

Trinitromethyl Ethers and Other Derivatives as Superior Oxidizers

WP-1766

Final Report



**Naval Air Warfare Center Weapons Division China Lake
Naval Air Systems Command**



**Principal Investigator:
Dr. Robert D. Chapman
Chemistry Branch (Code 4L4200D)
Research Division
Research & Intelligence Department
Naval Air Warfare Center Weapons Division
1900 N. Knox Rd. Stop 6303
China Lake, CA 93555-6106**

**Contributors:
Dr. Thomas J. Groshens
Dr. Matthew C. Davis
Dr. William W. Lai
Dr. Lawrence C. Baldwin
Dr. Richard A. Hollins
Collin A. Ladd (Naval Research Enterprise Intern Program, 2010)**

August 26, 2011

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.						
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.						
1. REPORT DATE (DD-MM-YYYY) 08-26-2011		2. REPORT TYPE Final		3. DATES COVERED (From - To) Nov 2009–Aug 2011		
4. TITLE AND SUBTITLE Trinitromethyl Ethers and Other Derivatives as Superior Oxidizers				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER 603716D		
6. AUTHOR(S) Chapman, Robert D. Groshens, Thomas J. Davis, Matthew C. Lai, William W. Baldwin, Lawrence C. Hollins, Richard A. Ladd, Collin A.				5d. PROJECT NUMBER WP-1766		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Chemistry Branch (Code 4L4200D) Naval Air Warfare Center Weapons Division 1900 N. Knox Rd. Stop 6303 China Lake, CA 93555-6106				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP & ESTCP Program Offices 901 North Stuart Street, Suite 303 Arlington, VA 22203-1853				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT There is no open-literature report of the preparation of trinitromethyl ethers, with the linkage (NO ₂) ₃ C–O–C, a class of compounds that might have promise as superior oxidizers to replace ammonium perchlorate. Several attempts by us to newly prepare examples of this potentially interesting class proved unsuccessful: first, trimethylsilyl trinitromethyl ether, followed by tert-butyl trinitromethyl ether. (Nevertheless, this class of compound still appears to be a fundamentally reasonable chemical linkage.) Some other unprecedented polynitroalkane products, such as nonanitroisobutane, were briefly pursued but proved less straightforward than hoped and were abandoned. Another promising target compound pursued here was 2,6,8,12-tetranitro-4,10-bis(trinitromethyl)hexaazaisowurtzitane ("DNIW," a decanitro-substituted hexaazaisowurtzitane), but synthetic strategies attempted in the course of this SEED project were unsuccessful, particularly to prepare unknown 4,10-diacetonyl-2,6,8,12-tetraacetylhexaazaisowurtzitane as a new intermediate. This target also remains of interest for pursuit outside the scope of the current project, as it has good oxygen balance and is expected to have good properties as an energetic ingredient (oxidizer or explosive).						
15. SUBJECT TERMS Trinitromethyl; trinitroethyl; oxidizers; hexaazaisowurtzitane						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT	b. ABSTRACT	c. THIS PAGE			Robert D. Chapman	
Unclassified	Unclassified	Unclassified	Unclassified Unlimited	22	19b. TELEPHONE NUMBER (Include area code) 760-939-1663	

Reset

Table of Contents

List of Tables	ii
List of Figures	ii
List of Schemes	ii
List of Acronyms	ii
Keywords	iii
Acknowledgements	iii
Executive Summary	1
Objective	2
Background	2
Materials and Methods	4
Results and Discussion	6
Conclusions and Implications for Future Research	15
Literature Cited	16

List of Tables

Table 1. Comparison of trinitroalkyl formal properties.....	5
---	---

List of Figures

Figure 1. X-ray structure of MDPI-15930: tetrakis(2,2,2-trinitroethyl) orthocarbonate	4
Figure 2. X-ray structure of MDPI-15933: bis(2,2,2-trinitroethyl) formal.....	4

List of Schemes

Scheme 1. Attempted nucleophilic substitutions in trinitromethanes by trimethylsilanolate.....	6
Scheme 2. Attempted preparations of silver trimethylsilanolate	7
Scheme 3. Preparation of and reaction of trimethylsilyl hypochlorite and silver nitroformate.....	8
Scheme 4. Reaction of <i>tert</i> -butyl hypochlorite plus silver nitroformate	9
Scheme 5. Formation of methanetrismalonate ester (5) [35] and its mechanism [36]	10
Scheme 6. Attempted preparation of methanetrismalonate hexa- <i>t</i> -butyl ester	10
Scheme 7. Preparation of a 1,1,1,3,3,3-hexanitropropane derivative (6) [39].....	11
Scheme 8. Proposed preparation of a decanitro-substituted hexaazaisowurtzitane (9)	12
Scheme 9. Attempts to alkylate TADA to diacetylhexaazaisowurtzitane (8).....	13
Scheme 10. Attempt to alkylate TADA with propylene oxide.....	14

List of Acronyms

AP	Ammonium Perchlorate
BOC	<i>tert</i> -Butyl carboxylate (<i>tert</i> -butoxycarbonyl)
CL-20	Hexanitrohexaazaisowurtzitane
DATA	4,10-Diacetyl-2,6,8,12-tetraacetylhexaazaisowurtzitane
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
MDPI	Molecular Diversity Preservation International
NAWCWD	Naval Air Warfare Center Weapons Division
NMR	Nuclear magnetic resonance
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
SEED	SERDP Exploratory Development
TADA	2,6,8,12-Tetraacetylhexaazaisowurtzitane

Keywords

Trinitromethyl; trinitroethyl; oxidizers; hexaazaisowurtzitane

Acknowledgements

In addition to the Principal Investigator, Dr. Thomas J. Groshens, Dr. Matthew C. Davis, Dr. William W. Lai, Dr. Lawrence C. Baldwin, and Dr. Richard A. Hollins (all of the Chemistry Branch, Research Division, Research Department, NAWCWD) plus Collin A. Ladd (participating in the Naval Research Enterprise Intern Program in Summer 2010) carried out the work described in this report.

Funding for some of the research described here was also provided by the Office of Naval Research (Dr. Clifford D. Bedford). The financial support of the Department of Defense Strategic Environmental Research and Development Program is acknowledged.

Executive Summary

SERDP Statement of Need WPSEED-10-01 called for novel materials that can replace ammonium perchlorate (AP) as rocket motor oxidizers. The main objective of this SEED project was to develop synthetic methodology leading to any example of the chemical class of trinitromethyl ethers—but especially ones that appeared competitive with AP as an oxidizer in rocket motor applications—as such methodology is currently unavailable even though such compounds were believed to exist elsewhere. Certain alternative target compounds were pursued in parallel as well.

There is no open-literature report of the *preparation of trinitromethyl ethers*, with the linkage $(\text{NO}_2)_3\text{C}-\text{O}-\text{C}$, a class of compounds that might have promise as superior oxidizers. This class of compound had been believed to exist because two particular examples were offered for sale by a commercial entity and other examples have been mentioned in a published journal article. Ultimately, both the offer for sale and the journal article were proven by our research to be erroneous, so the existence of that class of compounds remained unprecedented.

Several attempts by us to newly prepare examples of this potentially interesting class proved unsuccessful: first, trimethylsilyl trinitromethyl ether, followed by *tert*-butyl trinitromethyl ether. Nevertheless, this class of compound still appears to be a fundamentally reasonable chemical linkage.

Some other unprecedented polynitroalkane products, such as nonanitroisobutane, were briefly pursued but proved less straightforward than hoped and were abandoned.

One target considered early on, 5,5'-dinitro-2,2'-bis(trinitromethyl)-4,4'-bi-2*H*-1,2,3-triazole *N,N'*-dioxide, still appears particularly promising from a standpoint of properties that would provide superior performance as an oxidizer. However, synthetic strategies that were envisioned to produce it appeared beyond the scope of a SEED project and are likely impractical for a large-scale replacement of AP.

Another promising target compound that was ultimately pursued here was 2,6,8,12-tetranitro-4,10-bis(trinitromethyl)hexaazaisowurtzitane (“DNIW,” a decanitro-substituted hexaazaisowurtzitane), but synthetic strategies attempted in the course of this SEED project were unsuccessful, particularly to prepare unknown 4,10-diacetonyl-2,6,8,12-tetraacetylhexaazaisowurtzitane as a new intermediate. This target, DNIW, also remains of interest for pursuit outside the scope of the current project, as it has good oxygen balance and is expected to have good properties as an energetic ingredient (oxidizer or explosive).

Objective

SERDP Statement of Need WPSEED-10-01 called for novel materials that can replace ammonium perchlorate (AP) as rocket motor oxidizers. New alternatives are desired due to multiple environmental driving factors, among which are recently discovered deleterious health effects of environmental perchlorate as well as adverse local effects of hydrogen chloride combustion product from certain applications of AP. (The high solubility of perchlorate and its chemical stability in water make its contamination difficult to remediate by conventional water treatment methods. The U.S. Environmental Protection Agency and various states have been proposing stringent cleanup levels for perchlorate [1], which therefore represents a potential liability for the Department of Defense.) Totally carbon/hydrogen/nitrogen/oxygen-based alternative oxidizers are preferable to ones that incorporate halogens in other forms, in order to facilitate environmental benignity. Ideally, a superior oxidizer would possess an oxygen balance matching or surpassing that of AP (+34.04%), as well as comparable or superior energy content, so that its performance will be at least equivalent to that of AP. Oxygen balance (relative to CO₂) for CHNO-based compounds of composition C_aH_bN_cO_d is calculated according to the equation

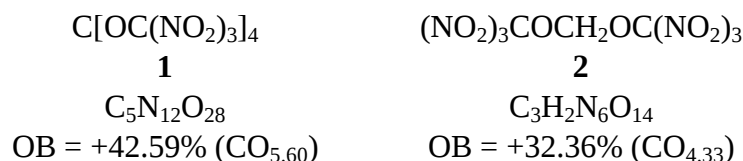
$$\text{OB}\% = -1599.94(2a + b/2 - d)M_w^{-1}$$

where M_w is the compound's molecular weight. Adequate chemical and hazard insensitivity are ultimately necessary for adoption of a replacement oxidizer.

The main objective of this SEED project was to develop synthetic methodology leading to any example of the chemical class of trinitromethyl ethers—but especially ones that appeared competitive with ammonium perchlorate as an oxidizer in rocket motor applications—as such methodology is currently unavailable even though such compounds were believed to exist elsewhere. Certain alternative target compounds were pursued. Other specific variations of trinitromethyl derivatives were of potential interest, and their pursuit was also a potential alternative objective of this project.

Background

There is no open-literature report of the preparation of *trinitromethyl ethers*, with the linkage (NO₂)₃C–O–C, as a class of compounds. At the outset of this SEED project, however, this class of compound was believed to exist because two particular examples, tetrakis(trinitromethyl) orthocarbonate (**1**) [2] and bis(trinitromethyl) formal (**2**), were offered for sale by a Swiss organization that collects small samples of exotic chemical compounds from research laboratories worldwide, Molecular Diversity Preservation International (MDPI) [3].



Compounds **1** (MDPI Catalog Reference #15930) and **2** (#15933) were offered for sale as samples of 100–400 mg. The original source of samples of **1** and **2**, if legitimate, might have

been the Russian Zelinsky Institute of Organic Chemistry, which is advertised to be a provider to libraries of organic compounds for screening [4]. Studies on trinitromethyl derivatives as a general class of compound have been published by Zelinsky chemists in the recent past, though most have been C-trinitromethyl derivatives, such as 2,4-dinitro-5-(trinitromethyl)imidazole [5]. The first open-literature report of synthesizing *het*-C(NO₂)₃ derivatives may have been by Khisamutdinov et al., who prepared 2,6-bis(trinitromethyl)benzo[1,2-*d*:4,5-*d'*]bistriazole-4,8(2*H*,6*H*)-dione by nitration of the corresponding bis(dinitromethyl) derivative's dianion [6]. In a presentation by Victor V. Semenov (Zelinsky Institute) at the August 1999 National Meeting of the American Chemical Society [7], various *N*-(trinitromethyl)azoles (pyrazoles, imidazoles, triazoles, and tetrazoles) were reported to be prepared by nitration of precursor *N*-(dinitromethyl)azoles, which had been prepared from *N*-acetonylazole "starting materials." The results from that presentation appear not to have been published in open print literature. (*O*-Trinitromethyl derivatives, such as **1** and **2**, were not mentioned in the presentation.) Other publications by other Zelinsky chemists on transformations leading to *N*-trinitromethyl are cited below.

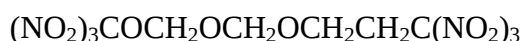
Aside from the recent offering of **1** and **2** by MDPI, the *existence* of trinitromethyl ethers as a specific class of known compound has been alluded to once in open literature (also co-authored by Zelinsky chemists) [8]: a table of 59 energetic structures (on which theoretical thermodynamic computations were performed) included two compounds, trinitromethyl 3,3,3-trinitropropyl formal (**3**) and trinitromethyl 3,3,3-trinitropropyl diformal (**4**), that were examples of trinitromethyl ethers and which also had *experimental* heats of formation listed. (Interestingly, *Chemical Abstracts* has not listed these particular compounds as being cited by that reference, and the compounds entered *Chemical Abstracts*' database only by appearance in a later Chinese paper [9] that reported newer theoretical computations about them and cited the precedent reference [8].)



3



OB = +4.28% (CO_{2.20})



4



OB = -3.96% (CO_{1.83})

Compounds **1** and **2** are particularly attractive examples of prospective AP-replacement oxidizers because the oxygen balance of **1** (+42.59%) significantly exceeds that of AP, and that of **2** (+32.36%) is comparable. Also impressively, according to Ammon's linear volume additivity method [10], **1** is predicted to have a density of 2.086 g cm⁻³ (676.117 Da/538.194 Å³). However, the entire specific class of trinitromethyl ethers has been essentially unrecognized: no synthetic methodology to prepare them has been published in open literature, and only the sparse information cited above is available at all. It should be understood that trinitromethyl derivatives need not behave chemically or thermally like 2,2,2-trinitroethyl derivatives, which have been well studied in the past and may be susceptible to chemical degradation related to deformylation of the methylene (CH₂) link to their substrates [11]. Simple trinitromethyl derivatives do not offer this mechanism for degradation.

Materials and Methods

This project commenced by ordering from MDPI samples of their advertised compounds **1** (MDPI Catalog Reference #15930) and **2** (#15933). Upon receipt, analysis of a small sample of #15930 by NMR in CD_2Cl_2 showed singlet absorptions unexpected for the intended structure of tetrakis(trinitromethyl) orthocarbonate: δ 4.96 (^1H) and δ 63.8 (^{13}C). The ^{13}C spectrum showed peaks consistent with trinitromethyl (δ 122.7) and orthocarbonate (δ 118.7) carbons. These analyses by NMR necessitated definitive identification of the sample by single-crystal X-ray crystallography. That analysis (Figure 1) confirmed the material as being actually tetrakis(2,2,2-trinitroethyl) orthocarbonate—a well known, old material originally patented by the U.S. Navy [12]—rather than the advertised trinitromethyl orthocarbonate. (The density measured for MDPI-15930, 1.801 g cm^{-3} , exactly matches a value previously published for the identified compound [13].) NMR spectra acquired in $\text{DMSO}-d_6$ (^1H δ 5.42; ^{13}C δ 62.24, 117.8, 123.6) essentially matched those reported by Sheremetev et al. [14] in that solvent.

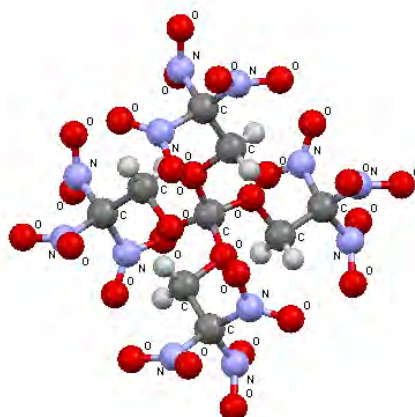


Figure 1. X-ray structure of MDPI-15930: tetrakis(2,2,2-trinitroethyl) orthocarbonate

Next, X-ray crystallographic analysis of MDPI-15933 (Figure 2) confirmed that it also was the corresponding trinitroethyl derivative, bis(2,2,2-trinitroethyl) formal, rather than the advertised trinitromethyl derivative. Bis(2,2,2-trinitroethyl) formal is also a well known, old material originally patented by the U.S. Navy [15]. NMR spectra were consistent with that identity: ^1H (CD_2Cl_2) δ 4.89 (s, 4 H), 5.00 (s, 2 H); ^{13}C (CD_2Cl_2) δ 67.6, 97.6, 124.4.

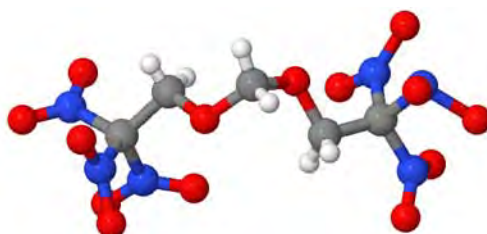


Figure 2. X-ray structure of MDPI-15933: bis(2,2,2-trinitroethyl) formal

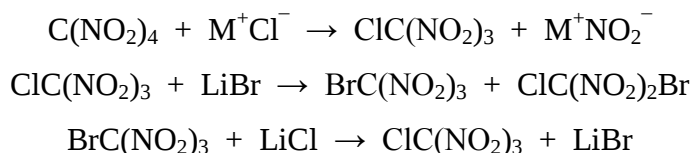
MDPI then provided original Submission Data Sheets showing that the original submitter misidentified both samples provided to MDPI.

Following this key misidentification of samples purported to be trinitromethyl ethers, a message was e-mailed to Prof. Tatyana Pivina of the Zelinsky Institute of Organic Chemistry, a co-author of the article [8] that cited other examples of trinitromethyl ethers, inquiring if the particular examples of that class shown in that paper were accurate representations of their structures. Her reply [16] corroborated a new suspicion that those structures also might have been erroneous; they should in fact have been the corresponding symmetrical bis(2,2,2-trinitroethyl) formal and diformal, which have empirical formulas identical to those of the unsymmetrical formals shown in the article. With this insight, it was then recognized that the enthalpies of formation reported therein exactly correspond to some previously published for the symmetrical formals (Table 1).

Table 1. Comparison of trinitroalkyl formal properties		
Reference	Sukhachev, D.V. et al. [8]	Kustova, L.V. et al. [17]
Formula	$\text{C}(\text{NO}_2)_3\text{OCH}_2\text{OCH}_2\text{CH}_2\text{C}(\text{NO}_2)_3$ $\text{C}_5\text{H}_6\text{N}_6\text{O}_{14}$	$\text{C}(\text{NO}_2)_3\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_3$ $\text{C}_5\text{H}_6\text{N}_6\text{O}_{14}$
Enthalpy of formation, ΔH_f	−96.1 kcal/mol	−402.1 kJ/mol = −96.1 kcal/mol
Formula	$\text{C}(\text{NO}_2)_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{C}(\text{NO}_2)_3$ $\text{C}_6\text{H}_8\text{N}_6\text{O}_{15}$	$\text{C}(\text{NO}_2)_3\text{CH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_3$ $\text{C}_6\text{H}_8\text{N}_6\text{O}_{15}$
Enthalpy of formation, ΔH_f	−142.7 kcal/mol	−597.1 kJ/mol = −142.7 kcal/mol

With no more evidence of actual existence of any trinitromethyl ethers, the premise of the original proposal was reconsidered. The following precedents for somewhat structurally similar molecules still suggested the reasonableness of the trinitromethyl ether linkage as a structural feature of a synthetically feasible material. Highly electronegative orthocarbonates are known, such as tetrakis(trifluoromethyl) orthocarbonate, $\text{C}(\text{OCF}_3)_4$ [18]. An electronegative trimethylsilyl ether has been prepared and isolated: tricyanomethyl trimethylsilyl ether, $(\text{CH}_3)_3\text{SiOC}(\text{CN})_3$ (boiling point 60 °C at 12 torr) [19]. Several molecules with the trinitromethyl group bonded to non-halogen heteroatoms (i.e., other than carbon) are known, such as tetranitromethane and $\text{N-C}(\text{NO}_2)_3$ in 3,5-dinitro-1-(trinitromethyl)-1,2,4-triazole [20]. On the basis of the feasibility of such molecules, trimethylsilyl trinitromethyl ether, $(\text{CH}_3)_3\text{SiOC}(\text{NO}_2)_3$, was chosen as a target worth pursuing, as it appeared to offer the prospect of being a potentially useful intermediate toward various other trinitromethyl ether products.

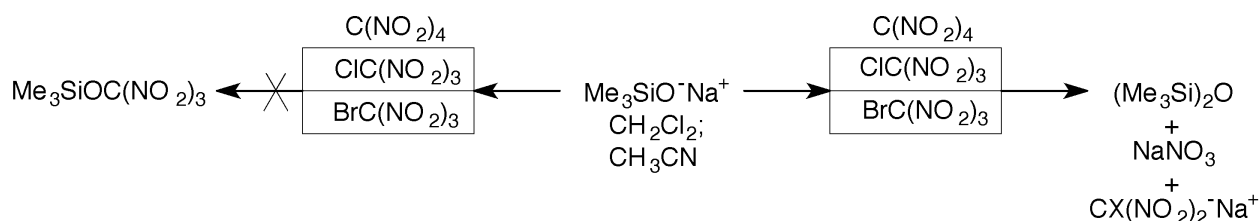
An initial approach toward this target was founded on observations of nucleophilic displacement of either halide or nitro substituents in various trinitromethane derivatives, as reviewed by Fridman et al. [21]:



It was desired that the well known trimethylsilanolate anion, $(\text{CH}_3)_3\text{SiO}^-$ (commercially available as the sodium and potassium salts), could similarly act as a nucleophile, forming the desired trimethylsilyl ether product.

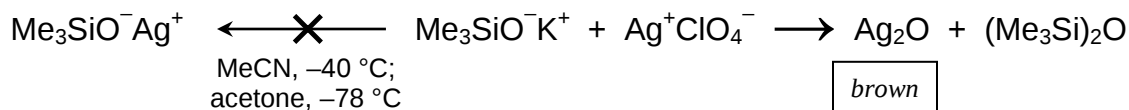
Results and Discussion

Treatment of several different trinitromethane derivatives—tetranitromethane, chlorotritromethane, and bromotritromethane—with sodium trimethylsilanolate under various conditions (acetonitrile or dichloromethane solvent) showed a different course of reaction (Scheme 1), according to multinuclear NMR (^1H , ^{13}C , ^{14}N , ^{29}Si) evidence. In no case was evidence of the desired trimethylsilyl trinitromethyl ether seen; but rather, hexamethyldisiloxane, sodium nitrate, and the anion of a dinitromethane derivative corresponding to the starting reactant were observed as final products. It is surmised that the trinitromethane derivatives act as *nitrating* agents toward trimethylsilanolate anion, resulting in trimethylsilyl nitrate intermediate (plus the sodium salt of substituted-dinitromethanide by-product), which then *trimethylsilylates* further sodium trimethylsilanolate reactant, forming hexamethyldisiloxane (plus sodium nitrate by-product).



Scheme 1. Attempted nucleophilic substitutions in trinitromethanes by trimethylsilanolate

An alternative reagent was considered in order to better drive abstraction of halide from a halotritromethane reactant: silver trimethylsilanolate, which is, however, unknown as a discrete, simple species—although adducts such as with complexed trimethylphosphine have been reported [22]. Schindler and Schmidbaur have reported that attempts to prepare simple silver trimethylsilanolate in many different solvents were unsuccessful [23], though details of their conditions were not reported. We tested the feasibility of similar reactions under very mild conditions, attempting a metathesis between potassium trimethylsilanolate and silver perchlorate, first in acetonitrile at approximately $-40\text{ }^\circ\text{C}$ and also in acetone at approximately $-78\text{ }^\circ\text{C}$, monitoring the progress of reaction by multinuclear NMR at low temperature. Rather than evidence of a new trimethylsilanolate salt, formation of a brown precipitate—consistent with silver(I) oxide—along with hexamethyldisiloxane product was always observed (Scheme 2). This behavior further corroborates previous reports of the instability of “silver trimethylsilanolate,” now even under very mild conditions.



Scheme 2. Attempted preparations of silver trimethylsilanolate

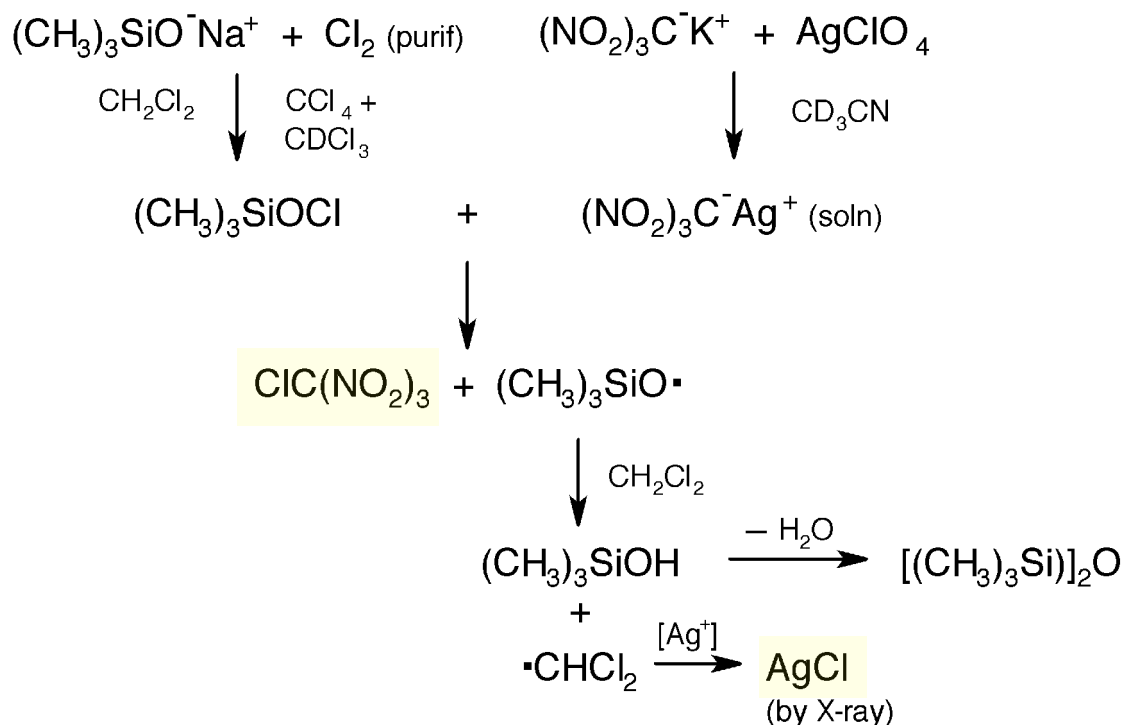
Since nucleophilic substitutions of halotrinitromethane derivatives by trimethylsilanolate ion proved unfeasible, an alternative approach toward the desired product was undertaken. The silver salt of trinitromethane (silver nitroformate) is well known. Trimethylsilyl hypochlorite, $(\text{CH}_3)_3\text{SiOCl}$, has also been reported in the literature [24]. It was envisioned that a metathetical reaction between these species might be driven by precipitation of silver chloride and produce the desired trimethylsilyl trinitromethyl ether, although it was also foreseeable that the hypochlorite might merely act as a chlorinating agent toward the nitroformate ion, producing chlorotrinitromethane instead.

Trimethylsilyl hypochlorite was prepared by chlorination of sodium trimethylsilanolate in dichloromethane solvent at 0 °C using a quantified solution of elemental chlorine in carbon tetrachloride. $(\text{CH}_3)_3\text{SiOCl}$ was newly characterized by NMR—since the earlier publication [24] reported no NMR data—in CH_2Cl_2 – CDCl_3 – CCl_4 mixtures: ^1H δ 0.28; ^{13}C δ 2.8 ± 0.2 ; ^{29}Si δ 39.8 ± 0.2 . In some preparations, trimethylsilanol (^{29}Si δ 16) and hexamethyldisiloxane (^{29}Si δ 7.2) were seen as side products.

Silver nitroformate solution was produced by the metathetical reaction between anhydrous silver perchlorate and potassium nitroformate in acetonitrile (separating the potassium perchlorate precipitate), analogous to that employed by Shevelev et al. using silver nitrate [25].

Mixing solutions of silver nitroformate (acetonitrile) and trimethylsilyl hypochlorite (CD_2Cl_2 – CCl_4) at low temperature and following their reaction by NMR at –20 °C showed no evidence of a new species consistent with $(\text{CH}_3)_3\text{SiOC}(\text{NO}_2)_3$, although significant trimethylsilanol appeared to form (according to ^{29}Si NMR) and the precipitate was darker than expected for silver chloride.

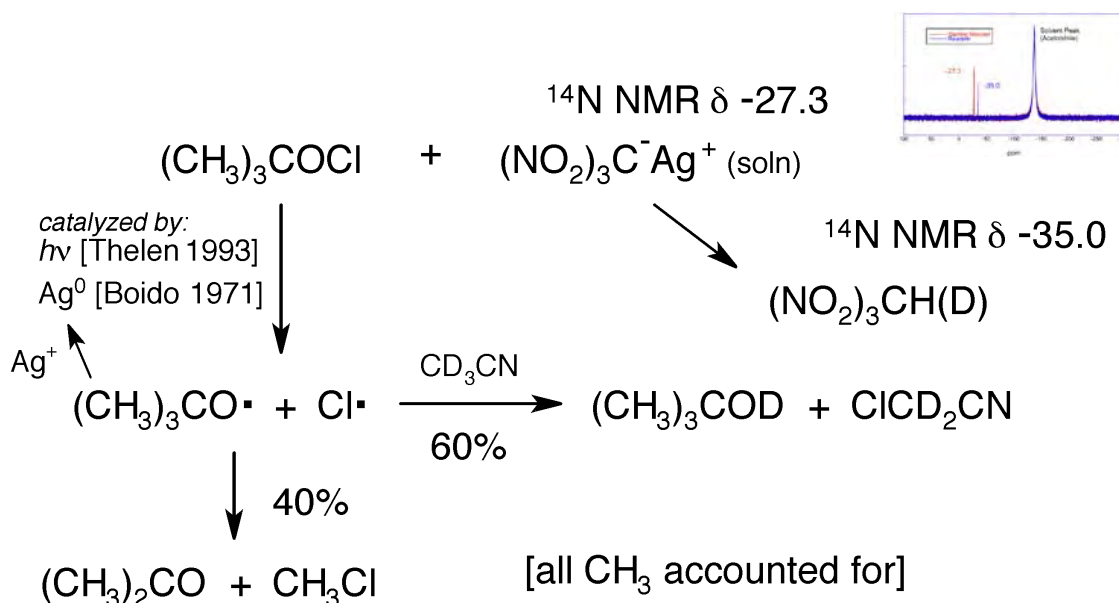
The reagent preparations and metathesis reaction were repeated more carefully to avoid any protic conditions: chlorine gas was purified to remove any hydrogen chloride contaminant; and silver perchlorate was azeotropically dried with benzene prior to its metathesis with dry potassium nitroformate. Soluble products from the metathesis between the reactants formed from these solutions were better characterized by multinuclear NMR as chlorotrinitromethane and trimethylsilanol. Interestingly, the precipitate lightened in color on standing (hours to overnight), and it was confirmed by X-ray powder diffraction to be silver chloride. Identification of trimethylsilanol as a product requires that hydrogen must be abstracted from a solvent, which is a well known reaction undergone by trimethylsiloxy radical [26,27,28], a reasonable by-product of the chlorination of nitroformate by trimethylsilyl hypochlorite. The formation of two chlorine-containing products, chlorotrinitromethane and silver chloride (highlighted in Scheme 3), requires that a chlorinated solvent in addition to trimethylsilyl hypochlorite contributes to their formation. Abstraction of hydrogen from dichloromethane by trimethylsiloxy radical should leave a dichloromethyl radical which may be further susceptible to reaction with the silver present in the system in order to produce the identified silver chloride.



Scheme 3. Preparation of and reaction of trimethylsilyl hypochlorite and silver nitroformate

As an alternative to trimethylsilyl trinitromethyl ether, the feasible formation of *any* trinitromethyl ether was hoped to be demonstrated by a preparation of *tert*-butyl trinitromethyl ether, an example that might be less useful as an intermediate toward other members of the class but which may have greater stability than the intractable trimethylsilyl ether. *tert*-Butyl hypochlorite is a well known, relatively stable material, which was freshly prepared [29]. Metathesis reactions between *t*-BuOCl and silver nitroformate in acetonitrile-*d*₃ solvent reproducibly produced organic products (according to multinuclear NMR) that allow the following processes to be identified (Scheme 4).

Precipitation of a brown solid is fairly rapid (seconds); acetone and chloromethane are formed in equimolar amounts; *tert*-butanol (apparently deuteriated *t*-BuOD) and chloroacetonitrile are additional by-products. The homolysis of tertiary alkyl hypochlorites to tertiary alkoxy and chlorine radicals is known to be initiated by various catalysts, including metallic silver [30] and light [31]; the resulting stable products in the case of *t*-BuOCl would be the observed acetone and chloromethane. This pathway accounts for approximately 40% of the identified methyl-containing products. The balance of ~60% of organic products arises from abstraction of hydrogen (a deuteron) from the solvent (CD₃CN), and chloroacetonitrile-*d*₂ similarly is formed by reaction of the chlorine radical intermediate with CD₃CN. The nature of the trinitromethyl by-product was not definitively identified, but its ¹⁴N NMR chemical shift (δ −35.0 vs. CD₃CN as

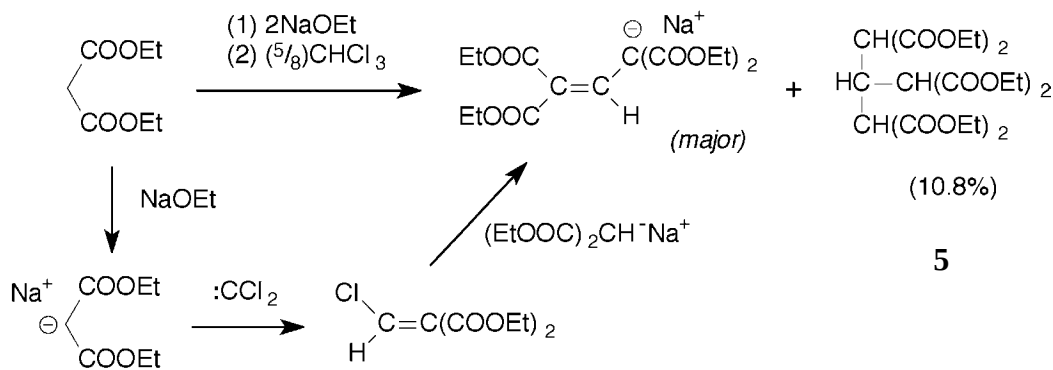


Scheme 4. Reaction of *tert*-butyl hypochlorite plus silver nitroformate

δ -139) is consistent with simple protonation of the nitroformate ion to trinitromethane; and the conversion is quite clean by NMR. The interaction of reactive silver species and *t*-butoxy radical is reminiscent of the attempted formation of silver *t*-butoxide—which is apparently unstable—via metathesis between silver perchlorate and lithium *t*-butoxide [32]: “...the precipitate appeared to be a mixture of varying composition, consisting of metallic silver as well as substances other than the silver alkoxide, containing silver, carbon and hydrogen.” Rapid degradation of reactant *t*-BuOCl may be similarly accelerated by silver in the present system.

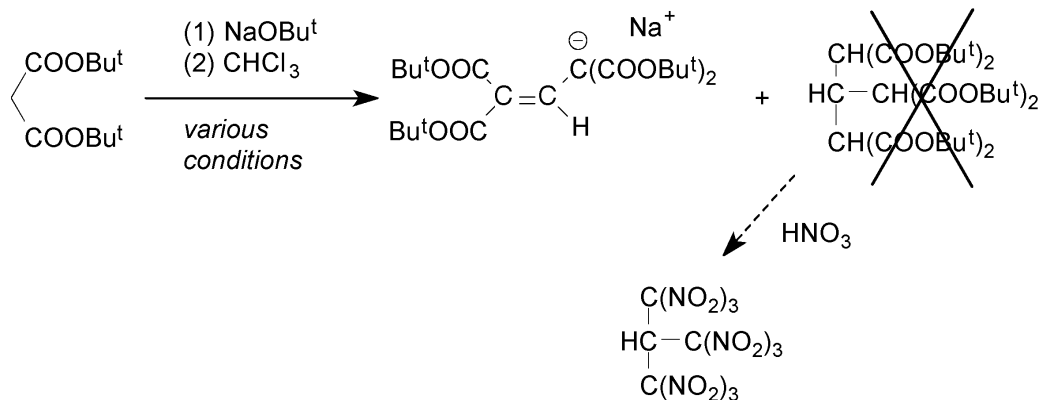
Interestingly, the participation of nitroformate appears to be necessary for the observed rapid reaction, however, as a similar mixture of *t*-butyl hypochlorite with silver *nitrate* in acetonitrile produced no significant precipitate or organic products even upon standing one day at ambient temperature. Only minor by-products consistent with adventitious degradation of *t*-BuOCl were apparent by NMR.

In parallel with the attempts above to prepare trinitromethyl ethers as an unprecedented class of compound, new trinitromethyl derivatives other than ethers were considered, namely, certain unknown polynitroalkanes with high oxygen balance. The known transformation that served as the basis for this approach is destructive nitration of malonic acids to corresponding trinitromethyl derivatives. For example, methylmalonic acid, $\text{CH}_3\text{CH}(\text{COOH})_2$, has been nitrated to 1,1,1-trinitroethane, $\text{CH}_3\text{C}(\text{NO}_2)_3$ [33]; and 1,3,5-triazine-2,4,6-trismalonic acid has been nitrated to 2,4,6-tris(trinitromethyl)triazine [34]. A potentially interesting malonate ester derivative has been reported by Coutelle [35]: hexaethyl methanetrismalonate (5), formed as a minor product from the reaction of diethyl malonate sodium salt with chloroform in the presence of excess sodium ethoxide (Scheme 5). The mechanism of the course of this reaction was later elucidated by Krapcho et al. [36].



Scheme 5. Formation of methanetrismalonate ester (**5**) [35] and its mechanism [36]

Although the decarboxylative nitration does not proceed successfully on ethyl malonate esters [34], *tert*-butyl carboxylate (BOC) esters are generally readily cleaved by acidic reagents, including nitric acid [37]. We therefore envisioned that if a hexa-*t*-butyl ester of methanetrismalonate (analogous to Coutelle's hexaethyl ester) could be prepared, it might be deprotected by nitric acid and each malonic acid substituent might be subsequently nitrated—tentatively in a one-pot reaction—to form “tris(trinitromethyl)methane,” i.e., nonanitroisobutane (Scheme 6). Unfortunately, despite a variety of conditions attempted, *no* evidence of the desired hexa-*t*-butyl methanetrismalonate ester was ever seen, even as a minor by-product; only the corresponding 1,1,3,3-propenetetracarboxylate ester (described by Krapcho et al. [36] for the ethyl ester) was formed in all cases.



Scheme 6. Attempted preparation of methanetrismalonate hexa-*t*-butyl ester

There was, however, some question about the stability of such a highly nitrated target structure. Pivina et al. [38] predicted that structures with a theoretical steric hindrance parameter $\alpha > 8.87$ would not be stable;

$$\alpha(\%) = U_{\text{strain}}/\Delta H_{\text{atomiz}}$$

where U_{strain} is the strain energy or the potential energy of the molecule in the minimum position, and ΔH_{atomiz} is the atomization enthalpy. Known hexanitroethane has $\alpha = 8.87$, but unknown 1,1,1,3,3,3-hexanitropropane has $\alpha(\text{theor}) = 15.08$ and was predicted to be unstable. Nonanitroisobutane might therefore be predicted as unstable as well. Note, however, that a compound with

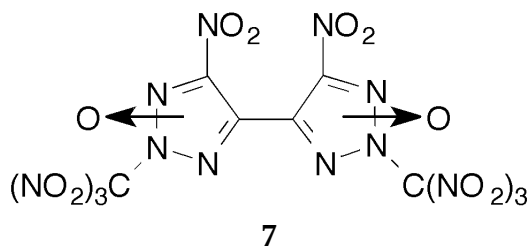
clearly greater steric hindrance than 1,1,1,3,3,3-hexanitropropane had been demonstrated—prior to the Pivina et al. prediction [38]—as stable enough to isolate and distill (Scheme 7): 2,2-bis-(bromomethyl)-1,1,1,3,3,3-hexanitropropane (**6**) [39].



Scheme 7. Preparation of a 1,1,1,3,3,3-hexanitropropane derivative (**6**) [39]

Another potentially interesting oxidizer candidate (or intermediate toward a better oxygen-balanced one) was briefly considered: the structure hexakis(nitratomethyl)ethane, $(\text{CH}_2\text{ONO}_2)_3\text{CC}(\text{CH}_2\text{ONO}_2)_3$, with a slightly better oxygen balance (−9.67%) than CL-20 (−10.95%), was first mentioned by Tarver [40], who cited some experimental properties for it, and it was subsequently mentioned again by Keshavarz in a theoretical context [41]. However, no literature was found on this compound’s preparation or experimental determination of properties. Thanks to a suggestion by John W. Fronabarger (Pacific Scientific Energetic Materials Co., Chandler, Arizona), who recognized that the cited molecule looked like a structural portion of well known “diPEHN” [“di(pentaerythryl hexanitrate)”], the compound shown by Tarver [40] was confirmed actually to be diPEHN, $(\text{CH}_2\text{ONO}_2)_3\text{C}[\text{CH}_2\text{OCH}_2]\text{C}(\text{CH}_2\text{ONO}_2)_3$, by matching Tarver’s tabulated density (1.63 g cm^{-3}) to the same experimental density for diPEHN reported earlier by Friederich and Brün [42].

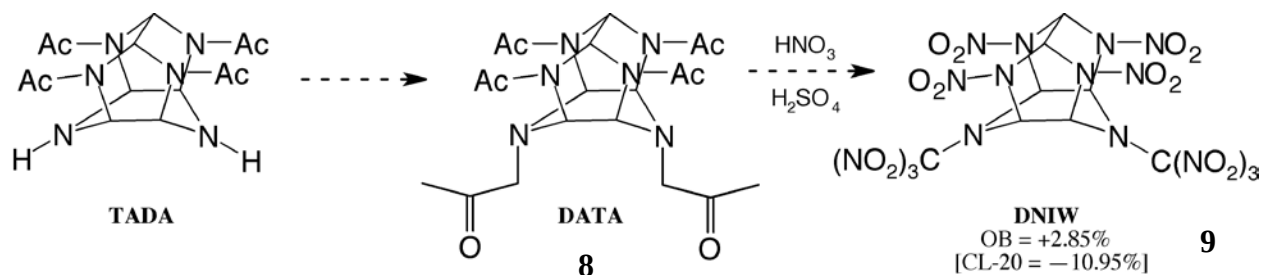
At the proposal stage of this SEED project, another structurally attractive compound was envisioned: 5,5'-dinitro-2,2'-bis(trinitromethyl)-4,4'-bi-2*H*-1,2,3-triazole *N,N'*-dioxide (**7**), either as the 1,1'-dioxide or 3,3'-dioxide, which has good oxygen balance (+17.26%) and should have good density and stability. Three different synthetic sequences were conceptually devised leading to at least one of the isomers, but they entailed seven, eight, or eleven steps from commodity chemical starting materials, and each one involved one step of uncertain (though reasonable) feasibility. This target was therefore deemed to be beyond the scope of this SEED project to develop a practical oxidizer replacement for AP.



Yet another unknown trinitromethyl derivative was envisioned as a potentially interesting oxidizer candidate. As background, 2,6,8,12-tetraacetylhexaazaisowurtzitane (TADA) is a well known intermediate for various other hexaazaisowurtzitane products, most importantly, hexanitrohexaazaisowurtzitane (CL-20) [43]. Furthermore, TADA is known to be functionalizable in ways other than direct nitration. For example, reactions with acetic anhydride and/or acetyl chloride [44] or substituted benzoyl chlorides [45] produce the corresponding 2,6,8,12-tetraacetyl-4,10-diacetylhexaazaisowurtzitanes. Also, the NH nitrogens of the piperazine ring (4,10-nitrogens in TADA) can react with various aldehydes to make a hemiaminal bridge between them [46].

Various *N*-(trinitromethyl) heterocycles have been prepared by destructive nitration of their *N*-acetyl derivatives [20,47], which precursors are generally prepared by *N*-alkylation with a suitable haloacetone [48].

It was therefore hoped that TADA might be derivatized by a reactive acetylonyl reagent to produce unknown 4,10-diacetylonyl-2,6,8,12-tetraacetylhexaazaisowurtzitane (**8**, “DATA”), which might subsequently undergo destructive nitration concomitantly with nitrolysis of *N*-acetyl (Scheme 8) to make 2,6,8,12-tetranitro-4,10-bis(trinitromethyl)hexaazaisowurtzitane (**9**, “DNIW”), i.e., a hexaazaisowurtzitane with ten nitro groups and an oxygen balance (+2.85%) significantly better than CL-20’s.



Scheme 8. Proposed preparation of a decanitro-substituted hexaazaisowurtzitane (**9**)

Several attempts were made to carry out this synthetic sequence (Scheme 9, below).

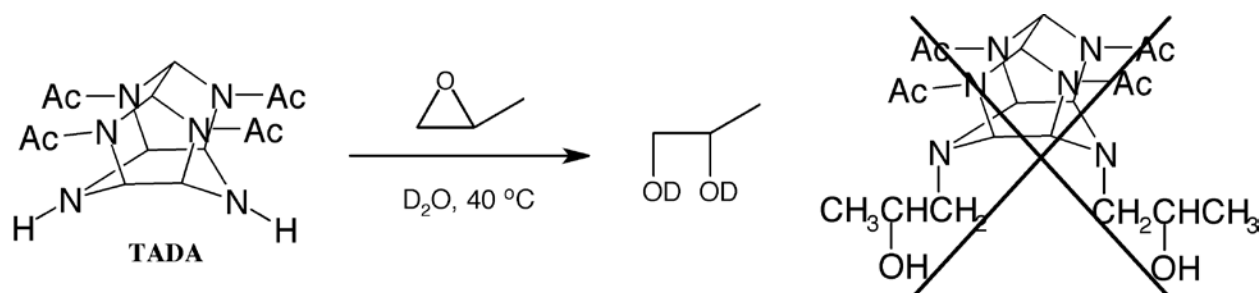
TADA has fairly poor solubility in nonaqueous solvents and is only slightly soluble, but usable, in polar aprotics such as dimethyl sulfoxide and dimethylformamide. Kawano and Kato have shown that alkylation of an amine by bromoacetone is feasible in DMSO [49]; however, without a competitive nucleophile, DMSO itself is susceptible to alkylation to an alkoxy-sulfonium salt. Similarly, amines may be alkylated by chloroacetone in tertiary amide solvents in the presence of base—for example, either triethylamine [50] or potassium carbonate (plus potassium iodide catalyst, presumably to activate the acetone further via chloride–iodide exchange to transient iodoacetone) [51]. Initially out of concern for the possible hydrolysis of activated haloacetones in water [52], we attempted alkylation of TADA with chloroacetone in DMSO in the presence of sodium iodide (1 equiv) and triethylamine base. Warming (80 °C) was necessitated in order to effect significant solubilization of TADA. The course of reaction was monitored by ¹H NMR (80 °C), but no significant change in absorptions of TADA was observed. A species was observed *in situ* that was consistent by NMR with an acetyltriethylammonium salt (via alkylation of triethylamine by chloroacetone), although Slates [52] has reported that this

at 80 °C, solvent was removed under high vacuum, and the residue was triturated with acetonitrile, producing an insoluble solid. This solid had a nondescript ^1H NMR spectrum with broad peaks different from TADA's and inconsistent with the desired product (DATA). The stability of TADA toward such a strong base at elevated temperature is questionable.

18-Crown-6 was tested as a phase transfer catalyst, using potassium carbonate as a base for alkylation by chloroacetone [51] and also employing sodium iodide catalyst: first, in acetonitrile at reflux temperature for 12 hours, and also in DMF at 80 °C for 4 h. Only unreacted TADA was recovered from both systems.

Diazoacetone [$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{N}_2$] was tested as a potentially reactive source of electrophilic acetyl [55]. Diazoacetone plus TADA in D_2O showed no reaction together after 18 hours at ambient temperature. Similarly, no reaction was seen in H_2O after 18 hours. Addition of dirhodium(II) tetraacetate as a potential catalyst for alkylation [56] induced no reaction with TADA after an additional 18 hours, although some diazoacetone had hydrolyzed to hydroxyacetone (by comparison to an authentic sample), according to NMR.

A modification of the reaction was attempted in order to prepare a suitable *precursor* to DATA. Piperazine has been alkylated by propylene oxide to prepare the 1,4-bis(2-hydroxypropyl) derivative [57]. A similar reaction was tested with TADA in D_2O in hopes of preparing the 4,10-bis(2-hydroxypropyl) derivative (Scheme 10) which might then be oxidized to DATA. The solution at 40 °C overnight showed some reaction between propylene oxide and D_2O to form 1,2-propanediol- d_2 but no significant change in TADA.



Scheme 10. Attempt to alkylate TADA with propylene oxide

Conclusions and Implications for Future Research

Despite two independent claims in literature (journal and online) of the existence of trinitromethyl ethers, this class of compounds proved not to be established by any precedence, as both claims were discovered to be erroneous. Several attempts to newly prepare examples of this potentially interesting class were unsuccessful, even though it appears to be a fundamentally reasonable chemical linkage.

Although some unprecedented polynitroalkane products, such as nonanitroisobutane, were briefly pursued, they too proved less straightforward than hoped and were abandoned.

One target considered early on, 5,5'-dinitro-2,2'-bis(trinitromethyl)-4,4'-bi-2*H*-1,2,3-triazole *N,N'*-dioxide (**7**), still appears particularly promising from a standpoint of properties expected to provide superior performance as an oxidizer. However, synthetic strategies that might produce it appeared to be beyond the scope of a SEED project and are likely impractical for a large-scale replacement of AP. It may be worth pursuing in the context of a research program independent of SERDP's goals.

A last target compound pursued, 2,6,8,12-tetranitro-4,10-bis(trinitromethyl)hexaaza-isowurtzitane (**9**), still appears conceptually interesting, but synthetic strategies attempted in the course of this SEED project—particularly routes via unknown diacetonilytetraacetylhexaaza-isowurtzitane (**8**) as a new intermediate—were unsuccessful. This target also remains of interest for pursuit outside the scope of the current project, as it has good oxygen balance and is expected to have good properties as an energetic ingredient (oxidizer or explosive).

Literature Cited

- [1] (a) http://www.epa.gov/fedfac/documents/emerging_contaminant_perchlorate.pdf ;
(b) <http://yosemite.epa.gov/opa/admpress.nsf/0/6348845793f4cc5d8525782b004d81ae>
[2] <http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=2752524>
[3] <http://www.mdpi.org/>
[4] http://www.bioscreening.com/companies/Zelinsky_Institute
[5] Lebedev, O.V.; Epishina, L.V.; Novikova, T.S.; Makhova, N.N.; Godovikova, T.I.; Golova, S.P.; Shastin, A.V.; Arnautova, E.A.; Pivana, T.S.; Khmel'nitskii, L.I. *International Annual Conference of ICT [Proc.]* **1998**, 29, 56/1.
[6] Khisamutdinov, G.Kh.; Korolev, V.L.; Kondyukov, I.Z.; Sbdrahmanov, I.Sh.; Smirnov, S.P.; Fainzilberg, A.A. *Russ. Chem. Bull.* **1993**, 42, 1559.
[7] Semenov, V.V. Presented at the 218th National Meeting of the American Chemical Society, New Orleans, LA, August 22–26, 1999; Paper ORGN 29.
[8] Sukhachev, D.V.; Pivina, T.S.; Volk, F.S. *Propell. Explos. Pyrotech.* **1994**, 19, 159.
[9] Xu, H.; Wang, C.-L.; Liu, Ji.-H. *Guti Huojian Jishu [J. Solid Rocket Technol.]* **2000**, 23, 48.
[10] Ammon, H.L. *Propell. Explos. Pyrotech.* **2008**, 33, 92.
[11] Frankel, M.B. *Tetrahedron* **1963**, 19(Suppl. 1), 213.
[12] Hill, M.E. Orthoesters of 2,2,2-trinitroethanol. U.S. Patent 3,306,939, February 28, 1967.
[13] Hatano, H.; Onda, T.; Shiino, K.; Matsuura, S.; Miyazaki, S. *Kayaku Gakkaishi* **1997**, 58, 147.
[14] Sheremetev, A.B.; Yudin, I.L. *Mendeleev Commun.* **2005**, 204.
[15] Hill, M.E.; Shipp, K.G. Process for acetal preparation. U.S. Patent 3,526,667, September 1, 1970.
[16] Pivina, T.S., Zelinsky Institute of Organic Chemistry, Moscow, Russia. Personal communication, February 12, 2010: "Yes, in our paper the incorrect structural formulae were presented... You have turned out to be the only attentive reader who noted it from 1994, - great!"
[17] Kustova, L.V.; Kirpichev, E.P.; Rubtsov, Yu.I.; Avdonin, V.V.; Korepin, A.G.; Eremenko, L.T. *Bull. Acad. Sci. USSR Div. Chem. Sci. [Engl. Transl.]* **1981**, 30, 1830.
[18] Adcock, J.L.; Robin, M.L.; Zuberi, S. *J. Fluorine Chem.* **1987**, 37, 327.
[19] Lidy, W.; Sundermeyer, W. *Chem. Ber.* **1973**, 106, 587.
[20] Kofman, T.P.; Uspenskaja, T.L.; Malygina, L.V.; Pevzner, M.S. 1-Trinitromethyl-3-nitro-5-R-1,2,4-triazole and its production method. Soviet Patent SU 1,840,302 A1, August 27, 2006.
[21] Fridman, A.L.; Surkov, V.D.; Novikov, S.S. *Russ. Chem. Rev.* **1980**, 49, 1068.
[22] Schmidbaur, H.; Adlkofer, J.; Shiotani, A. *Chem. Ber.* **1972**, 105, 3389.
[23] Schindler, F.; Schmidbaur, H. *Angew. Chem. Int. Ed. Engl.* **1967**, 6, 683.
[24] Dahlmann, J.; Rieche, A.; Austenat, L. *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 727.
[25] Shevelev, S.A.; Erashko, V.I.; Sankov, B.G.; Fainzil'berg, A.A. *Bull. Acad. Sci. USSR Div. Chem. Sci. [Engl. Transl.]* **1968**, 368.
[26] Davies, A.G.; Roberts, B.P.; Tse, M.-W. *J. Chem. Soc. Perkin Trans. 2* **1977**, 1499.
[27] Gara, W.B.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. 2* **1977**, 1709.
[28] Baban, J.A.; Goddard, J.P.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. 2* **1986**, 1269.
[29] Mintz, M.J.; Walling, C. *Org. Synth.* **1969**, 49, 9.
[30] Boido, V.; Edwards, O.E. *Can. J. Chem.* **1971**, 49, 2664.
[31] Thelen, M.-A.; Felder, P.; Frey, J.G.; Huber, J.R. *J. Phys. Chem.* **1993**, 97, 6220.

-
- [32] Macomber, R.S.; Ford, J.C.; Wenzel, J.H. *Synth. React. Inorg. Metal-Org. Chem.* **1977**, *7*, 111.
- [33] Franchimont, A.P.N. *Rec. Trav. Chim. Pays-Bas* **1886**, *5*, 281.
- [34] Shastin, A.V.; Godovikova, T.I.; Golova, S.P.; Kuz'min, V.S.; Khmel'nitskii, L.I.; Korsunskii, B.L. *Mendeleev Commun.* **1995**, 17.
- [35] Coutelle, C. *J. Prakt. Chem. [2]* **1906**, *73*, 49.
- [36] Krapcho, A.P.; Huyffer, P.S.; Starer, I. *J. Org. Chem.* **1962**, *27*, 3096.
- [37] Strazzolini, P.; Scuccato, M.; Giumanini, A.G. *Tetrahedron* **2000**, *56*, 3625.
- [38] Pivina, T.S.; Gritsaev, E.I.; Smirnov, B.B.; Shlyapochnikov, V.A.; Novikov, S.S. *Bull. Acad. Sci. USSR Div. Chem. Sci. [Engl. Transl.]* **1977**, 158.
- [39] Szwechgejmer, G.A. *Rocz. Chem.* **1973**, *47*, 1249.
- [40] Tarver, C.M. *J. Chem. Eng. Data* **1979**, *24*, 136.
- [41] Keshavarz, M.H. *J. Hazard. Mater.* **2007**, *143*, 437.
- [42] Friederich, W.; Brün, W. *Chem. Ber.* **1930**, *63B*, 2681.
- [43] Hamilton, R.S. Crystallization of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{5,9}.0^{3,11}]dodecane. U.S. Patent 6,992,185, January 31, 2006.
- [44] Kodama, T.; Tojo, M.; Ikeda, M. Hexaazaisowurtzitane derivatives and process for producing the same. PCT Patent WO 96/23792, August 8, 1996.
- [45] Wu, X.; Wang, Y.; Ou, Y.; Liu, J. *Hanneng Cailiao [Chin. J. Energ. Mater.]* **2006**, *14*, 343.
- [46] Sun, C.; Zhao, X. *Hanneng Cailiao [Chin. J. Energ. Mater.]* **2008**, *16*, 669.
- [47] Kofman, T.P.; Kartseva, G.Yu.; Glazkova, E.Yu.; Krasnov, K.N. *Russ. J. Org. Chem.* **2005**, *41*, 753.
- [48] Kofman, T.P.; Uspenskaya, T.L.; Medvedeva, N.Yu.; Pevzner, M.S. *Chem. Heterocycl. Comp. [Engl. Transl.]* **1976**, 821.
- [49] Kawano, T.; Kato, N. *Chem. Letters* **2006**, *35*, 270.
- [50] Ohba, N.; Ikeda, A.; Matsunari, K.; Yamada, Y.; Hirata, M.; Nakamura, Y.; Takeuchi, A.; Karino, H. 1,2,5,6-Tetrahydropyridine-2-one compounds which are useful herbicides. U.S. Patent 5,076,834, December 31, 1991.
- [51] Fusaka, T.; Yamato, S.; Kajiwarra, T.; Kamiyama, H.; Itoh, S.; Tanaka, Y. *J. Pesticide Sci. (Tokyo)* **2004**, *29*, 339.
- [52] Slates, H.L.; Weber, S.; Wendler, N.L. *J. Org. Chem.* **1969**, *34*, 458.
- [53] Major, R.T.; Cline, J.K. *J. Am. Chem. Soc.* **1932**, *54*, 242.
- [54] Rao, P.N.P.; Amini, M.; Li, H.; Habeeb, A.G.; Knaus, E.E. *J. Med. Chem.* **2003**, *46*, 4872.
- [55] Hendrickson, J.B.; Wolf, W.A. *J. Org. Chem.* **1968**, *33*, 3610.
- [56] Yee, T.; McKervey, M.A. *Chem. Rev.* **1994**, *94*, 1091.
- [57] Paul, K.; Blanton, C.D. Jr. *J. Med. Chem.* **1973**, *16*, 1391.