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The feasibility of tetranitratoborates and tetranitratoaluminates as high-oxygen carriers for oxidizer balanced green solid and ionic liquid energetic materials was demonstrated. The predicted performances of the ionic liquids represent a marked improvement over the presently used hydrazine while avoiding at the same time its high vapor toxicity. Simple, one-pot, one-step syntheses from inexpensive and readily available starting materials have also been developed for these materials. However, the long-term thermal stability of these compound is marginal , and work on an alternate high-oxygen carrying anion has been started.

A second area of significant interest was the synthesis of DTTO and iso-DDTO. Theoretical performance calculations were carried out for both using the latest density and heat of formation values, and show that both compounds would provide significantly higher detonation pressures than HMX and CL20 . Efforts were started to develop suitable methodology for their syntheses.

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# SYNTHESIS OF NEW HIGH-OXYGEN CARRIERS AND DITETRAZINETETROXIDE (DTTO)

## FINAL REPORT

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# PREFACE

The research reported herein was supported by the Office of Naval Research with Daniel Tam serving as Scientific Officer and Drs. Cliff Bedford and Al Stern as Scientific Advisers. This report summarizes the work done during the period 21 February 2008 through 21 February 2009. The program has been directed by Professor Karl Christe and the scientific effort was carried out by Drs. Ralf Haiges, Ross Wagner, and the late CJ Jones.

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## Abstract

This program had two main objectives. The first task was the demonstration of the feasibility of using complex anions $BX_4^-$ anions, such as $[B(NO_2)_4]^-$, as high-oxygen carriers for halogen-free green ingredients for propellants or explosives. The second task involved the synthesis of explosives which can outperform CL20 by at least 20%.

Our approach toward the synthesis of the $[B(NO_2)_4]^-$ anion involved Umpolung reactions. For this purpose, two $B(NX)_4^-$ skeletons, $B(N_3)_4^-$ and $B(imidazolate)_4^-$, were prepared and subjected to oxidative cleavage reactions. Using ozone, partial cleavage of the imidazole ring yielded the tetrakis-(diformylamido)borate anion, but further oxidation with stronger oxidizers resulted in cleavage of the B-N bonds. Because azides could not be ozonized directly, they were first converted to the corresponding phosphazenes. Treatment of the phosphazenes with HOF yielded $BF_4^-$ and $NO_3^-$.

As an alternate and synthetically easier approach, a complex $BX_4^-$ anion was synthesized in which X is a dinitro-substituted 1,3,4-triazole (DNT). Performance calculations were carried out for $NH_4^+B(DNT)_4^-$ and indicate that it would outperform $NH_4^+ClO_4^-$ in typical formulations. Starting from $BH_4^-$, the tetramethylammonium (TMA) salts of the $[H_3BDNT]^-$, $[H_2B(DNT)_2]^-$, $[HB(DNT)_3]^-$, and $[B(DNT)_4]^-$ anions were successfully prepared and characterized. It was shown that $[TMA]^+[B(DNT)_4]^-$ is thermally and hydrolytically stable and insensitive. Starting from $BCl_4^-$, the half-substituted $[Cl_2B(DNT)_2]^-$ anion was prepared, and the crystal structures of the $[H_2B(DNT)_2]^-$ and $[Cl_2B(DNT)_2]^-$ anions were determined.

The second area of significant interest was the synthesis of DTTO and *iso*-DDTO. Theoretical performance calculations were carried out for both using the latest density and heat of formation values, and show that both compounds would provide significantly higher detonation pressures (567 and 581 kbar, respectively) than HMX (359 kbar) and CL20 (468 kbar). The known compound, 6-phenyl[1,2,3]triazolo[4,5-e]-1,2,3,4-tetrazine, was chosen as a model compound to test the hypothesis that alternating oxygen substitution on the nitrogen atoms indeed results in a pronounced increase in thermal stability. For its synthesis, the first 10 of 15 steps were successfully completed with an overall yield of 13 %.

## Introduction

Ammonium perchlorate (AP) is the most commonly used oxidizing ingredient in solid propellant formulations.[1] It carries a sufficient excess of oxygen to allow for the combustion of the required binder and added metal, such as aluminum. The major drawback of AP is its chlorine content which results in the formation of large amounts of HCl as a combustion product and causes severe environmental problems, such as acid rain. In addition, perchlorate contamination in the groundwater, even at the ppm level, causes thyroid problems. It is therefore desirable to find a halogen-free replacement for AP.

## Objectives

This program had two main objectives aimed at the synthesis of novel high power explosives which might benefit many programs, including underwater explosives. The goal of the first task was the identification, synthesis and characterization of novel compounds that can provide equal amounts or an excess of oxygen compared to AP, result in similar or better performance than AP, have high densities, good thermal and hydrolytic stability, and eliminate the formation of undesirable halogen or other compounds which might be of damage to the environment or could cause ozone depletion. The second task was aimed at the synthesis of more powerful explosives which can outperform CL20 by at least 20%.

## Approaches

Ordinary oxidizer anions, such as nitrate or dinitramide, do not carry enough oxygen for the complete combustion of either the large organic cations typically used in ionic liquids, or the metal powders and binders used in solid propellant formulations. This problem of under-oxidation can be overcome by the use complex anions and has been patented by the author for ionic-liquid based monopropellants.[2] Variation of the physical properties for the different applications can be achieved by crystal engineering. For low melting ionic-liquids, bulky singly charged cations with long asymmetric side-chains which pack poorly in a crystal lattice, are being used, whereas for a high-melting solid propellant ingredient, multiply charged, hard spherical ions that pack well and result in high lattice energies, are advantageous.

Our original approach involved the use of polynitrato anions as oxygen carriers. While a substantial amount of research in this area had been carried out between 1960 and 1980 in this country, the USSR and Europe,[3-9] the available data did not allow evaluation of these materials for our intended applications. We successfully demonstrated the potential of tetranitratoborates and tetranitratoaluminates[10] as high-oxygen carriers and their ability to form ionic-liquids. However, their long-term thermal stability was not quite good enough for practical applications. We, therefore, started to explore the synthesis of a novel anion, $[B(NO_2)_4]^-$, which does not contain the weak N-O single bond linkage of the nitrates and is expected to provide a thermally more stable anion. The synthetic approach involves "Umpolung" reactions, i.e., the synthesis of $BN_4^-$ skeletons, followed by the oxidation of the nitrogen containing ligands to nitro groups. In particular, the synthesis of $[NH_4]^+[B(NO_2)_4]^-$ might provide a green high-performing replacement for $NH_4^+ClO_4^-$.

Under the second task, we started to develop methodology for the synthesis of the elusive DTTO and *iso*-DTTO molecules. These compounds have been predicted to have outstanding densities and heats of formation, but their syntheses have not been accomplished in spite of many attempts, both in Russia and the US. At the Zelinsky Institute, Churakov and Tartakovsky have shown[11] that the addition of an oxygen atom to every second nitrogen atom in polynitrogen chains, creating alternating positive and negative charges, greatly increases their thermal stability, but their synthetic approaches involved diazonium salt intermediates which require a phenyl substituent for their stabilization. Furthermore, they did not test strong enough oxidizers and could add only one oxygen atom but not two oxygen atoms to a four nitrogen atom chain. These shortcomings might be overcome by using a century old literature method to construct a 1-,2-,3-,4-tetrazine ring and use more powerful oxidizers, such as HOF,[12] to oxygenate two of the four ring nitrogen atoms.

## RESULTS and DISCUSSION

### *TASK 1. Synthesis of New High-Oxygen Anions*

In previous work, we had evaluated the potential of complex nitrates of boron and aluminum as high-oxygen carriers. Although these compounds were excellent oxygen carriers, they were abandoned because of their limited thermal stability, and our efforts were shifted towards the preparation of the novel $[B(NO_2)_4]^-$ anion which does not contain N-O single bonds and, therefore, should have better thermal stability while maintaining the high performance of the tetranitratoaluminates.

Since the $[B(NO_2)_4]^-$ anion is unknown, we have carried out calculations at the B3LYP/6-31+G(d) level of theory which showed that this anion is vibrationally stable.

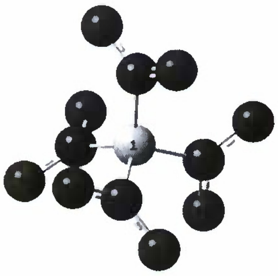


Figure 1. Predicted structure of the tetranitroborate anion

Furthermore, the thermal stability of $[B(NO_2)_4]^-$ should be higher than that of the corresponding nitrato complexes, because both oxygen atoms of the nitro groups are equivalent and possess bond orders of 1.5, thus imparting increased stability to the N-O bonds. The corresponding nitrato or nitrito compounds contain weak N-O single bonds. Although the tetranitroborate anion is unknown, mononitroborate anions, such as $[(R_f)_3BNO_2]^-$,[13,14] have been prepared and were shown to be thermally stable up to 260 °C, to have low solubility in water and to be nonhygroscopic. The tetrahedral $BN_4$ skeleton is also a very favorable and stable building motif. It is the building block of cubic ß-boron nitride, BN, a material with outstanding physical properties. It is thermally stable at temperatures higher than 2000 °C and is the second hardest known material after diamond.[15]

The ammonium tetranitroborate salt (ATNB), $[NH_4][B(NO_2)_4]$, has great potential as a green replacement for ammonium perchlorate (AP). It is expected to have a high melting point and good thermal stability because the oxygen atoms in $[B(NO_2)_4]^-$ are well suited for the formation of strong hydrogen bonds with the $NH_4^+$ counter-ions which should increase the lattice energy, stability and density of $[NH_4]^+[B(NO_2)_4]^-$. We have carried out theoretical calculations and have estimated the heat of formation and density of $[NH_4]^+[B(NO_2)_4]^-$ as -613 kJ/mol and 1.79 g/cm$^3$, respectively. Performance calculations were carried out using the Cheetah program. It was shown that optimized propellant formulations, using either aluminum or alane as a fuel and hydroxyl terminated polybutadiene as a binder, predict ATNB to deliver specific impulses comparable to those of $NH_4ClO_4$ formulations.

The synthesis of the tetranitroborate anion is challenging. Traditional direct nitration methods using $NO_2^+$-type reagents fail because the nitrogen atom carries a positive charge and the oxygen atoms carry partial negative charges. This results in attack of boron by $NO_2^+$ through the oxygen atoms and in the formation of an oxygen bonded isomer, the $[B(ONO)_4]^-$ anion (see Figure 2).

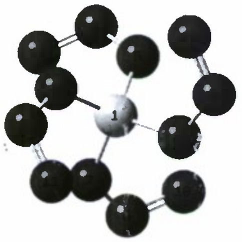
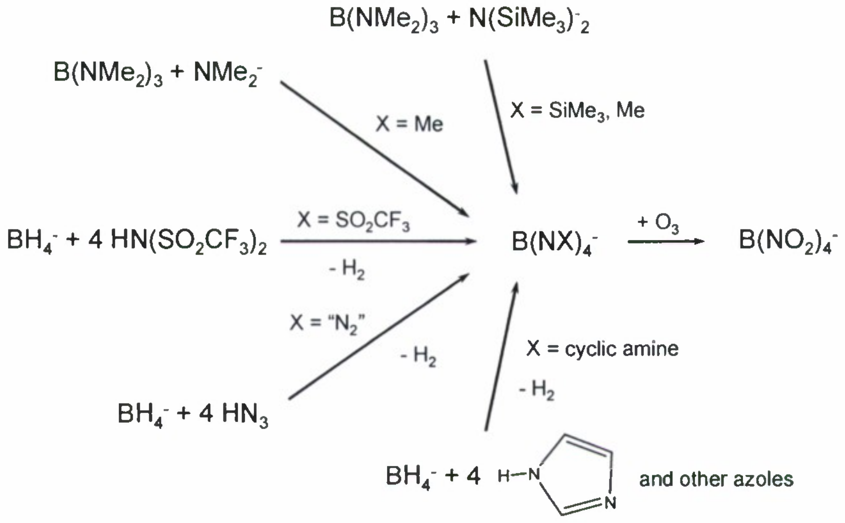


Figure 2. Predicted structure of the $[B(ONO)_4]^-$ anion

Although this isomer is also vibrationally stable, as shown by our theoretical calculations, we do not favor this isomer for the following reasons. Its energy content is 33.5 kJ/mol lower than that of $[B(NO_2)_4]^-$, and its thermal stability is predicted to be much lower because of the presence of two non equivalent N-O bonds, one single and one double bond. The N-O single bond represents the weakest link in this system and would rupture relatively easily, as was previously found for the analogous tetranitratoborate anions.

Therefore, efforts were undertaken to build the $BN_4^-$ skeleton first and then introduce the oxygen atoms. This can be achieved by “Umpolung” reactions, using amide or similar anions in which the nitrogen atom carries the desired negative charge. Different approaches for constructing such $BN_4^-$ skeletons are shown in Scheme 1.



Scheme 1

Two suitable B(NX)$_4^-$ skeletons, tetra-azidoborate and tetrakis-imidazolatoborate, were synthesized and subjected to cleavage by ozone, HOF, RuO$_4$, PbO$_2$, basic peroxide, or acid cleavage. Spectroscopic analyses of the reaction products showed that the desired cleavage reactions might have been achieved, but confirmation by crystal structures was not possible during the limited time frame, except for the products from the ozonization of the [B(imidazolate)$_4$]$^-$ anion which produced the tetrakis-bis-formyl amido borate anion which was characterized by its crystal structure (see Figure 3).

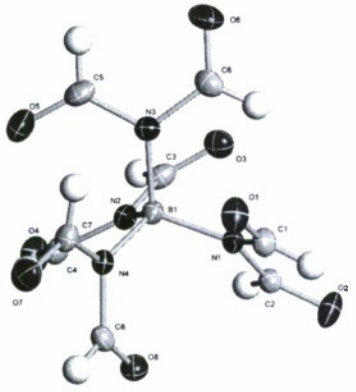


Figure 3. Crystal structure of the tetrakis(diformylamido)borate anion

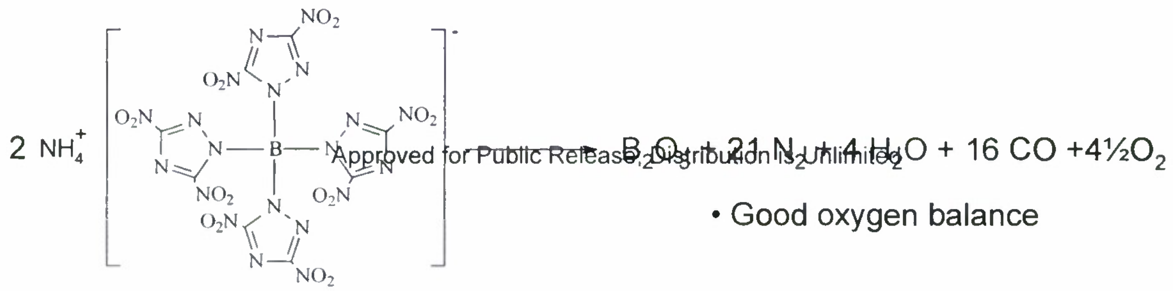
Attempts were made to oxidatively remove these aldehyde groups while forming a nitro-group at the same time by increasing the oxidative power of ozone by simultaneous UV-irradiation of the aqueous reaction medium. This resulted in the formation of the NO$_3^-$

anion and some unknowns. Other strong oxidizing agents were also studied. Using $Na[B(imid)_4]$ and $RuO_4$ in aqueous solution resulted in cleavage of the B-N bonds and in the formation of the $NO_3^-$ anion. The use of HOF[16] and $[PPh_4]^+[B[N(CHO)_2]_4]^-$ in $CH_3CN$ solution at room temperature produced some $NH_4^+BF_4^-$ due to attack of the starting material by HF. The latter was formed during the generation of the HOF from $H_2O$ and $F_2$ in $CH_3CN$. Similar results were obtained when we used $Na[B(imid)_4]$ and HOF in $CH_3CN$ solution at -10 °C. Since HOF is the intermediate product of the hydrolysis of $F_2$, we have also carried out reactions with $OF_2$ which is the final product of the hydrolysis of $F_2$. Since $OF_2$ is more stable than HOF and can be readily separated from the HF by-product, this approach offered an opportunity to avoid the competing side reaction of the starting material with HF. However, a mixture of 10 % of $OF_2$ in $N_2$ was found not to react with $Na[B(imid)_4]$ at -20 °C in $CH_3CN$ solution. Attempts to hydrolyze aqueous $[PPh_4]^+[B[N(CHO)_2]_4]^-$ to the corresponding $[B(NH_2)_4]^-$ amine and $CH_2O$ using UV-photolysis were also unsuccessful.

In order to cleave the B-N bonds in the tetra-azido borate anion, we have prepared the $Li^+$, $Na^+$ and $[N(CH_3)_4]^+$ salts of the $[B(N_3)_4]^-$ anion[17] and have studied their oxidative cleavage. Because an azido group cannot be directly converted into a nitro group by the use of ozone, it was first transformed into a phosphazene by reaction with trimethylphosphine.

$$Li[B(N_3)_4] + 4\ PMe_3 \rightarrow Li[B(N{=}PMe_3)_4] + 4\ N_2$$

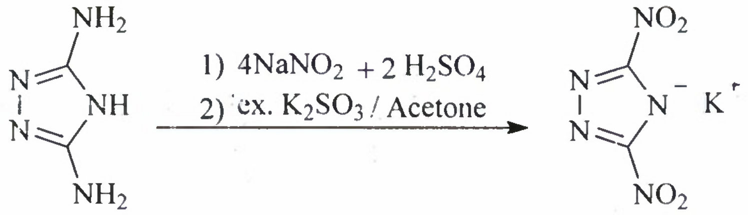
Cleavage reactions of the phosphazene using ozone gave again nitrate and borate ions. When HOF was used as an oxidizer, $BF_4^-$ and $NO_3^-$ were obtained as reaction products. Because the oxidative cleavage of the $B(NX)_4^-$ skeletons required more systematic studies, alternate candidates were also explored. The most promising compound was the ammonium salt of the tetrakis(3,5-dinitro-1,2,4-triazolyl)borate, $[B(DNT)_4]^-$, anion. It has a good oxygen balance and, based on our theoretical calculations, it could outperform $NH_4ClO_4$ (Scheme 2).



- Good oxygen balance

Scheme 2

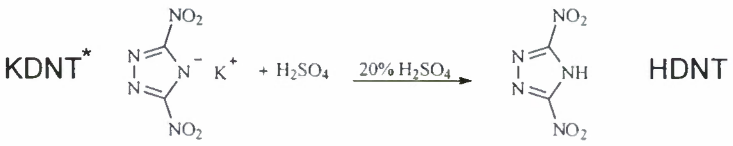
The starting material for the synthesis of DNT compounds is its potassium salt (KDNT). was readily prepared (Scheme 3) from commercially available compounds using a literature method.[18]



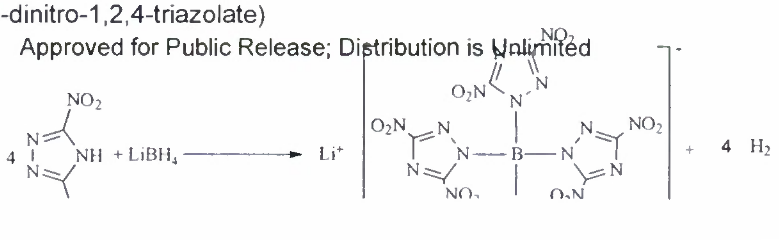
KDNT

Scheme 3

To prepare the desired borate salt, KDNT it was converted (Scheme 4) by acidification with 20% aqueous $H_2SO_4$ to the free triazole (HDNT) which contains an acidic hydrogen. It was found that the crude HDNT obtained by this method was yellowish-brown. It was purified by vacuum sublimation, yielding a white product. The reaction of HDNT with $BH_4^-$ then offered a route to the corresponding borate anion (Scheme 4).



Potassium (3,5-dinitro-1,2,4-triazolate)



Scheme 4

The reaction of HDNT with $LiBH_4$ was studied in diethyl ether as a solvent at room temperature and produced 50 % of the hydrogen expected for a substitution of all four hydrogen ligands. To obtain single crystals suitable for x-ray diffraction, the lithium salt was converted to the $PPh_4^+$ salt, and the partial substitution was confirmed by x-ray crystallography (see Figure 4) which showed the replacement of two ligands in accord with the observed hydrogen evolution.

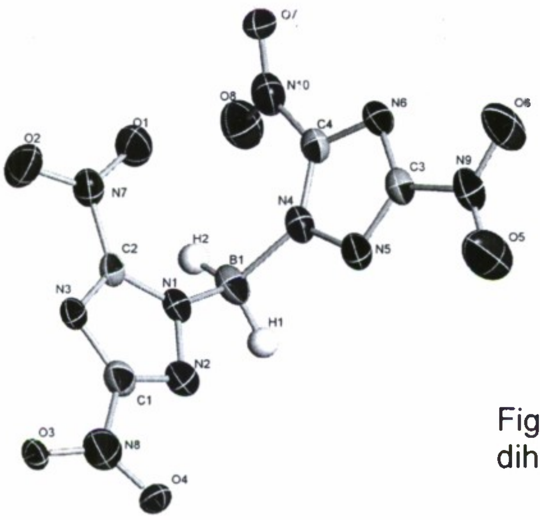


Figure 4. Crystal structure of the dihydrido-bis(dinitro-triazolato)borate

A similar reaction under the same conditions with the $N(CH_3)_4^+$ salt instead of the lithium salt also resulted only in the replacement of two hydrogen atoms. Because the dihydrido-salt might already be of significant interest as a HEDM, a larger batch of the lithium dihydrido-bis-dinitrotriazoloborate was prepared, but detonated on handling in the drybox. Therefore, it appears that dihydrido-bis-dinitrotriazoloborates might be too sensitive for practical applications. Attempts to prepare its tetramethylammonium salt from the reaction of $N(CH_3)_4{}^+BH_4{}^-$ with only 2 equivalents of dinitro-triazole in diethylether at room temperature resulted only in the evolution of one mole of $H_2$, but succeeded at 85 °C in THF solution (see below).

To achieve further ligand exchange, the reaction was repeated at higher temperature using a higher boiling solvent such as THF. The reactions of $TMA^+BH_4{}^-$ with 2 and 4 equivalents of HDNT in THF solution at 85°C resulted in quantitative $H_2$ evolution of 2 and 4 moles, respectively. The reaction of $P(C_6H_5)_4{}^+$ $BH_4{}^-$ with excess of dinitrotriazole in toluene at 110 °C also produced four equivalents of $H_2$. Furthermore, the Raman spectrum of the solid reaction product no longer showed any B-H bands. This is a strong indication that all four hydrogen atoms were successfully replaced by dinitrotriazolo groups. The product had some solubility in $CH_3CN$ and toluene, and attempts will be made in the future to obtain single crystals for a structural analysis.

The stepwise synthesis of tetrakis-dinitrotriazolatoborate from $BH_4{}^-$ and dinitro-triazole was established by a multinuclear ($^1H$, $^{13}C$, $^{11}B$, and $^{14}N$) NMR study in $CD_3CN$ solution. The reactions of $TMA^+BH_4{}^-$ with 1, 2, 3 and 4 equivalents of HDNT were studied in THF solution at 85°C. In all cases, quantitative $H_2$ evolution of 1, 2, 3 and 4 moles, respectively, was observed. In the cases of 1:1 and 2:1 ratios, the observed products were $TMA^+HB(DNT)_3{}^-$ and $TMA^+H_2B(DNT)_2{}^-$, respectively. In the case of a 3:1 ratio, the main products were $TMA^+H_2B(DNT)_2{}^-$ and $TMA^+B(DNT)_4{}^-$, with only a small amount of $TMA^+HB(DNT)_3{}^-$ being present, indicating a tendency of the tri-substituted anion to dismutate to the di- and tetra-substituted anions. In the case of a 4:1 ratio, $TMA^+B(DNT)_4{}^-$ was the main product (Fig. 5).

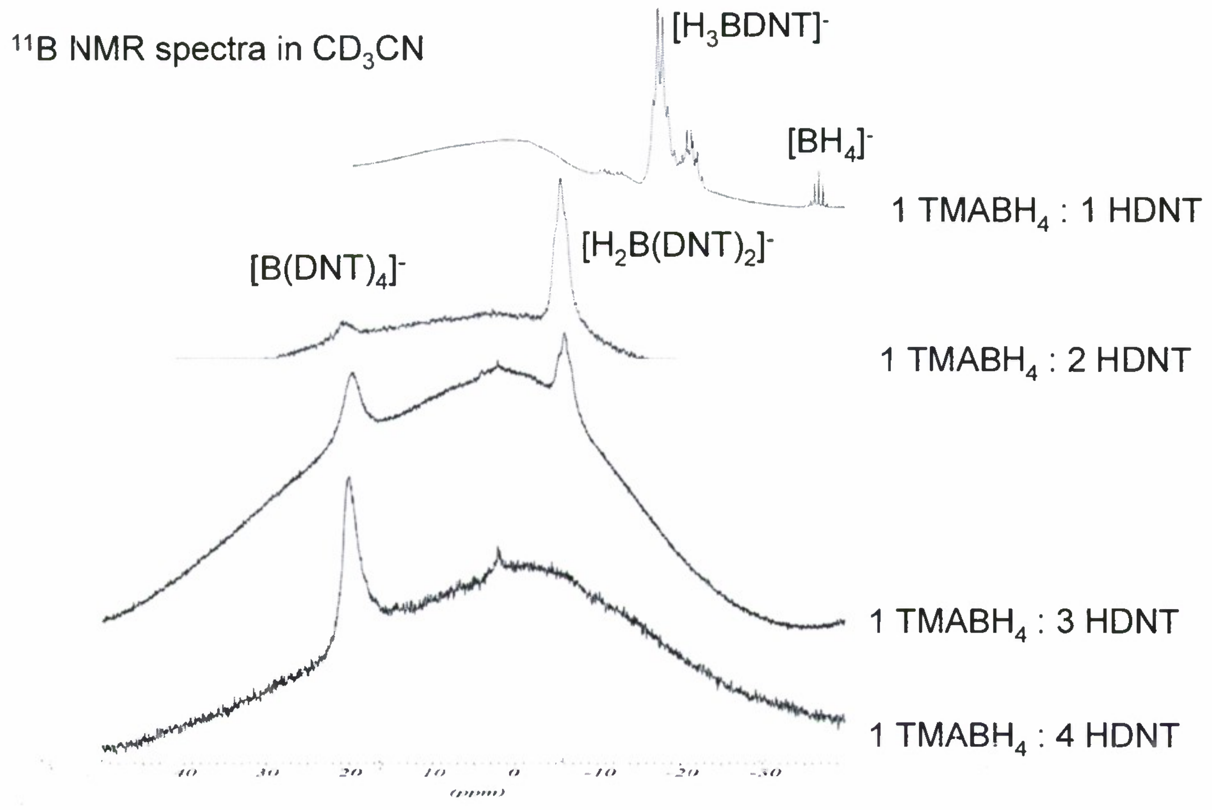


Figure 5. $^{11}$B NMR spectra of $[H_3B(DNT)]^-$, $[H_2B(DNT)_2]^-$, $[HB(DNT)_3]^-$, and $[B(DNT)_4]^-$.

The composition of the products was further demonstrated by Raman spectroscopy (Fig. 6). The thermal stability of these tetramethylammonium salts was studied by thermal gravimetric analysis. The compound of greatest interest, $TMA^+B(DNT)_4^-$, lost 75 % of its weight at about 180 °C (Fig. 7), and $TMA^+H_3B(DNT)^-$ salt also underwent a sharp weight loss of 74 % at 177 °C (Fig. 8). These results demonstrate that we have achieved one of our main goals, i.e., significantly improving the thermal stability of our high-oxygen carrying anion without sacrificing its theoretical performance compared to those of $B(ONO_2)_4^-$ and $Al(ONO_2)_4^-$.[10] Efforts to obtain crystal structures for these salts succeeded for $[N(CH_3)_4]^+$ $[H_2B(DNT)_2]^-$ and further confirms the nature of these compounds.

While the $H_2B(DNT)_2^-$ anion might have sensitivity issues because its lithium salts detonated on one occasion without provocation during its handling in the glove box, the

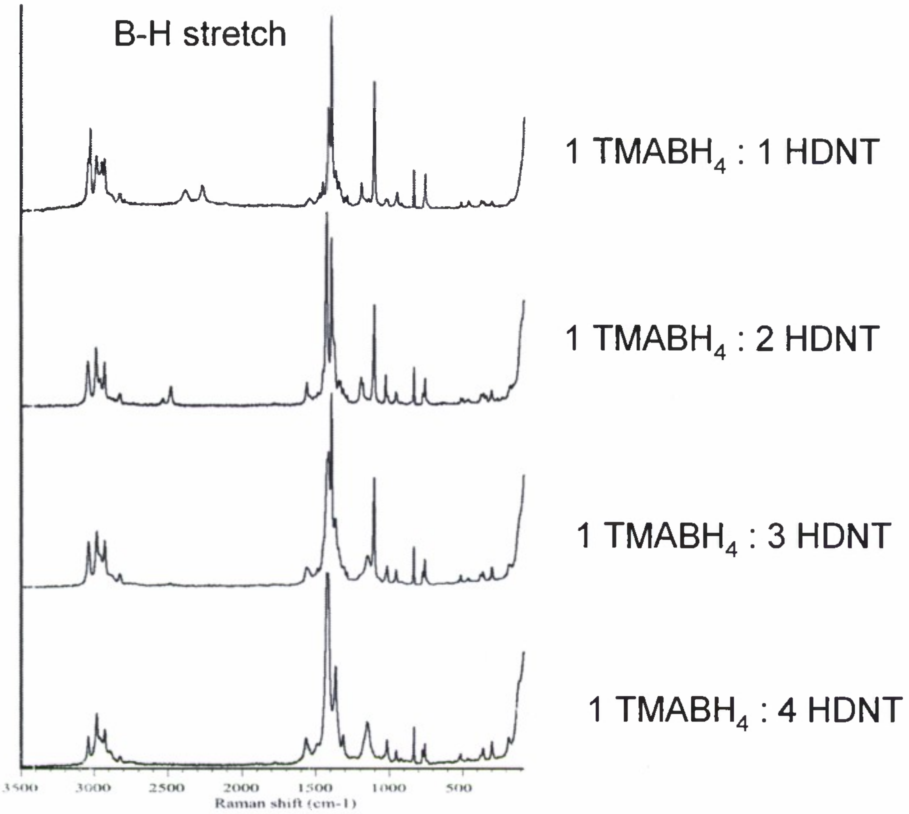


Figure 6. Raman spectra of the TMA$^+$ salts of $[H_3B(DNT)]^-$, $[H_2B(DNT)_2]^-$, $[HB(DNT)_3]^-$ and $[B(DNT)_4]^-$

Figure 7. TGA curve of $[TMA][B(DNT)_4]$

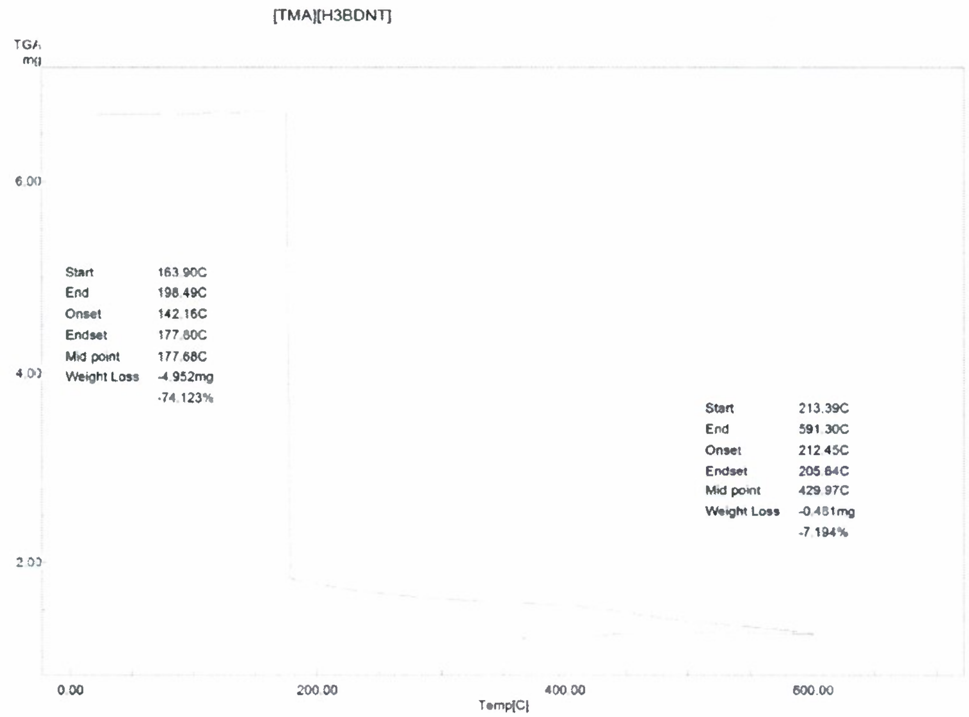


Figure 8. TGA curve of [TMA][$H_3B(DNT)$]

tetra-substituted compound appears to be much less sensitive. It was shown that the $TMA^+B(DNT)_4^-$ salt is insensitive to blows with a hammer, and friction tests with a spatula were negative. It also burns smoothly in an open flame without explosion. Furthermore, it decomposed smoothly during the TGA runs. It was also shown that it is hydrolytically completely stable. For example, a sample of the $TMA^+$ salt was dissolved in water. The water was pumped of and the solid residue was shown by vibrational and NMR spectroscopy to be the unchanged starting material (Fig. 9).

As an alternate synthesis route for $B(DNT)_4^-$, we have also studied the replacement of halide ligands by DNT ligands. To this end, we have reacted tetramethylammonium (TMA) chloride, $BCl_3$ and KDNT in $SO_2$ solution at room temperature and obtained a crystalline product whose structure was determined by x-ray diffraction. It was shown that two of the four chloride ligands had successfully been replaced by DNT groups (see Fig. 10). This partially substituted product also exhibited good thermal stability, low sensitivity and was hydrolytically stable. We have also studied the reaction of $BI_3$ with 4

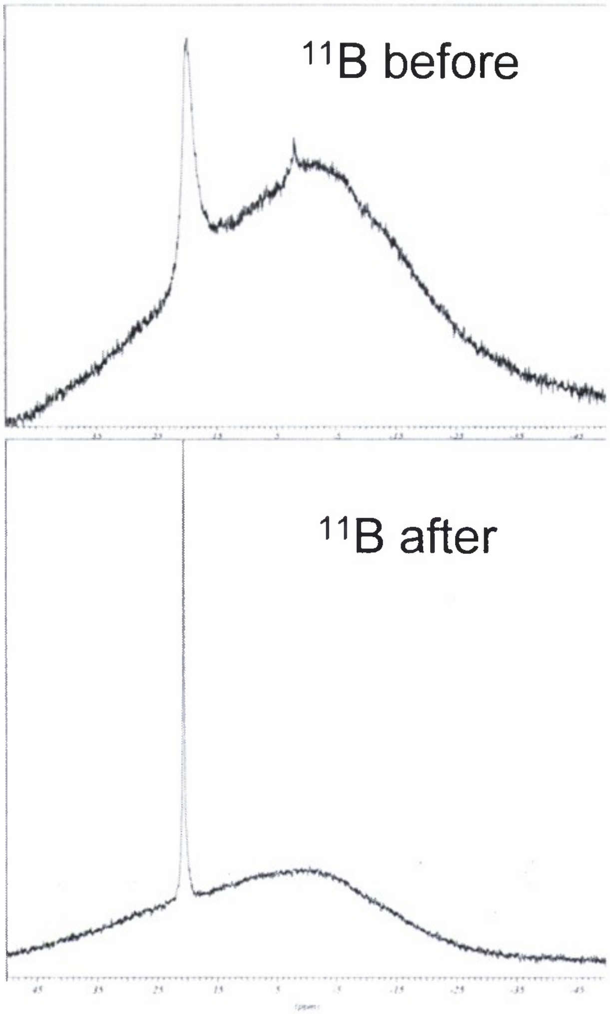


Figure 9. $^{11}$B NMR spectra of [TMA][B(DNT)$_4$] before and after exposure to water.

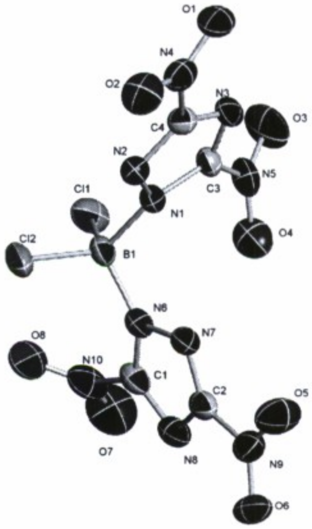


Figure 10. Crystal structure of the dichloro-bis(3,5-dinitro-1,2,4-triazolyl)borate anion.

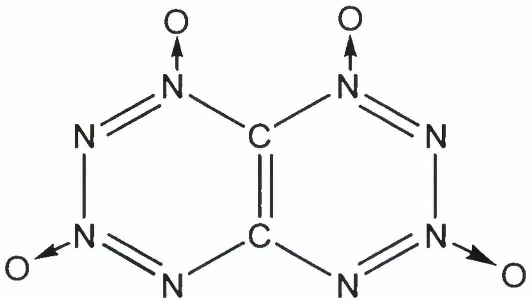
equivalents of AgDNT in $CH_3CN$ solution, and the correct amount of AgI precipitate, expected for a complete replacement of all four I atoms, was obtained.

### Task 1, Summary

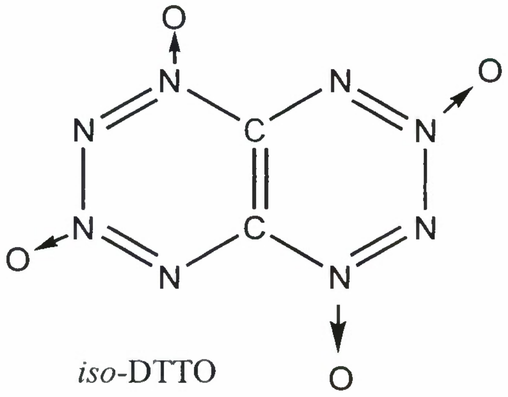
The results obtained under this Task are highly encouraging. The B(DNT)$_4^-$ anion is an excellent candidate for the replacement of the perchlorate anion in high-oxygen carrier applications. It has sufficient thermal stability, is hydrolytically stable, is insensitive, and the predicted performance of its ammonium salt is slightly higher than that of ammonium perchlorate. Although much progress was made during this program, further work is required to develop this $B(DNT)_4^-$ chemistry. For example, the crystal structure of the anion needs to be determined, the alkali metal or tetramethylammonium salts need to be converted to the ammonium salt, the ammonium salt needs to be fully characterized and its compatibility with other formulation ingredients needs to be established. Furthermore, modification of the cations should be studied to obtain low-melting compounds for ionic-liquid liquid monopropellant applications. These compounds would be of great interest for the replacement of the presently used highly carcinogenic hydrazine.

### *TASK 2. Syntheses of DTTO and iso-DTTO*

Over the past 20 years, the late Prof. Harold Schechter from Ohio State University had been an adamant advocate for pursuing the syntheses of the new explosives DiTetrazineTetrOxide (DTTO for short) and its isomer, *iso*-DDTO.



DTTO



*iso*-DTTO

The scientific basis for his faith in DTTO was the extensive work carried out by the group of Churakov and Tartakovsky at the Zelinsky Institute for Organic Chemistry of the Russian Academy of Sciences in Moscow. In a series of papers,[11] these scientists have demonstrated that catenated cyclic nitrogen compounds can be stabilized by creating alternating positive and negative charges through the addition of an oxygen atom to every second nitrogen atom. Using the density and heat of formation predictions of Harold Schechter, we have calculated for DTTO, using the Cheetah program,[19] a detonation pressure of 1142 kbar which is more than three times the value for HMX (359 kbar). Since this value appeared unrealistically high, we have asked Herman Ammon to re-estimate the densities[20] and Jerry Boatz and Dave Dixon to redo the heats of formation. Using their best estimates, we recalculated the detonation pressures and velocities and obtained much more realistic values (see Table 1).

**Table 1. Calculated detonation pressures and velocities for DTTO and *iso*-DTTO compared to those for HMX and CL20.**

| compound | ρ (gcm$^{-3}$) | $\Delta H_f^0$ (kJmol$^{-1}$) | deton pressure (kbar) | det veloc (msec$^{-1}$) |
|---|---|---|---|---|
| HMX | 1.9050 | 75.0 | 359 | 9123 |
| CL20 | 2.044 | 377.2 | 468 | 9867 |
| DTTO | 1.970 | 901.7 | 558 | 1027 |
| *iso*-DTTO | 1.994 | 887.0 | 571 | 1037 |

Although the values predicted for DTTO and *iso*-DTTO do not approach Schechter's values, they are still much higher than those of HMX and CL20 and *demonstrate the great merit and potential pay-off of pursuing the syntheses of DTTO and iso-DTTO.*

Since the synthetic approach of Churakov and Tartakovsky, using phenyl diazonium salts, permitted only the synthesis of phenyltetrazinedioxides but not of ditetrazine-tetroxides, we decided to explore different methodologies for preparing tetrazine-dioxides which are not attached to a phenyl group. A literature search was carried out and revealed that a 1,2,3,4-tetrazine ring can be constructed from triazoles in which the two carbon atoms are not part of a phenyl ring. The resulting compound, 6-phenyl-[1,2,3]triazolo[4,5-e]-1,2,3,4-tetrazine, PTAT, was characterized by Japanese workers[21] by its low-temperature crystal structure (Figure 11), but is thermally unstable.

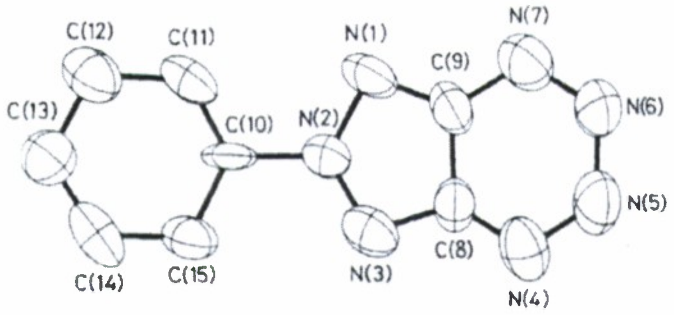
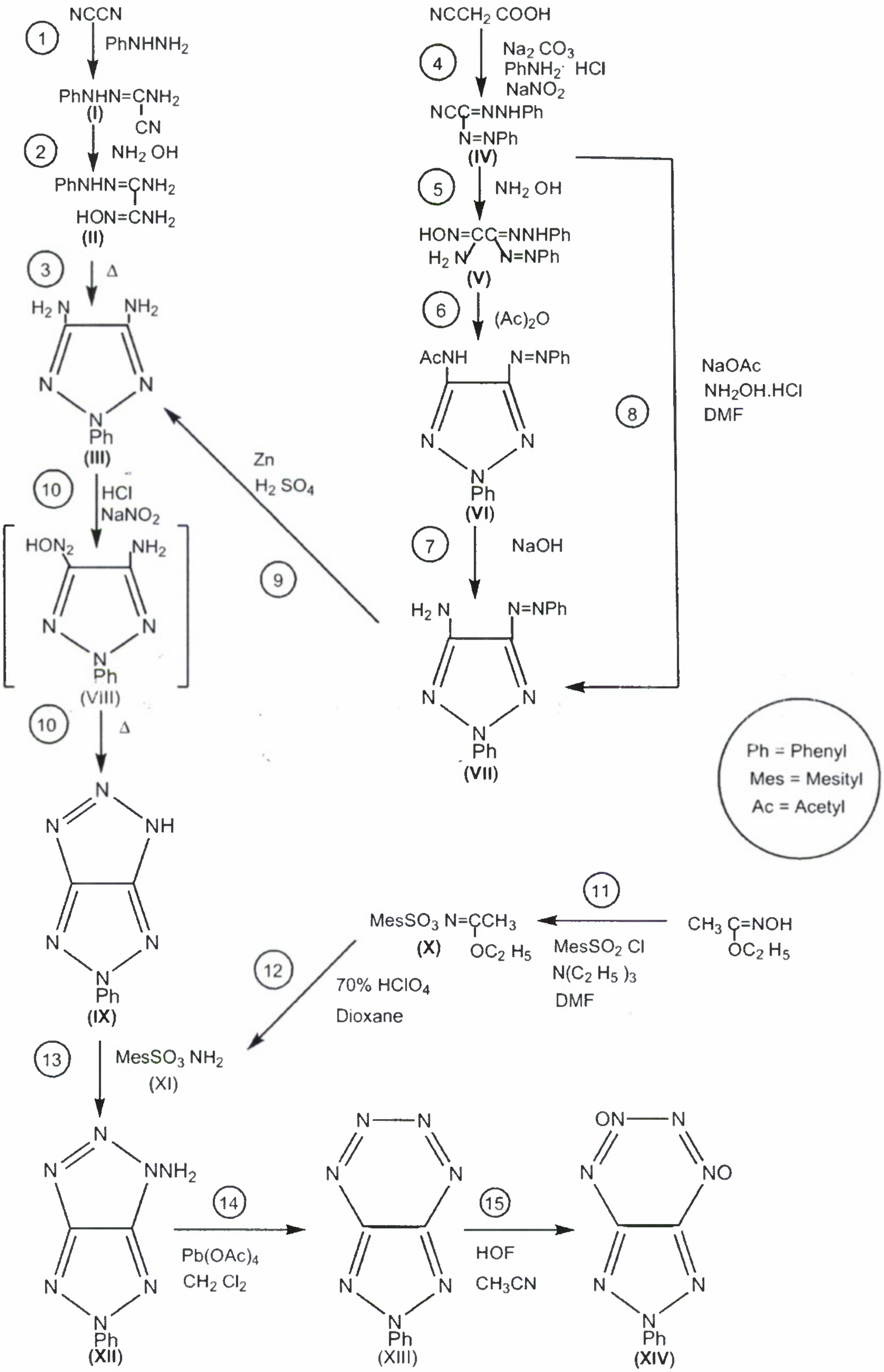


Figure 11. Crystal structure of 6-phenyl[1,2,3]triazolo[4,5-e]-1,2,3,4-tetrazine (PTAT)

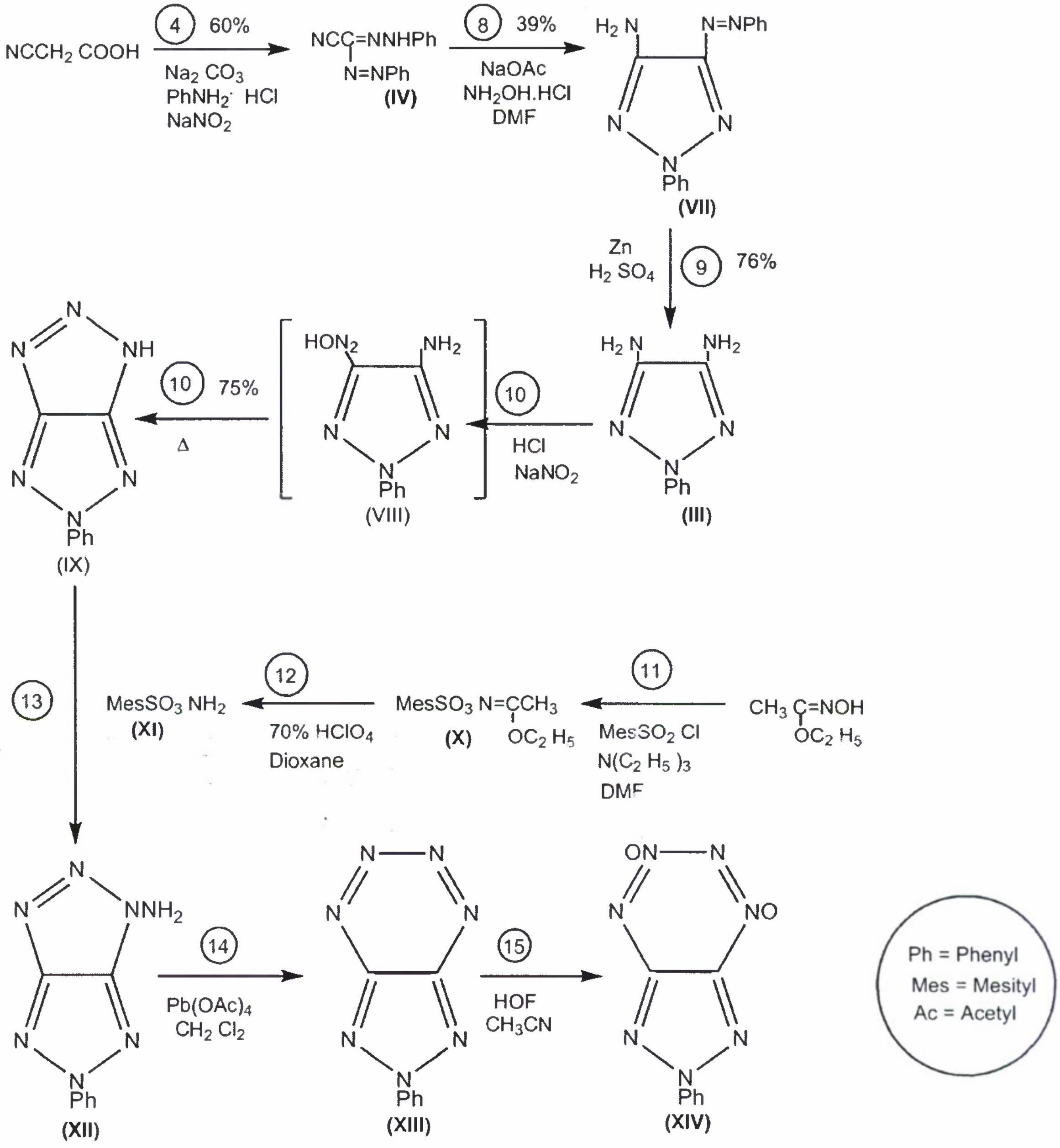
Our goal was to prepare and characterize some small amounts of DDTO or *iso*-DTTO. If their properties, such as density and stability, were good, improved synthetic methods would be developed. Our approach for the synthesis of DTTO involved the following strategy. Using HOF, the tetrazine ring of the Japanese compound would be oxidized to a more stable dioxotetrazine, then the triazole ring would be converted by ring expansion into a tetrazine, and oxidized again with HOF to DTTO.

The initially proposed synthetic sequence together with subsequent modifications is shown in Scheme 5. Although this plan appeared at first to be straightforward, a number of the procedures reported for some of the intermediate compounds were vague and in our hands not reproducible, necessitating multiple experiments to improve yields and/or evoke alternate preparative procedures. As a result of these unforeseen delays, the entire synthetic sequence could not be completed in the contractual timeframe. In the following chronological discussion of each of the reaction steps which were completed, the agreement with or the difference from the literature results are summarized to serve as a guide for future work in this area.

Based on the experimental work a number of the reaction steps in Scheme 5 have been deleted to obtain the recommended reaction sequence outlined in Scheme 6. In this sequence the experimentally determined overall yield of the intermediate compound (IX) was 13.3% based on cyanoaceticacid.



Scheme 5. Originally proposed synthesis of PTAT



Scheme 6. Improved synthesis of PTAT

*Step 1. Synthesis of 2-Amino-2-phenylhydrazonoacetonitrile (I) from Phenylhydrazine and Cyanogen*

The procedure of Fischer[22] simply states that passage of cyanogen into aqueous 10% phenylhydrazine, cooled in an ice bath, until it is no longer absorbed provides the water insoluble title compound which is then isolated by filtration and purified by carbon decolorization and crystallization from 20% ethanol. No information is provided on the cyanogen addition rate, the actual reaction temperature or the yield of product.

A series of eight experiments was conducted using in each case 0.2-0.4 mol of phenylhydrazine. The cyanogen was not metered as it was mixed into a slow nitrogen stream used to prevent suck back of the phenylhydrazine solution into the gas inlet until a rapid cyanogen flow was attained. The exit gases from the reactor were flared to destroy the highly toxic cyanogen. When the cyanogen passed through the reaction mixture the pale clear blue flame of the flared exit gas changed to an opaque white. The bright orange product precipitated as it formed in the initially white phenylhydrazine emulsion (an aqueous 10% phenylhydrazine solution separates into two liquid phases on cooling in an ice bath). At the end of the cyanogen addition, filtration of the thick creamy orange reaction mixture produced an inordinately large amount of solid, the bulk volume of which decreased to about one-third of its initial volume on washing with water. In one experiment where the introduction of cyanogen was inadvertently delayed for 30 min the emulsified phenylhydrazine was transformed into a thick white cream having the same consistency as the final reaction mixture. The color of the washed product varied from a dark brownish orange to a bright orange as the mol ratio of $(CN)_2/C_6H_5N_2H_3$ decreased over the range 2.74 to 0.81. An excess of cyanogen appears to react further with the initial product albeit more slowly to form a darker colored by-product requiring carbon decolorization for its removal. The yield of product after crystallization from 20% ethanol was 25-33%. From these experiments it is apparent that phenylhydrazine is partially converted into a form which is non-reactive with cyanogen. Possible species might be the soluble ionic phenylhydrazinium hydroxide (a monohydrate) or the bis(phenylhydrazinium) oxide (a hemihydrate, m.p.25.6°).[23] On the basis of this hypothesis, simultaneous addition of both reactants should afford higher product yields because of a lesser formation of the unreactive form.

A further series of four experiments was conducted using simultaneous addition of reactants while monitoring the reaction temperature. The best purified product yield (45%) was obtained when the cyanogen flowrate was about half of that of the phenylhydrazine. At cyanogen flowrates equal or higher than that of the phenylhydrazine, yields ranged from 34-36%. The temperature of the reaction mixture increased about 4-5° during the 4-9 min addition. The crude product formed by this simultaneous addition procedure was much lighter in color than that from addition of cyanogen to phenylhydrazine with the consequence that purification was much simplified.

<u>Step 2</u>. *Synthesis of Phenylhydrazonooxamide Oxime (II) from 2-Amino-phenylhydrazonoacetonitrile (I) and Hydroxylamine*

The procedure described by Thiele[24] was reasonably straightforward, rapid and readily reproducible. The reaction was repeated five times by combining near saturated solutions of 2-amino-2-phenylhydrazonoacetonitrile (I) in refluxing ethanol with equimolar quantities of hydroxylamine prepared from stoichiometric amounts of hydroxylamine hydrochloride and sodium carbonate in a minimum amount of water. The significantly smaller 72-78% yield of product could be increased to the reported range (90-100%) by secondary recovery from the product mother liquor and washings, but with slightly lower purity. This difference in the initial yield may be due to a lower water concentration than that used by Thiele who probably worked with 95% ethanol rather than 100% and may have used more water for the hydroxylamine preparation in order to dissolve the by-product sodium chloride. The solid oxime undergoes slow oxidation on exposure to air at ambient temperature, particularly when wet, and more rapidly at higher temperatures to give black char. Oxime solutions oxidize rapidly turning wine red.

<u>Step 3.</u> *Synthesis of 4,5-Diamino-2-phenyl-1,2,3-triazole (III) from 2-Phenylhydrazidooxamide Oxime (II)*

Thiele[5] states that heating 2-phenylhydrazidooxamide oxime (II) in an autoclave to 150° for 2 hours with a six-fold excess of water forms 4,5-diamino-2-phenyl-1,2,3-triazole (III) in 40-50% yield with longer time or higher temperature having little effect. The results of a series of seven experiments were quite erratic, perhaps the direct consequence of varying experimental conditions, but in all cases quite different from that reported. Since solutions of the oxime air oxidize readily, only the first experiment was conducted in the presence of air. When air in the autoclave was displaced with nitrogen a smaller amount of by-product tar of a lighter color was observed. The crude product was (with one exception) a mixture of somewhat water soluble colorless crystals and a brown tar. The exception occurred after a reaction time of 5 hours, when nothing crystallized from the aqueous phase and a brown oil replaced the tar. From this observation one might conclude that the tar is a mixture of the crystals with less of the oil (a presumed by-product or degradation product). The operation common to each of these experiments was the separation of the crystals from the tar either mechanically from cold mixtures or by aqueous extraction of the more soluble crystals from warm mixtures. However, purification of the product by recrystallization never gave a product having the reported melting point of 143°. In two of the experiments needles melting at 110-12° were obtained which were comprised of two components as demonstrated by thin layer chromatography. $^1$H and $^{13}$C NMR spectra were consistent with the calculated spectra for the title triazole containing about 18% of an oxime derived from the starting material by substitution of a hydroxyl- group for one of the amino- groups. In other experiments the isolated products had higher melting points, namely 160°, 152-64° and 165-70°. In the last case the crystals were plates (characteristic of the starting oxime, m.p. 174°) whereas in the first two cases they were needles (characteristic of both the diaminotriazole derivative (III), m.p. 143° and an impurity reported by Thiele[5] to occur in 3% yield where one of the amino- groups has been replaced by a hydroxyl- group in the triazole, m.p. 173°).

An attempt to facilitate the cyclization reaction with ultrasound was unsuccessful as were attempts at the same 150° temperature to remove water azeotropicly with cumene or by using urea as a solvent.

This approach to 4,5-diamino-2-phenyl-1,2,3-triazole (III) (Steps 1-3) was abandoned as a consequence of the poor results obtained in Step 3 and was replaced with another sequence of reactions wherein a phenylazo- group is substituted for the first aminogroup introduced (initially Steps 4, 5, 6, 7 and 9) and subsequently by a further modification (Steps 4,8 and 9: see Scheme 1).

*Step 4. Synthesis of 2-Phenylazo-2-phenylhydrazonoacetonitrile (IV) from Cyanoacetic Acid and Phenyldiazonium Chloride*

The procedure for the preparation of the title compound was reported[25] in the patent literature without stating a yield. Only the melting point was given for characterization of the material. A series of three experiments established that the material is produced in near quantitative yield as an extremely fine and voluminous solid which required extensive washing to remove inorganic salts and vacuum drying near ambient temperature to prevent air oxidation and/or thermal decomposition. Most of the water insoluble compound (91%) is produced as a thick floating foam over the remainder which occurs as a thin slurry. Both forms were shown to be identical by thin layer chromatography and $^{1}H$ and $^{13}C$ NMR spectroscopy. The thoroughly washed wet product isolated by filtration had an inordinately high water content namely 78% for the foam and 83% for the slurry. Soxhlet extraction of the crude dry product with chloroform was complete and left less than 1% residual salts. However, two recrystallizations from ethanol were required to raise the melting point to the reported value with recovery of only 60% of the material in each crystallization. An attempt to purify the material by high vacuum sublimation was unsuccessful due to extensive decomposition.

*Step 5. Synthesis of 2-Phenylazo-2-phenylhydrazonoacetamide Oxime (V) from 2-Phenylazo-2-phenylhydrazonoacetonitrile (IV) and Hydroxylamine*

A series of seven experiments was carried out with variations in reaction conditions in the conversion of the title nitrile (IV) to the oxime (V). The principal differences among syntheses reported in the literature were the solvents used, reactant concentrations, reaction time, temperature and the preparative method for hydroxylamine from its hydrochloride. An attempt to follow the procedure of Henderson[25] failed to give any solid product. A reinvestigation of Henderson's procedure by Nikitin[26] reported a 98% oxime yield but in our hands over 80% of the starting nitrile was recovered. Much better results were obtained with the procedure of Thiele[24] (see Step 2 above) with some modifications namely extending the reaction time and adding a 2.5-fold excess of hydroxylamine to the nitrile (reverse addition) under a nitrogen atmosphere. With these modifications pure product was obtained in 70% yield.

<u>Step 6.</u> *Synthesis of 4-Acetamido-5-phenylazo-2-phenyl-1,2,3-triazole (VI) from 2-Phenylazo-2-phenylhydrazonoacetamide Oxime (V) and Acetic Anhydride*

Two attempts were made to reproduce the synthesis by Nikitin[26] wherein acetic anhydride is used as the reaction solvent for this ring closure instead of water as was used in Step 3 above. In this process the by-product water forms acetic acid which acetylates the initially formed amino- group. In each attempt the reaction did not proceed as rapidly as reported leaving the product contaminated with much starting material. Rather than trying to improve the synthesis of the 4-acetamido- derivative which then requires a basic hydrolysis Step 7 to form the 4-amino- derivative, a newly reported[8] process which could be adapted for a single step conversion of 2-phenylazo-2-phenylhydrazono-acetonitrile (IV) to the title compound was investigated (see Step 8).

<u>Step 7.</u> *Synthesis of 4-Amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII) from 4-Acetamido-5-phenylazo-2-phenyl-1,2,3-triazole (VI) and Aqueous Base*

Despite the low purity of the 4-acetamino-derivative available it was subjected to basic hydrolysis to obtain a crude sample of the corresponding 4-amino- derivative following the Nikitin[26] report. Separation of the mixture was accomplished on a thin layer chromatographic plate and the components were identified by $^1$H and $^{13}$C NMR spectra as the desired product (VII) and the starting material (VI).

<u>Step 8.</u> *Synthesis of 4-Amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII) from 2-Phenylazo-2-phenylhydrazonoacetonitrile (IV) and Hydroxylamine*

A procedure reported by Badahdah[27] for the one step conversion of 2-(heterocyclic radical)-2-phenylhydrazoacetonitrile to the 4-amino-5-(heterocyclic radical)-2-phenyl-1,2,3-triazole was adapted by substituting the title nitrile (IV) for the nitrile containing the heterocyclic radical in this process. The nitrile (IV) reacts with hydroxylamine (generated *in situ* as its acetate salt from its chloride salt and sodium acetate) to produce the amide oxime (V) which in turn cyclizes to the title triazole (VII) in the refluxing dimethylformamide solvent. A series of seven experiments using purified nitrile indicated that the yield of the recrystallized triazole was increased from 16% to 39% when the reaction time was extended from 2 to 4 hr but further extension to 8 hr was without effect. In one 4 hr experiment where crude nitrile was used in place of recrystallized material the yield was only 15% although up to an additional 8-15% yield of a slightly less pure triazole derivative could be obtained from the concentrated mother liquor.

_Step 9._ *Synthesis of 4,5-Diamino-2-phenyl-1,2,3-triazole (III) from 4-amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII) and Zinc/Sulfuric Acid*

Three experiments were conducted following the procedure of Nikitin[26] reported to give an 80% yield (88% with secondary recovery). For reasons unknown, the reduction was far from complete in the first experiment where 29% of the starting material was recovered chromatographically. The product yield was 60% based on reacted starting material. On repetition of the reaction the reduction was virtually complete with only about 4% of the starting material contaminating the diamino- derivative obtained in 69% yield and on scale-up in 76% yield. $^1H$ and $^{13}C$ NMR spectroscopy was used to characterize the product.

_Step 10._ *Synthesis of 4,5-Triazolo-2-phenyl-1,2,3-triazole (IX) from 4.5-Diamino-2-phenyl-1,2,3-triazole (III)*

The procedure of Thiele[24] was followed wherein 4,5-diamino-2-phenyl-1,2,3-triazole (III) was diazotized to form 4-amino-5-diazono-2-phenyl-1,2,3-triazole (VIII) which without being isolated was allowed to decompose to give a 75% yield of 4,5-triazolo-2-phenyl-1,2,3-triazole (IX).

_Step 11._ *Synthesis of Ethyl O-(mesitylenesulfonyl)acetohydroxamate (X) from Ethyl Acetohydroxamate and Mesitylenesulfonyl Chloride*

The preparative procedure reported by Tamura[28] was used to prepare (X) which is one of the more stable acetohydroxamate derivatives. The initial product in the two experiments conducted was liquid rather than the solid reported. Whether or not this difference was due to the effect of possible deviations from Tamura's experimental conditions could not be decided because additional experiments were precluded by lack of contractual time. A crystalline solid recovered from the initial liquid appeared to be primarily (X) by NMR spectroscopy although the melting point was 7-8° lower than reported.[28] Other tentatively identified materials were the reaction solvent DMF, O-

(mesitylene-sulfonyl)hydroxylamine (XI) (possibly in the form of a salt) and mesitylenesulfonic acid.

A possible explanation for the above observations is that the reaction did not go to completion before the reaction mixture was poured into water. If this were the case it would be expected that mesitylenesulfonyl chloride would be hydrolyzed to mesitylenesulfonic acid and hydrochloric acid which could cause acid catalized hydrolysis of part of (X) to form ethyl acetate and O-(mesitylene-sulfonyl)hydroxylamine (XI). In neither of the experiments conducted nor in the reported[28] procedure were temperatures of the reaction mixtures noted; only the terms "ice cooling" and "stirring at $0^{o}$" were used. Our experiments might have been colder with the consequence that insufficient time was allowed for completion of the reaction.

## Task 2, Experimental

*Step 1.* *2-Amino-2-phenylhydrazonoacetonitrile (I)*

The first preparative procedure consisted of passing a known amount of cyanogen gas as an unmetered stream in about 10 min into a rapidly stirred (600 rpm) aqueous 10% phenylhydrazine solution cooled in an ice bath. The crude insoluble product was isolated by filtration and partially purified by recrystallization from aqueous 20% ethanol. Further purification was effected by precipitation from an ethereal solution by pouring it into 6.5-8.7 times its volume of hexane. The results are summarized in Table 1.

The second preparative procedure utilized simultaneous addition of phenylhydrazine and cyanogen to ice cooled water with all other experimental conditions from the previous eight runs remaining unchanged. The results are summarized in Table 2.

*Step 2.* *Phenylhydrazidooxamide Oxime (II)*

A near saturated solution of hydroxylamine containing a slurry of sodium chloride was prepared at ambient temperature from its hydrochloride by neutralization with the stoichiometric amount of sodium carbonate. To this mixture on a steam bath a near saturated refluxing solution of the stoichiometric amount of 2-amino-2-phenylhydrazonoacetonitrile (I) in 100% ethanol was added rapidly. After refluxing for 5 min

**Table 1. Addition of Cyanogen to Phenylhydrazine**

| Expt. | $C_6H_5N_2H_3$ mmol | $(CN)_2$ mmol | Mol Ratio $(CN)_2$/ $C_6H_5N_2H_3$ | % Yield, Recrystallized Aqueous Ethanol | % Yield, Ppt'd Ether/Hexane |
|---|---|---|---|---|---|
| 1 | 121 | 173 | 1.43 | 26.8[a] | 24.3[b] |
| 2 | 119 | 33 | 0.28 | -[a, c, d] | |
| 3 | 353 | 365 | 1.03 | 22.9[a] | 17.5[e] |
| 4 | 365 | 442 | 1.21 | -[a, d] | - |
| 5 | 362 | 461 | 1.27 | 22.9[a] | 21.9[e] |
| 6 | 380 | 308 | 0.81 | 29.6 | |
| 7 | 387 | 385 | 0.99 | 32.9 | |
| 8 | 394 | 346 | 0.88 | 25.3 | |

---

(a) Aqueous 80% ethanol used inadvertently

(b) Hexane/ether volume ratio, 6.5

(c) Visually observed as less than half of that in Expt. 1

(d) Decomposed during drying in 100° oven

(e) Hexane/ether volume ratio, 8.7

**Table 2. Simultanious Addition of Phenylhydrazine and Cyanogen**

| Expt. | $C_6H_5N_2H_3$ mmol (mmol/min) | $(CN)_2$ mmol (mmol/min.) | $H_2O$ mL | Mol Ratio $(CN)_2/C_6H_5N_2H_3$ | Temp. Range during addition, °C | % Yield Recrystallized from 20% ethanol |
|---|---|---|---|---|---|---|
| 9 | 366 (37) | 750 (66) | 410 | 2.03 | 3.6-11.3 | 34.6 |
| 10 | 375 (59 | 211 (29) | 420 | 0.56 | 3.1-7.4 | 45.6 |
| 11 | 390 (78) | 461 (59) | 420 | 1.18 | 1.1-7.8 | 35.8 |
| 12 | 401 (31) | 423 (30) | 440 | 1.05 | 8.9-14.1 | 33.9 |

the reaction mixture was cooled in an ice bath before isolating the product by filtration. The product was washed with ethanol and water and oven dried at 62° (100° drying is satisfactory for small amounts which dry quickly but larger quantities are prone to rapid oxidative degradation). The results are summarized in Table 3.

**Table 3. Phenylhydrazidooxamide Oxime**

| Expt. | Nitrile, mmols | Ethanol, mL | $NH_2OH$, mmols | $H_2O$, mL | Wash Ethanol, mL | Wash $H_2O$, mL | % Yield, prim. (sec) | m.p.,°C |
|---|---|---|---|---|---|---|---|---|
| 1 | 57.5 | 70 | 57.7 | 5.0 | 15 | 250 | 59 (-) | 172.3[a,b] |
| 2 | 33.2 | 40 | 33.2 | 2.9 | 9 | 150 | 72 (17) | |
| 3 | 79.4 | 100 | 79.4 | 7.0 | 22 | 360 | 74 (14) | |
| 4 | 306 | 380 | 306 | 27 | 170 | 1400 | -[c] (-)[c] | |
| 5 | 330 | 412 | 330 | 29 | 170 | 2000 | 79 (13) | 173.4<br>(168-71) |

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(a) Reported[5] m.p.174°

(b) Recrystallized from ethyl acetate (extremely thin plates unsuitable for single crystal X-ray diffraction)

(c) Both primary and secondary recovered product decomposed to a black brittle foam on attempted drying at 100°

*Step 3. 4,5-Diamino-2-phenyl-1,2,3-triazole (III) (Aqueous Thermolysis of 2-Phenylhydrazonooxamide Oxime (II)*

The general procedure for the cyclization of the title oxime to the triazole by loss of water was to load 5-8 g of the oxime (II) and a 6-fold excess of water into the glass liner of a 300 mL Parr bomb and sweep the air out with a nitrogen purge. After the apparatus was immersed in a thermostated 150° oil bath about 15 min were required to reestablish the temperature. Upon completion of the heating the apparatus was cooled to ambient temperature before venting to atmospheric pressure. The resulting mixture of nearly colorless crystals and brown resinous tar was treated with aqueous 5% $Na_2CO_3$ solution and steam distilled for about 1 hr to remove a very small amount of volatile degradation products. After carbon decolorization and separation of the tar the volume of the aqueous solution was reduced to its initial volume on a rotary evaporator before the crystalline product was isolated. The experimental results for seven runs using the above process conditions are summarized in Table 4.

## Table 4. Aqueous Thermolysis of 2-Phenylhydrazonooxamide Oxime

| Expt | Oxime, mmols | $H_2O$, mL | Min at 150° | Products | Steam Distill | $Na_2CO_3$ Treatment | Observations |
|---|---|---|---|---|---|---|---|
| 1 | 29.2 | 34 | 120[a] | needles, tar | yes | yes | No crystals from aqueous solution |
| 2 | 29.2 | 34 | 120 | needles, tar | no | no | Crystals (m.p.160°) in solution appeared to decompose to tar |
| 3 | 34.7 | 40 | 60[b] | plates, tar | - | - | Crystals (m.p.152-64°)[d] mostly oxime by $^{1}$H and $^{13}$C NMR |
|  |  |  | 120[c] | needles, tar | yes | yes |  |
| 4 | 34.0 | 39 | 120 | needles, tar | no | no | Crystals separated by aqueous extraction; m.p. of 1st and 3rd extracts and residue were 110-12°, 110-40° and 154-6°, respectively |
| 5 | 42.9 | 50 | 120[e] | needles, tar | yes | yes | Crude needles extracted with ether and recrystallized from water (m.p.109-10°) showed two partially separated components by ether developed TLC which appeared to be the diammino-substituted triazole (yield ~23%) and an amino-hydroxyl-substituted triazole by $^{1}$H and $^{13}$C NMR |
| 6 | 41.6 | 48 | 300 | oil | yes | yes | Large prismatic crystals (no m.p. up to 300°, $Na_2CO_3$ ?) |
| 7 | 41.4 | 48 | 90 | plates, tar | yes | yes | Plates m.p.165-7° (~33% recovered oxime) |

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(a) In the presence of air; (b) 30 min. at 122° prior to attaining 150°; (c) Reheated reaction mixture; (d) M.p. 143° reported by Thiele;[24] (e) Thermostat malfunction caused 45 min temperature oscillation 145-50°.

Three additional experiments were conducted to investigate alternative means of effecting the cyclization reaction. In one case the addition of ultrasound energy to the above described experimental conditions was without effect. In the second case molten urea was used in lieu of water as the reaction solvent but again without effect. In the third case refluxing cumene was used as the reactrion solvent in an attempt to remove water as an azeotrope. These results are summarized in Table 5.

*Step 4. 2-Phenylazo-2-phenylhydrazonoacetonitrile (IV)*

The first two preparations of the title nitrile were compromised because of the large quantity of thick foam produced the consequences of which were that (1) the reactor was undersized, (2) stirrer malfunctions reduced the rate of addition of reactants because of poor heat dissipation, and (3) removal of by-product salts by water washing was incomplete. These problems were largely overcome in the third preparation which is described below.

A 5 gal plastic bucket cooled in an ice bath and equipt with a large Teflon paddle stirrer and a thermocouple was used to prepare sodium cyanoacetate solution from 85.1 g $CNCH_2COOH$ (1.00 mol) and 420.0 g $Na_2CO_3$ (3.96 mol) in 2500 mL water. A solution of the benzene diazonium salt was prepared similarly in a 4 L Erlynmeyer flask cooled in an ice bath from 186.3 g $C_6H_5NH_2$ (2.00 mol) and 500 g 36.5% HCl (5.00 mol) in 1500 mL water to which was added 143.8 g 98% $NaNO_2$ (2.00 mol) in 500 mL water. The cold diazonium salt solution was poured into the rapidly stirred cold (1.7°) $NaOOCCH_2CN/Na_2CO_3$ solution over the course of 5 min while maintaining the temperature in the 0-5° range. On mixing an immediate precipitation of a brick red solid occurred accompanied by $CO_2$ evolution to form a thick stiff foam which caused a stirrer failure 15 min after addition was complete (The mixture was unstirred for 1 hr while repairs were made). The reaction mixture was then stirred at 2.7° for 3.5 hr before isolation of the solid by filtration.

Because of the large volume of solids and the limited size of the filter funnel the following procedure was used to wash salts from the product. A 350 mL coarse fritted

**Table 5. Alternate Conditions for Thermolysis of 2-Phenylhydrazonooxamide Oxime**

| Expt. | Oxime, mmol | Solvent | min at 150° | Observations |
|---|---|---|---|---|
| 5 | 27.7 | 100 mL Cumene, 99% | 180 | ~0.05-0.1 mL $H_2O$ (~10-20%) plus tar |
| 9 | 0.067 | 0.076 g urea[a] | 20[b] | $^1H$ and $^{13}C$ NMR spectra in $CD_3OD$ showed in addition to urea and biuret (in $^1H$ spectrum) aromatic protons in the range 5.8-7.8 ppm and 9 peaks (in $^{13}C$ spectrum) in the range 113.2-129.5 ppm of which 8 could be interpreted as two sets of aromatic carbons; the 9th peak is presumably virtually superimposed ipso carbons. Weakness of the peaks indicated low product yield. |
| 10 | ~0.25 | 1.5 mL $H_2O$ | 5[c] | Tar and crystals, m.p. 173-5° (recovered oxime) |

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(a) Based on a successful preparation of 4-amino-5-nitro-2-phenyl-1,2,3-triazole[24]

(b) Temperature 142°

(c) With ultrasound

funnel was filled to capacity and vacuum filtered. The filter cake was twice reslurried with 200 mL water and the washed filter cake was transferred to a stirred 5 gal bucket containing 3000 mL water. This batch process was repeated until all of the insoluble solids had been transferred. The resulting slurry was allowed to stand unstirred overnight. The thick foam was reslurried before the wash procedure was repeated (with the exception that each of the filter cake batches was not reslurried during washing). Again the resulting slurry was allowed to stand overnight unstirred before reslurrying for the final filtration where each batch of moist filter cake was transferred to a tared crystallizing dish for drying. The foam and the solids which settled in the liquid below it were collected separately for vacuum drying to constant weight at ambient temperature; (1) foam, 75 hr to obtain 218 g from 1002 g moist filter cake and (2) settled solids, 51 hr to obtain 27 g from 160 g moist filter cake.

Micro TLC of both the crude dry foam and slurry products on silica gel developed with either chloroform or a 10/6/5 volume ratio pentane/ether/ethyl acetate gave identical chromatograms with respect to the number of components and there measured $R_F$ values, namely 0.13 (fluoresces blue under uv), 0.30, 0.55 (largest spot), and 0.63 with chloroform; 0.29 (fluoresces blue under uv), 0.50, 0.59 (largest spot) and 0.68 with the 10/6/5 mixture. In neither case, however, did the $R_F$ of the major component match that of ethanol recrystallized (IV), namely 0.38 ($CHCl_3$) or 0.69 (10/6/5 mixture). Presumably the impurities present allow (IV) to move more rapidly. NMR spectra of the crude foam, crude slurry and ethanol recrystallized (IV) are collected in Table 6.

Extraction of a 1.006 g sample of the dried foam with $CHCl_3$ 10 times in a Soxhlet left only 0.010 g colorless residue. Recrystallization of the settled solids (26 g) from 250 mL of refluxing 100% ethanol on cooling to ambient temperature recovered 14.7 g (56%); cooling to ice bath temperature recovered 64%. An attempt to recover additional product from the concentrated recrystallization mother liquor yielded only a reddish black oil. Twice recrystallized product had the same m.p.155-8°, as reported by Henderson.[25]

In an attempt to purify (IV) by sublimation a 0.647 g sample of the foam was heated to 82° under dynamic high vacuum for 66 hr to give at a sticky red sublimate (5.2% condensed at 22°), a black residue (57.4%) and by difference volatiles (37.4%).

Step 5. *2-Phenylazo-2-phenylhydrazonoacetamide Oxime (V)*

The Henderson[6] procedure was repeated on a 10 mmol scale wherein solid 2-phenylazo-2-phenylhydrazonoacetonitrile (IV) was added to 10 mL of an ethanol solution of 15 mmol of $NH_2OH$ (prepared from $NH_2OH.HCl$ and KOH) and heating for 4 hr at reflux. No solid product appeared on cooling the reaction mixture in an ice bath. In view of this negative result the procedure was amended by addition of 40 mL $H_2O$ which proved to be ineffective as a precipitating agent for the slightly soluble title oxime (V).

Next the improved procedure of Henderson[25] as reported by Nikitin[26] was repeated on a 125 mmol scale. A solution of $NH_2OH$ was prepared in 50 mL $H_2O$ from its hydrochloride and $K_2CO_3$ and added to an equimolar amount of 2- phenylazo-2-phenylhydrazonoacetonitrile dissolved in 300 mL of 2-propanol. During the ensuing 4.3

**Table 6. NMR spectra of 2-Phenylazo-2-phenylhydrazonoacetonitrile**

| | Crude Foam | Crude Slurry | Ethanol Recrystallized[a] (m.p. 155-8°) |
|---|---|---|---|
| $^1$H Spectrum (δ in ppm in acetone-$d_6$) | | | |
| NH | 3.31 | (absent) | 2.97 |
| Arom. CH | | | |
| para (s) | 7.32 | 7.33 | 7.33 |
| meta (t) | 7.45, 7.46, 7.48 | 7.46, 7.47, 7.49 | 7.46, 7.47, 7.49 |
| ortho (d) | 7.72, 7,74 | 7.73, 7.75 | 7.73, 7.75 |
| $^{13}$C Spectrum (δ in ppm in acetone-$d_6$) | | | |
| CN | 112.66 | 112.84 | 112.62 |
| Arom. C | | | |
| ortho | 120.56 | 120.59 | 120.60 |
| para | 128.94 | 129.02 | 129.00 |
| meta | 130.24 | 130.28 | 130.31 |
| ipso | 148.96 | 148.89 | 148.84 |
| $C^2$ | 148.96 | 148.89 | 148.84 |

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(a) The $^{13}$C spectrum did not exactly match that reported by Nikitin[26]

hr at 50° the dark orange-brown solution changed to wine red (indicating air oxidation of the oxime) with precipitation of a solid near the end of the reaction period. The solvent was stripped from the mixture on a rotary evaporator and 200 mL $H_2O$ was added before isolation of the dark red solid by filtration, water washing and air drying at approximately 60°. The resulting 29.0 g of solid had a m.p. 145-7° unchanged after crystallization from 95% ethanol with 56% recovery (oxime (V)[24] m.p. 160-2°, nitrile (IV)[23] m.p. 155-8°). A micro TLC on silica gel developed with a 10/6/5 volume ratio of pentane/ ether/ethyl acetate had a $R_F$=0.67 (nitrile(IV) from Step 4, $R_F$=0.69) suggesting the material was primarily recovered starting material. NMR spectra $^1$H (aromatic protons, (s) p 7.32, (t) m 7.46, 7.47, 7.49, (d) o 7.73, 7.74) and $^{13}$C (CN, 112.79, aromatic carbons, o, 120.54, p, 128.95, m, 130.23, i, 148.85) confirm (*cf.*, Table 6) the TLC results.

The above two negative results prompted a change in the procedure for preparation of $NH_2OH$ to that of Thiele[24] wherein a near saturated aqueous solution of its hydrochloride salt is neutralized with a solid base (or its nonaqueous solution) to minimize the amount of water in the subsequent reaction with 2-phenylazo-2-phenylhydrazonoacetonitrile (IV). This procedure was utilized in a reaction on a 10 mmol scale wherein (IV), dissolved in 50 mL of boiling ethanol, was added to a mixture of 10 mmol of $NH_2OH$ dissolved in an aqueous slurry of NaCl (prepared from equivalent amounts of its hydrochloride salt and $Na_2CO_3$ in 0.90 mL water). The mixture was refluxed for 15 min before cooling in an ice bath and filtering off the solids which were washed with 2 x 3 mL of cold ethanol and vacuum dried at ambient temperature. The 2.270 g of dried crude solid appeared to be a mixture of dark red (m.p. 182°) and colorless (probably NaCl not melting up to 200°) materials. $^1H$ and $^{13}C$ NMR spectra were recorded for the red solid (see Table 7) before additional washing with water until the washings gave only a faint turbidity with $AgNO_3$. The water washed product was again vacuum dried before determining the weight, 1.397 g (approximately 5.0 mmol), the m.p.162°(lit [26] oxime (V) m.p.162°) and the $^1H$ and $^{13}C$ NMR spectra (Table 7). After standing a week the combined aqueous ethanolic reaction mixture filtrate and washings deposited a second crop of product (0.858 g after drying, approximately 3.0 mmol) shown to be less pure by $^1H$ and $^{13}C$ NMR spectra (Table 7). A micro TLC analysis on silica gel of this secondary recovery showed on development with 10/6/5 volume ratio pentane/ether/ethyl acetate in addition to spots at $R_F$=0.14 ((V) $R_F$=0.17) and $R_F$=0.70 ((IV) $R_F$=0.69) an unknown at $R_F$=0.61).

A 1.397 g amount of vacuum dried product (equivalent to 4.95 mmols "oxime" if pure) was recrystallized from 100% ethanol to recover 0.858 g "oxime" (3.04 mmol, 60% yield) m.p. 162°. $^{13}C$ NMR (acetone-$d_6$) showed in addition to the 10 peaks reported[24] 8 weaker peaks perhaps due to the "nitrile" starting material. A second crop of crystals recovered from the mixed ethanolic mother liquor plus aqueous washings was assayed by micro TLC on silica gel. Development with 10/6/5 volume ratio pentane/ ether/ethyl acetate showed spots at $R_F$=0.14 ("oxime" $R_F$=0.17), $R_F$=0.61 (unknown) and $R_F$=0.70 ("nitrile" $R_F$=0.69). A $^{13}C$ NMR spectrum showed 25 peaks commensurate with its lesser purity.

Two additional preparations were done using the above procedure to determine the effect on product yield of (1) doubling the reaction time and (2) using an excess of $NH_2OH$ with the following results: (1) a 43% yield with a 30 min reaction time and a $NH_2OH$/"nitrile" ratio = 1 and (2) a 57% yield with a 15 min reaction time and a $NH_2OH$/'nitrile" ratio = 1.5.

For the final two preparations some additional changes in experimental conditions were invoked. First, (IV) was recrystallized from 95% ethanol saturated at reflux and cooled to ice bath temperature which eliminated an insoluble impurity (probably $Na_2CO_3$) with the recovery of about one-third of the initial weight, m.p. 158-62°. Second, air was excluded from the reaction, isolation, and drying processes by employing either a nitrogen or a vacuum atmosphere. Third, a reverse addition of reactants (*i.e.*, $NH_2OH$ was added to (IV)) was expedited by mixing the concentrated aqueous $NH_2OH$ with 100% ethanol and filtering out the by-product NaCl. Fourth, the course of the reaction was followed by periodic sampling for micro TLC analysis. In the first of these two final experiments the reaction was conducted on a 10 mmol scale initially with equivalent amounts of reactants but ultimately with addition of 100% excess of $NH_2OH$ after three-fourths of the total 2 hr reaction time to drive the reaction to completion. Although TLC indicated complete utilization of (IV) and only (V) as the sole product its melting point range was higher and wider (m.p. 162-74°) than pure (V) probably the consequence of partialoxidation during air drying at 62°. As a result the observed 75% yield is probably higher than the actual yield.

The last experiment done on a 40 mmol scale will be described in more detail. The $NH_2OH$ solution was prepared in a mortar in three separate batches of 70, 20 and 10 mmol size. For example, the 70 mmol batch used 4.868 g $NH_2OH.HCl$ (70.0 mmol), 3.711 g $Na_2CO_3$ (35.0 mmol), 4.0 mL $H_2O$ and 20 mL 100% ethanol. The solid by-product NaCl was filtered out before loading the solution into an addition funnel on the magnetically stirred reactor which also carried a reflux condenser and a septum sampling port. A solution of 2-phenylazo-2-phenylhydrazonoacetonitrile (IV) 9.970 g (40.0 mmol) in 100 mL 100% ethanol was prepared under reflux in the nitrogen-filled reactor before addition of the $NH_2OH$ solution (5 min required). Aliquots of the reaction

## Table 7. NMR Spectra of 2-Phenylazo-2-Phenylhydrazonoacetamide Oxime

| | Crude Product m.p. 182° | Washed Product m.p. 182° | Secondary Recovery | Literature[26] |
|---|---|---|---|---|
| $^1$H spectrum (δ in ppm in acetone-$d_6$) | | | | |
| NHPh | (s) 5.61 | (s) 5.61 | (s) 5.62 | (s) 5.56 |
| $NH_2$ | (s) 6.57 | (s) 6.56 | (s) 6.57 | (s) 6.54 |
| Arom. H | (m) 7.07-7.87 | (m) 7.05-7.86 | (m) 7.05-7,87 | (m) 7.09-7.95 |
| OH | (s) 9.65 | (s) 9.65 | (s) 9.67 | (s) 10.54 |
| Unknowns | 2.91,13.40,14.81 | 2.9013.41,14.81 | 2.92,7.21,7.22<br>7.76,7.79,8.17,<br>13.41,14.82 | |
| $^{13}$C spectrum (δ in ppm in acetone-$d_6$) | | | | |
| $C^1$ | 138.93 | 139.35 | 139.32 | 136.82 |
| $C^2$ | 148.21 | 148.62 | 148.57 | 148.27 |
| N=NPh | | | | |
| ortho | 119.51 | 119.92 | 119.90 | 119.34 |
| para | 128.30 | 124.18 | 124.16 | 128.10 |
| meta | 129.99 | 130.13 | 130.27 | 129.55 |
| ipso | 153.20 | 153.62 | 153.56 | 153.11 |
| NHNPh | | | | |
| ortho | 115.49 | 115.89 | 115.88 | 115.37 |
| para | 122.79 | 123.20 | 123.18 | 122.62 |
| meta | 129.89 | 128.70 | 128.69 | 129.73 |
| ipso | 150.85 | 151.25 | 151.22 | 150.72 |
| Impurity (possibly (IV) , *cf.* Table 6) | | | | |
| $C^2$ | 115.41 | | | |
| Arom. C | | | | |
| ortho | 119.47,119.47 | | | |
| para | 123.78,129.73 | | | |
| meta | 130.97,130.97 | | | |
| ipso | 143.69,148,21 | | | |

mixture were withdrawn at 10, 30 and 60 min after completion of the $NH_2OH$ addition to monitor the formation of (V) and the depletion of (IV). At 105 min, an additional 20.0 mmols of $NH_2OH$ was added rapidly and aliquots were withdrawn at 120, 150, 180 and 240 min. At 270 min, another 10.0 mmols of $NH_2OH$ was introduced slowly during the next 15 min. The final aliquot, withdrawn at 300 min, showed only a very small amount of unreacted (IV). The reaction mixture was allowed to stand overnight, while maintaining the nitrogen atmosphere. The solids were isolated quickly by filtration under a nitrogen blanket and then dried in the funnel in a dessicator at ambient temperature under dynamic vacuum. The 7.86 g of 2-phenylazo-2-phenylhydrazonooxalamide oxime (V) (27.8 mmol, 69.6% yield) had a m.p=160-2° and was stored under nitrogen.

*<u>Step 6.</u> 4-Acetamido-5-phenylazo-2-phenyl-1,2,3-triazole (VI)*

Two experiments were done each using different batches of 2-phenylazo-2-phenylhydrazonoacetamide oxime (V) the NMR spectra of which were consistent with the structure. Nonetheless the samples were of dubious purity as indicated by their melting points, namely 182° and 178-80° for the first and second experiments, respectively (reported[24] m.p.160-2°). In the first experiment 1.34 g (V) was added to 10.0 mL acetic anhydride and heated to 50° for 65 min before allowing the mixture to stand overnight at ambient temperature. The resulting orange crystals were filtered out, washed with water and dried under high vacuum at 50°. The melting point (150-85°) of the 1.29 g of product indicated it to be of low purity.

In the second experiment 1.13 g (V) was added to 10 mL of freshly distilled acetic anhydride and heated at 50-60° for 60 min before being allowed to cool to 30° with stirring overnight. The resulting orange crystals were filtered out, water washed and vacuum dried at 50°. The resulting 1.16 g of solids had a m.p.=120-2°, again indicating low purity. Micro TLC (same as in Step 5 above) indicated two components of which the one in lesser amount was the starting material (V).

The $^1H$ and $^{13}C$ NMR spectra of the product obtained in each of the above experiments, when compared with the spectra reported by Nikitin[26] suggest that (VI) was obtained albeit of low purity. The data are summarized in Table 8. An infra-red spectrum (in KBr) showed 37 absorption bands in the 4000-400 $cm^{-1}$ region including the five reported by Nikitin[26] for (VII).

*<u>Steps 7 and 8.</u> 4-Amino-5-phenylazo-1,2,3-triazole*

Two approaches to the title compound were made the first of which consisted of a single experiment wherein basic hydrolysis of the corresponding 4-acetamido-derivative (VI) was attempted despite the low purity of the starting material (from the first experiment Step 6).

(Step 7). A 1.26 g sample of the orange acetamido-derivative was stirred at 100° for 1 hr with 0.50 g NaOH and 10 mL water. The resulting yellow solids were filtered out, repeatedly water washed and dried in a 100° oven. The melting point of the approximately 1 g of crude product indicated low purity (sintered 170°, mostly melting 180-90° and finishing at 205°). Recrytstallization from 100% ethanol and vacuum drying gave approximately 0.5 g of material, m.p.170-5°, which was used for a TLC analysis. Approximately 0.042 g of this material as an ethyl acetate solution was placed as a line on an 8"x8"x2mm silica gel TLC plate and developed with 10/6/5 volume ratio pentane/ether/ethyl acetate to give two bands with $R_F$ values at 0.37 and 0.67. The two materials were recovered by acetone extraction of the silica gel from the mechanically separated bands and had melting points of 197-8° and 211-3°, respectively. For the 4-acetamido- (VI) and 4-amino- (VII) derivatives of 5-phenylazo-2-phenyl-1,2,3-triazole the reported[26] melting points are 209° and 215°, respectively. $^1H$ and $^{13}C$ NMR spectra although having broad peaks were consistent with the respective structures.

(Step 8). A second approach to the title compound was investigated because of the difficulties encountered in Steps 5 (ease of air oxidation of the "oxime"), and 6 and 7 (incomplete reactions giving low purity products). A new procedure was reported on arylhydrazonitriles as building blocks in heterocyclic synthesis[27] wherein the intermediate oxime formed on reaction with hydroxylamine is not isolated but reacts *in situ* to form the title triazole derivative in a single step. Using this process a series of eight experiments was conducted, one using crude "nitrile" and seven using "nitrile" purified by recrystallization from ethanol. The general procedure described below sets forth the

## Table 8. NMR Spectra of 4-Acetamido-5-phenylazo-2-phenyl-1,2,3-triazole

| | Expt. 1 | Expt. 2 | | Literature[26] |
|---|---|---|---|---|
| $^1$H spectra (δ in ppm) | (in chloroform-d) | (in benzene-$d_6$) | (in chloroform-d) | (in benzene-$d_6$) |
| $CH_3$ | (s) 1.62 | (s) 1.84 | s) 1.25 | (s) 1.18 |
| NH | (broad) 5.0 | - | (s) 5.50 | (s) 4.85 |
| Arom. H | (m) 6.58-6.97,(m) 7.95-8.06 | (m) 7.04-7.37 | (m) 7.12-8.18 | - |
| Unknowns | 7.28,7.29,7.50 | 0.50,2.26 | 0.077,0.091 | |
| $^{13}$C spectra (δ in ppm) | | | | (in chloroform-d) |
| $CH_3$ | 24.74 | - | 24.92 | 24.71 |
| CO | (absent) | - | - | 172.30 |
| NHNPh | | ( )[a] | ( )[b] | |
| ortho | 118.78 | | | 118.71 |
| para | 128,20 | | | 128.07 |
| meta | 129.38 | | | 129.30 |
| ipso | 139.18 | | | 139.13 |
| N=NPh | | ( )[a] | ( )[b] | |
| ortho | 122.89 | | | 122.77 |
| para | 132.33 | | | 132.19 |
| meta | 129.38 | | | 129.30 |
| ipso | 151.88 | | | 151.86 |

(a) Multiplet of 17 peaks in aromatic region suggesting two compounds each containing a phenylazo- and a phenyl-triazole moiety.

(b) Complex multiplet of 33 peaks in aromatic region suggesting four compounds each containing a phenylazo- and a phenyl- triazole moiety or perhaps two compounds each containing two pair of the aromatic moieties.

conditions which produced the best yield of "triazole". Air was displaced by a slow stream of nitrogen after 2.49 g 2-phenyl-azo-2-phenylhydrazonoacetonitrile (IV) (10.0 mmol), 2.78 g $NH_2OH \cdot HCl$ (40.0 mmol) and 3.28 g $NaOOCCH_3$ (40.0 mmol) were charged into a magnetically stirred 100 mL reactor fitted with a septum sampling port and a reflux condenser vented through an oil bubbler. Injection of 20 mL of anhydrous dimethylformamide through the septum sampling port resulted in vigorous gas evolution. Heating with a mantle required approximately 15 min to bring the orange mixture to reflux which was maintained for 4 hr during which time the condensation and dissolution of a white solid (probably $NH_2OH \cdot HOOCCH_3$) in the reflux condenser and precipitation of a white solid (probably NaCl) in the reactor were observed. The cooled reaction mixture was transferred to a rotary evaporator with the aid of an ethanol rinse and the solvents were removed under vacuum at 75°. The residue was triturated with 4 x 10 mL water to remove salts, isolated by filtration, dissolved in the minimum amount of refluxing ethanol and filtered hot. The crystals recovered from the filtrate at 0-3° after vacuum drying weighed ~1.0 g (approximately 55% of the crude product weight) and had a m.p.=211-3°, Yield 39%. When this procedure was repeated with crude (IV) the yield was 16%.

Similarly, if the reaction time were halved the yield fell to 16%. Doubling the reaction time had little effect on the yield (37%). Using chloroform as the developer the product was assayed by TLC on silica gel micro plates which had been pretreated with a 15/1 volume ratio of chloroform/ethanolamine. The recrystallized product showed only (VII) ($R_F$=0.67) while the mother liquor from which it was obtained showed small amounts of starting material (IV) ($R_F$=0.41) and two unknowns ($R_F$=0.27 and $R_F$=0.73) in addition to (VII).

The reagents used and the results obtained for the duplicate preliminary experiments are summarized in Table 9. For unknown reasons the extent of reduction of the phenylazo- group to an amino- group is far less in the first experiment than in the second where only the sublimation time was substantially different. A 0.598 g portion of the crude sublimate from the product from Experiment 1 was chromatographed on a column of silica gel as a chloroform solution. An orange band was eluted leaving a blue band at the top of the column. Evaporation of the eluate gave 0.363 g of an orange solid m.p.=210-3° (m.p.215-6° for starting material (VII)) representing a 29% recovery. A $^1H$ NMR spectrum of this eluate showed two sets of aromatic ortho-, meta- and para- peaks at 7.40-7.42 ppm and 7.23-7.25 ppm (o- doublets), 6.8-6.9 ppm (superimposed m- triplets) 6.65-6.665-6.68 ppm (p- triplet) and 6.58 ppm (p- singlet). Interaction of the chloroform solvent with the $NH_2$- group resulted in a very broad band ~4.0 ppm. The $^{13}C$ spectrum showed the expected ten carbons: o-, p-, m-, and ipso in each of the two

**Table 9. 4,5-Diamino-2-phenyl-1,2,3-triazole**

| Reactants and Conditions | Expt. 1 | Expt. 2 |
|---|---|---|
| 4-Amino-5-phenylazo-1,2,3-triazole | 1.319 g (5.01 mmol) | 1.316 g (5.00 mmol) |
| Dioxane | 13.2 mL | 13.2 mL |
| 96% $H_2SO_4$ | 2.66 mL (48.0 mmol) | 2.77 mL (50,0 mmol) |
| 95% zinc, 1st increment | 0.851 g (12.4 mmol) | 0.895 g (13.0 mmol) |
| 2nd increment | 0.140 g (2.03 mmol) | 0.155 g (2.25 mmol) |
| Water wash | 3 x 10 mL | 1 x 12.5 mL |
| | | 2 x 2.5 mL |
| $K_2CO_3$ | 0.705 g (5.10 mmol) | 0.705 g (5.10 mmol) |
| Sublimation time and temperature | 9 hr, 130° plus 1 hr,160° | 64 hr,130° |
| Sublimate weight | 0.634 g | 0.608 g |
| Sublimate m.p. | 138-74° | 142-5° |
| | - | 142-4° |

aromatic rings plus C-NH2 and C-N=N-. An attempt to displace the presumed diammino- product on the column with acetone appeared instead to react to give unknown products.

*<u>Step 9.</u> 4,5-Diamino-2-phenyl-1,2,3-triazole (III) (Zinc/Sulfuric Acid Reduction of 4-Amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII))*

The diamino- product was easily separated from the ~4% starting material in the crude sublimate from Experiment 2 by dissolution in hot water from which about 60% could be recovered on cooling. However, since the diamino- product is used in Step 10 as an aqueous solution there is no need to isolate the crystalline solid. The scaled-up experiment is described below.

A slurry of 6.042 g 4-amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII) (22.9 mmol) in 61 mL dioxane was cooled in an ice bath and 12.6 mL 96% $H_2SO_4$ was added dropwise. The wine red slurry changed to yellow on addition of 25 mL $H_2O$. The ice cooling was discontinued and 4.14 g 95% Zn dust (60.1 mmol) was added at 20° resulting in a temperature rise to 35° accompanying moderate gas evolution. The temperature was raised to 50-53° for 2 hr during which time most of the yellow solid dissolved. Another 0.681 g of Zn dust (9.89 mmol) was added and the heating was extended for an additional 1 hr during which time the light yellow solution faded to almost colorless.

The solvents were stripped from the reaction mixture at 57° on a rotary evaporator under high vacuum before adding 57 mL $H_2O$ to the residue. The resulting slurry was cooled to 3° before the solids were filtered out and washed with 2 x 11.5 mL of cold (5°) water. The moist filter cake was transferred to a beaker containing 3.267 g $K_2CO_3$, mixed to a uniform paste and air dried at 50°. The dry residue was ground in a mortar before isolating the 3.165 g of crude product by sublimation at 131° under dynamic high vacuum. A 3.160 g portion of the sublimate was dissolved in 150 mL of hot water leaving a small insoluble residue which weighed 0.111 g (3.5% of the sublimate) after drying. Thus the water soluble 3.049 g of 4,5-diamino-2-phenyl-1,2,3-triazole (III) (17.4 mmol) represents a 76% yield.

<u>Step 10.</u> *4,5-Azimido-2-phenyl-1,2,3-triazole (IX)*

The aqueous filtrate containing 3.049 g of 4.5-diamino-2-phenyl-1,2,3-triazole (III) (17.4 mmol) obtained in Step 9 above was diluted to 200 mL at ambient temperature and acidified with 3.2 mL conc. HCl before adding it dropwise to a stirred solution containing 2.538 g of $NaNO_2$ (36.78 mmol) and 12.6 mL conc. HCl in 300 mL $H_2O$ and maintained at 0.8-3.6° during the 40 min addition. The orange solution which became increasingly darker during the addition was filtered immediately after completion of the addition to remove a small amount of black precipitate. The stirred filtrate was allowed to warm to ambient temperature resulting in an initial gas evolution and gradual formation of a precipitate over the course of 6 d. The solid was isolated by filtration and dried at ambient temperature under a dynamic vacuum. The yield was 2.124 g (IX) (12.96 mmol) or 74.5%. On heating, the solid turned brown at 135° and exploded at 140° (lit.[26] browning 130-40°, explodes 147°).

*Step 11. Ethyl O-(mesitylenesulfonyl)acetohydroximate (X)*

Two attempts were made to prepare (X) following the report of Tamura[28] wherein mesitylenesulfonyl chloride is added incrementally to a DMF solution containing equimolar amounts of ethylacetohydroximate and triethylamine each at approximately 3.6 molar concentration with ice cooling and stirring for 30-60 min. In each of the experiments, (one at a 225 mmol scale and the other at 35 mmol) gave a liquid rather than a solid product precipitating when the reaction mixtures were poured into about 15 times their volume of ice water. As a consequence further attempts to isolate the reported solid product (X) from the liquids obtained were without precedent.

The liquid (with some accompanying aqueous phase) when cooled in a -25° freezer until ice formation was initiated gave a supercooled liquid which could be induced to crystallize by mechanical agitation. The resulting crystals had a m.p.=50-1° (reported[28] (X) m.p.57-8°) and were not entirely soluble in dioxane as reported.[28] The dioxane insoluble material melted in the range 140-50° for the material retained on a filter and 154-60° for that crystallizing from the filtrate. Both solids were strongly acidic (litmus test). $^1$H and $^{13}$C NMR spectra were of poor quality for each of the isolated materials and served only to suggest rather than define their components.

## Task 2, Summary

A sequence of reactions leading to 6-phenyl[1,2,3]triazolo[4,5-e]-[1,2,3,4]-tetrazine (XIII) (see Scheme 1) had all been reported in the literature. However, many of the experimental details were vague and not always reproducible in our laboratory. As a consequence of the failure of step 3 to give 4,5-diamino-2-phenyl-1,2,3-triazole (III) free of 4-amino-5-hydroxy-2-phenyl-1,2,3-triazole, the first three steps of our initial approach had to be abandoned and replaced by another series of reactions (steps 4, 5, 6, 7, and 9). Unfortunately each of the products from reaction steps 5, 6 and 7 were grossly contaminated with unreacted starting materials as well as by-products of unknown constitution. Fortunately a reaction (step 8) was found which combined steps 5, 6 and 7 thereby precluding isolation of intermediate compounds (V) and (VI) and leading directly to 4-amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII). Thus the sequence of reactions (steps 4, 8 and 9) in the second approach has the same number of steps as were in the first approach to prepare 4,5-diamino-2-phenyl-1,2,3-triazole (III) but the overall yield of pure (III) was more than doubled at 17% (based on cyanoacetic acid) compared with 8% of an impure material (based on cyanogen). The next reaction (step 10) provided 4,5-azimido-2-phenyl-1,2,3-triazole (IX) cleanly to give an overall yield of 13% (based on cyanoacetic acid) at this stage of the synthetic sequence. The first reaction (step 11) of the two reaction sequence to prepare the aminating agent (XI) was attempted but the product obtained instead of being the reported solid was a liquid, tentatively assumed to be a consequence of incomplete reaction. No further time was available to resolve this discrepancy or to test the last three reactions (steps 12-15) leading to the final product (XIII).

## Publications

In addition to the work discussed above, the following 5 papers were published under this program with partial funding from ONR.

"Energetics and Mechanism of the Decomposition of Trifluoromethanol," J. Phys. Chem. A, 112, 1298 (2008), M. T. Nguyen, M. H. Matus, V. T. Ngan, R. Haiges, K. O. Christe, D. A. Dixon.

"Bond Dissociation Energies in Second Row Compounds," J. Phys. Chem. A, 112, 3145 (2008), D. J. Grant, M. H. Matus, J. R. Switzer, D. A. Dixon, J. S. Francisco, K. O. Christe.

"Thermochemical Parameters of CHFO and $CF_2O$," J. Phys. Chem. A, 112, 4973 (2008), with M. H. Matus, M. T. Nguyen, D. A. Dixon, K. O. Christe.

"The Structure and Heats of Formation of Iodine Fluorides and the Respective Closed Shell Ions from CCSD(T) Electronic Structure Calculations and Reliable Prediction of the Sterical Activity of the Free Valence Electron Pair in $ClF_6^-$, $BrF_6^-$ and $IF_6^-$," Inorg. Chem., 47, 5485 (2008), with D. A. Dixon, D. J. Grant, K. O. Christe, K. A. Peterson.

"Neil Bartlett, Founder of Noble-Gas Chemistry," Nature 455 (11 September, 2008).

## Interactions/Transitions

**Lectures (12)** were presented at the following conferences and universities:

AFOSR Molecular Dynamics Conference, Vienna, VA, May 2008

Gordon Research Conference on Energetic Materials, Tilton School, NH, June 2008

Pyrotechnics Conference, Fort Collins, CO, July 2008

AFOSR Workshop on Ionic Liquids, Colorado Springs, CO, July 2008

Intersib Fluorine 2008, Vladivostok, Russia, September 2008

Halchem IV, Platja d'Aro, Spain, September 2008

DTRA Basic Research Technical Review, Springfield, VA, November 2008

Invited Lecture, Universidad Autonoma de Barcelona, Bellaterra, Spain, November, 2008

19th ACS Winter Fluorine Conference, St. Pete Beach, FL, January 2009 (4 papers)

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