-nitro-1,3-dioxide anion by elimination of the blocking group "R" on oxygen. This anion could then be rendered as its hydroxyl ammonium salt (Figure 30).

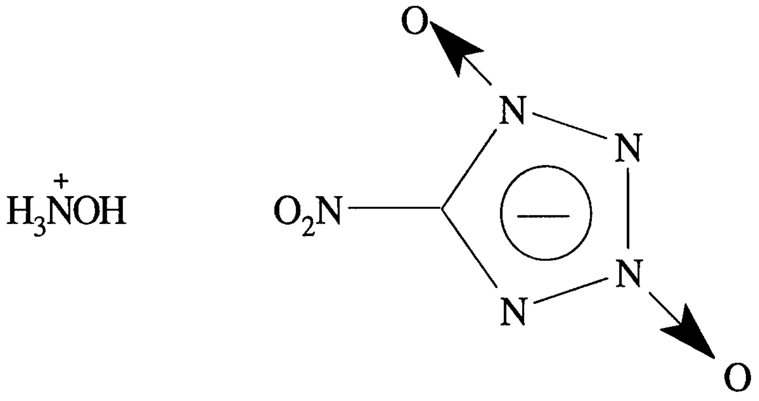


Figure 30. Hydroxyl ammonium salt.

This material enjoys the advantages of two extra oxygen atoms peer 180 daltons of molecular weight, along with a high (~ +50 kcal per mole) enthalpy of formation and is one of our most practical targets in this program.

CONCLUSIONS

A vast array of unprecedented, but nevertheless theoretically intriguing heterocycles and functional groups have been explored experimentally, based on their potential technological payoff. A small subset of these has been realized and are undergoing scale up and performance characterization. The pentazole-N-oxides, hexazine N-oxides, and N-nitro imine ylides remain unsolved problems with considerable prospect for payoff. All of these functional groups promise to advance the causes of higher density, higher oxygen balance, and higher energy simultaneously. As for the diazanitrate and triazanitrate, these goals are being pursued at a steady pace. They too promise the simultaneous rewards of oxygen, density, and energy. It is hoped that the final year of the program will find a solution to a growing subset of these admittedly high-risk goals.

EXPERIMENTAL

SYNTHESIS OF 5-NITROTETRAZOLE-2-N-OXIDE

5-Nitrotetrazole sodium salt (12.5 g, 100 mmol) was dissolved in 50 mL H_2O and treated with 45 g (1.5 oxidizing equivalents) of "OXONE" peroxy monosulfate and 20 g (200 mmol) of potassium acetate buffer and was stirred for 48 h at 50°C and worked up.

WORKUP: Added a solution of 90 mmol of Bu_3NH^+ $NaSO_4^-$ in 200 mL H_2O and extracted 1 x 300 mL EtoAc. The yellow product, which resides in the EtoAc layer, can be purified by flash chromatography followed by crystallization from ethyl acetate/toluene yield = 75% of yellow plates, upon slow evaporation of volatile in vacuo after originally seeding the solution with a crystal of the desired product. This product can be ion exchanged by dissolving it in CH_3OH and eluting it through a column five times its weight of "AMBERLYST 15" polystyrene sulfonate resin charged with the desired cation, at a slow enough rate to permit full equilibration (~ 15 min). The products are each crystallized from solvents of polarity appropriate to the cation at hand. Recovery on crystallization was excellent (≥90%).

APPENDIX A

SUPPORTING DATA FOR STRUCTURE ASSIGNMENTS

Table 1. Crystal data and structure refinement for bott88f.

Identification code	bott88f	
Empirical formula	C14 H22 N18	
Formula weight	442.50	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.8797(11) Å	α= 90°.
	b = 9.8665(12) Å	β= 96.103(2)°.
	c = 11.2386(14) Å	γ = 90°.
Volume	979.1(2) $\mathrm{\AA}^3$	
Z	2	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	0.108 mm^{-1}	
F(000)	464	
Crystal size	0.32 x 0.22 x 0.20 mm^3	
Theta range for data collection	2.31 to 28.31°.	
Index ranges	-11<=h<=11, -12<=k<=13, -14<=l<=15	
Reflections collected	7919	
Reflections 'observed'	1999 [I>2sigma(I)]	
Independent reflections	2389 [R(int) = 0.0266]	
Completeness to theta = 28.31°	98.4 %	
Absorption correction	Integration	
Max. and min. transmission	0.981 and 0.965	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2389 / 0 / 159	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0964	
R indices (all data)	R1 = 0.0458, wR2 = 0.1002	
Largest diff. peak and hole	0.320 and -0.203 e.$\mathrm{\AA}^{-3}$	

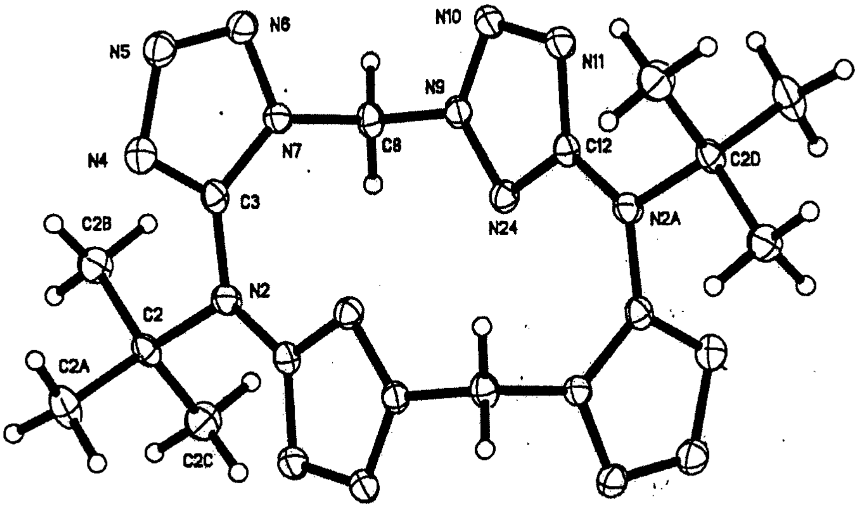
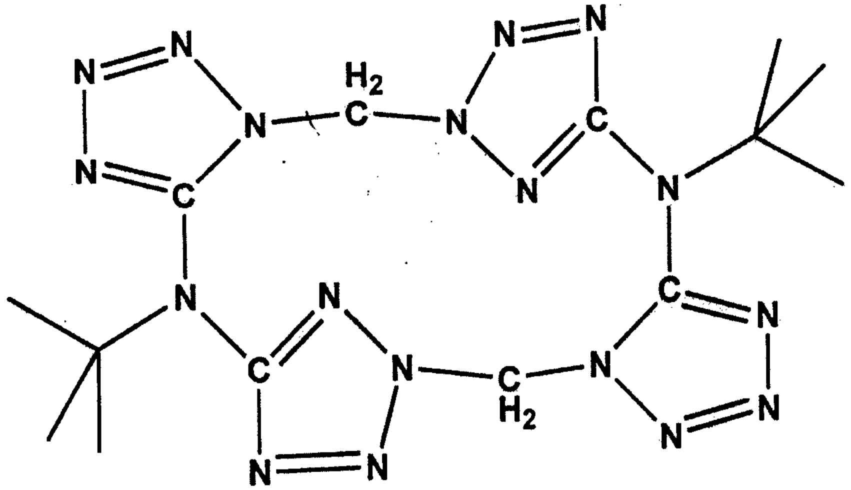


Figure 1. Thermal-ellipsoid drawing of the large-ring tetra-tetrazole compound. At first glance it appears to be a simple dimer of the suggested structure, but note that the tetrazoles are not all inserted into the large ring in the same way.



APPENDIX B

HYDROXYL AMMONIUM 5-NITROTETRAZOLE-2-OXIDE

Table 1. Crystal data and structure refinement for srip23tc.

Identification code	srip23tc	
Empirical formula	C H4 N6 O4	
Formula weight	164.10	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.5335(11) Å	α= 90°.
	b = 12.2327(16) Å	β= 92.076(2)°.
	c = 5.5796(7) Å	γ = 90°.
Volume	582.06(13) Å^3	
Z	4	
Density (calculated)	1.873 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	336	
Crystal size	0.46 x 0.43 x 0.07 mm^3	
Theta range for data collection	2.39 to 28.26°.	
Index ranges	-11<=h<=11, -14<=k<=15, -7<=l<=7	
Reflections collected	4329	
Reflections 'observed'	1226 [I>2sigma(I)]	
Independent reflections	1416 [R(int) = 0.0377]	
Completeness to theta = 28.26°	97.7 %	
Absorption correction	Integration	
Max. and min. transmission	0.9876 and 0.9326	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1416 / 0 / 113	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0742	
R indices (all data)	R1 = 0.0345, wR2 = 0.0774	
Extinction coefficient	0.006(3)	
Largest diff. peak and hole	0.336 and -0.254 e.Å^{-3}	

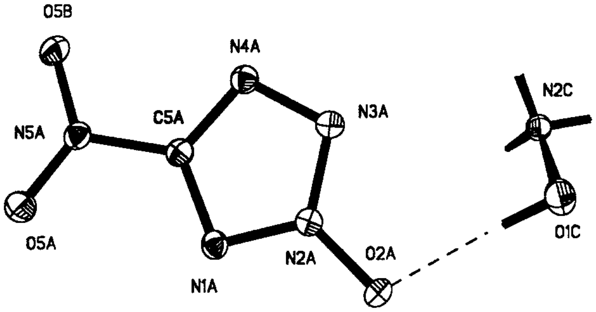


Figure 1. Drawing of one ion pair in the crystal SRIP23, which was grown from a portion of the contents of vial 14074-66 from butyl acetate solvent. [The original material was an acetonitrile solvate.]

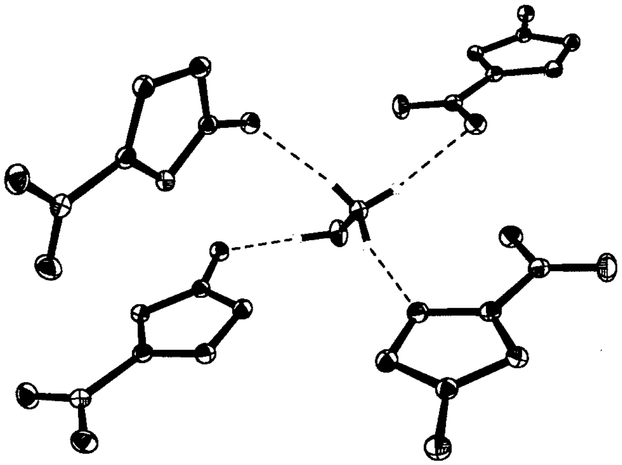


Figure 2. A drawing showing the four strong H-bonds that connect each cation to four anions in SRIP23.

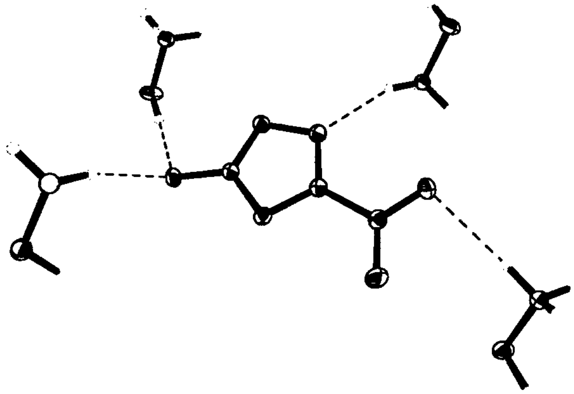


Figure 3. Each anion in SRIP23 is tightly bound to four neighboring cations.

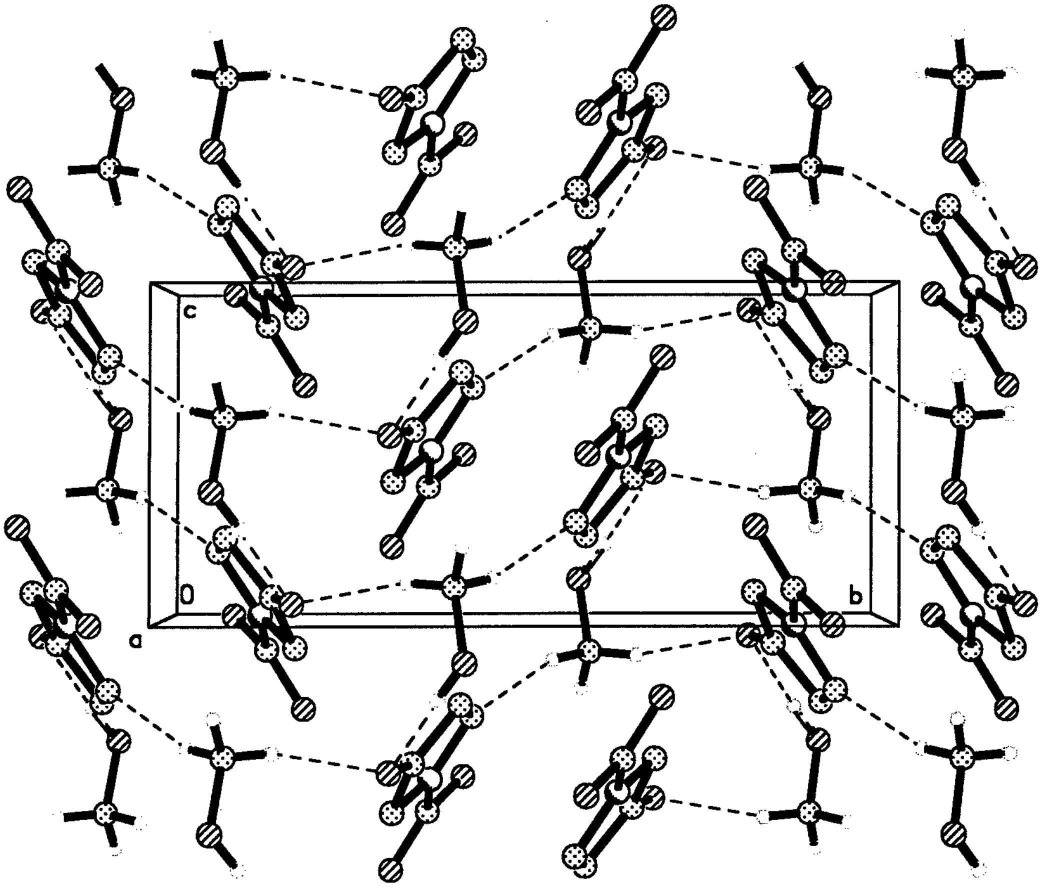


Figure 4. Packing in crystal SRIP23. Hydrogen bonding links the ions in all directions. This leads to hard crystals of density ~1.82 at RT (1.873 at −180C). The crystals may be slightly hygroscopic (damp surfaces in high humidity).