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FINAL TECHNICAL REPORT

"SCHOLARLY RESEARCH IN EXPLOSIVE RESEARCH & CHARACTERIZATION"

PREPARED FOR

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PREPARED BY

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GEO-CENTERS, INC.

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TASK 1:

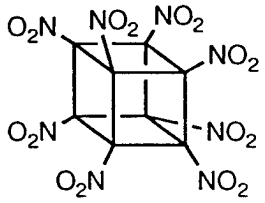
CONDENSED PHASE STUDIES

Objective 1:

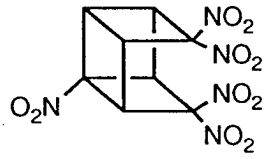
Polynitrocage Compounds

(Dr. A. Bashir-Hashemi)

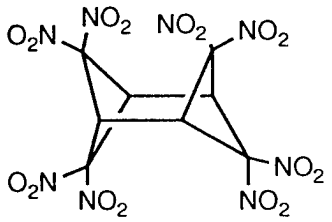
There is considerable current interest in the synthesis and chemistry of polynitrocage compounds, mainly due to their high density and strain energy. New classes of cage molecules that are predicted to have high thermal stability and low sensitivity are polynitrocubanes, polynitrosecocubanes and polynitrodiasteranes.



Octanitrocubane



Pentanitrosecocubane

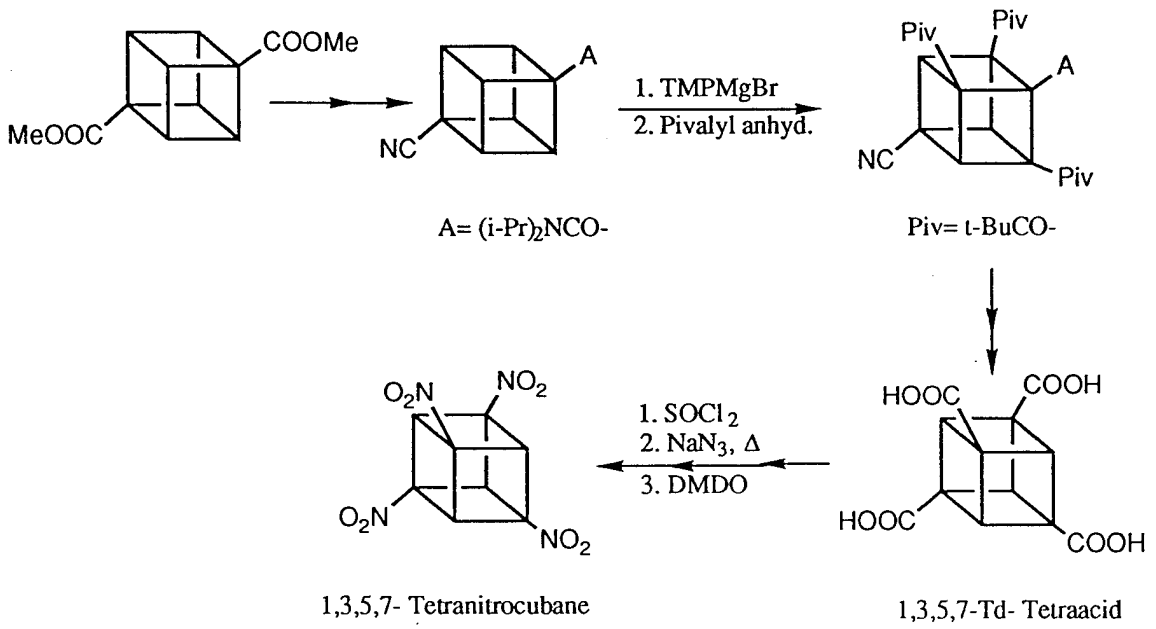


Octanitrodiasterane

Polynitrocubanes:

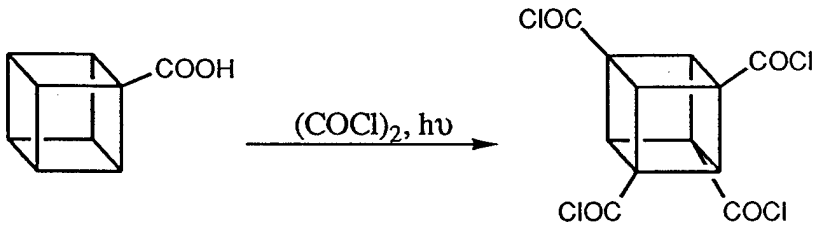
Preliminary estimations suggest that octanitrocubane should have a molecular density of 2.10 g/cc and a positive heat of formation of 88.0 kcal/mol. The srain energy for this compound is predicted to be 170 kcal/mol.

The synthesis of 1,3,5,7-tetranitrocubane,the highest polynitrated cubane so far, has been achieved from commercially available 1,4-dicarbomethoxycubane by Eaton, et al. in 26 synthetic steps. The key step in this synthesis was the introduction of three functionalities ortho to the amido group. We have discovered that the reaction of 1-amido-4-cyanocubane with an excess of TMPMgBr followed by



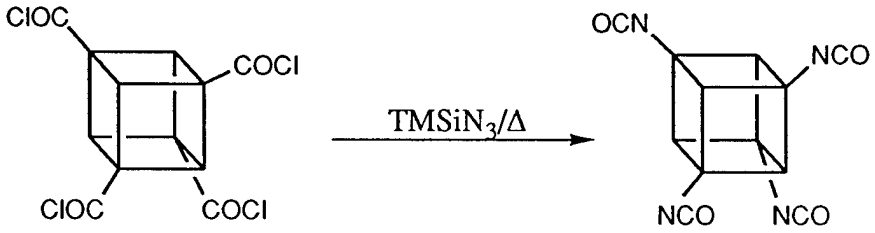
the addition of pivalic anhydride at room temperature gives pentasubstituted cubane in 40-60% yield. This approach shortens the original synthetic route by eight steps.

Very recently, however, a significant breakthrough was achieved in the synthesis of cubanes. We have developed a methodology in which the cubane skeleton can be functionalized selectively and simultaneously in several positions in one simple step using oxalyl chloride and light. Application of this procedure to carboxycubane **1** led to the synthesis of 1,3,5,7-tetrachlorocarbonylcubane **2**, an immediate precursor to tetranitrocubane. Compound **2** can be isolated from the reaction mixture by trituration with ether, and the excess oxalyl chloride can be recovered and recycled without any pollution problem.



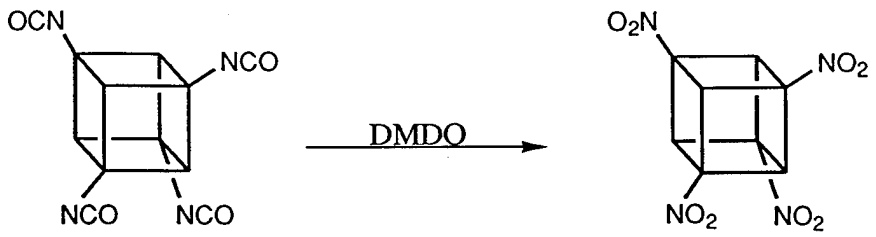
1 2

1,3,5,7-Tetrachlorocarbonylcubane **2** is very pure (94%) and can be converted to tetranitrocubane by the modified procedure provided by Professor P.E. Eaton, University of Chicago. For example in one run, compound **2** was treated with trimethylsilyl azide in the presence of a catalytic amount of 2,6-di-tert-butylpyridine in a hot chloroform solution to give the corresponding tetraisocyantocubane **3**. In this reaction the isolation of tetraacyl azide intermediate, a very sensitive explosive, was avoided.



2 3

Compound **3** was treated with aqueous dimethyldioxirane/acetone solution to give tetranitrocubane **4** in a reasonable yield. Tetranitrocubane was purified using column chromatography.



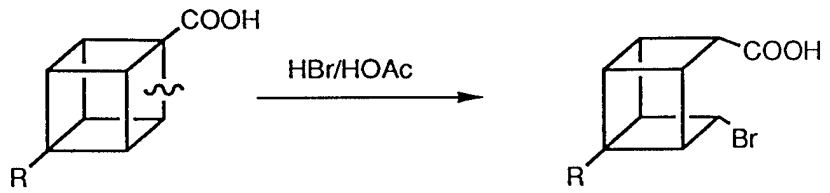
3 4

The synthesis of sufficient amounts of tetranitrocubane for necessary performance tests is underway.

Secocubanes and Diasteranes:

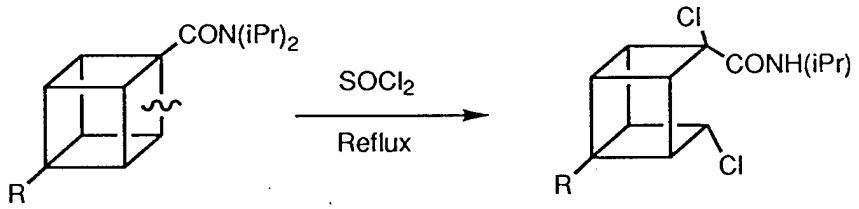
In principle, the secocubane ring system is accessible by scission of a cubane C-C bond, and the successive cleavage of a second parallel cubane C-C bond provides entrance into the diasterane ring system. To the extent that this strategy of selectively severing endocyclic C-C bonds in appropriately functionalized cubanes can be developed, an important route to critical intermediates essential to the synthesis of the target polynitro systems becomes available.

Fortunately, it is now possible to produce secocubanes by the regiospecific ring-opening of the cubane framework by two essentially complementary methods. In one method, when cubane carboxylic acid was treated with HBr/CH_3COOH rapid addition of HBr occurred producing secocubane in excellent yield.



R = H, COOH

The second procedure, developed by us at GEO-CENTERS, INC. involves the reaction of amidocubanes with thionyl chloride to afford secocubanes in high yields.



R = COOMe, CN, CON(iPr)$_2$

In our hands, when amidocubanes were treated with thionyl chloride under reflux, secocubanes were obtained in high yields. Again, the reaction was found to be regiospecific in that the cleavage occurred only at the C-C bond adjacent to the amido group.

Experiments with substituted cubanes have shown that these reactions are complementary and mutually exclusive; i.e., thionyl chloride cleaves amidocubanes only, while HBr reacts with cubane carboxylic acids only.

With the availability of methods to selectively cleave cubane bonds to give other cage systems and based on theoretical calculations tabulated below, two target molecules have been selected for future synthesis:

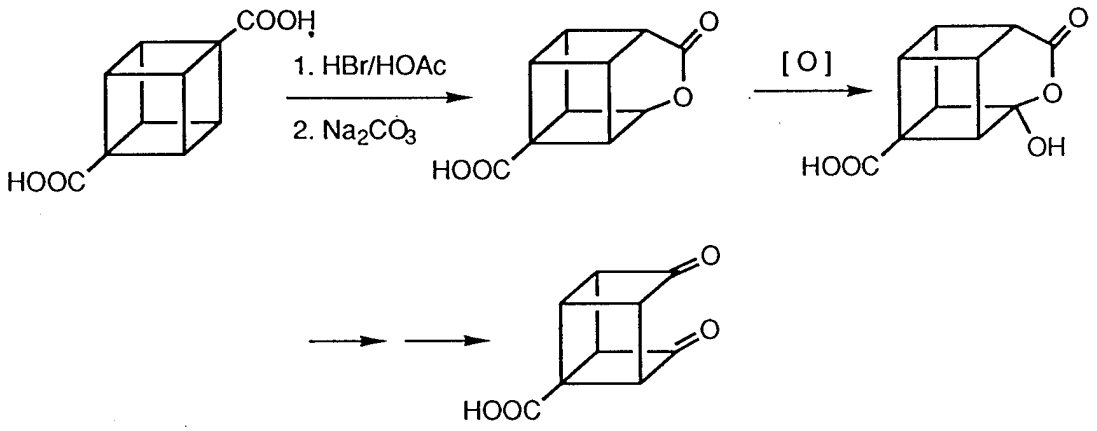
pentanitrosecocubane and octanitrodiasterane. Although calculated performance of pentanitrosecocubane is below that of HMX, the molecule is proposed as a model for other higher nitrosecocubnanes.

Table 1

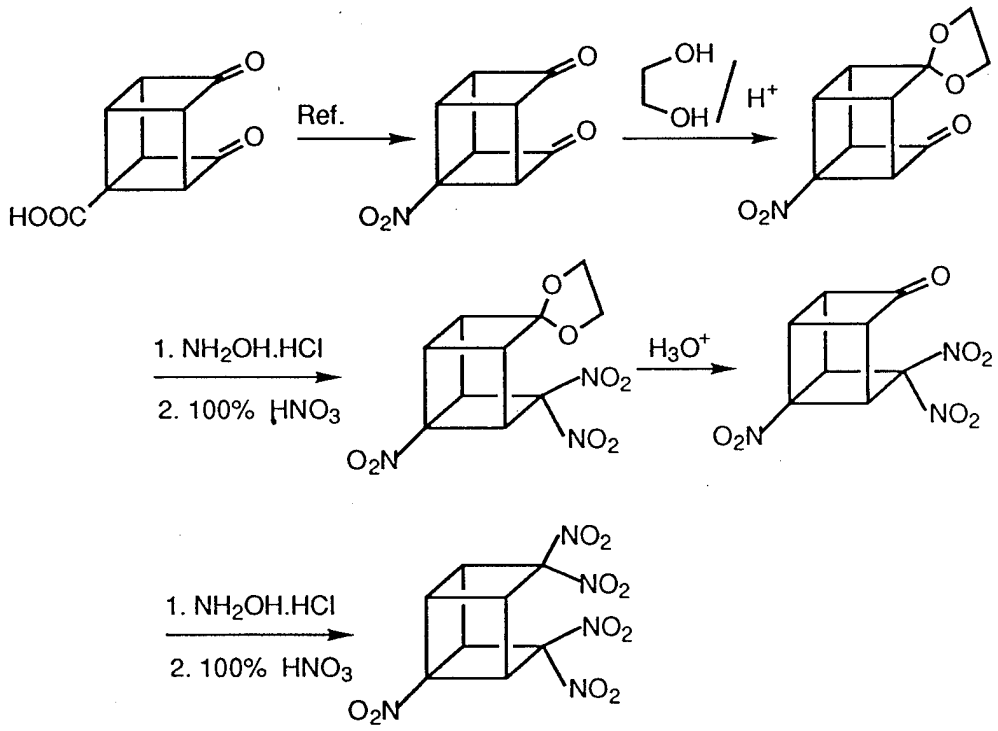
Calculated Physical and Energetic Performance Data

Compound	Density (g/cc)	DHf (kcal/mol)	Det'n vel (m/s)	P_{C-J} (kbar)
HMX	1.94	+17.9	9130	389
Pentanitrosecocubane	1.81	+172.3	8399	346
Octanitrodiasterane	1.954	+297.2	942	453

Octanitrodiasterane is expected to exhibit high thermal stability and low sensitivity characteristics consistent with other polynitro polycyclic and gem dinitro compounds. The proposed synthetic approaches to these molecules follow.

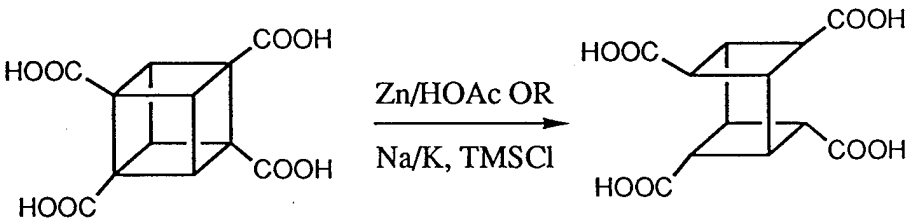


Treatment of cubane-1,4-dicarboxylic acid with HBr/CH_3COOH followed by reaction with base has been shown by Eaton et al to yield the lactone. Oxidation of the lactone function has been carried out using RuO_4. Transformation of the oxidized lactone to diketosecocubane carboxylic acid would be achieved by standard methods. The carboxylic acid group would then be converted to a nitro group via the isocyanate intermediate. Conversion of the carbonyl functions to geminal dinitro groups would be carried out sequentially owing to their mutual steric proximity based on the successful strategy developed in similar targets; e.g., 2,2,4,4-tetranitroadamantane. This synthetic sequence will serve as a model for the proposed synthesis of octanitrodiasterane (vide infra).

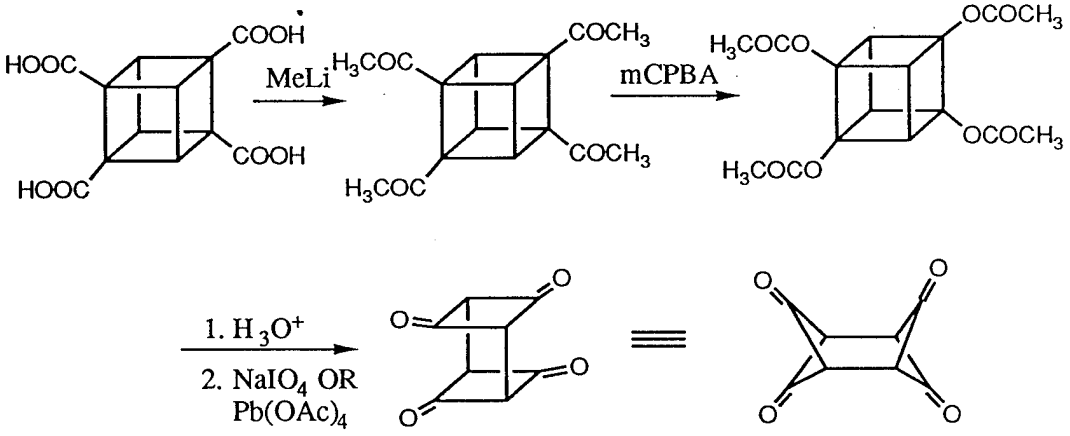


Controlled cleavage of the two parallel bonds will be needed to assure the synthesis of diasteranes. A number of such pathways can be visualized that would lead to the required cleavage. These are outlined following.

The ready availability of cubane 1,2,4,7-tetracarboxylic acid via our new synthetic strategy, makes it an attractive starting material for this purpose. Reductive cleavage of the succinyl bonds in this compound using Zn/HOAc or Na/K alloy would yield diasterane tetracarboxylic acid.



Alternatively, the tetracarboxylic acid can be converted to the corresponding tetrakis methylketone. Baeyer-Villiger reaction would yield cubane 1,2,4,7-tetraacetate. Hydrolysis of the acetate function followed by cleavage of the 1,2-diol units using either $NaIO_4$ or $Pb(OAc)_4$ would directly yield the diasterane tetrone as depicted below.



This diasterane tetrone is an ideal precursor to octanitrodiasterane, since the strategy for conversion of multiple ketones to geminal dinitro units has already been developed. We are currently pursuing possible transformations towards the synthesis of these attractive polynitrocage compounds.

It is interesting to note that for the purpose of health and environmental concerns, a series of substituted cubanes (54 compounds) were submitted to NIH for toxicity tests. None of these compounds posed any health hazard. Two of the cubane derivitives exhibited moderate anti-HIV and anti-cancer activity.

Objective 2:

Design of New Explosive Molecules

(Dr. Keerthi Jayasuriya)

Summary:

Computer-assisted molecular design is a new approach to energetic molecular research using methods from theoretical chemistry and computational techniques. The interest of this technique stems from the desire to understand the molecular reactivity and properties of energetic molecules at the molecular level. Based on this information, one could rationally design energetic materials having both good thermal stability, impact and shock sensitivity with enhanced explosive performance. Quantum mechanical techniques are necessary for the investigation of electronic properties of molecules of interest. In this context, both ab initio and semi-empirical methods have been used to determine the electronic properties of potential explosive and propellant molecules. Preferred positions for electrophilic or nucleophilic attack can be identified from the analysis of electron density distribution of the molecule. Energy differences between the reactants and products can be related to the thermodynamic stability of the products. Information of this nature will undoubtedly help in the search for novel explosive molecules. Significant progress has been made in understanding the explosive properties at the molecular level.

Introduction:

Computational techniques can easily be used to evaluate reactivity and molecular properties of many compounds where experimental information is either lacking or is difficult to obtain. During this period, computational techniques have been succesfully applied to understand the energetic compounds of interest at the molecular level. This information has been used to identify potential energetic materials with suitable insensitivity and performance suitable for DOD applications. Quantum mechanical techniques are necessary for the investigation of electronic properties. A population analysis permits the characterization of charge distribution in terms of effective charges and hybridizations. The complete electric field of the system can be determined by using the charge distribution effectively. Energy differences of reactions can give vital information about the energy hypersurface of the reaction. The geometry of a molecule is one of the important factors determining affinity and activity of molecules. The geometries of all the molecules contained in this report are optimized completely. Optimizing the geometry is equivalent to locating the deepest minimum of the energy hypersurface.

1) Stabilization Energy of Cyclic Compounds:

The stabilization energy, E_{stab}, is the difference in energy between the product and reactants, and this energy has been investigated for several cyclic compounds using MINDO/3 methods. If the stabilization is negative, it indicates that the products are thermodynamically stable with respect to the reactants, whereas if E_{stab} is positive, the product is

thermodynamically not very stable with respect to the reactants. The stabilization energy for the dimerization of acetylene to give cyclobutadiene is -2.32 kcal/mol, and the negative sign indicates that cyclobutadiene is about 2.32 kcal/mol thermodynamically more stable than acetylene. The dimerization reaction of 1,2-dinitroacetylene to yield 1,2,3,4-tetranitrocyclobutadiene is thermodynamically more stable in favor of the product by about 6.12 kcal/mol. The dimerization of 1,2,3,4-tetranitrocyclobutadine yields octanitrocubane and the stabilization energy for this [2+2] reaction is -5.08 kcal/mol in favor of the product. According to these calculations, it is thermodynamically feasible to synthesize octanitrocubane starting from 1,2-dinitroacetylene via a [2+2] cycloaddition approach. Although, 1,2-dinitroacetylene is not yet available to attempt this reaction, it is interesting to note that octatrifluoromethyl cubane is made starting from 1,2-ditrifluoromethylacetylene via a [2+2] cycloaddition approach. It is also important to emphasize that the stabilization energy does not indicate the activation energy barrier involved for this cycloaddition reaction. The activation energy is the energy of the transition structure with respect to the reactants, whereas the stabilization energy indicates the stability of the products with respect to the reactants.

2) Energy Performance Calculations:

Major emphasis was focused on the development of the TIGER code, which is used for the calculation of thermodynamic state in a nonideal heterogeneous system of known atomic composition containing gases, liquids and solids

with arbitrary equations of state. Since some of the binders contain phosphorus atoms, the TIGER code was modified to include phosphorus and its possible stable products. The covolumes of these products were calculated using the DENCAL program. The modified TIGER code was used in the calculation of thermodynamic properties of various HMX compositions.

During this period, energy performance calculations were carried out on several TNAZ based plastic moldable C-4 formulations. Table 1 gives the type of formulation, percentage by weight and volume, theoretical maximum density (TMD), and calculated detonation velocity and pressure for each formulation studied. These calculations were carried out using the TIGER code. It is quite clear from the performance evaluation, TNAZ based formulations offer better energy output than the C-4 formulation by about 15-30 percent.

Table 1

Energy Performace Index of New High Energteic Explosives and In-Service Explosives

Explosive Molecule	Calculated Density (gm/cc)	Heat of Formation (kcal/mol)	Energy Performance Index (%) (ee-eer/eer)*100
1,3,5,7-tetranitro-2,4,6,8tetraaza cubane*	2.21	165.1	49
Octanitrocubane*	2.2	81	39
TNAZ	1.841	3.7	0.7
HMX	1.905	17.9	-
RDX	1.806	14.7	-6.8
TNT	1.654	-16.0	-46

Note: (*) Experimental Stage New Explosives

The two most important parameters used to screen potential explosive molecules are the density and the heat of formation of the molecule. Based on these two parameters alone, one could focus on potential explosive molecules more effectively. The energy performance calculations were carried out using the TIGER hydrodynamic code to evaluate the detonation performance of octanitrocubane (ONC), which is

predicted to be one of the most powerful explosives. These calculations were carried out at different densities and different heats of formation values to determine the effect of these parameters on the overall energy performance of the explosive. The densities used in the calculation are as follows:

1) 2.03 gm/cc
2) 2.13 gm/cc
3) 2.23 gm/cc

The energy performance of ONC calculated at the density of 2.03 gm/cc gives 20% more energy output than HMX. When the density is set to 2.13 gm/cc, which is 5% more than the previous density, the energy performance improves over 30% than HMX. The final energy performance curve is calculated at density of 2.23 gm/cc, which increases the energy output to over 40% than the current bench mark explosive. The energy performance of ONC with respect to HMX at three different heats of formation reflects the changes in the strain energy of ONC. The density is held constant at 2.03 gm/cc for these calcualtions. The three different heats of formation were used in the calculation.

1) 44 kcal/mol (strain energy is 116 kcal/mol)
2) 81 kcal/mol (strain energy is 156 kcal/mol)
3) 121 kcal/mol (strain energy is 196 kcal/mol)

The energy output calculated using 44 kcal/mol as the heat of formation gives about 16% better performance than the HMX, while the heat of formation of 81 kcal/mol shows a 20% better performance than HMX. The difference between these

two heats of formation values is about 50%, yet the energy performance is improved by only about 4%. The energy performance of ONC calculated using the heat of formation as 121 kcal/mol improves the energy output to about 24% over the bench mark explosive, HMX. These calculations indicate the importance of density and, to a lesser extent, the heats of formation as useful parameters in screening potential explosive molecules.

In an effort to find more powerful explosive molecules, special attention is being placed on explosive structures with three-dimensional structures. These structures can be viewed as fused structures joined with two or more bonds. For example, octanitrocubane, which is hailed as the 'superexplosive', is made up of fusing two 1,2,3,4-tetranitro cyclobutane rings with four bonds. Another worthy member in this class of compounds is CL-20, in which two seven-membered rings with a common bond are fused together to give a three-dimensional structure. Along this line of thought, it is possible to conceive the structure of two fused 1,3,3-trinitroazetidine (TNAZ) structures to give a fused dimer of TNAZ. The explosive properties of this fused TNAZ structure was studied by using both quantum chemical (MINDO/3) and hydrodynamic (TIGER) calculations. The calculated density of TNAZ and its dimer are 1.84 and 2.03 gm/cc, respectively. The energy performance of TNAZ dimer is better than TNAZ by about 16%.

According to the energy performance index, (EPI), both octanitrocubane and tetranitrotetraazacubane gives more power than HMX by 39% and 49%, respectively. The current developmental stage explosive, TNAZ, gives about 0.7% more

power than HMX. In this index, 2,2,4,4,6,6-hexanitroadamantane is -13% less powerful than HMX.

3) Decomposition Pathways:

The elucidation of reaction mechanisms is a major challenge for chemists. Although the geometries of reactants and products can be obtained experimentally, the transition states local energy maxima along reaction pathways are not easily subject to experimental scrutiny. Computational techniques can be utilized to provide structural and reactive properties of short-lived reactive intermediates.

The characterization of the decomposition pathways of azacubane is being carried out using ab initio molecular orbital (MO) methods to determine the stability of azacubane systems. The optimizations were carried out at 6-31G level of basis set and the first transition state is determined by using the eigenvalue T.S# search technique. It is important to remember that it is difficult to rule out completely the posibility of alternative routes proceeding through other transition states of even lower energy. The major objective in determining the reaction pathway is the location of the stationary points. These may be characterized as a local energy minimum, a local energy maximum and a local energy saddle point. If the stationary point is an energy minimum, it corresponds to a particular equilibirum structure. The local energy saddle point is defined as the stationary point with one, and only one, negative eigenvalue. The reaction profile of 1,5-diazacubane molecule depicts the decomposition pathway via a ring opened transition state. The activation energy barrier for this ring opening pathway is 16.26

kcal/mol. The activation energy barrier for cubane for the same reaction pathway under exactly same conditions is 34 kcal/mol. The frequency calculation on the transition structure indicate a single negative frequency vibration confirming the transition state for this pathway.

As part of a continuing study of the explosive characteristics of strained molecules, MINDO calculations were carried out on triprismane, tetranitrotriprismane and diasterane molecules. Triprismane is an interesting molecule with two different types of C-C bonds. The C-C bonds in the three-sided faces are very much like those in cyclopropane (the bond deviation indices is 0.080 for these C-C bonds), while the C-C bonds in the four-sided faces are quite similar to those in cubane (the bond deviation indices is 0.033 for these C-C bonds). Thus, triprismane can be regarded, in this context, as two cyclopropane rings linked by three cubane-like bonds. This bonding pattern is fully confirmed by the negative electrostatic potentials associated with the C-C bonds in triprismane, which are very much like the corresponding potentials in cyclopropane and in cubane.

A study of the decomposition pathways of cubane is being carried out using ab initio MO method to determine the most feasible ring opening mechanism(s). This study is expanded further to include azacubanes and their ring opening mechanisms. The number of N atoms in these azacubanes will be systematically increased up to 8 N atoms. In a recent article, the stability of N_8 cubane type molecule was predicted on the basis of calculated vibrational frequencies. This study on azacubane decomposition pathways will be able to confirm the stability of the N_8 cubane molecule.

4) DNI-24: A New Insensitive Energetic Material:

In modern ordnance there is a strong requirement for explosives having both good thermal stability, impact and shock insensitivity and better explosive performance. However, these requirements are somewhat mutually exclusive. Those explosives having good thermal stability and impact insensitivity usually exhibit poorer explosive performances and vice versa. A new energetic material, 2,4-dinitroimidazole (DNI-24) was discovered using CAMD techniques. DNI-24 has good thermal stability and impact insensitivity with relatively good performance with respect to HMX. DNI-24 is made by thermal rearrangement of DNI-14 (1,4-dinitroimidazole). The bond dissociation energy (BDE) of a typical $N-NO_2$ bond is about 47 kcal/mol. In the presence of two double bonds as in DNI-14, this $N-NO_2$ bond is expected to weaken further. Therefore, the NO_2 group attached to ring N atom rearranges to its isomer, DNI-24, which is calculated to be about 27 kcal/mol more stable than DNI-14. The energy performance of DNI-24 is significantly better than RDX and TATB. This material is being evaluated at DOE as a possible replacement for TATB.

TASK 2:

SYNTHESIS

Objective 1:

Synthesis of Specific Polynitrocubanes

(Prof. Philip E. Eaton)
(University of Chicago)

SYNTHESIS OF SPECIFIC POLYNITROCUBANES

FINAL PROGRESS REPORT

SUBCONTRACT AGREEMENT NUMBER: GC 1853-89-006
ISSUED BY GEO-CENTERS, INC.

TO THE UNIVERSITY OF CHICAGO
PHILIP E. EATON, PRINCIPAL INVESTIGATOR

COVERING THE PERIOD SEPTEMBER 1, 1989
THROUGH OCTOBER 31, 1992

SUBMITTED:

PHILIP E. EATON

DECEMBER 18, 1992

This is the final technical report reviewing progress over the entire contract period March 1, 19 89 through October 31, 1992 under contract GC 1853-89-006 entitled "Synthesis of Specific Polynitro Compounds".

The work under this contract was divided into two major areas:

1. Investigation of substitution reactions on the cubane nucleus.

2. Development of new oxidation methods for the conversion of aminocubanes to nitrocubanes

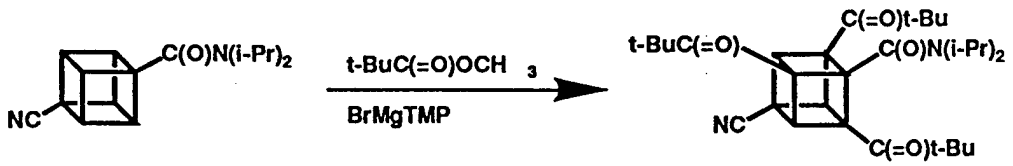
1. Investigation of substitution reactions on the cubane nucleus.

Much of the research in this area was focused on the possibility of developing one-pot, multi-functionalization reactions of activated cubanes so as to simplify the synthesis of 1,3,5-trinitrocubane and 1,3,5,7-tetranitrocubane accomplished here earlier. These original syntheses provided the first samples of these critical polynitro compounds and allowed us to demonstrate that the compounds are stable and come up to expectations vis-à-vis density and energy. Unfortunately, the original syntheses were far too long to be practical.

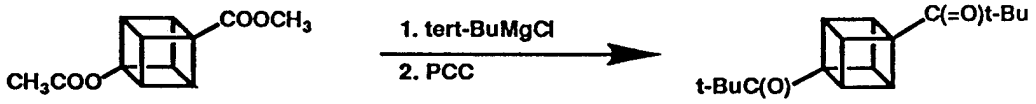
4-Cyano-1-carboxamidocubane was synthesized and its reactions under a variety of basic conditions with a large variety of electrophiles were examined. Most of the early work was done with lithium tetramethylpiperidide as the base in THF as solvent. Electrophiles employed included: carbon dioxide, ethyl formate, methyl chloroformate, phenylcyanate, hindered phenylcyanates, diethylformamide, various carbamates, etc.

Significant success was achieved with the combination lithium tetramethylpiperidide (LiTMP)-tetrahydrofuran-phenylcyanate. Sequential reactions *in a single pot* of 4-cyano-N,N-diisopropylcarboxamidocubane in THF with portions of LiTMP followed by portions of phenylcyanate lead to the introduction of *two* cyano groups onto the cubane frame (in addition to the one already in the starting material). This was the first time two new substituents other than metals had been added successfully in a single pot reaction. The yield of 2,4,6-tricyano-N,N-diisopropylcarboxamidocubane is over 50% by this procedure. This new method saved 7 steps (!) over the original procedure, but it was still tedious.

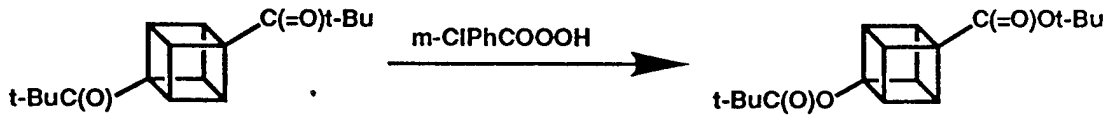
We next examined the reactions of 4-cyano-1-carboxamidocubane under a variety of conditions with methyl pivalate. Most of the work was done with bromomagnesium tetramethylpiperidide as the base with THF as solvent. Very significant success was achieved. Reactions *in a single pot* of 4-cyano-N,N-diisopropylcarboxamidocubane in THF with excess BrMgTMP along with excess methyl pivalate led to the direct introduction of *three tert*-butyl groups onto the cubane frame. This was the first time three new substituents other than metals had been added successfully in a single pot reaction. The yield of 4-cyano-2,6,8-tris(*tert.*-butylcarbonyl)-N,N-diisopropylcarboxamidocubane is over 60% by this procedure.



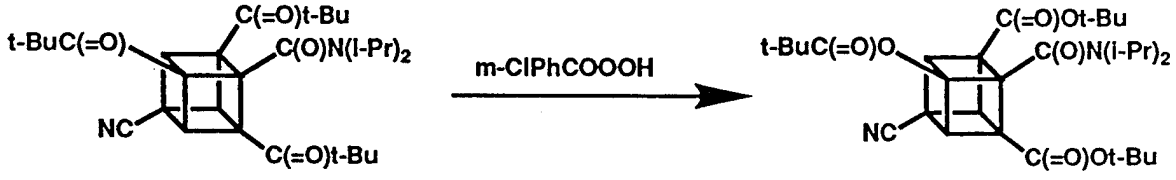
This new method seemed to open the way to a ready and practical synthesis of T_d-tetranitrocubanes provided that a way could be worked out a way to degrade a *tert*-butyl carbonyl group attached to the cubane nucleus to a carboxylic acid. We looked as the possibility of using Baeyer-Villiger oxidations. The first work was done on a model cubane system synthesized specially for the purpose:



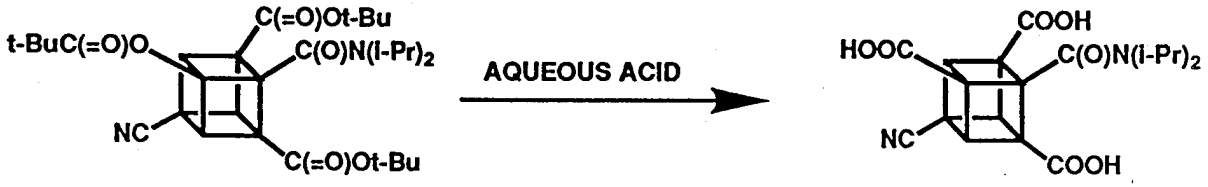
With this material in hand we were able to run many different variants of the Baeyer-Villiger oxidation. We found, *exactly as hoped for*, that there were indeed conditions that brought about oxidation of *tert*-butyl cubyl ketones regiospecifically -- that is, with specific insertion of oxygen in between the carbonyl carbon and the *tert*-butyl group and not between the carbonyl carbon and the *tert*-butyl group . The product of the oxidation with excess *m*-chloroperbenzoic acid in refluxing methylene chloride is specifically the bis(*tert*-butyl ester) of cubane diacid; none of the unuseful cubyl ester of pivalic acid is formed under these correct conditions.



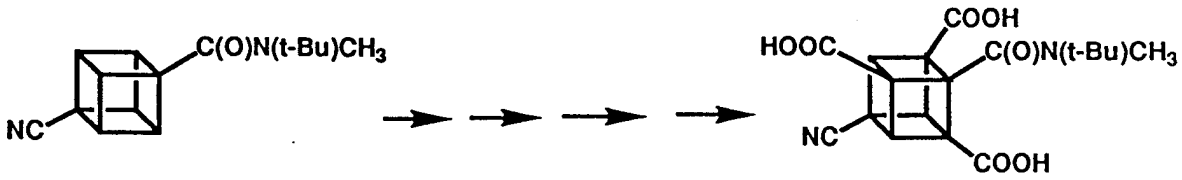
Now we turned to applying this conversion to the product of the multiple direct substitution reaction achieved earlier. We found that treatment of this pentasubstituted cubane with a large excess of *m*-chlorobenzoic acid effected completely regiospecific oxidation of *each and every* *tert*-butyl carbonyl substituent on the cubane frame.



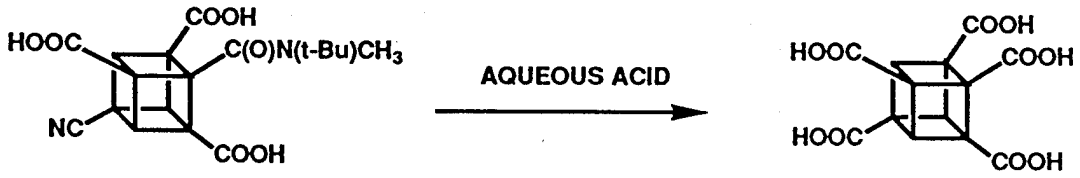
As expected, it proved easy to hydrolyze each of the three *tert*-butyl esters so-formed. This produces a cubane tri-acid in which the acid groups are disposed with C_{3v} symmetry about an axis that passes through the other substituents, the cyano and amide groups. This is exactly what we wanted to continue our work to simplify the original syntheses of C_{3v}-1,3,5-trinitrocubane and T_d-1,3,5,7-tetranitrocubane.



It also provided the possibility to prepare for the first time a cubane pentacarboxylic acid. Success requires the hydrolysis of both the cyano and amide groups. The first was readily accomplished, but the second could not be done in direct fashion. Diisopropylamides are notoriously resistant to cleavage. To circumvent this and to open the way to easy removal of the amide we repeated the entire sequence of reactions now starting with a methyl *tert*-butyl amide derivative of cyanocubane carboxylic acid. Everything worked beautifully.



And, most importantly, now we were able to hydrolyze all the substituents.

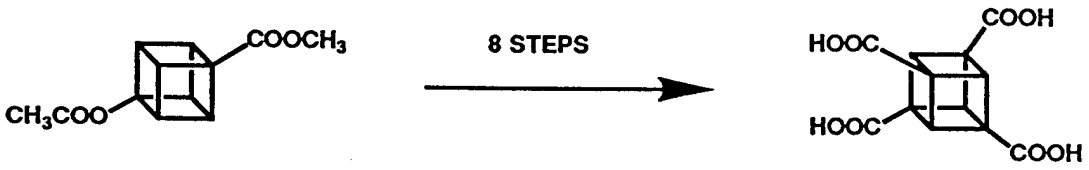


This work was reported in full detail at the successful 1990 U. S. Army ARDEC Workshop on High Energy Materials organized by Geo-Centers, Inc.

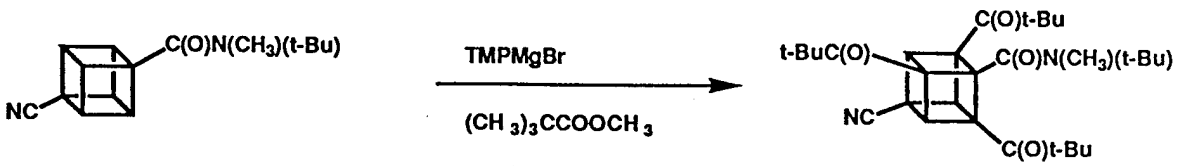
A substantial effort was put into effecting direct decarboxylation of the "surrounded" carboxyl group. So far this has failed.

Putting everything together that we had discovered about direct multiple substitution and multiple functional group transformations on the cubane framework. Doing this provided the practical synthesis of the T_d-1,3,5,7-tetraacid which was the object of whole plan. *The original 26*

step synthesis was shortened to 8 steps.



Enormous amounts of time and manpower were spent refining the actual laboratory manipulations associated with this multistep procedure and in accumulating substantial quantities of the product. The sequence was run repeatedly. (University regulations require that the scale of reactions be limited in light of prudent safety regulations.) The main problem addressed was how to achieve reproducibility in the tris-*tert*-butylcarbonylation of the 4-cyanoamido cubane: *viz.*,



Three leads were developed and followed up in so far as possible:

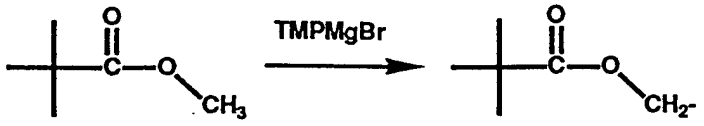
1. Commercially available magnesium bromide was found to be of quite variable quality; certain lots worked far better than others. We encountered similar variability with "home-made" magnesium bromide. Therefore, it was best to prove out each lot of magnesium bromide in small scale runs (20 mg) before using it in larger (1 gram) runs.

2. On numerous occasions the addition of lithium bromide to the reaction mixture enhanced the yield of product. No sense could ever be made of this chemically, for the observation was not always reproducible. Finally, on the idea that the LiBr might be somewhat wet, we considered the effects of small amounts of water on the the reaction.

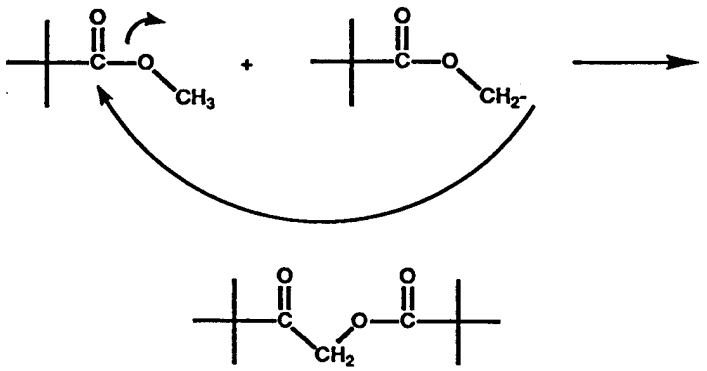
3. The addition of 1-3 equivalents of water to the reaction mixture led on occasion to cleaner reactions mixtures. Nonetheless, the results were frequently not reproducible.

Unfortunately, none of this led anywhere.

We next examined the reactions between the base, TMPMgBr, and the carbonylating agent, methyl pivalate. We discovered, much to our amazement, that the base is strong enough to deprotonate the methyl group of the ester effectively:



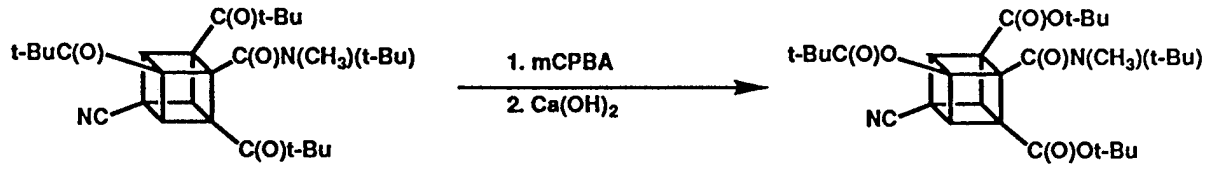
The anion so formed then enters into various aldol reactions: *viz*,



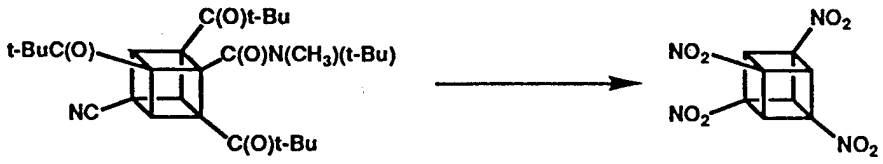
This goes on to give a terrible mess.

We had just begun a search for a better *tert*-butylcarbonylation reagent (looking at the more sterically hindered reagent ethyl pivalate), when A. Bashir-Hashemi of Geo-Centers informed us that pivalic anhydride could be employed successfully as replacement for methyl pivalate in our synthesis scheme for T_d-tetrasubstituted cubanes. In our hands this proved a boon forward but, nonetheless, reproducibility was elusive. Finally, we discovered that the "trick" to obtain reproducible results is to use base prepared directly from ethyl Grignard. (Apparently, there are so many variables in the preparation of the Hauser base from LiTMP that irreproducible results are obtained no matter how careful one is.) We are now able to get 61% yield of the tris-ketone *each time* even on 5 gram scale.

The second critical step in the synthesis of the precursors for T_d-tetranitrocubane is the Baeyer-Villiger oxidation of the tris-ketone to the corresponding tris-ester with *m*-chloroperbenzoic acid. It has always been clear that the chemistry of this step is dandy, but there has been a disagreement amongst investigators as to how to bring it off in the lab. Some have felt that elevated temperature was necessary and did the reaction starting in chloroform and then heating on the steam bath until the solvent was gone. This gets things up to about 95 °C, too hot in our opinion for safe operation on larger scales. However, if the reaction was done at lower temperatures there was substantial difficulty in removing "unreacted" excess peracid and the product *m*-chlorobenzoic acid. We have now worked out a procedure that solves both problems. The reaction is done in refluxing methylene chloride; the pot temperature is about 45 °C and is easily maintained by reflux of the solvent. Scale-up is simple, for temperature control is simple. After the reaction is complete, the precipitated chlorobenzoic acid is filtered and finely powdered calcium hydroxide is added to the mother liquor to react with the excess peracid and benzoic acid still in solution. Filtration removes these by-products quantitatively as the calcium salts. Evaporation gives the desired tris-ester pure and in 95+% yield!



With the crucial problems of the early stages of the T_d synthesis finally resolved, we were to embark on a crash program to obtain sufficient T_d-tetranitrocubane from it for the necessary "frontier" research critical to ARDEC's, Geo-Centers' and our research.



However, with the discovery by Bashir-Hashemi of a totally new way to the synthesis of the T_d-tetraacid we decided to retain the 70 grams of tris-ketone for future work on pentasubstituted cubanes.

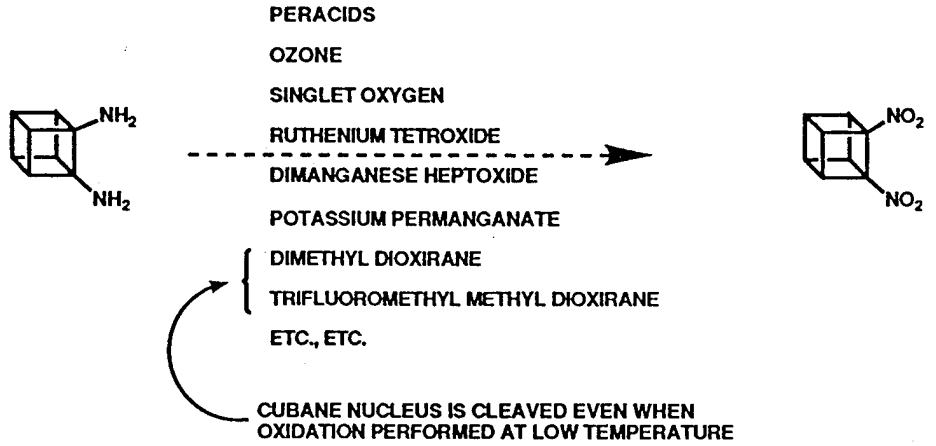
2. Development of new oxidation methods for the conversion of aminocubanes to nitrocubanes

We investigated in depth the preparation of 1,2-disubstituted cubanes with particular reference to cubanes containing two adjacent nitrogen functionalities. The purpose of this work was 1) to improve the preparation of these compounds with particular reference to safety and 2) to continue the search for a way to prepare vicinal dinitrocubanes by oxidation of potential precursors. The matter of safety comes up importantly in the conversion of cubane acids to cubane amines by way of cubyl acyl azides. These cubane acyl azide compounds are shock sensitive when crystalline and very dangerous explosives. Thus, we sought a method which would proceed without ever having a cubyl acyl azide present at a concentration high enough to permit crystallization.

In the early work the azides were made by reaction of the cubane acid chlorides with trimethylsilylazide neat so as to promote rapid reaction at room temperature. (The reaction was run at this temperature as at higher temperature rearrangement of the azide to the corresponding isocyanate occurs (desirable), but the isocyanate so formed reacts with trimethylsilylazide present in excess and with the trimethylsilylchloride produced in the original reaction (undesirable).) Subsequently, the excess silylazide and the silylchloride are removed, the reaction mixture is diluted and heated to reflux, whereupon rearrangement to the desired isocyanate occurs in the absence of interfering reactants. This procedure ordinarily gives excellent yields, but unfortunately it permits crystallization of the intermediate azide and the hazards thereof. We have now found that

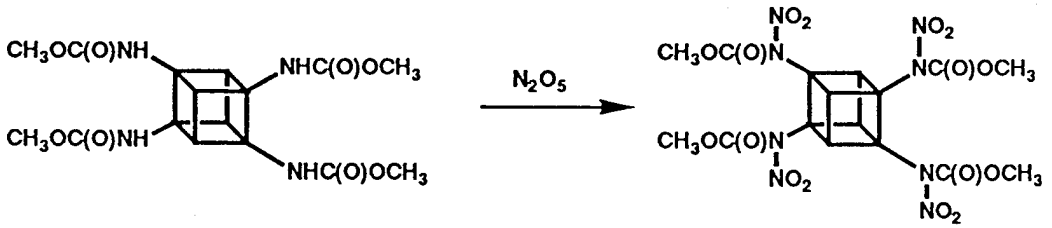
almost as good conversions can be obtained by diluting the original mixture somewhat and running the reaction at reflux from the beginning. In this way the acyl azide is rearranged *immediately upon formation* and, as there is no concentration build-up, it cannot crystallize.

The fundamental problem in the synthesis of vicinal dinitrocubanes by oxidation of vicinal diamines is the ring opening of intermediates by a push-pull mechanism. Repeated attempts made during this project period to void this difficulty have been unsuccessful, even when low temperature techniques were applied to dioxirane oxidation processes.



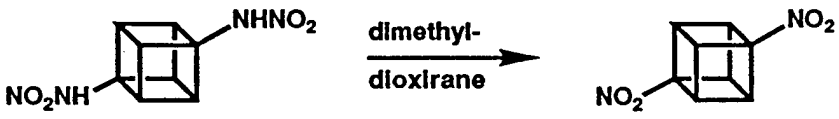
We believe that if we could find a new, non-electron rich source for nitrocubanes we could surmount the problem. At lot of effort was put previously into the oxidation of isocyanatocubanes, but this was completely unsuccessful; no oxidation occurs at all -- the isocyanate group is too "non-electron rich".

Following up on a lead generated at Thiokol Corp. we examined the N-nitration of the tetra-methylcarbamate of cubane-1,2,4,7-tetramine using dinitrogen pentoxide (generated from ozonation of dinitrogen tetroxide) as the nitrating agent.

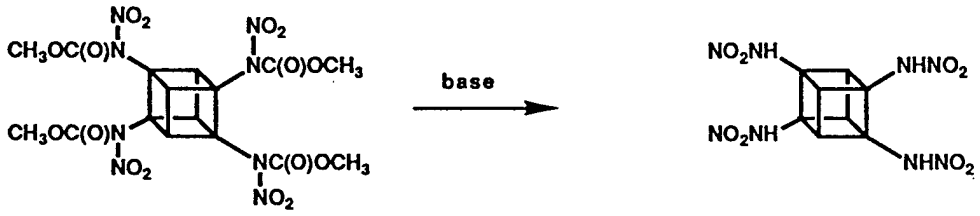


X-ray analysis by Gilardi at ONR Laboratory in Washington confirmed the structure of the product first isolated by Rod Willer & Al Stern at Thiokol. In collaboration with Willer and Stern we confirmed the formation of the product, demonstrated a somewhat higher yield, and provided a better isolation procedure. We developed a low temperature NMR technique for following the nitration.

When we applied this sort of chemistry to the carbamate of 1,4-diaminocubane we succeeded in the preparation of the bis-nitraminocarbamate. Hydrolysis gives the bis-nitramine in good yield. We discovered that the relatively electron poor N-nitroamines of cubyl amines can be oxidized directly to nitrocubanes. This is the first new source of nitrocubanes.



This reaction is easily done and proceeds in excellent yield. The key question now is "Will it apply to the oxidation of the 1,2,4,7-tetranitramino compound?". We have started an examination of the hydrolysis of cubane 1,2,4,7-tetra-N-nitrocarbamate to the corresponding tetra-N-nitramine and its oxidation.



TASK 3:

MOLECULAR PHYSICAL AND CHEMICAL STUDIES

Objective 1:

New Methods of Synthesis of
1,3,3-Trinitroazetidine (TNAZ)

(Prof. Harold Shechter)
(Ohio State University)

T · H · E
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STATE
UNIVERSITY

Research Foundation

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Columbus, OH 43210-1063

TECHNICAL REPORT

"New Methods of Synthesis of 1, 3, 3-Trinitroazetidine (TNAZ)"

Prime Contract DAAA21-89-C-001V
Subcontract Number GC-1853-91-013

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New Methods of Synthesis of 1,3,3-Trinitroazetidine (TNAZ)

Harold Shechter

Department of Chemistry, The Ohio State University

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Abstract

Study is being made of practical syntheses of 1,3,3-trinitroazetidine (TNAZ) and its 1-substituted-3-azetidine precursors by (1) reactions of aminonucleophiles with 2-nitroallyl reagents, (2) preparation and elaboration of 1-substituted-3-azetidinone and its derivatives, and (3) consecutive ring-opening and cyclizative-displacements of epichlorohydrin with N,N-dimetallosulfonamide reagents.

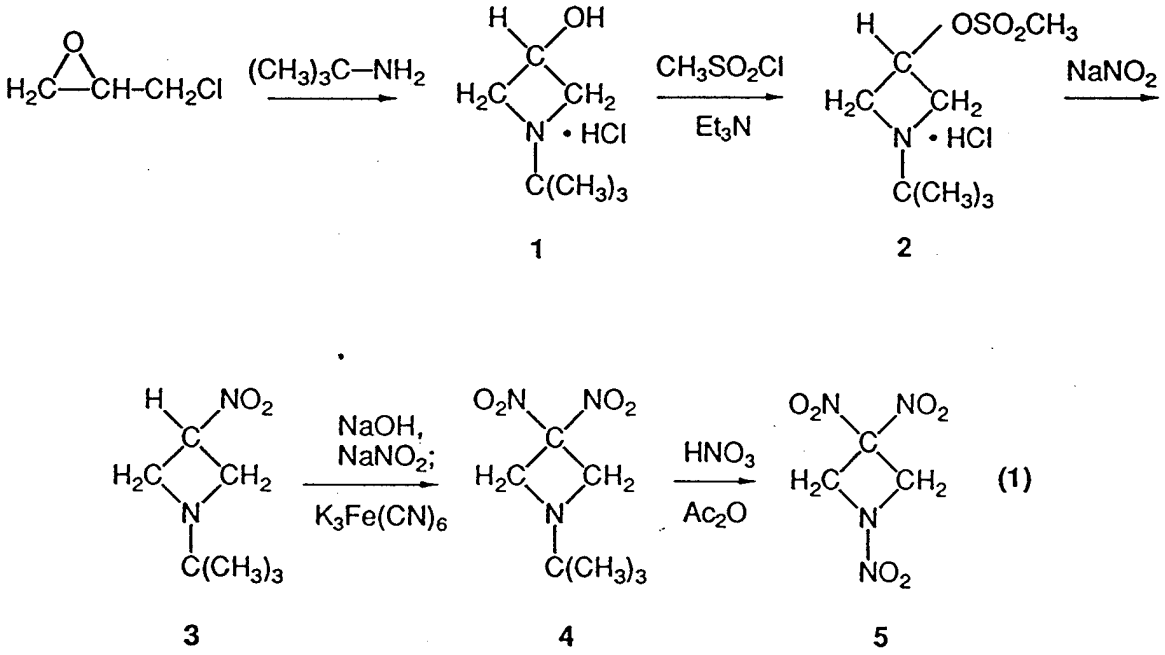
New Methods of Synthesis of 1,3,3-Trinitroazetidine (TNAZ)

Harold Shechter

Department of Chemistry, The Ohio State University

Columbus, Ohio 43210

1,3,3-Trinitroazetidine (TNAZ, 5) is a powerful strained-ring explosive of military interest. TNAZ (5) is presently prepared (Eq 1) by: (1) reaction of tert-butylamine and epichlorohydrin to give 1-tert-butyl-3-azetidinol hydrochloride (1), (2) conversion of 1 by methanesulfonyl chloride and triethylamine to 1-tert-butyl-3-azetidinyl mesylate hydrochloride (2) and then by sodium nitrite to 1-tert-butyl-3-nitroazetidine (3), (3) oxidative-

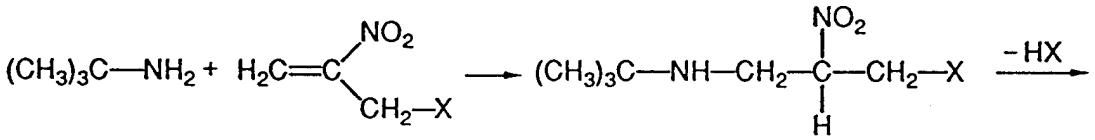


nitration of the sodium salt of 3 by sodium nitrite, sodium persulfate, and potassium ferricyanide to 1-tert-butyl-3,3-dinitroazetidine (4), and (4) nitrolysis of 4 with 98% nitric acid in acetic anhydride.[1] The present method for synthesis of 5 is complicated, inefficient, and expensive. Study has been

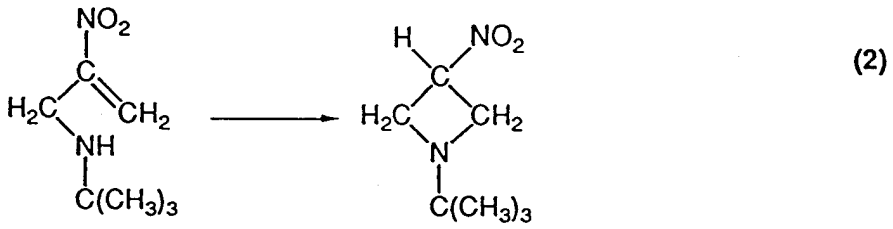
made of new, shorter and more practical methods for preparing intermediates to 5 on Geo-Centers AC-D-RFP-91-1853-011. The new routes to these important intermediates are summarized as follows:

1. Reactions of Tert-butylamine and 2-Nitroallyl Reagents.

Study has been initiated of synthesis of 1-tert-butyl-3-nitroazetidine (3, Eq 2) by reactions of tert-butylamine (6) with 2-nitroallyl reagents [7; X = $OCOCH_3$ and $OCOC(CH_3)_3$].



6 7 8

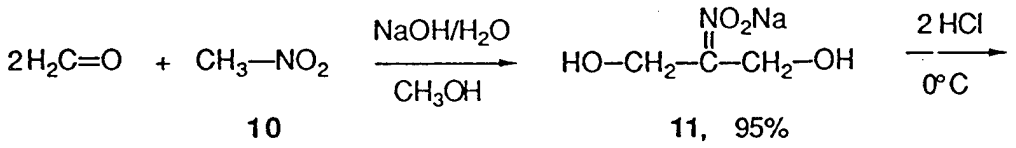


(2)

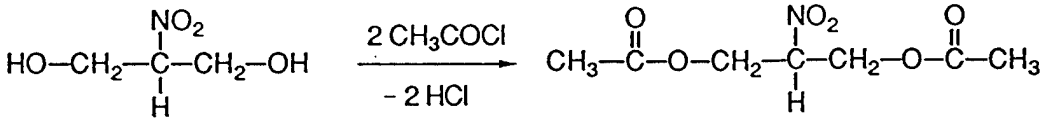
9 3

Effective small-scale methodology for synthesis of 3 has now been developed (Eq 3) involving (1) conversion of nitromethane (10, 1 equiv), formaldehyde (2 equiv) and sodium methoxide (1 equiv) in methanol/water at 25°C to sodium 2-nitronato-1,3-propanediol (11, 95%) which, upon neutralization with hydrochloric acid at 30-40°C and ether extraction, yields 2-nitro-1,3-propanediol (12, >75%), (2) diacetylation of 12 with acetyl chloride (2 equiv) in ether to give 2-nitro-1,3-propanediol diacetate (13, 95%), (3) preparation of 2-nitroallyl acetate[2,3] (14, 50-55%) from 13 and sodium acetate (1.5 equiv) in tert-butyl methyl ether at 40°C, followed by an aqueous wash and vacuum distillation, and (4) addition of tert-butylamine (6, 1.2 equiv) to 14 in tetrahydrofuran at -78°C to form 3-tert-butylamino-2-nitro-1-propyl

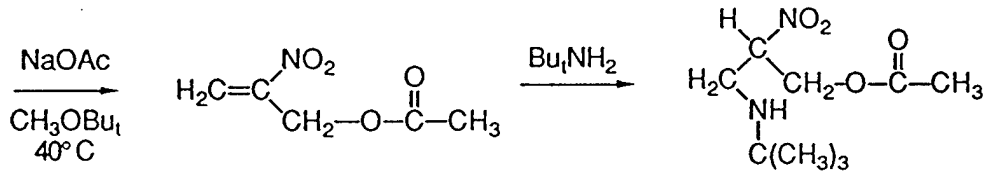
acetate (15) which, upon addition of triethylamine (1.2 equiv) and warming to 0°C, eliminates to 9 which cyclizes to 3 (97%). The present conversion of nitromethane (10) to 3 is 45-50%. The inefficiency in the present sequence arises primarily from incomplete elimination of 13 and handling losses and polymerization of 14 during vacuum distillation. The method summarized shows promise for improvement and for large scale use as now discussed.



10 11, 95%



12, >75% 13, 95%



14, 55% 15

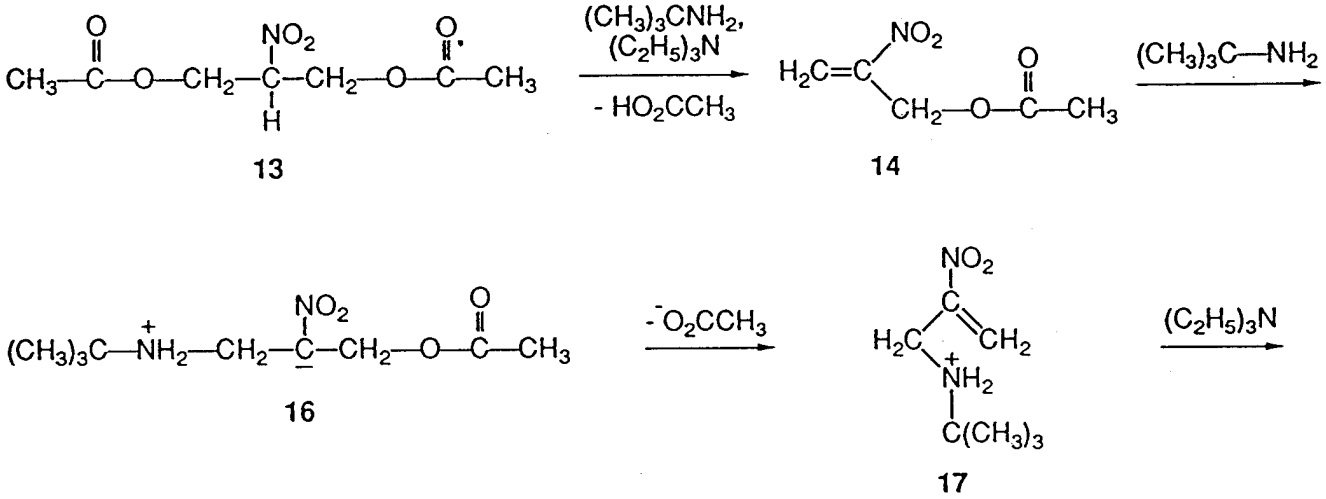
9 3 97% (3)

2-Nitro-1,3-propanediol (12) is preparable in bulk quantities by base-catalyzed condensation of formaldehyde (2 equiv) and nitromethane (10) and by deformylation of 2-hydroxymethyl-2-nitro-1,3-propanediol as derived from

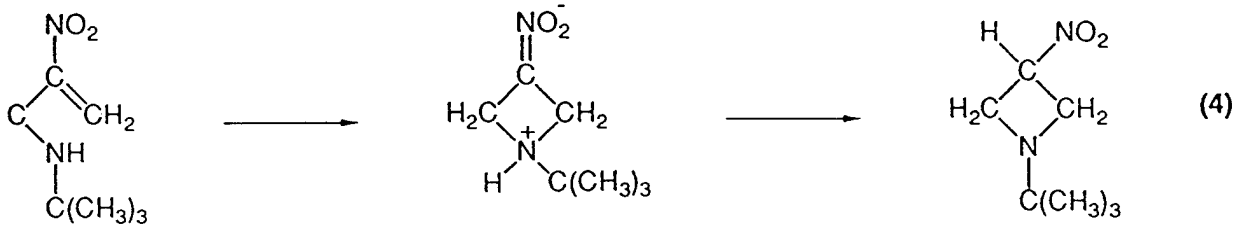
nitromethane (10) and formaldehyde (3 equiv). Diacetylation of 12 by acetic anhydride should be essentially quantitative and cheaper than with acetyl chloride. Further, nitromethane (10) may be convertible by formaldehyde and then acetic anhydride to 13 in a single reactor.

Elimination of 13 to 2-nitroallyl acetate (14) with inexpensive bases [NaO_2CCH_3, Na_2CO_3, $NaHCO_3$, $(C_2H_5)_3N$, and CaO, etc.] may be possible at moderate temperatures in solvents from which acetate salts and acetic acid can be extracted with water. Vacuum distillation and purification of 14 may be avoidable. Addition of tert-butylamine to 14 in ether, subsequent elimination of 15 by triethylamine to 16, and cyclization of 16 to 3 are excellent reactions (Eq 3). Elimination-cyclization of 15 may be improved by use of cheap inorganic bases (Na_2CO_3, $NaHCO_3$, and NaO_2CCH_3), purification of crude 3 should be satisfactory by aqueous extraction, and 3 may then be usable without distillation for oxidative-nitration to 4.

Of particular interest is conversion of 2-nitropropanediol diacetate (13) by tert-butylamine (6, 2 equiv) and triethylamine (1 equiv) in a <u>single unit process</u> (Eq 4) to 1-tert-butyl-3-nitroazetidine (3). <u>Indeed, such an</u>



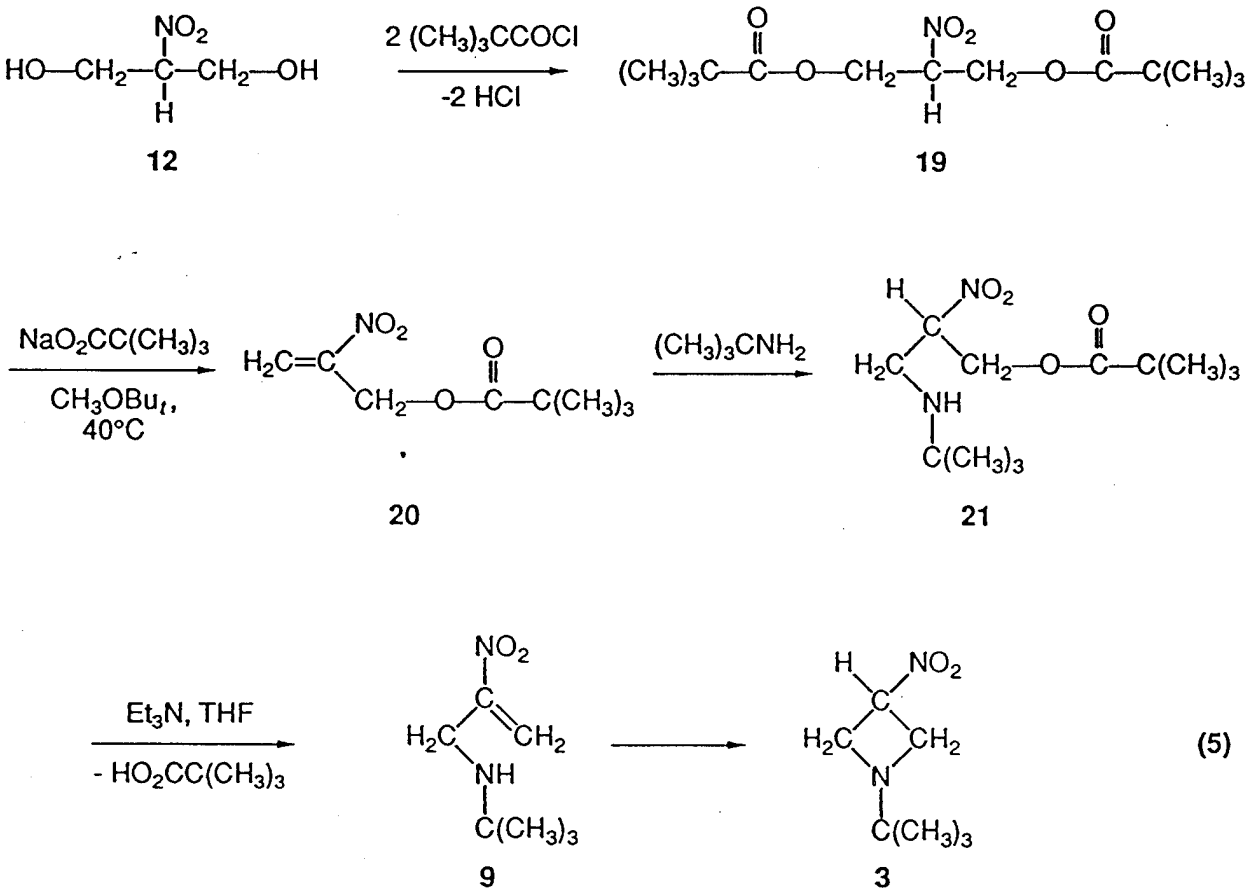
13 14 16 17



9 18 3 (4)

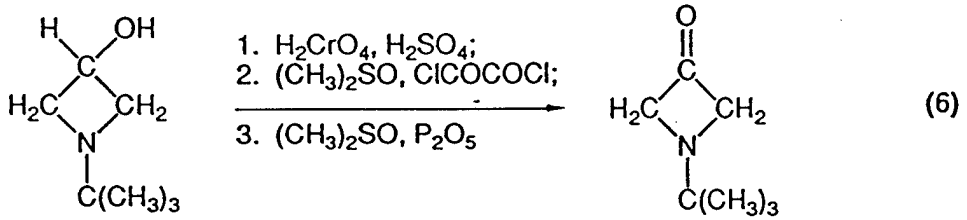
overall conversion of 13 to 3 can be effected (45% yield) at moderate dilutions at -78 to 0°C on small scale. Much development of this system (Eq 4) will be needed for its adaptation to large scale synthesis of 3.

Study is also being made of synthesis of 3 from 2-nitro-1,3-propanediol dipivalate (19) as summarized in Eq 5. Of importance is that 2-nitroallyl pivalate (20)[3], as prepared by elimination of 19 with sodium pivalate and vacuum distillation, reacts well with tert-butylamine (6) and triethylamine to give 1-tert-butyl-3-nitroazetidine (3, > 45%) via 21 and 9. Although very promising, the sequence in Eq 5 has not been further developed as in Eq 4 because of the cost of pivaloyl chloride.



2. Synthesis and Nitrative Transformations of 1-tert-Butyl-3-azetidinone Derivatives.

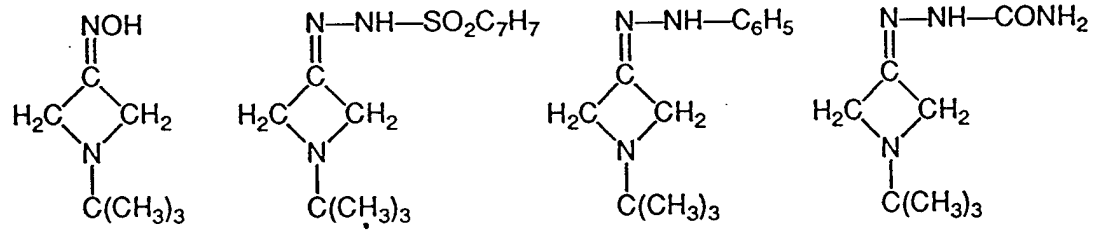
1-tert-Butyl-3-azetidinone (22) is obtained in 60-70% yields on small scale by oxidations of 1-tert-butyl-3-azetidinol (Eq 6, 1) with (1) chromic acid/sulfuric acid, (2) dimethyl sulfoxide/oxalyl chloride in methylene chloride, or (3) dimethyl sulfoxide/phosphorous pentoxide in methylene chloride, respectively. Azetidinone 22 is storable for long periods at 0°C



(6)

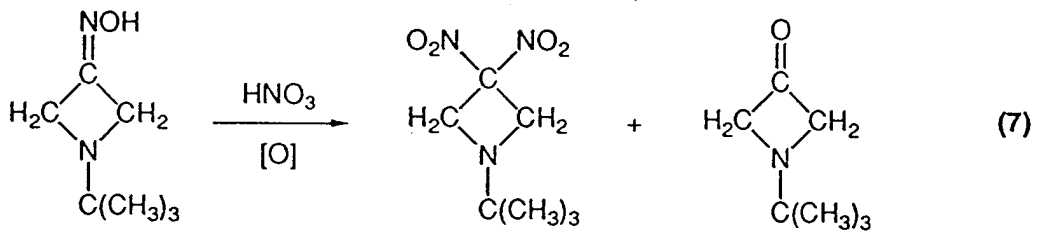
1 22

and is readily converted to its oxime (23), p-toluenesulfonylhydrazone (24), phenylhydrazone (25), and semicarbazone (26). Of further importance is that



23 24 25 26

oxime 23 is oxidatively-nitrated (Eq 7) by 100% nitric acid to 1-tert-butyl-3,3-dinitroazetidine (4, 55%) and 1-tert-butyl-3-azetidinone (22). Study is



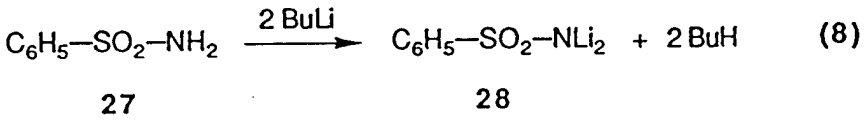
(7)

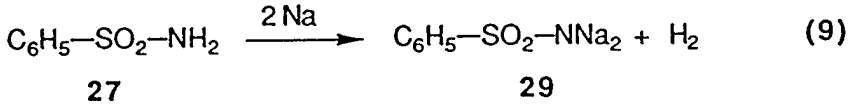
23 4 22

to be made of (1) large scale oxidation of 1 to 22 by $ClS(CH_3)_2Cl$ as generated from chlorine and dimethyl sulfide, (2) catalyzed large scale oxy-nitrations of 23 to 4, (3) nitrative conversions of 23 and of 4 to 1,3,3-dinitroazetidine (5, TNAZ), (4) one-pot conversions of 1 to 23, 4 or 5, and (5) improved nitrative-dealkylative transformation of 4 to 5.

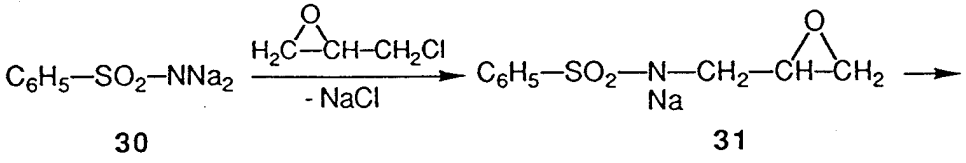
3. Displacements of Epichlorohydrin with N,N-Dimetallosulfonamide Reagents

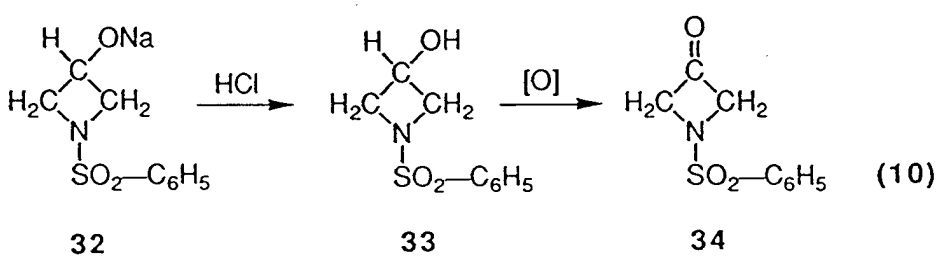
Study is being made of conversions of benzenesulfonamide (27) by butyllithium (Eq 8) and by sodium (Eq 9) to N,N-dilithiobenzenesulfonamide (28) and N,N-disodiobenzenesulfonamide (29), respectively. Dimetallobenzenesulfonamides





28 and 29 are of interest in reactions (as in Eq 10) with epichlorohydrin followed by acidification to give 1-benzenesulfonyl-3-azetidinol (32) which should be oxidizable to 1-benzenesulfonyl-3-azetidinone (33), an established important precursor to 5.[4] Investigations of reactions of epichlorohydrin with 29 and with 28 are as yet incomplete.





References

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2. (a) K. Klager, J. Org. Chem., 20, 650 (1955). (b) K. Klager, Monstshefte für Chemie, 96, 1 (1965).

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4. Private communication by Dr. T. Axenrod, City College of New York, New York and Dr. P. R. Dave, Geo-Centers Inc., Lake Hopatcong, NJ.

Objective 2:

Studies of Novel Oxidative Nitration Methods

(Dr. Walter W. Zajac, Jr.)
(Villanova University)

STUDIES OF NOVEL OXIDATIVE NITRATION METHODS

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Department of Chemistry
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FINAL REPORT

DECEMBER 1992

Contract No. DAAA21-89-C-0012
Subcontract No. GC-1852-089-002
GEO-CENTERS, INC.
7 Wells Ave.
Newton Centre, MA 02159

TABLE OF CONTENTS

I INTRODUCTION

An important aspect of the U. S. Army's need to have available a wide range of energetic materials involves the synthesis of organic compounds. Polynitropolycyclic cage molecules are a class of compounds that have been predicted to have high density and high energy properties. A review by Marchand "Synthesis and Chemistry of Novel Polynitropolycyclic Cage Molecules" (Tetrahedron, 1988, 44, 2377) summarizes the methods employed for introducing nitro groups into cage systems. Even though considerable success has been achieved there still is a need to find inexpensive, environmentally safe and easy to handle oxidants capable of converting amino groups into nitro groups as well as a need to develop methods of synthesis of polycyclic cage molecules containing vicinal dinitro groups. For the success of the Army's ongoing program on the synthesis of high energy density materials it is necessary to find a solution to these problems.

II STATEMENT OF WORK

TASK TITLE:

Oxidation Of Nitrogen Functionalities Into Nitro Groups

TASK OBJECTIVE:

The Use Of New Oxidation Techniques In Nitro Group Synthesis

III SIGNIFICANT ACCOMPLISHMENTS

The tasks set forth in the statement of work have been carried out. The specific accomplishments are summarized in this section.

In order to facilitate the ease in reading this final report, the progress reports submitted during the course of this contract are included as part of the Final Report. The appropriate references to these progress reports are placed at the end of each of the sections for easy referel to the pertinent material.

A. SYNTHETIC METHODOLOGY

1. The use of safe, environmentally compatable, inexpensive and easy to handle hydrogen peroxide equivalents (sodium perborate, sodium percarbonate and percarbamide) in the presence of activators (e.g. N,N,N',N'-tetraacetylethylenediamine) to oxidize primary amines to C-nitroso compounds was demonstrated. In some instances nitro compounds are the products of oxidation of primary amines under these conditions. (August 1989, p 1; December 1989, pp 3-4; October 1990, pp 4-5; 9th Working Group Meeting 1990, p 242, pp 246-249; 10th Working group Meeting 1991, pp 187-190, slides 1-15.)

2. The use of the Paquette procedure (*meta* chloroperoxybenzoic acid, urea, sodium dihydrogen phosphate in refluxing acetonitrile) for the oxidative coupling of bis oximes to polycyclic cage compounds containing vicinal dinitro groups was demonstrated. This method is also effective for the conversion of the oximino group to the nitro group in those compounds where cyclization is precluded. (August 1989, p 4, p 6; December 1989, p 28, p 28, p 30; 8th Working Group Report 1989, p 201, p 203, p 205; 9th Working Group Meeting 1990, pp 242-244, slides, 8, 9, 15, 16, 21, 23, 27, 28; November 1991, M. S. Thesis, G. Speier; 11th Working Group Meeting 1992. slides 5, 6, 7, 11.)

3. The oxidation of secondary amines to nitrones and subsequent ozonolysis of nitrones to nitro compounds was demonstrated to be a useful method for the indirect conversion of an amine, an amide or an isocyanate into a nitro compound. (May 1989, p 10; August 1989,

p 1; December 1989 pp 4-5, 12, 21; 8th Working Group Report 1989, p 211; 9th Working Group Report 1990, p 242, slide 5; 10th Working Group Report 1991, slide 36.)

4. The succesful and unsuccessful methods for the synthesis of polycyclic cage compounds contining vicinal dinitro groups was reviewed. (11th Working Group Report 1992.)

B. SYNTHESIS OF POLYNITRO POLYCYCLIC CAGE COMPOUNDS.

1. Three new polynitronoradamantanes (3,7,9-trinitro-, 3,7,9,9-tetranitro- and 2,2,6,6-tetranitro) were synthesized and the crystal densities and the thermal stabilities (by differential scanning calorimetry) were determined. Except for 2,2,6,6-tetranitro-noradamantane, the other two nitronoradamantanes have a pair of vicinal nitro groups. (August 1989, pp 4-6; December 1989, pp 26-34; 8th Working Group Report 1989, pp 200-201, 204-205; October 1990, p 6, pp 67-85; 9th Working Group Report 1990, p 243, pp 253-264; 10th Working Group Meeting 1991, pp 192-193, slides 27-31; November 1991, pp 1-2, pp 4-8; 11th Working Group Meeting 1992, slide 24; U. S. Patent # 1,105,031.)

2. 1,5-Dinitrobicyclo[3.3.0]octane was synthesized and the X-ray structure determined. This compound has the dinitro groups vicinal. (9th Working Group Report 1990, pp 243-244, pp 267-268; November 1991, M. S. Thesis, G. Speier)

3. The bis imine of 2,3-diamino-2,3-dimethylbutane, N,N'-dibenzylidine-2,3-diamino-2,3-dimethylbutane, was oxidatively cyclized to 3-benzoyl-4,4,5,5-tetramethyl-2-phenylimidazoline. Subsequent peroxy acid oxidation of this heterocycle to 2-nitro-3-benzamido-2,3-dimethylbutane was acheived. These observations suggest the potential use of this sequence of reactions for the conversion of vicinal diamino groups ultimately to vicinal dinitro groups in cage compounds. (May 1989, pp 6-9; August 1989, pp 1-4; December 1989, pp 12-25; October 1990, pp 1-3; 8th Working Group Meeting Report 1989, pp 206-210; 10th Working Group Report 1991, pp 190-191, slides 16-26.)

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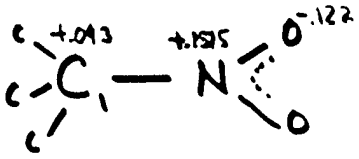
Figure 5

Non-nearest neighbor effects

NA is a nearest neighbor scheme. It can be extended indefinitely by weighting atoms according to the influence of their next nearest neighbors. Example



← usual LL_A charges

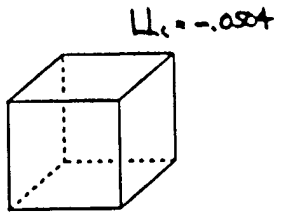
To take account of Oxygen influence on C_1 note that instead of 5 elec. around N there are only 5.0 − .1515 = 4.8485. Therefore N does not offer 1 elec. for sharing but only $\frac{5.0-.1515}{5} = .9699$ elec.

$$\therefore LL_{C_1} = 4 - \left(3 + \frac{2\chi_C}{\chi_C+\chi_H}(.9699)\right) = +.1205$$

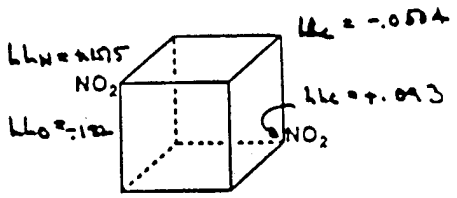
(instead of +.093)

Figure 6

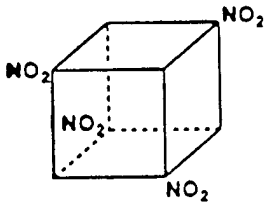
Nitro cubanes



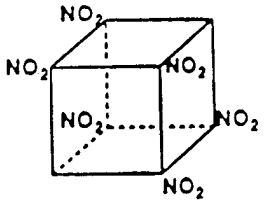
cubane
0



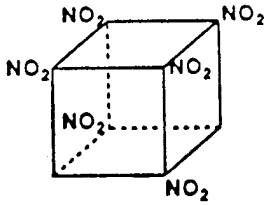
1,4-dinitro cubane
2



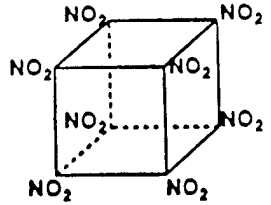
1,3,5,7-tetranitro cubane
4



1,2,3,4,6,7-hexanitro cubane
6(3/3)



1,2,3,5,6,7-hexanitro cubane
6(4/2)



1,2,3,4,5,6,7,8-octanitro cubane
8

Figure 7

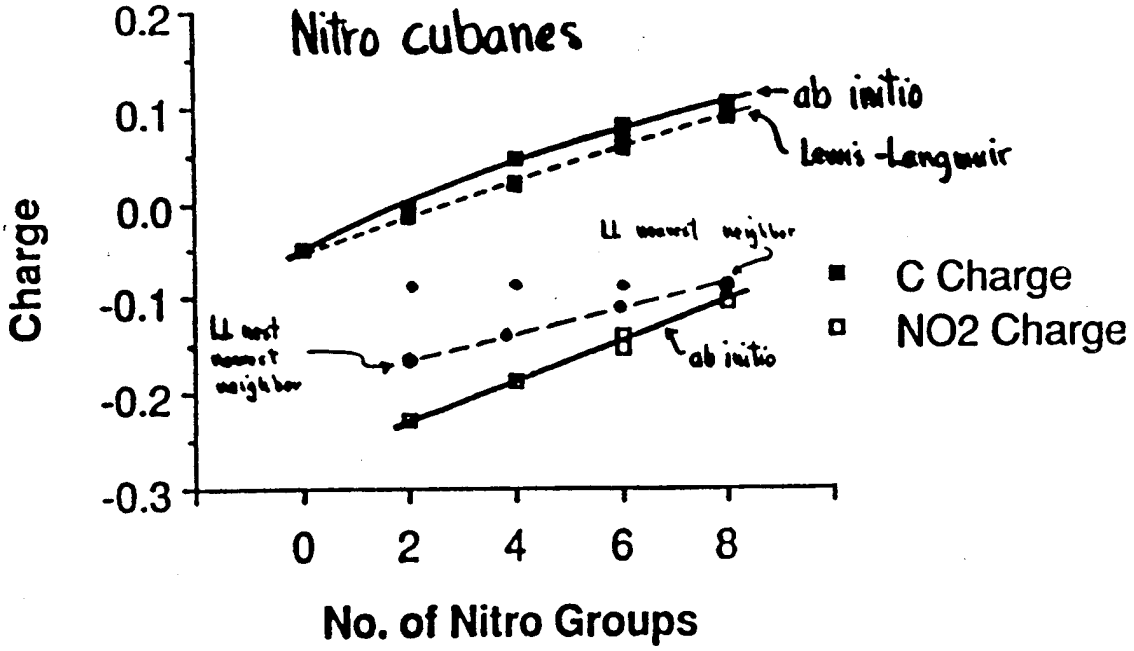
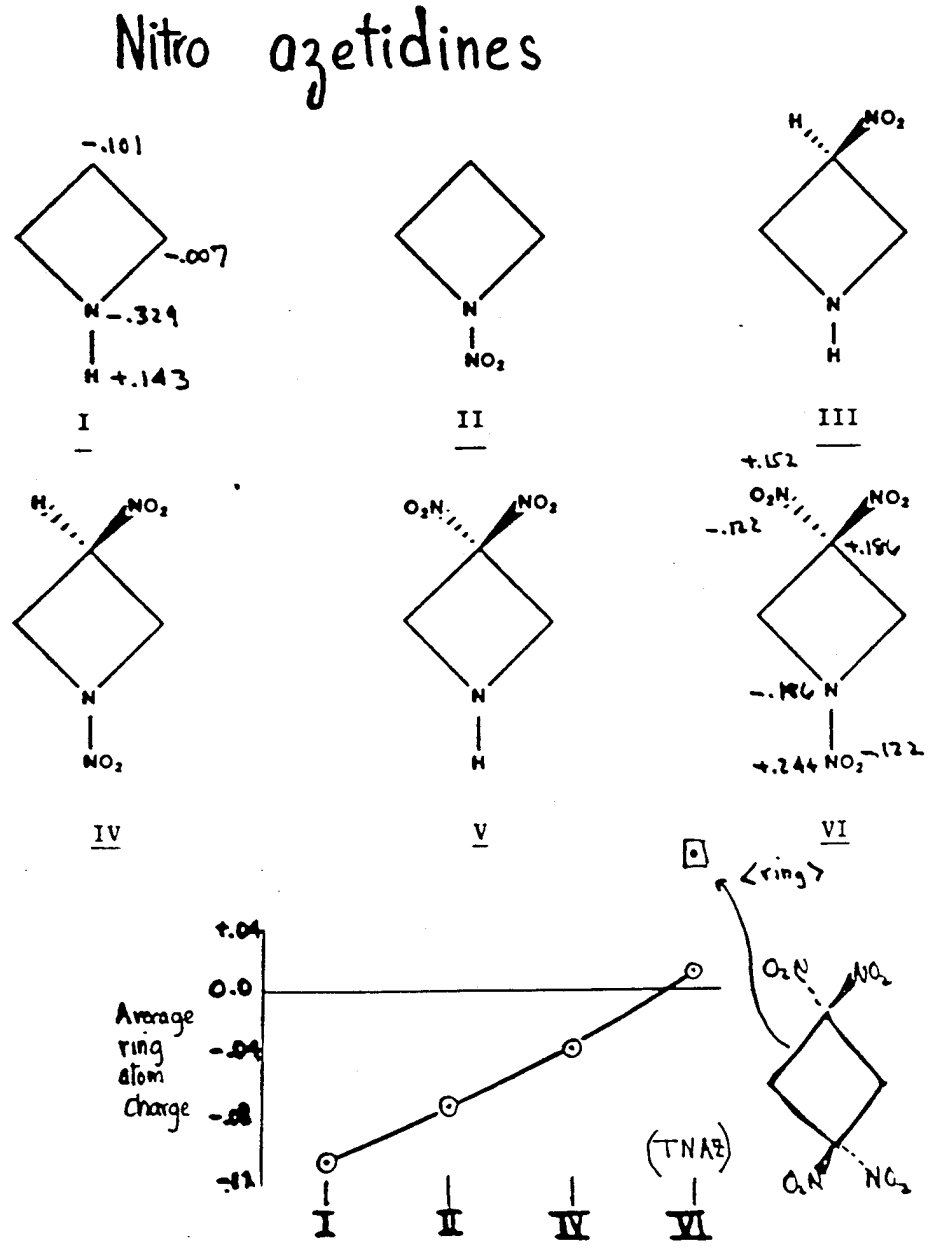


Figure 8



agreement. Now, however, if we use LL_N plus $2LL_O$ to evaluate the charge on $-NO_2$ we get no change as we change the number of nitro-groups as long as we ignore the changes occurring on the carbon atoms (thus, the horizontal series of points on the LL nearest neighbor line). When the carbon charge changes are taken into account the proper trend is established (dashed line Figure 7).

Nitro Azetidines

The nitro-azetidines, particularly trinitroazetidine (TNAZ), have proved to be valuable new explosives and analysis of the ring charges on these species combined with that given above for the nitrocubanes provides the basis for a hypothesis regarding stability under successive nitration. For the azetidines, successive nitration reduces the average number of electron per ring atom (averaging is now over the nitrogen as well as the carbons) producing a less bound, but still stable, TNAZ (Figure 8). We now calculate the average ring atom charge, <ring>, for 1,1,3,3 tetranitro cyclobutane and obtain a value significantly more positive than TNAZ suggesting reduced ring binding relative to TNAZ (Figure 8), but still a stable molecule, as proved several years ago by Kurt Baum, *et al.* of Fluorchem Inc. For various reasons outside of our analysis, 1,1,3,3 tetranitro cyclobutane is not an interesting explosive, but its <ring> is in the same region as we found for tetranitrocubane and these results help connect knowledge about nitrocubanes and the standard RDX and HMX reference systems, since TNAZ may be regarded as a 'four membered ring RDX'. In our analysis of nitrocubane cubane nitration two years ago we concluded that even though the carbon cage is becoming successively less tightly bound as $-NO_2$ groups were added (reflected in the rising <ring> of Figure 7), octanitrocubane was nevertheless predicted to be a thermodynamically stable molecule. On the other hand, <ring> for hexa- or octa-nitro cyclobutanes immediately indicates

that these molecules cannot be thermodynamically stable (even if there were no steric or electrostatic interactions between the nitro-groups).

RDX, HMX, and Wurtzitane

Figure 9, RDX and HMX, show the <ring> = -0.051, to be quite negative, therefore containing quite stable rings. Nielsen's hexnitrohexaazaisowurtzitane (HNW) from NWC, China Lake (CL-20), retains about half this stability and probably accounts for success of this new explosive as a sequel to HMX (Figure 10).

Polycyclic Nitramines

Representative examples are given in Figure 11 and this class also appears to enjoy favorable <ring> values, but their more crowded geometry relative to RDX, HMX and CL-20, suggests more difficulty with steric repulsions and less favorable realizations.

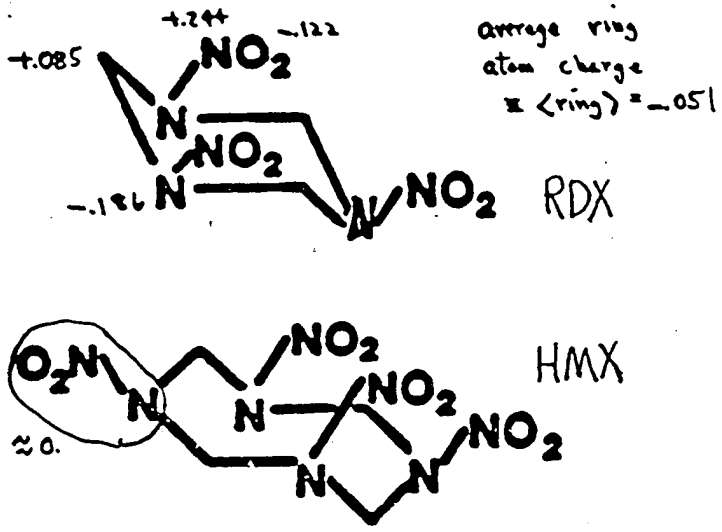
Substituent Group Comparison

The ring atom $-NO_2$ comparison for the three most frequently occurring cases (top of Figure 12) shows the advantage of incorporating N into rings and cages and likewise the pronounced tendency toward destabilization when two nitro-groups are substituted on the same carbon. It also suggests that $-C(NO_2)_3$ will not destabilize rings or cages to which it is attached and may be a useful way to add nitro-groups if the density of the material is not reduced significantly.

Cages and Rings Being Currently Developed

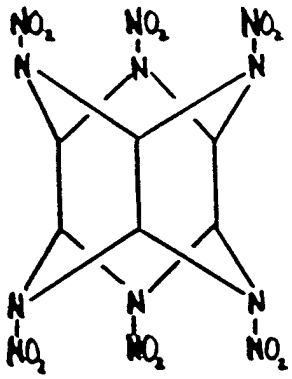
Figures 13 (Zajac), 14 (Paquette) and 15 (NWC, China Lake), are species currently under development. Paquette's peristylane cage appears to be somewhat less destablizied by successive nitration than Zajac's system and thus it is

Figure 9



average ring atom charge = <ring> = -.051

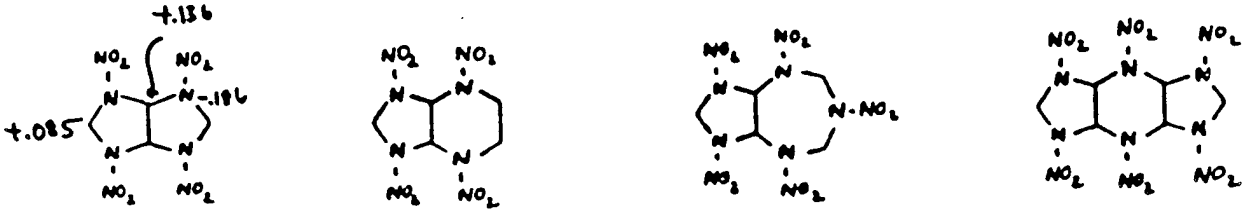
Figure 10



<ring> = -.025

Figure 11

Polycyclic Nitramines



Bicyclo-HMX

<ring> = -.038 <ring> = -.045 <ring> = -.040

Figure 12

Substituent Group Comparison

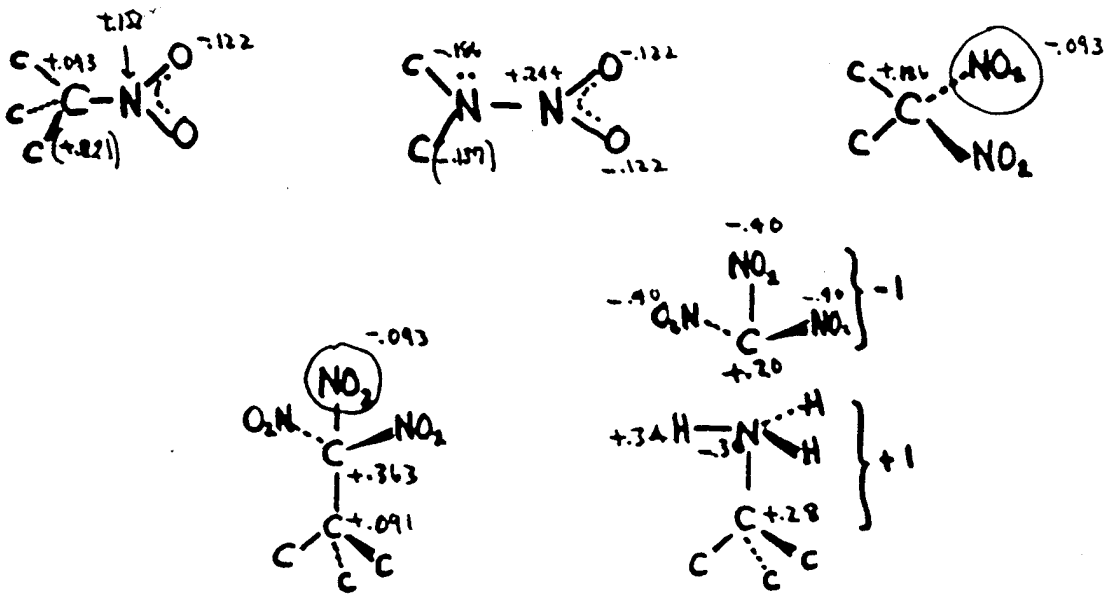
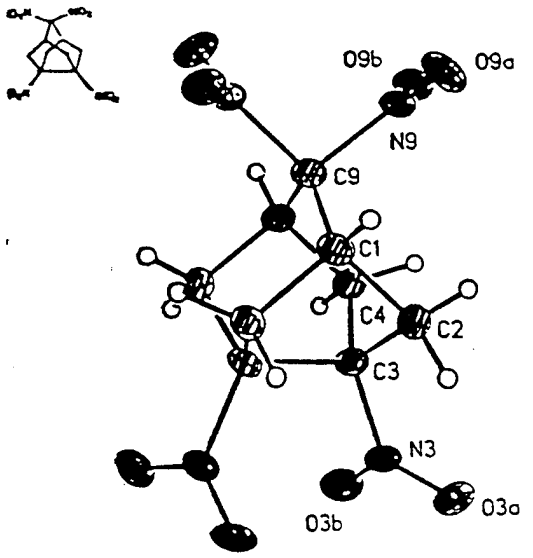


Figure 13



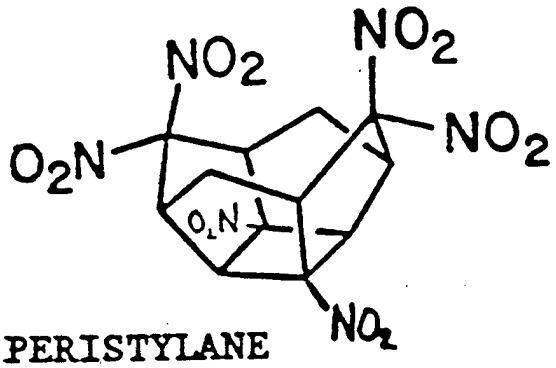
Zajac

4 Hs ⟨ring⟩ = -.078

4 NO_2 ⟨ring⟩ = -.015

Density 1.725 g/cc

Figure 14



PERISTYLANE

1.70 g/cm^3

Paquette

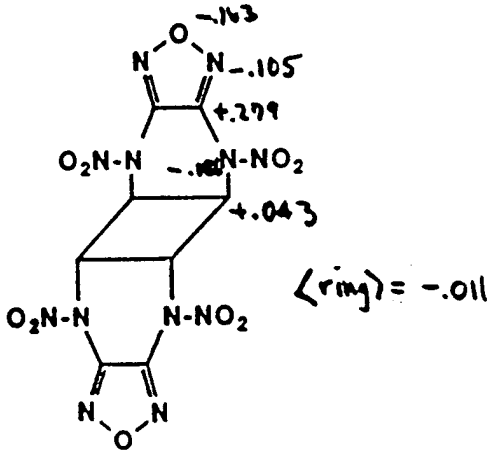
all Hs ⟨ring⟩ = -.067

4 NO_2 ⟨ring⟩ = -.019

5 NO_2 ⟨ring⟩ = -.007

6 NO_2 ⟨ring⟩ = +.008

Figure 15



⟨ring⟩ = -.011

GOAL: TO EXCEED HMX (CL-20)

reasonable to suggest that addition of a sixth $-NO_2$ group might well be realizable. The resultant <ring> is not greater than that of tetranitrocubane, but might provide six nitro-groups with a molecular density not appreciably greater than 1.70 q/cm^3.

Insensitive Explosives

These are of high current interest for many practical considerations and some of those under active development are shown in Figure 16. In all of these molecules there is an appreciable decrease in cage stability as $-NO_2$ groups are substituted for H, especially for Marchand's $C_7H_6(NO_2)_6$, however, none of them appear less stable than tetranitrocubane and therefore all of the types in Figure 16 should be realizable thermodynamically.

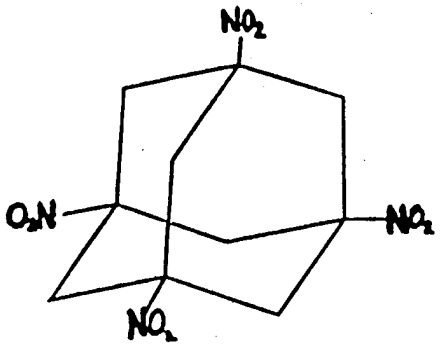
Summary

(1) A trivially simple method of obtaining atomic charges at chemically useful accuracy is presented that is immediately accessible, both computationally and conceptually, to all practicing chemists.

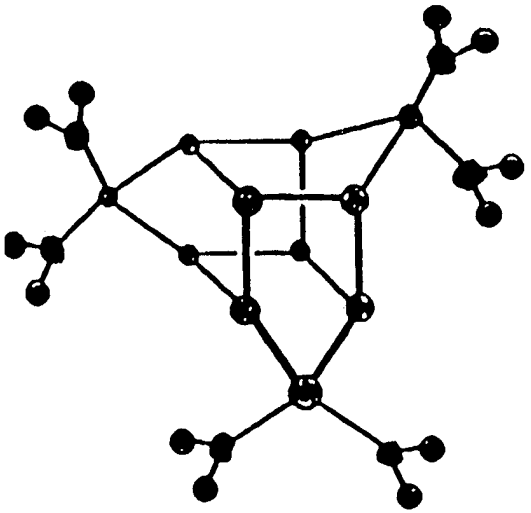
(2) These molecular atomic charges can be employed to deduce bonding and reactivity patterns between diverse classes of molecules.

(3) Results for one type of application, assaying ring and cage stability under successive nitration, has been given in this report for most of the classes of species studied by the Working Group Institute on High Energy Density Materials.

Insensitive Explosives

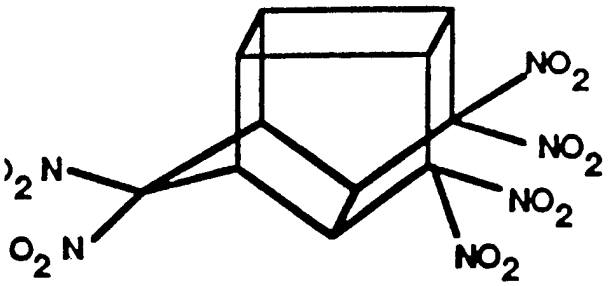


Sollott & Gilbert
adamantane <ring> = -.081
Tetra nitro <ring> = +.007



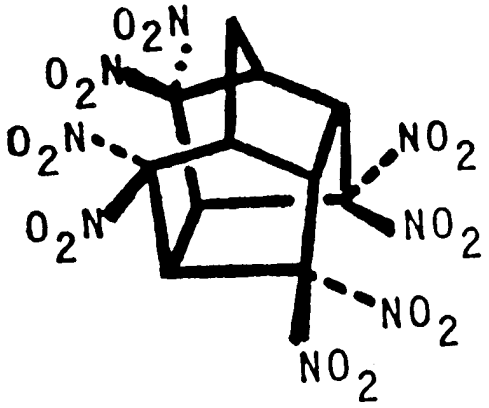
Marchand
6 Hs <ring> = -.064
6 NO2 <ring> = +.014

HEXANITROTRISHOMOCUBANE



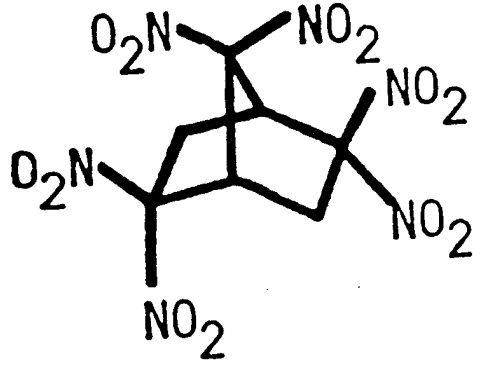
Marchand
6 Hs <ring> = -.064
6 NO2 <ring> = +.014

HEXANITRO PENTACYCLOUNDECANE



Marchand
8 Hs <ring> = -.073
8 NO2 <ring> = +.031

$[C_{11}H_8(NO_2)_8]$



Marchand
6 Hs <ring> = -.085
6 NO2 <ring> = +.023

$[C_7H_6(NO_2)_6]$

TASK 5:

FORMULATIONS AND MANUFACTURING

Objective 1:

Synthesis of Suitable Precursors to New Energetic Polynitropolycyclic Compounds

(Dr. Alan P. Marchand)
(University of North Texas)

Note: Information included in Appendix I is on file at the GEO-CENTERS, INC. office and is available for review.

SYNTHESES OF SUITABLE PRECURSORS TO NEW ENERGETIC POLYNITROPOLYCYCLIC COMPOUNDS

Principal Investigator: Dr. Alan P. Marchand

Postdoctoral Research Associates: Drs. V. R. Gadgil, R. Sharma, and U. R. Zope

Department of Chemistry, University of North Texas, Denton, TX 76203-0068

Contract Number DAAA21-89-C-0012

Reference: GC-1853-89-003

FINAL REPORT

Period Covered: January 7, 1991 through June 30, 1992

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INTRODUCTION

As part of the U. S. Army's Improved Performance on Target (IPOT) program, we have been involved in an intensive effort to synthesize new polynitropolyhedranes. The objective of our work is stated in FIGURE 1; the rationale for studying polynitropolycyclic cage compounds as a new class of energetic materials is presented in FIGURE 2.

Our basic synthetic approach is outlined in the retrosynthetic perspective shown in FIGURE 3. The key features of this approach are as follows:

(i) The basic cage system is constructed first.

(ii) The cage system thereby constructed contains suitable functional groups (e.g., ketone and ester functionalities), each of which can be converted subsequently into nitro groups by using standard literature procedures.

Importantly, such methodology makes it possible to take advantage of standard synthetic techniques; in this manner, several novel polynitropolycyclic systems have been synthesized in several different laboratories.[1,2] A major advantage to this approach is that it avoids the complications potentially attendant with the manipulation of polynitro-containing synthetic intermediates. A further advantage is that NO_2 groups are introduced sequentially. Hence, the effect of increasing the degree of nitro-substitution on various chemical and thermodynamic properties of a given cage system can be assessed in a gradual and orderly fashion. This same philosophy has continued to guide us in performing the studies that are reported herein.[2]

The target molecule, 2,2,5,5,7,7-hexanitronorbornane (HNN, 4) was chosen for several reasons:

(i) The results of calculations performed by Dr. Keerthi Jayasuriya (GEO-CENTERS, Inc., Dover, NJ), shown in the table in FIGURE 4, suggest that 4 may be a powerful explosive. Its calculated explosive performance characteristics appear to be competitive with those of HMX.

(ii) Our research group has considerable experience in the synthesis of substituted cage molecules in general[1,2] and substituted norbornanes in particular.[3]

(iii) Rational approaches to the synthesis of 4 can be modeled conveniently via investigation of the syntheses of 2,2,5,5- and 2,2,7,7-tetranitronorbornanes and also 3,3,5,5-tetranitroquadricyclane (see below).

RESULTS & DISCUSSION

We originally envisioned some potentially serious problems that are likely to be encountered in a rational approach to the synthesis of the target molecule, 4. Inspection of molecular models suggests that there may be considerable steric crowding in this molecule brought about by nonbonded interactions between the exo-2- and exo-5- nitro groups on one hand and the syn- and anti-7- nitro groups, respectively, on the other. Also, the potential for Haller-Bauer cleavage[4] of this strained bicyclic system exists if the route chosen for the synthesis of 4 proceeds via a synthetic intermediate which contains a 1,3-dione moiety. For these reasons, we initiated three model studies wherein the syntheses of 2,2,5,5-tetranitronorbornane (1), 2,2,7,7-tetranitronorbornane (2), and 3,3,5,5-tetranitronortricyclane (3) were undertaken. Of these three studies, the syntheses of 1 and 3 were deemed initially to be most critical, since it would be necessary to address both of the potential problems listed above (i.e., steric crowding and the potential for Haller-Bauer cleavage) when executing the synthesis of each of these compounds.

Model Study 1: Synthesis of 2,2,5,5-Tetranitronorbornane (1; Dr. Rajiv Sharma). A straightforward synthesis of 1 is presented in FIGURE 5. We have utilized the basic approach, i.e., multistep conversion of an oxime functionality to geminal dinitro groups, on several past occasions.[2]

The X-ray crystal structure of 1 is shown in FIGURE 6; the density of 1, calculated from the X-ray derived unit cell parameters, is 1.710 $g\text{-}cm^{-1}$. A DSC thermogram of 1 is shown in FIGURE 7. Proton (300 MHz) and carbon-13 (75 MHz) NMR spectra of 1 are presented in FIGURES 8 and 9, respectively.

Model Study 2: Synthesis of 2,2,7,7-Tetranitronorbornane (2; Dr. Rajiv Sharma). Our successful synthesis of **2** is shown in FIGURE 10. The approach shown therein was chosen to avoid the intermediacy of norbornane-2,7-dione, for which Haller-Bauer cleavage under either acidic or basic conditions was considered to be a potential problem. Indeed, when a solution of 7,7-dimethoxynorbornan-2-one (one of the intermediates in our synthesis of **2**) in 10% aqueous sulfuric acid-THF was refluxed for 7 h, Haller-Bauer cleavage indeed occured concomitant with hydrolysis of the ketal group, thereby affording 3-oxocyclohexanecarboxylic acid. None of the desired product of simple ketal hydrolysis, i.e., norbornane-2,7-dione, could be isolated from this reaction.

At the time of preparation of this long abstract, we have been unable (despite several attempts) to prepare a suitable single crystal of **2** for X-ray structural analysis. A DSC thermogram of **2** is shown in FIGURE 11.

Proton (300 MHz) and carbon-13 (75 MHz) NMR spectra of **2** are presented in FIGURES 12 and 13, respectively. Of particular interest is the fact that the C(1) bridgehead proton in **2** is unusually highly deshielded (δ4.4). Similar deshielding of the C(3) bridghead proton in 2,2,4,4-tetranitroadamantane (δ4.7) was noted by Dave and coworkers (FIGURE 14).[5] This unsual deshielding might simply reflect cumulative magnetic anisotropic effects of the adjacent nitro groups in both of these compounds. Alternatively, deshielding of the the bridghead proton in these compounds that is flanked by four NO_2 groups might reflect the cumulative electron withdrawing inductive effect of the nitro substituents.

If indeed electronic (rather than magnetic) effects are responsible for this unusual deshielding phenomenon, then it is possible that electron density in such bridghead C-H bonds might be unusually low, reflecting unusually high acidity of these C-H bonds (and, consequently, also reflecting unusually high stability of the anion derived via heterolysis of such C-H bonds!). In view of this latter possibility, it seems worthwhile to attempt to generate the corresponding anion at C(1) in 2 in the hope that it might prove possible to capture this species by an electrophile, e.g., nitronium ion (see FIGURE 15). Metalation at C(1) might be "directed" by the adjacent nitro groups in 2, in much the same way that Eaton and coworkers have successfully utilized amides of secondary amines to direct "ortho-lithiation" in appropriately substituted cubanes.[6] A model for the transiton state of nitro-directed bridgehead lithiation of 2 is shown in FIGURE 16.

A manuscript which describes our syntheses of 2,2,5,5- and 2,2,7,7-tetranitronorbornanes has been prepared. We plan to submit this manuscript to the Journal of Organic Chemistry for publication. A copy of the manuscript is appended to this report (APPENDIX I).

Model Study 3: Progress Toward the Synthesis of 3,3,5,5-Tetranitronortricyclane (3; Dr. V. R. Gadgil). Compound 3 is of particular interest, as it embodies similar elements of steric crowding due to nonbonded interactions among NO_2 groups that motivated us to synthesize 2,2,7,7-tetranitronorbornane (2). In addition, the inclusion of a cyclopropane ring in the nortricyclane σ-framework of 3 renders this compound more highly strained than either 1 or 2.

Initially, we pursued three parallel approaches in an attempt to generate suitable precursors to **3** [see Paths (a), (b), and (c) in FIGURE 17]. Of the three synthetic pathways that are shown in this figure, Path (b) appears to be the most tractable. We recently completed the synthesis of 5,5-dinitronortricylane-anti-3-carboxylic acid. The proton noise decoupled ^{13}C NMR spectrum of the corresponding ethyl ester, which displays the expected ten resonances, is shown in FIGURE 18. At present, we are attempting to introduce a carbonyl functionality at C(3) by using the strategy shown in Path (b), FIGURE 17. We recently utilized a similar approach to convert a bridging $CHCO_2H$ group into a C=O functionality as part of our successful synthesis of homopentaprismane-8-carboxylic acid (FIGURE 19).[7]

Progress Toward the Synthesis of 2,2,5,5,7,7-Hexanitronorbornane (4; Dr. Umesh R. Zope). One approach to target molecule **4** is summarized in FIGURE 20. Thus far, we have successfully synthesized norbornane-2,5-dione-7-carboxylic acid, a key intermediate in our projected synthesis of **4**. NMR spectra of the corresponding methyl ester have been obtained; pertinent NMR spectra are shown in FIGURES 21, 22, and 23.

The method shown in FIGURE 20 involves synthesis of an appropriate 7-substituted-2,2,5,5-tetranitronorbornane (i.e., NO_2 groups are introduced into the norbornane ring "from the bottom up"), An alternative approach for synthesizing **4**, shown in FIGURE 24, involves the preparation of 7,7-dinitronorbornane-2,5-dione (i.e., NO_2 groups are introduced "from the top down"). Three key intermediates in the reaction sequence which leads to this dinitronorbornanes dione have been synthesized; relevant carbon-13 NMR spectra are shown in FIGURES 25, 26, 27, and 28.

Acknowledgments are expressed in FIGURE 29.

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7. Marchand, A. P.; Deshpande, M. N. J. Org. Chem. 1989, 54, 3226.

SYNTHESIS OF NEW POLYNITROPOLYCYCLIC COMPOUNDS

OBJECTIVE: To synthesize new polynitropolycyclic "cage" compounds. These compounds are expected to possess high densities and to constitute a new class of high energy explosives and propellants.

Figure 1

FIGURE 2

POLYNITROPOLYCYCLIC CAGE COMPOUNDS: A NEW CLASS OF ENERGETIC MATERIALS

1. COMPACT STRUCTURES ⟹ HIGH DENSITIES

2. STRAIN ENERGY PRESENT IN CAGE SYSTEMS:
   WILL THIS FACTOR CONTRIBUTE SIGNIFICANTLY TO OVERALL EXPLOSIVE PERFORMANCE?

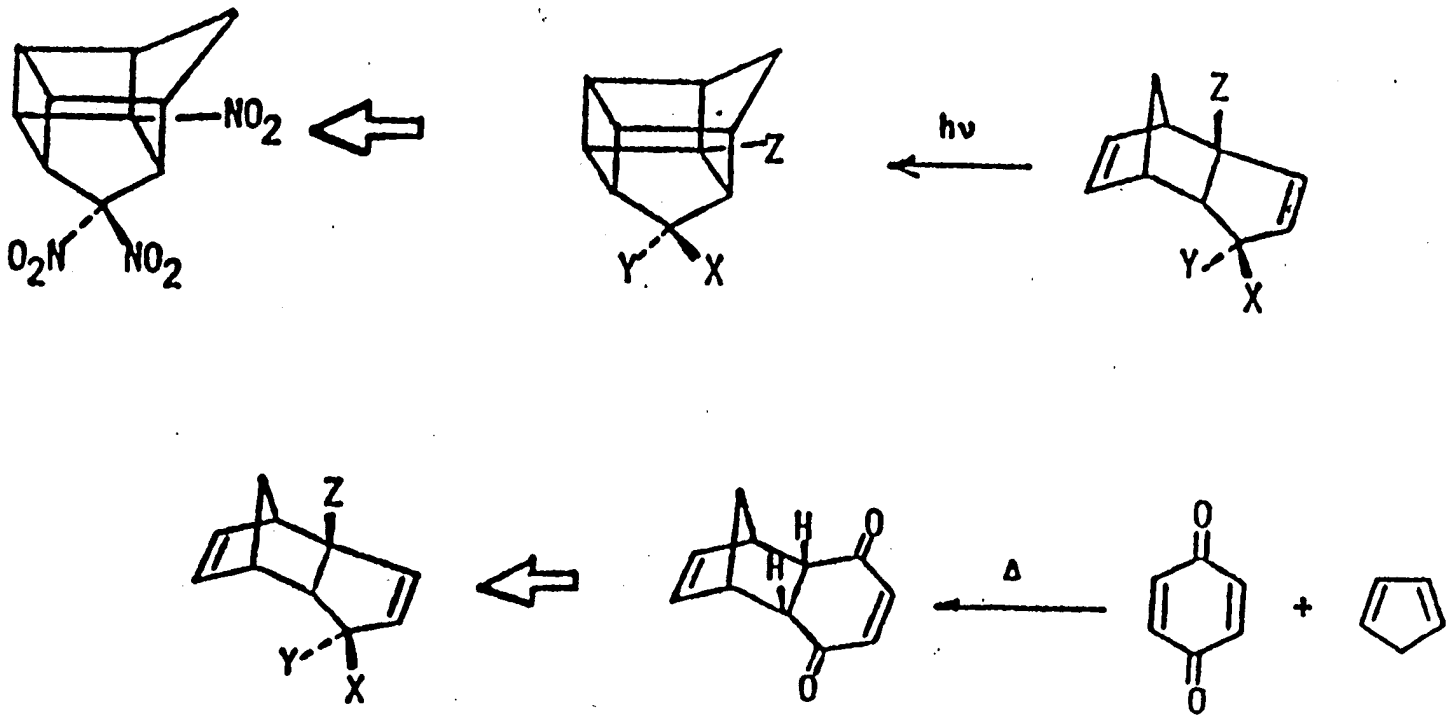
3. INCREASE DEGREE OF NO_2-SUBSTITUTION IN A SYSTEMATIC FASHION:
   GAUGE CUMULATIVE EFFECTS OF INCREASING NO_2-SUBSTITUTION UPON PHYSICAL AND CHEMICAL PROPERTIES OF THE CAGE SYSTEM

4. PROVIDE EXPERIMENTAL TEST/VERIFICATION OF PREDICTIONS BASED UPON THE RESULTS OF THEORETICAL CALCULATIONS:
   (DENSITY, HEAT OF FORMATION, DETONATION PRESSURE, DETONATION VELOCITY, ETC.)

5. RECENT EXPERIMENTAL EVIDENCE SUGGESTS THAT POLYNITROPOLYCYCLIC CAGE MOLECULES COMPRISE A NEW CLASS OF <u>POWERFUL</u> AND <u>RELATIVELY INSENSITIVE</u> EXPLOSIVES

FIGURE 3

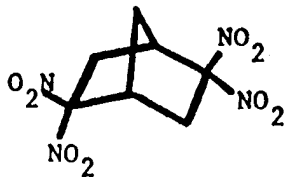
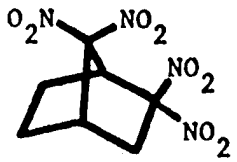
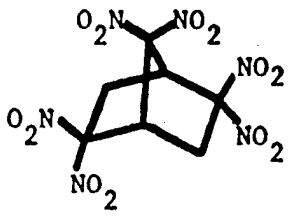
RETROSYNTHETIC PERSPECTIVE:



(X,Y = CARBONYL OXYGEN;
Z = CO_2Me)

REFERENCE: A. P. MARCHAND AND S. C. SURI, J. ORG. CHEM., 49, 2041 (1984).

Table I. Thermodynamic Calculations for Polynitronorbornanes.

COMPOUND	Density ($g\text{-}cm^{-3}$)	ΔH_f (kcal/mol)	P_{CJ} (kBar)	D (m/sec)
	1.80 (1.71, X-ray)	+32	308	8137
	1.81	+35	330	8174
	1.90	+72	410	8914

Calculations performed by Dr. Keerthi Jayasuriya, GEO-CENTERS, Inc., Picatinny Arsenal, NJ.
(For comparison: HMX: P_{CJ} = 389 kBar; D = 9130 m/sec)

Figure 4

Synthesis of 2,2,5,5-Tetranitronorbornane

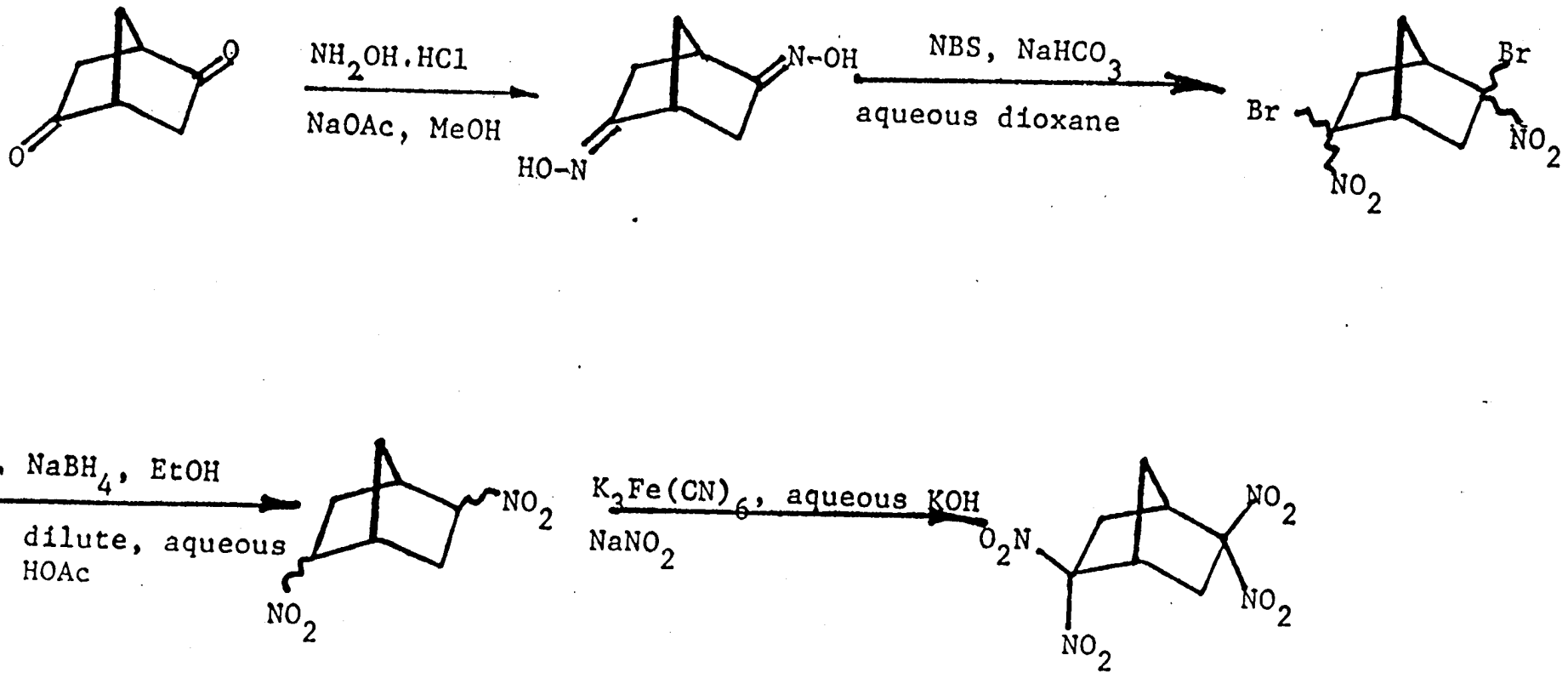
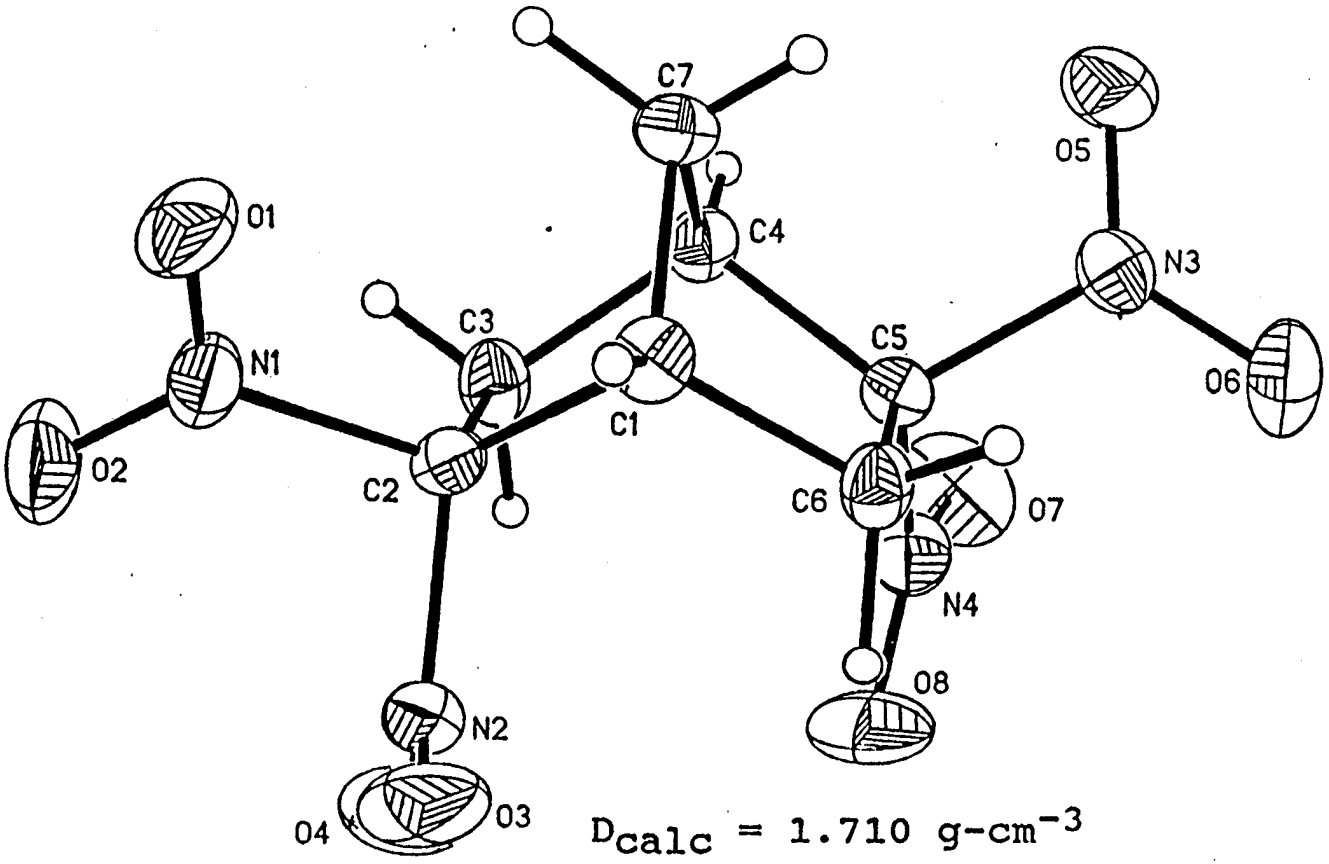


Figure 5

Figure 6

X-Ray Crystal Structure of 2,2,5,5-Tetranitronorbornane



D_{calc} = 1.710 g-cm^{-3}

Synthesis: Dr. Rajiv Sharma
University of North Texas

X-ray Crystallography: Professor William H. Watson
Dr. Ram P. Kashyap
Texas Christian University

DSC OF 2,2,5,5-TETRANITRONORBORNANE

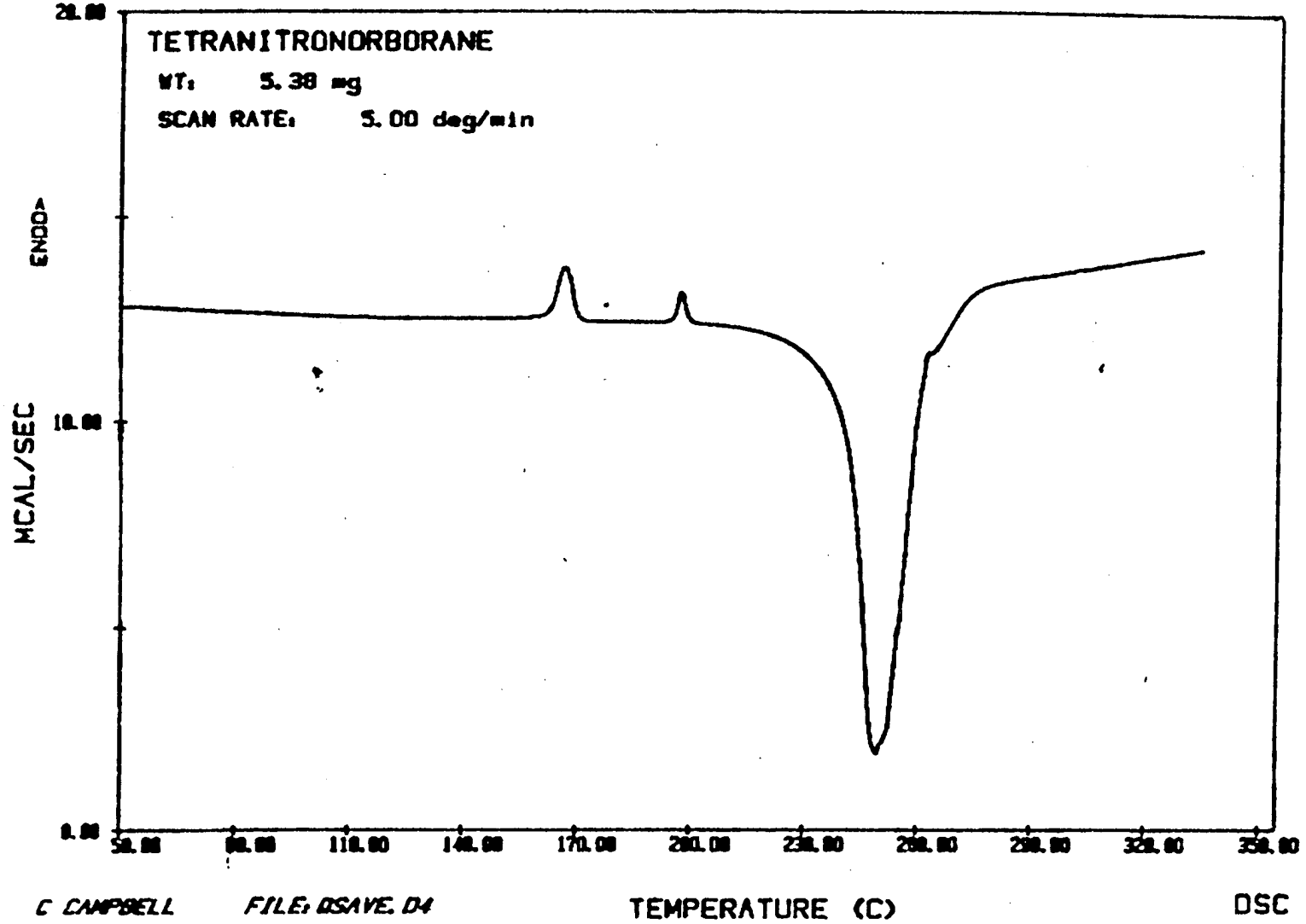


Figure 7

Figure 8

300 MHz Proton NMR Spectrum of 2,2,5,5-Tetranitronorbornane

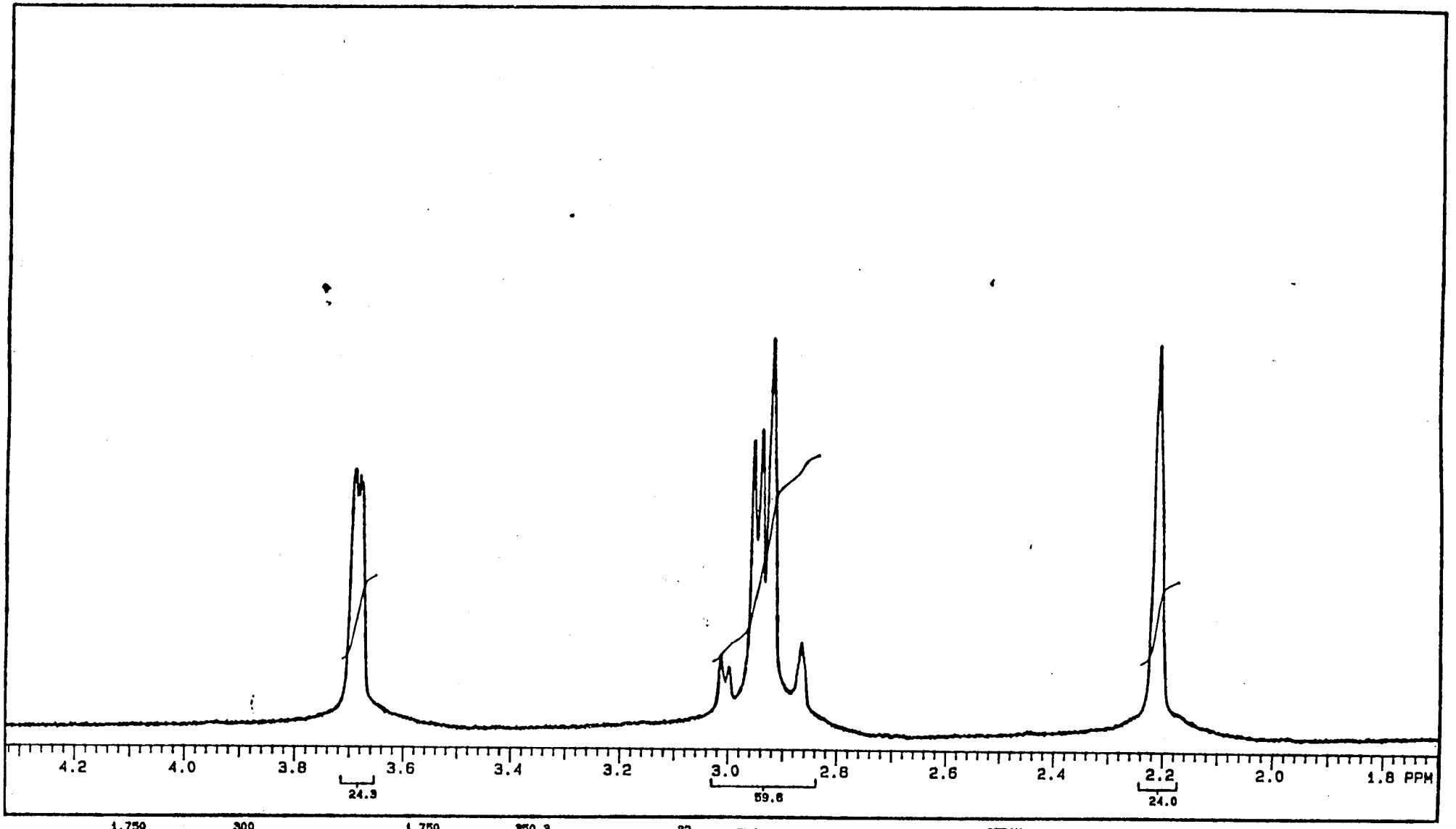
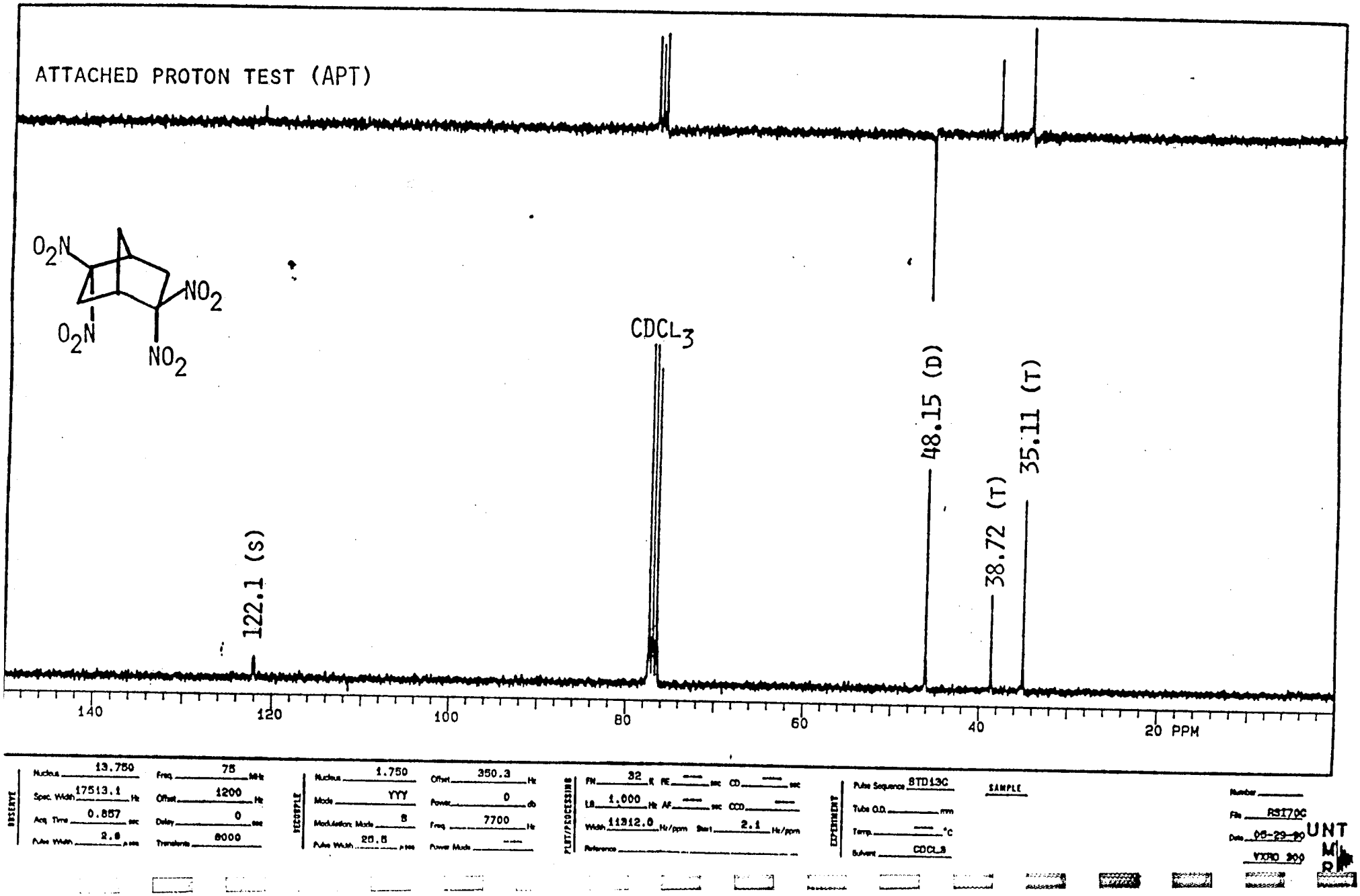


Figure 9

75 MHz Carbon-13 NMR Spectrum of 2,2,5,5-Tetranitronorbornane



Synthesis of 2,2,7,7-Tetranitronorbornane

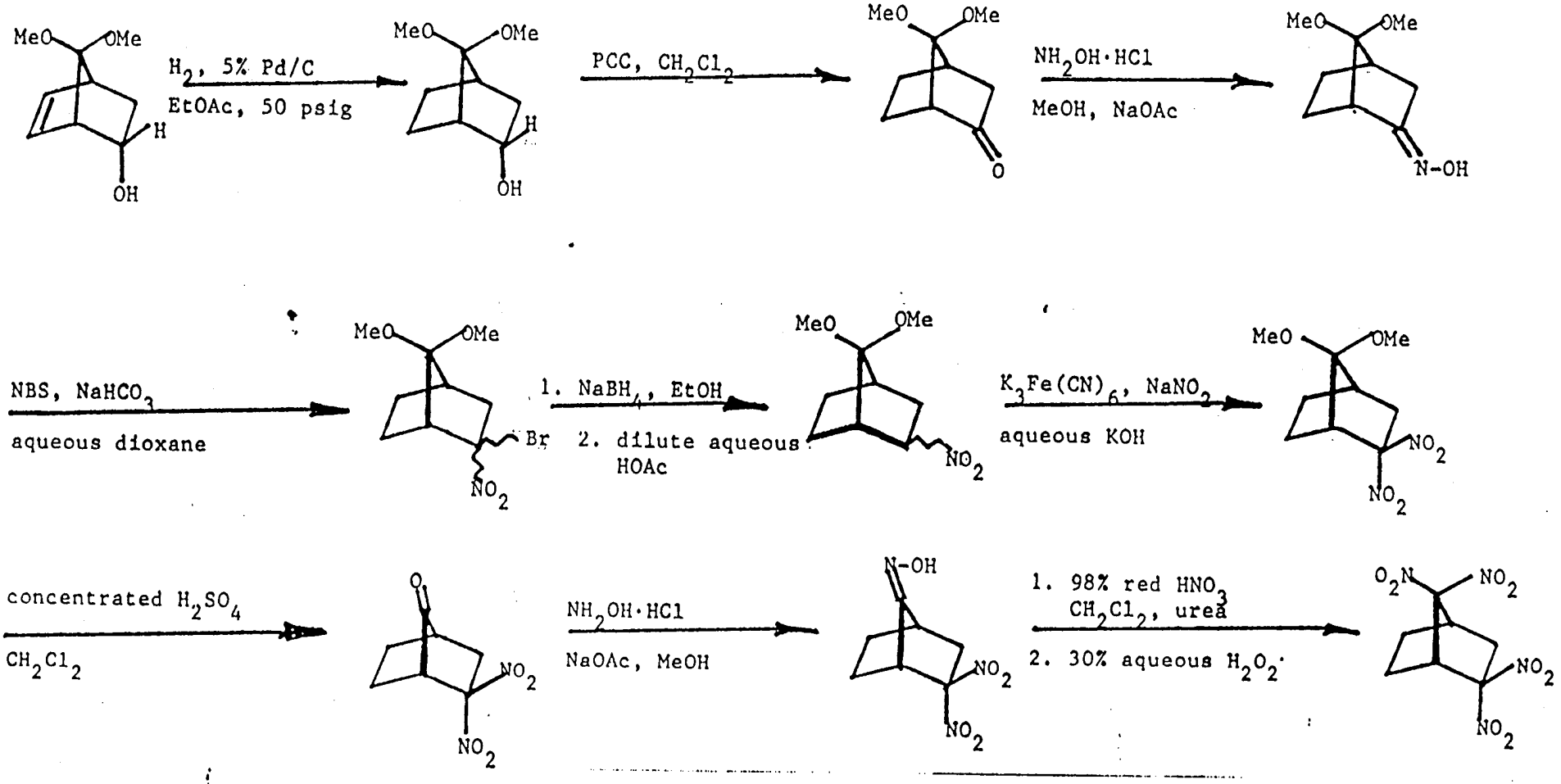


Figure 10

DSC OF 2,2,7,7-TETRANITRONORBORNANE

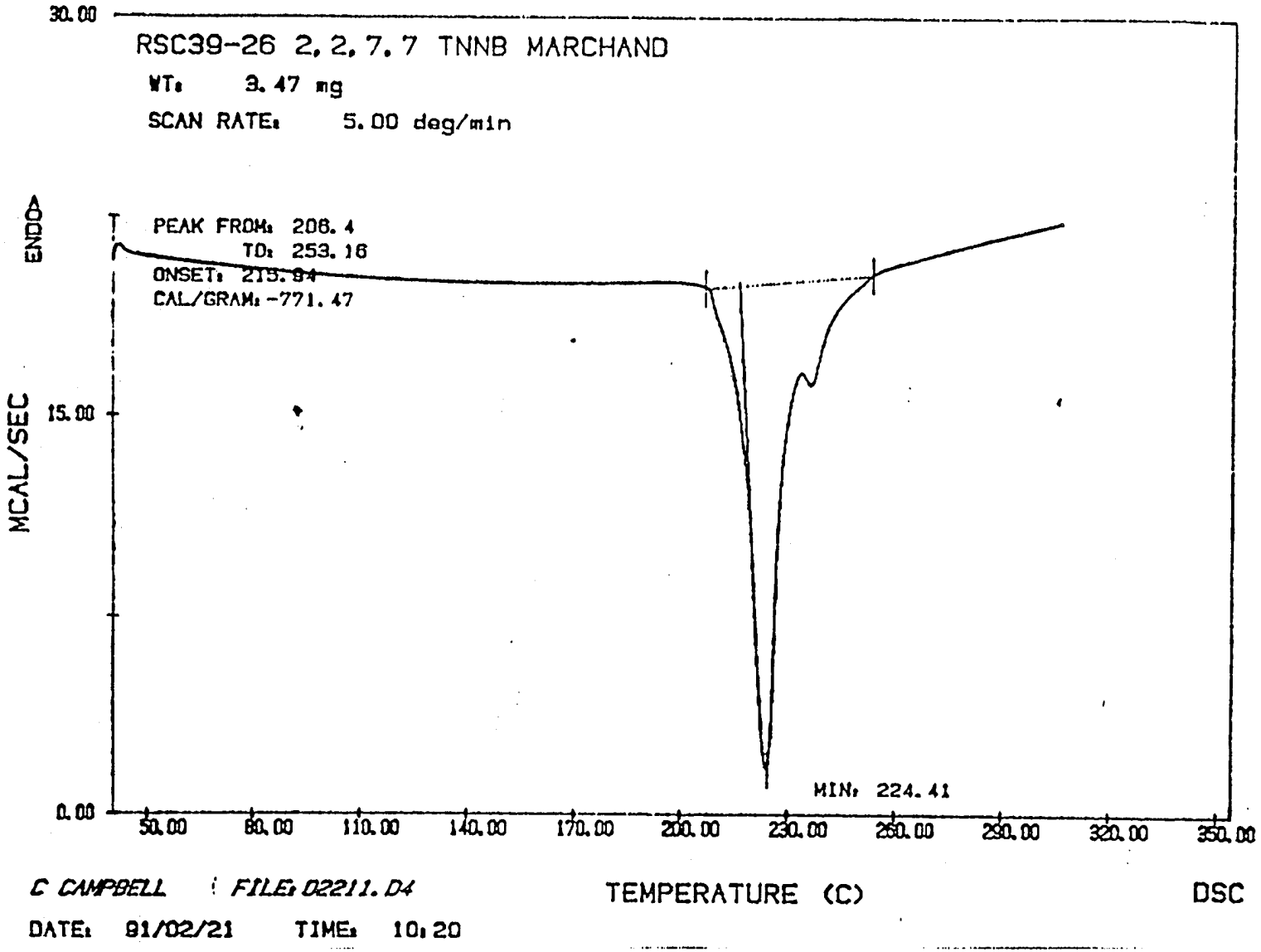


Figure 11

Figure 12

300 MHz Proton NMR Spectrum of 2,2,7,7-Tetranitronorbornane

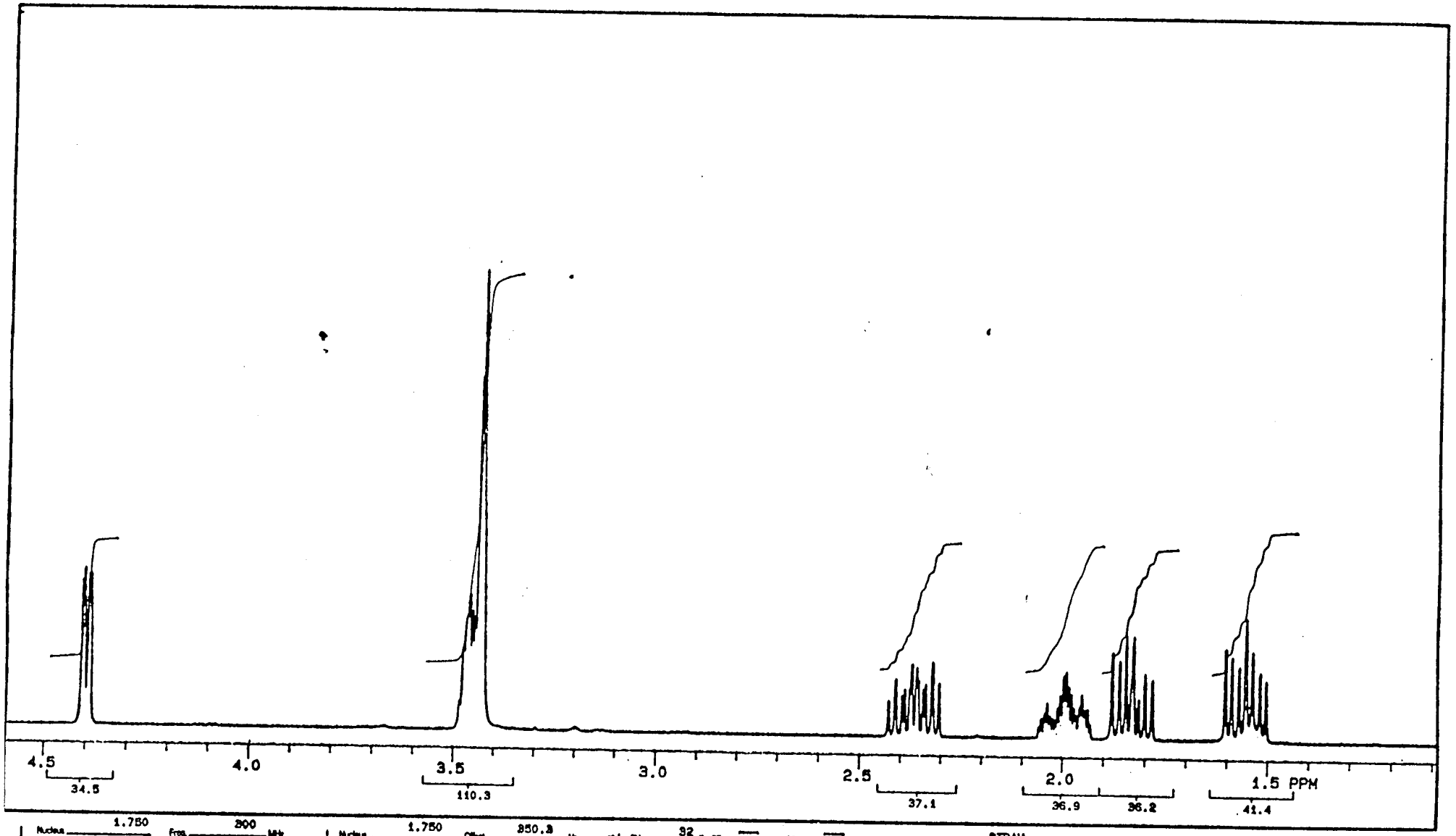


Figure 13

75 MHz Carbon-13 NMR Spectrum of 2,2,7,7-Tetranitronorbornane

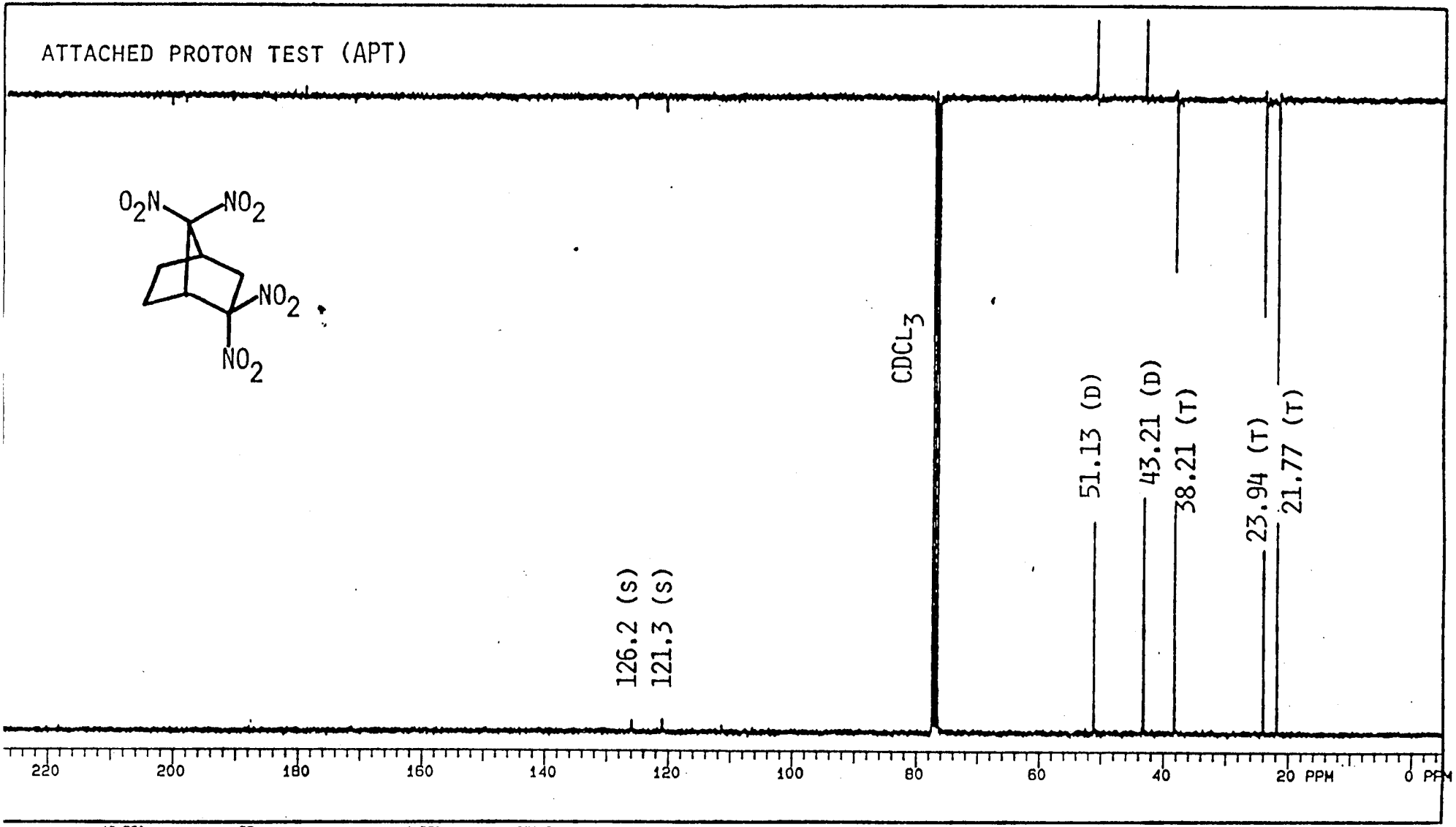
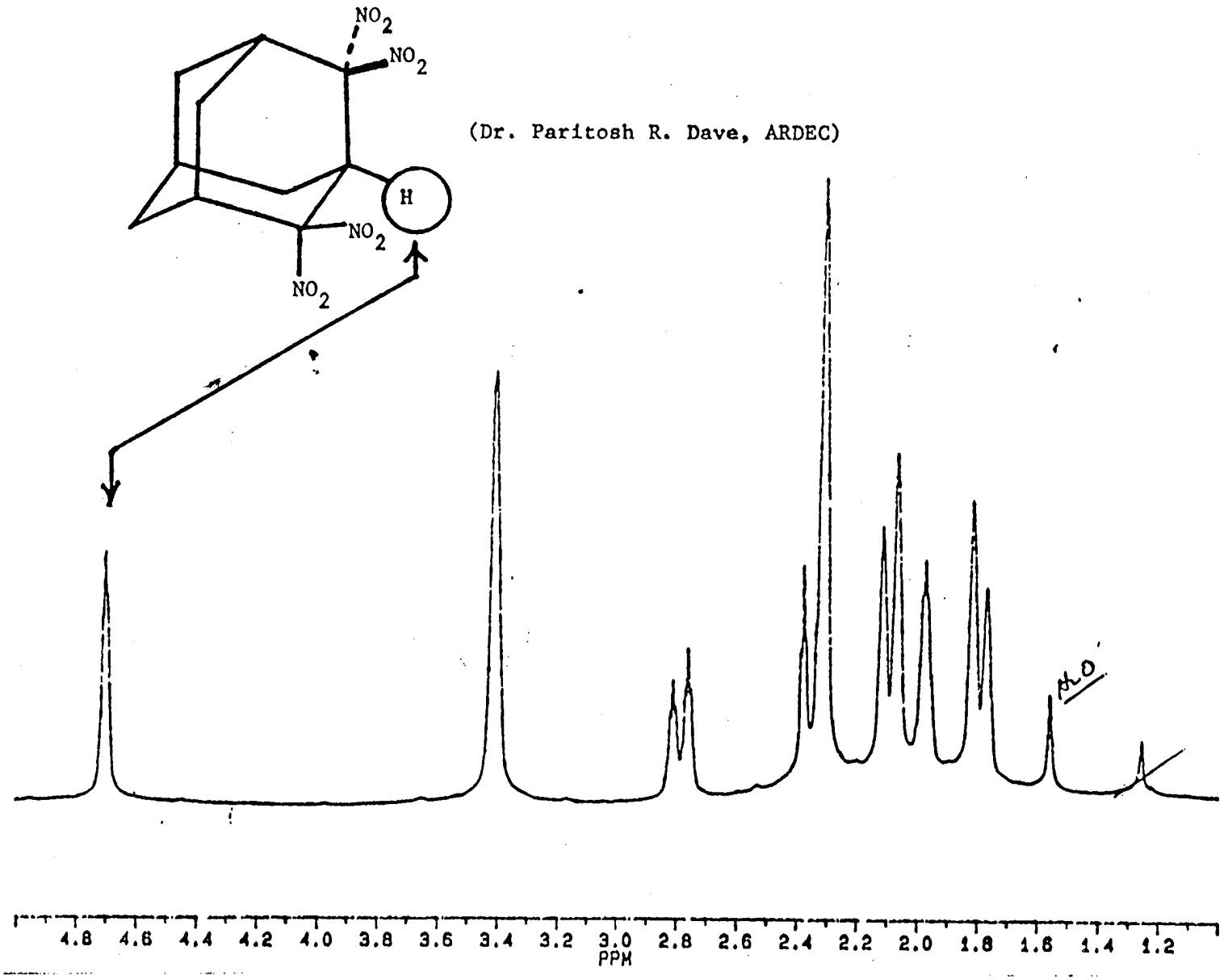


Figure 14



(Dr. Paritosh R. Dave, ARDEC)

OBJECTIVE:

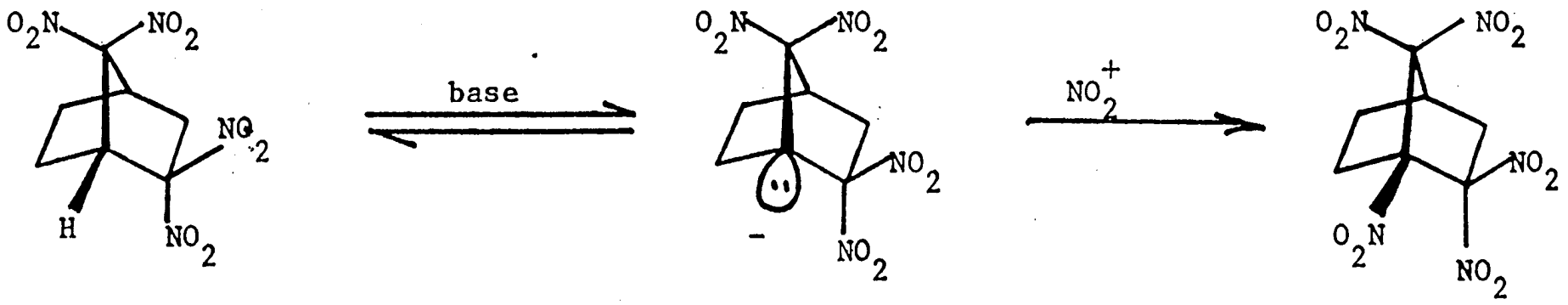


Figure 15

MODEL FOR THE TRANSITION STATE OF NITRO-DIRECTED BRIDGEHEAD LITHIATION OF 2,2,7,7-TETRANITRONORBORNANE

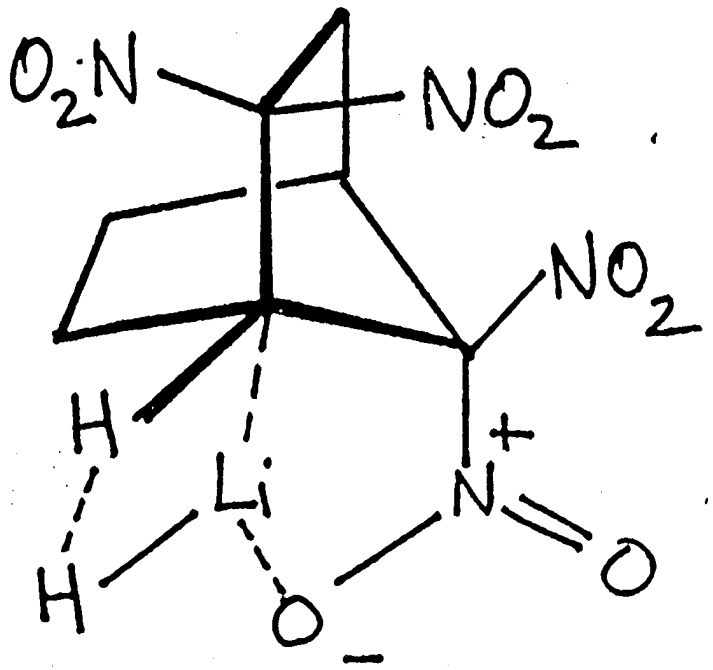


Figure 16

APPROACHES TO THE SYNTHESIS OF A TETRANITRONORTRICYCLANE

(Dr. V. R. Gadgil)

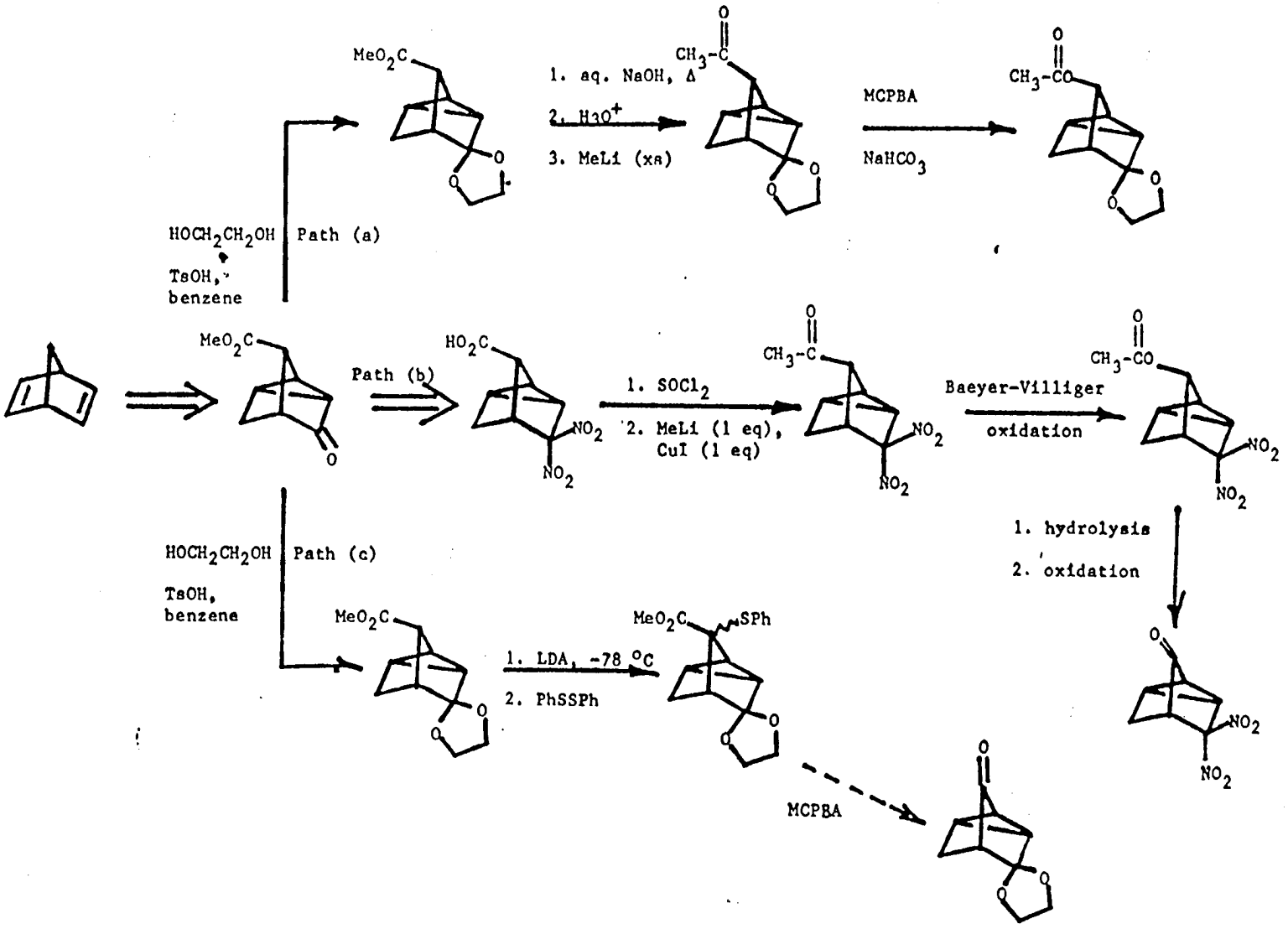
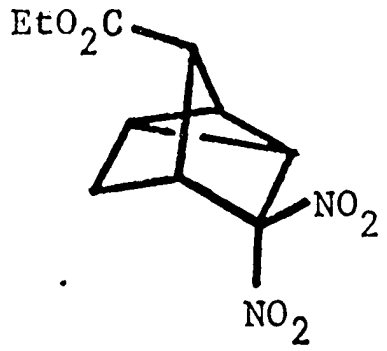


Figure 17



Proton Noise-Decoupled

Carbon-13 NMR Spectrum

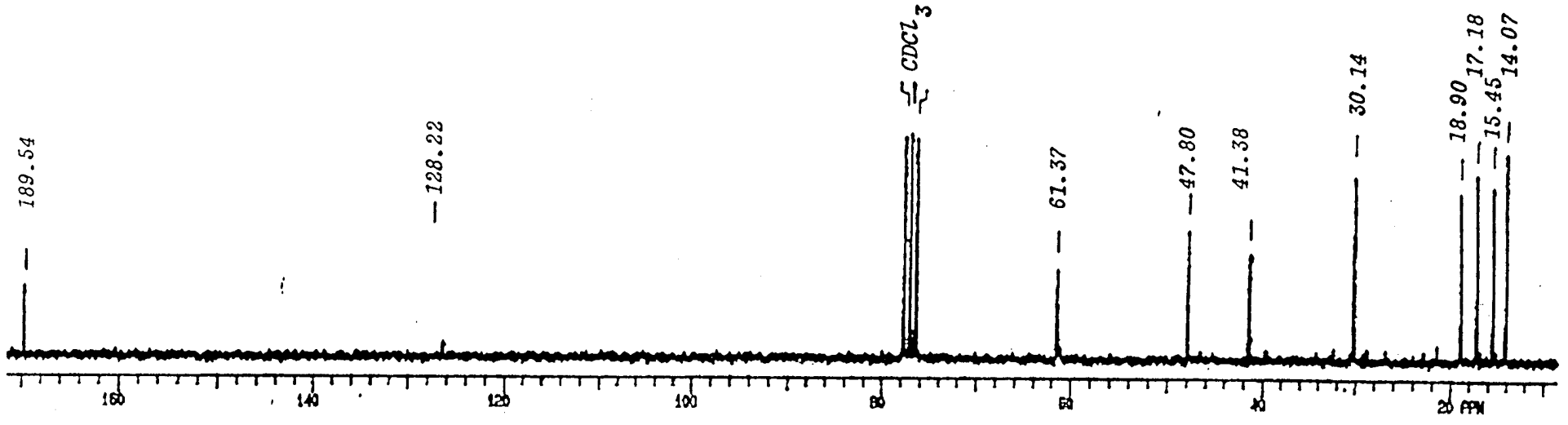


Figure 18

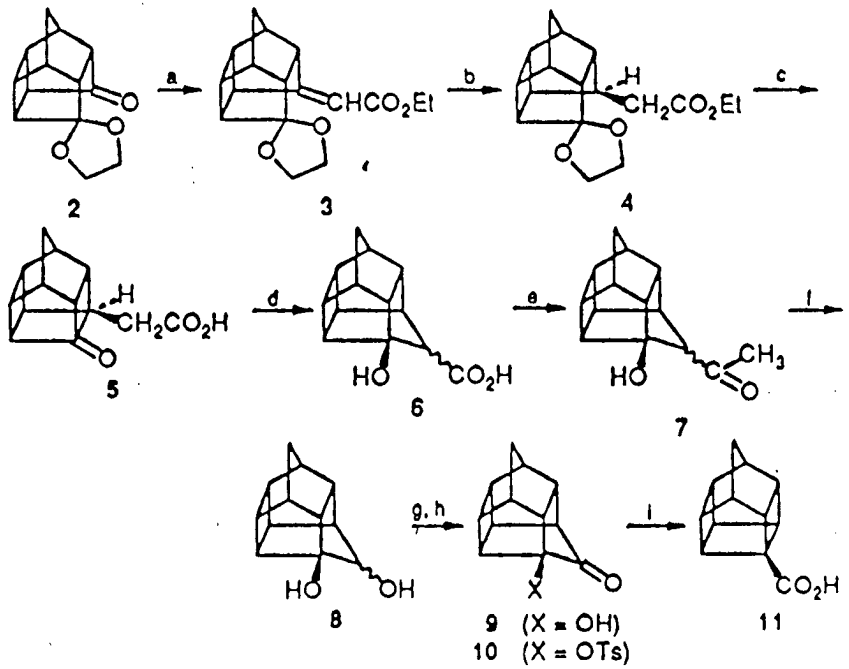
Reprinted from The Journal of Organic Chemistry, 1989, Vol. *54*, *page* 3226.

Synthesis of Hexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane-8-carboxylic Acid (Homopentaprismane-8-carboxylic Acid)

Alan P. Marchand* and Mahendra N. Deshpande

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068

Scheme II[a]



[a] (a) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, reflux 36 h (93%); (b) H_2 (1 atm), Pd–C, EtOAc, room temperature, 2 days (100%); (c) 10% aqueous H_2SO_4, dioxane, reflux 2 days (90%); (d) NaH, DMF–THF, 20 h (91%); (e) MeLi, THF (80%); (f) $(CF_3CO)_2O$, 90% aqueous H_2O_2, 1 day, followed by 5% aqueous NaOH, MeOH, 50 °C, 17 h (60%); (g) NCS, Me_2S, Et_3N, −25 °C (77%) *or* $(COCl)_2$–DMSO, −60 °C → −40 °C (42%); (h) TsCl, py (88%); (i) 20% aqueous KOH, reflux 7 h (94%).

Figure 19

APPROACH TO THE SYNTHESIS OF 2,2,5,5,7,7-HEXANITRONORBORNANE

(Dr. Umesh R. Zope)

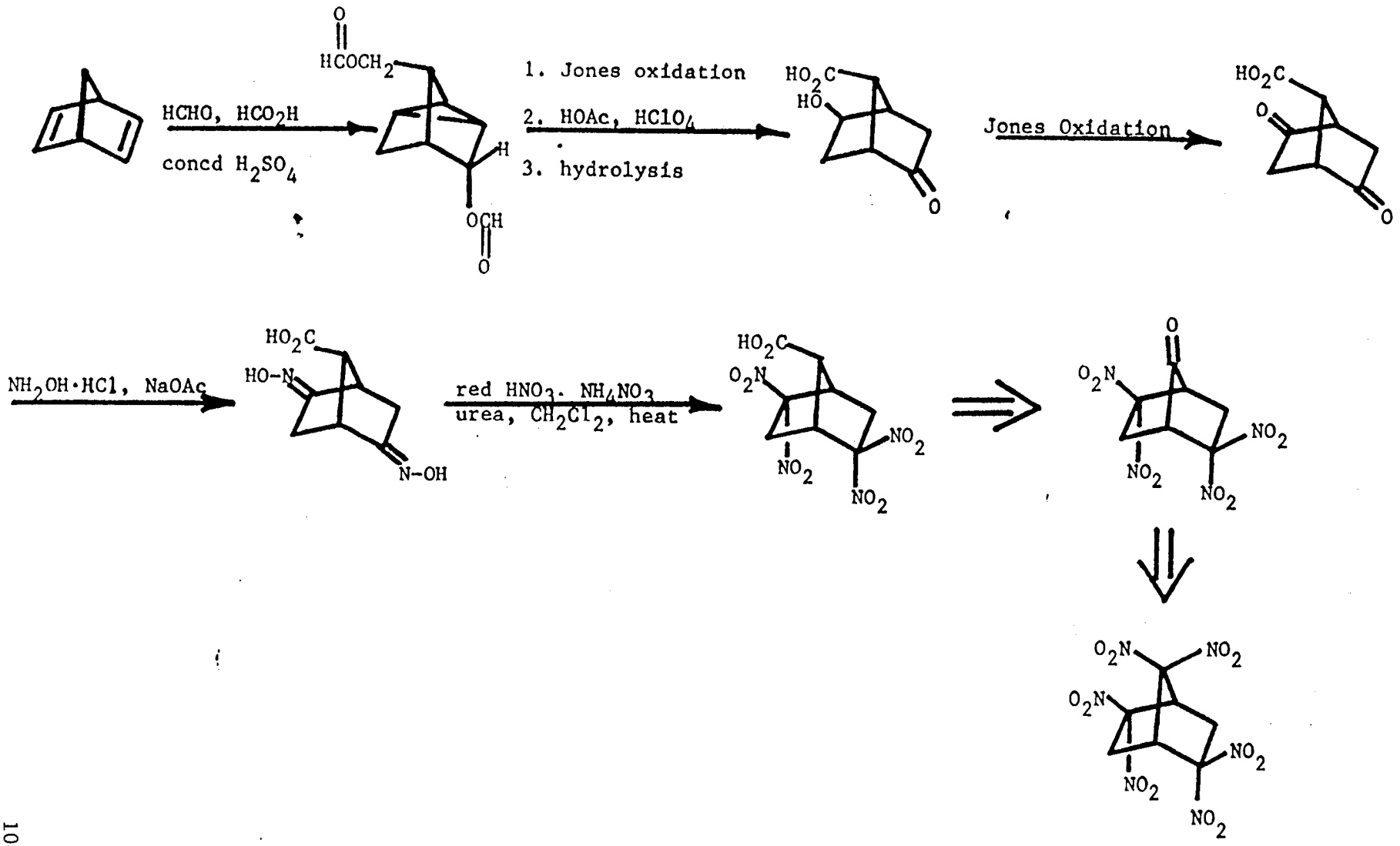


Figure 20

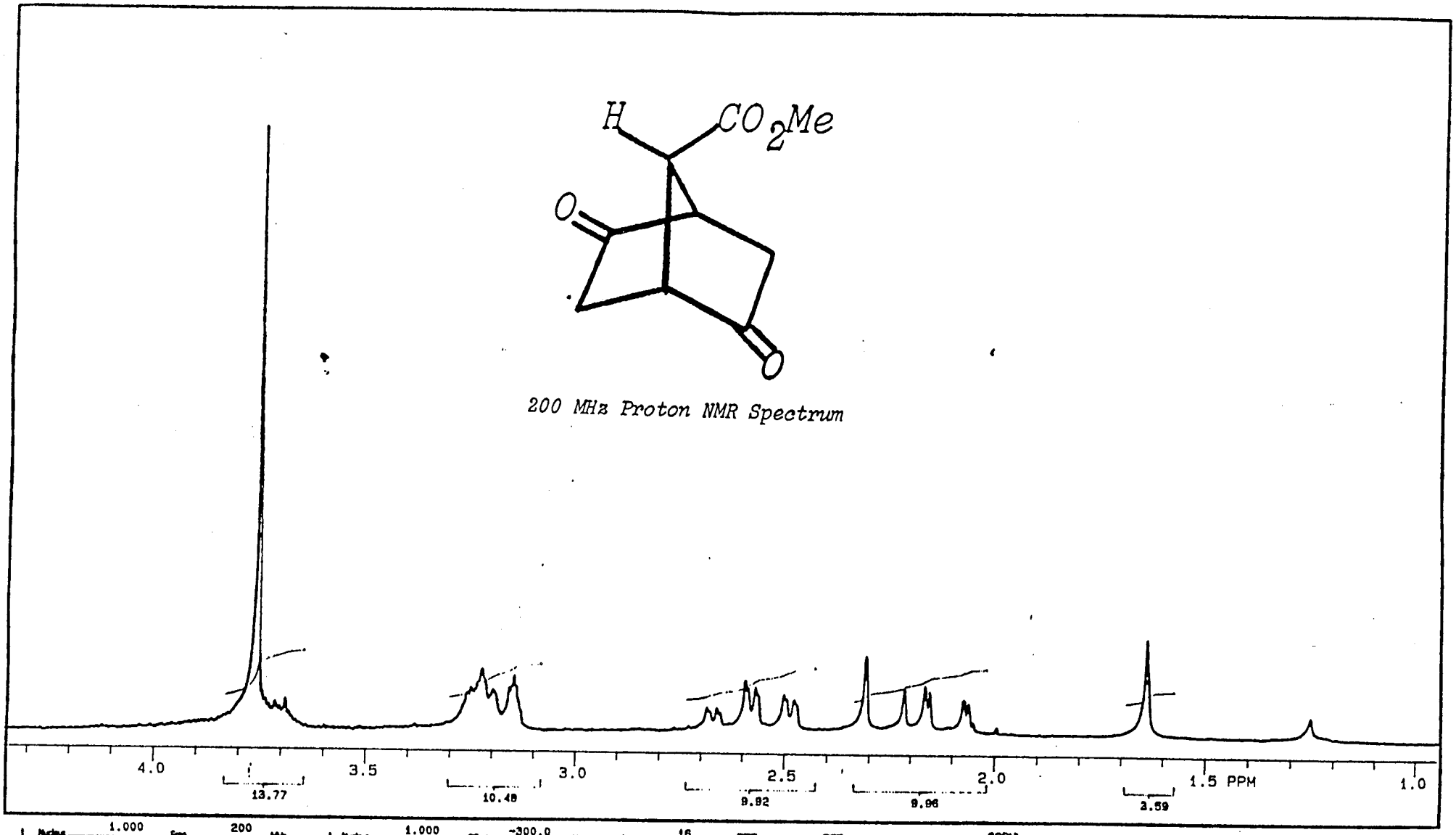
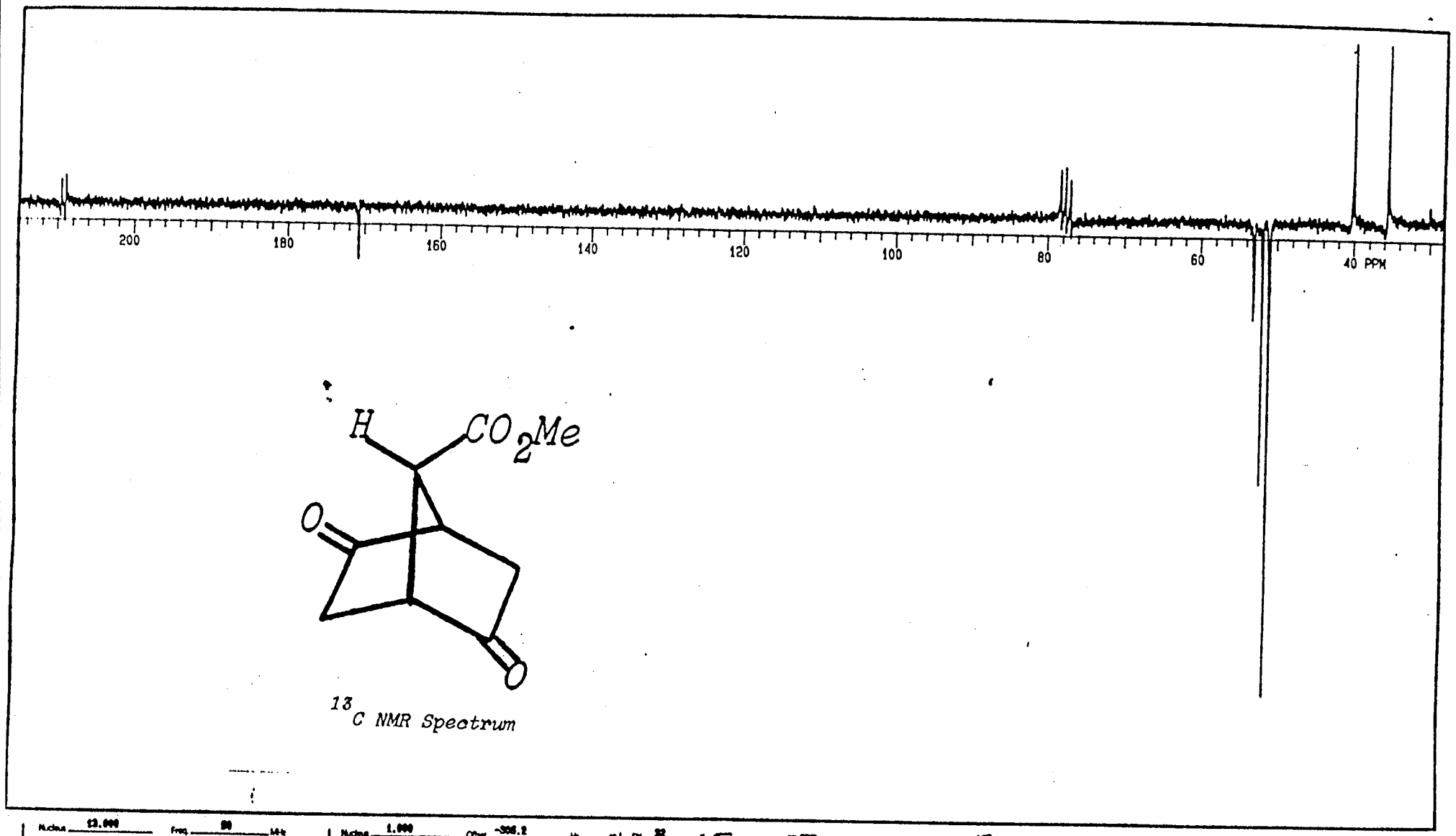

H
CO2Me
O
200 MHz Proton NMR Spectrum
4.0
3.5
3.0
2.5
2.0
1.5 PPM
1.0
13.77
10.48
9.92
9.96
3.59
OBSERVE
Nucleus 1.000
Freq. 200 MHz
Spec. Width 3000.3 Hz
Offset 0 Hz
Acq. Time 1.994 sec
Delay 0 sec
Pulse Width 9.3 μsec
Transients 144
DECOUPLE
Nucleus 1.000
Offset -300.0 Hz
Mode NNN
Power 20 db
Modulation Mode C
Freq. 10000 Hz
Pulse Width μsec
Power Mode 1.0
PLOT/PROCESSING
FN 16 R RE sec CD sec
LB Hz AF sec CCD
Width 681.7 Hz/ppm Start 189.0 Hz/ppm
Reference
EXPERIMENT
Pulse Sequence S2PUL
Tube O.D. mm
Temp. °C
Solvent CDCL3
SAMPLE
ESR
Number
File ESTH
Date 01-03-91
VXRD 200
UNT
NMR

Figure 21



^{13}C NMR Spectrum

Figure 22

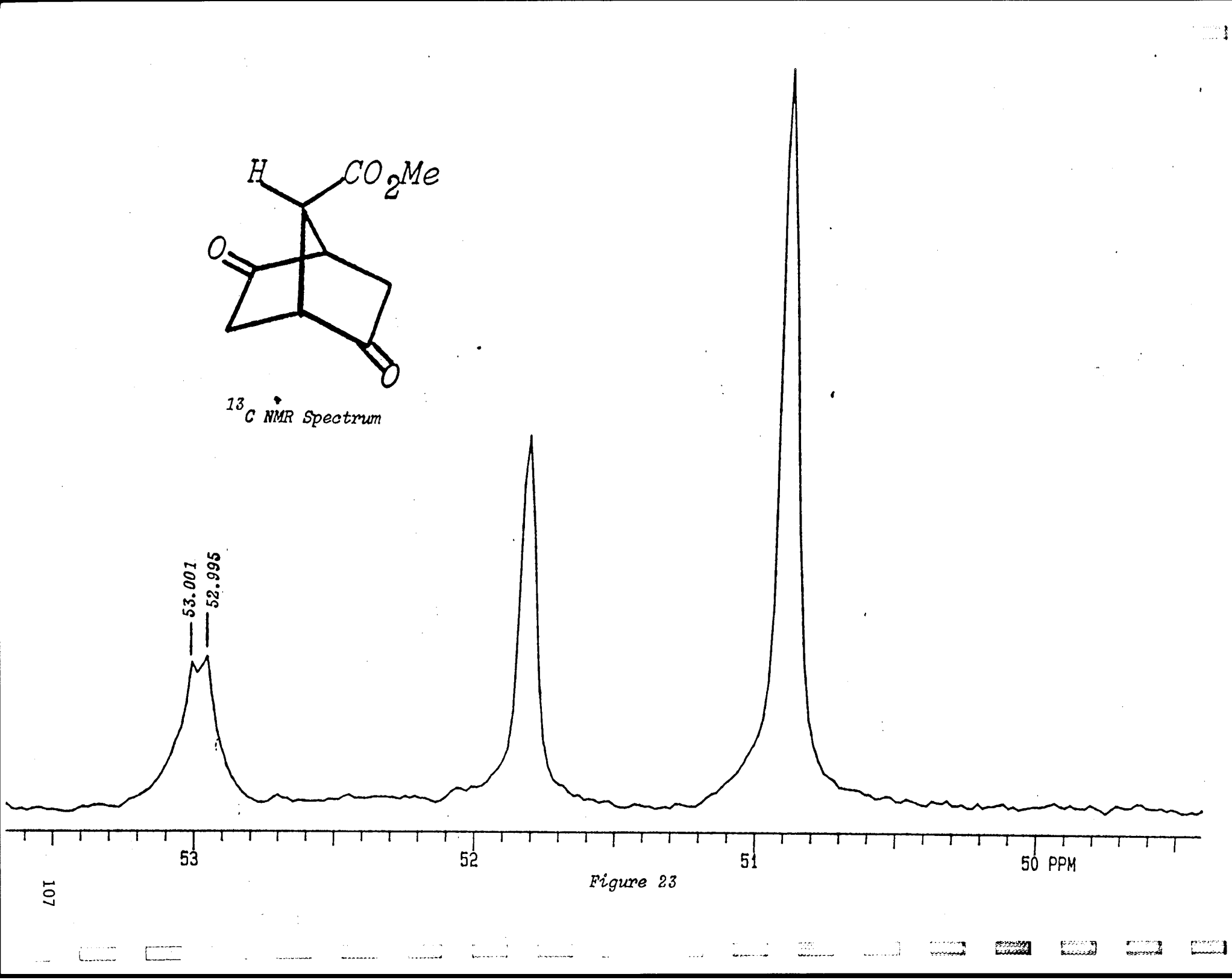


Figure 23

AN ALTERNATIVE APPROACH TO THE SYNTHESIS OF 2,2,5,5,7,7-HEXANITRONORBORNANE (DR. V. R. GADGIL).

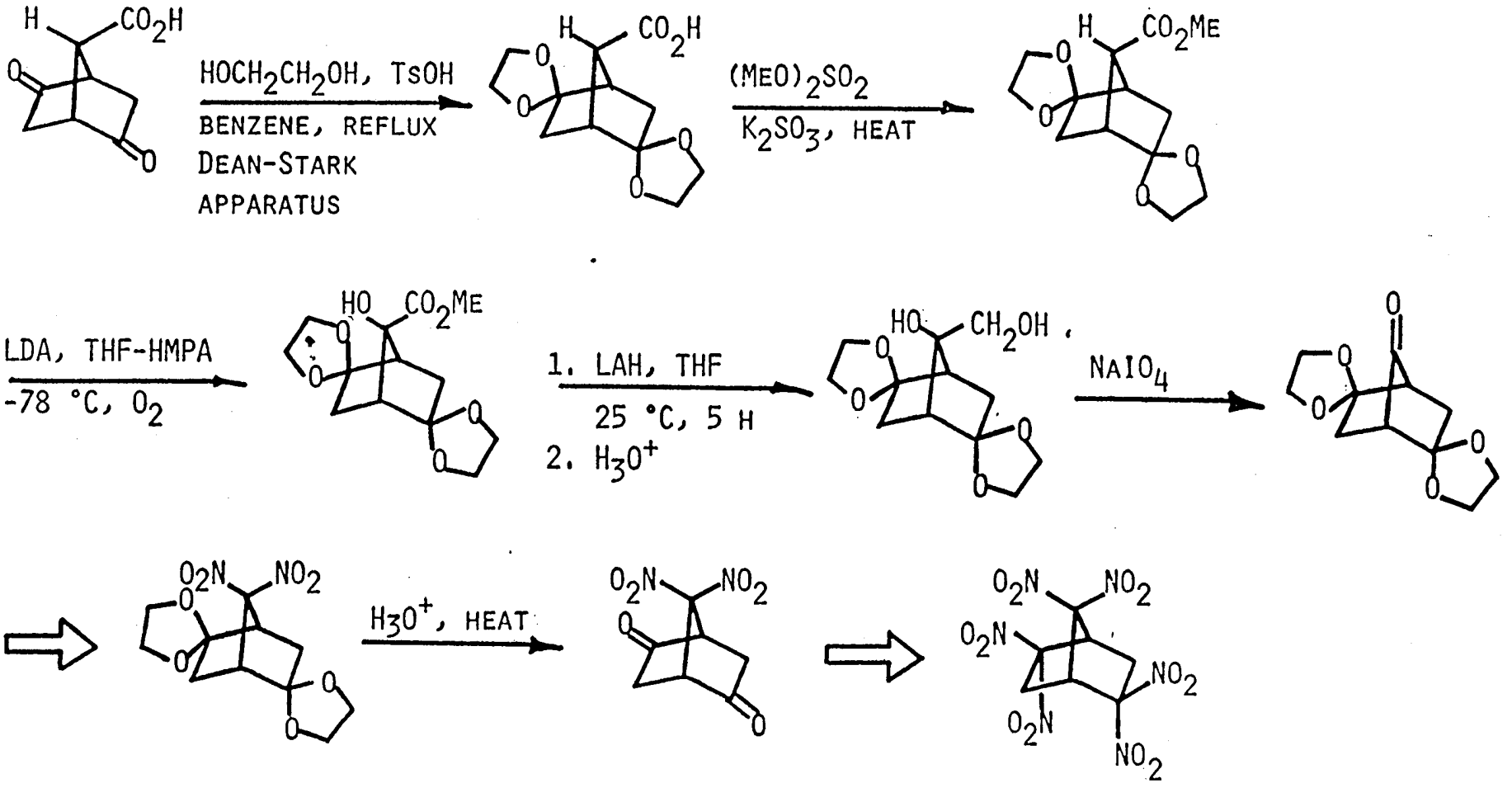


Figure 24

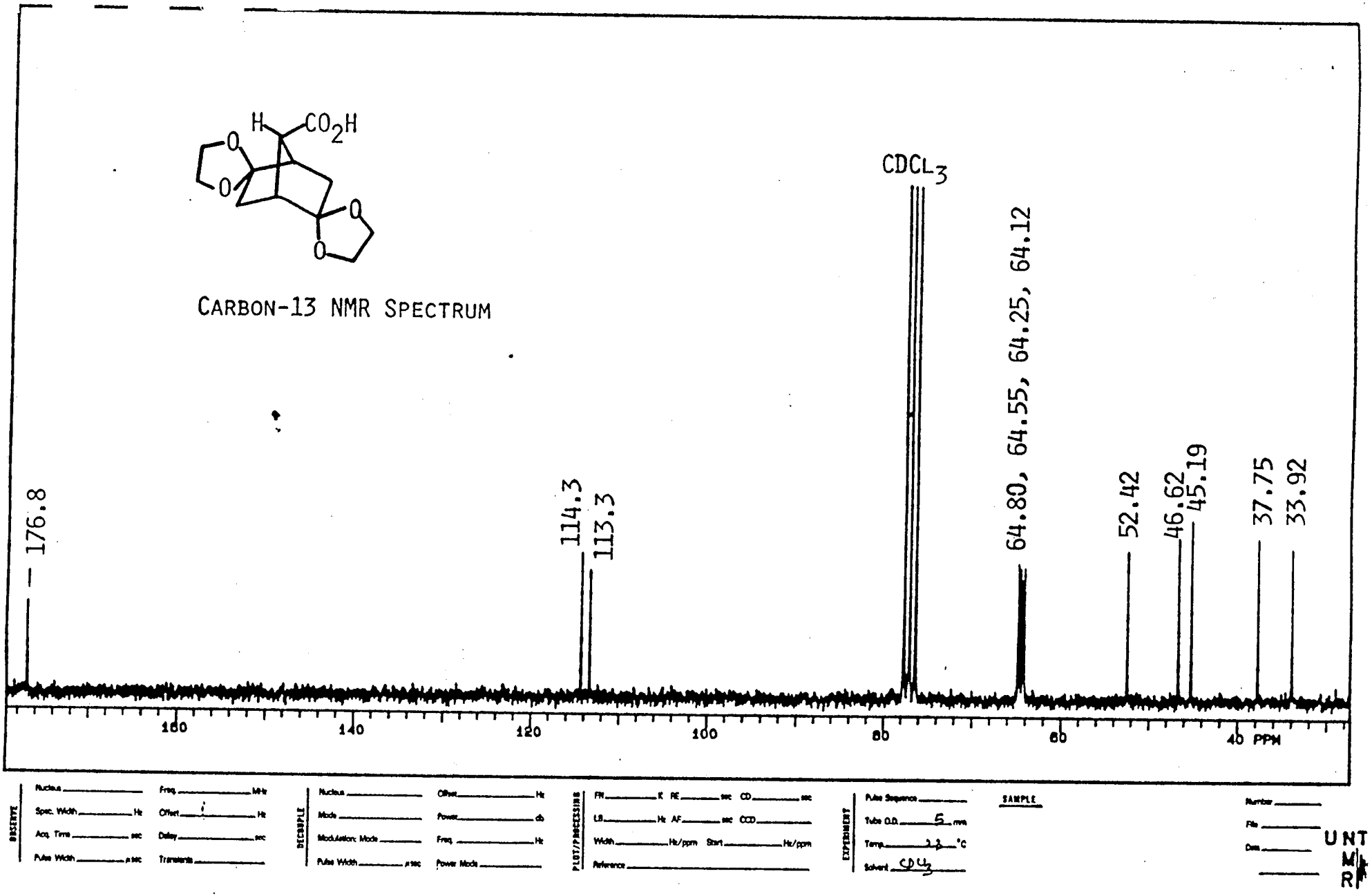

H
CO2H
O
O
O
O
CARBON-13 NMR SPECTRUM
CDCL3
64.80, 64.55, 64.25, 64.12
176.8
114.3
113.3
52.42
46.62
45.19
37.75
33.92
160
140
120
100
80
60
40 PPM
RESERVE
Nucleus
Freq. MHz
Spec. Width Hz
Offset Hz
Acq. Time sec
Delay sec
Pulse Width μsec
Transients
DECOUPLE
Nucleus
Offset Hz
Mode
Power db
Modulation Mode
Freq. Hz
Pulse Width μsec
Power Mode
PLOT/PROCESSING
FN R RE sec CD sec
LB Hz AF sec CCD
Width Hz/ppm Start Hz/ppm
Reference
EXPERIMENT
Pulse Sequence
Tube O.D. 5 mm
Temp. 23 °C
Solvent CDCl3
SAMPLE
Number
File
Date
UNITY

Figure 25

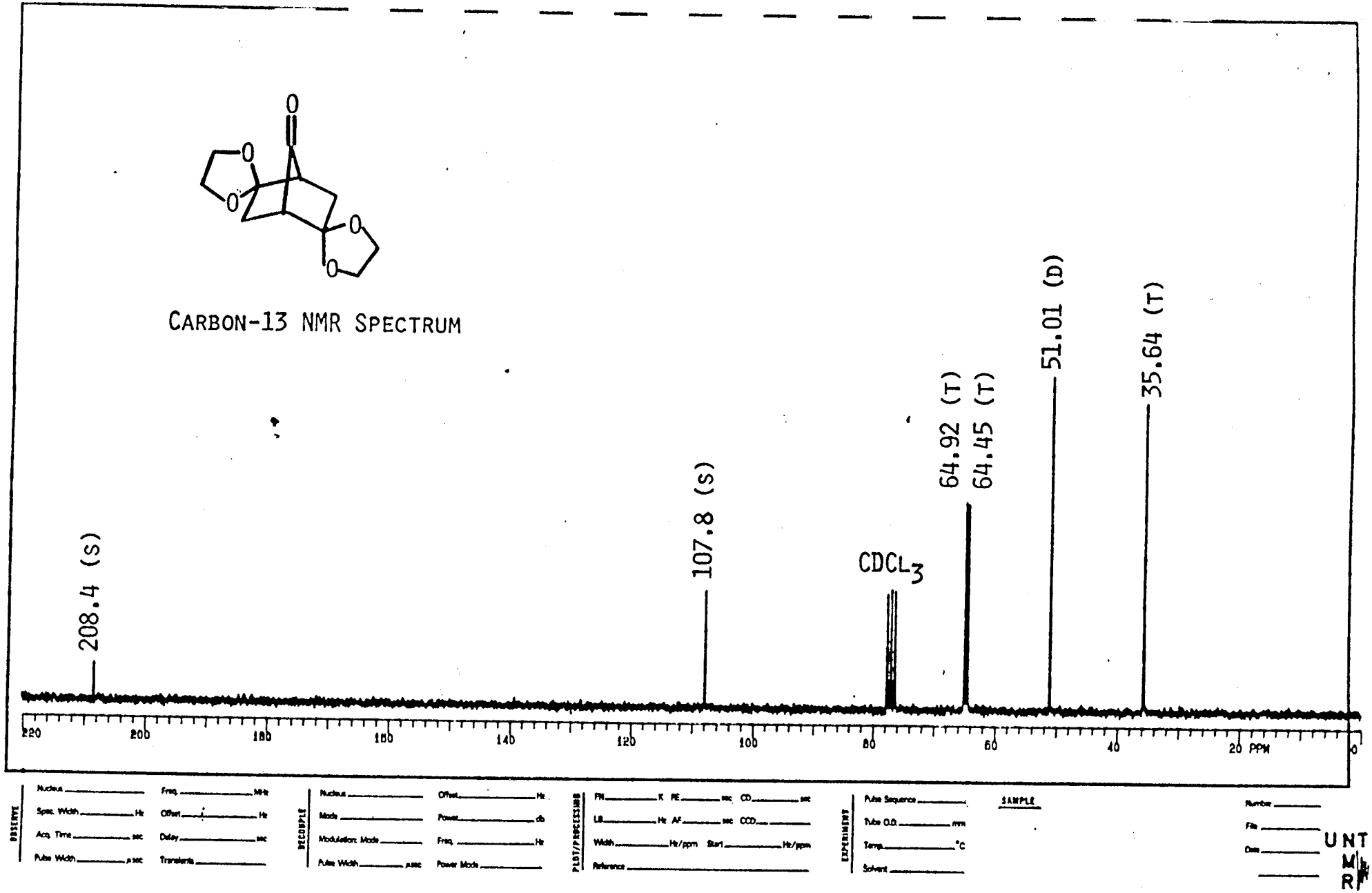

CARBON-13 NMR SPECTRUM
208.4 (S)
107.8 (S)
CDCL3
64.92 (T)
64.45 (T)
51.01 (D)
35.64 (T)
220
200
180
160
140
120
100
80
60
40
20 PPM
0
OBSERVE
DECOUPLE
PLOT/PROCESSING
EXPERIMENT
SAMPLE
UNT
MR

Figure 26

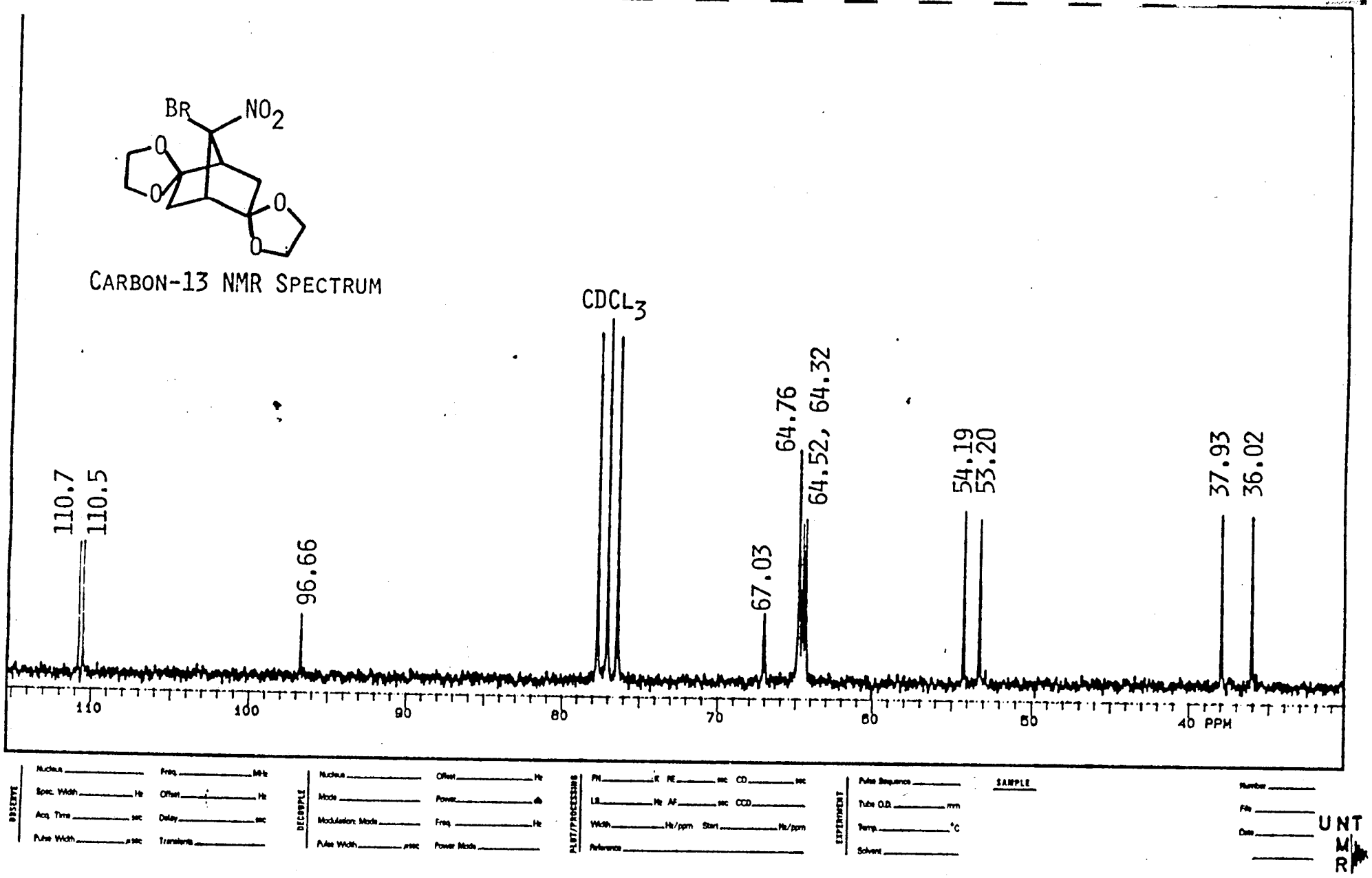

BR
NO2
O
O
O
O
CARBON-13 NMR SPECTRUM
CDCL3
110.7
110.5
96.66
67.03
64.76
64.52, 64.32
54.19
53.20
37.93
36.02
110
100
90
80
70
60
50
40 PPM
OBSERVE
Nucleus
Freq. MHz
Spec. Width Hz
Offset Hz
Acq. Time sec
Delay sec
Pulse Width μsec
Transients
DECOUPLE
Nucleus
Offset Hz
Mode
Power db
Modulation Mode
Freq. Hz
Pulse Width μsec
Power Mode
PLOT/PROCESSING
FN IT FE sec CD sec
LB Hz AF sec CCD
Width Hz/ppm Start Hz/ppm
Reference
EXPERIMENT
Pulse Sequence
Tube O.D. mm
Temp. °C
Solvent
SAMPLE
Number
File
Date
UNT
M
R

Figure 27

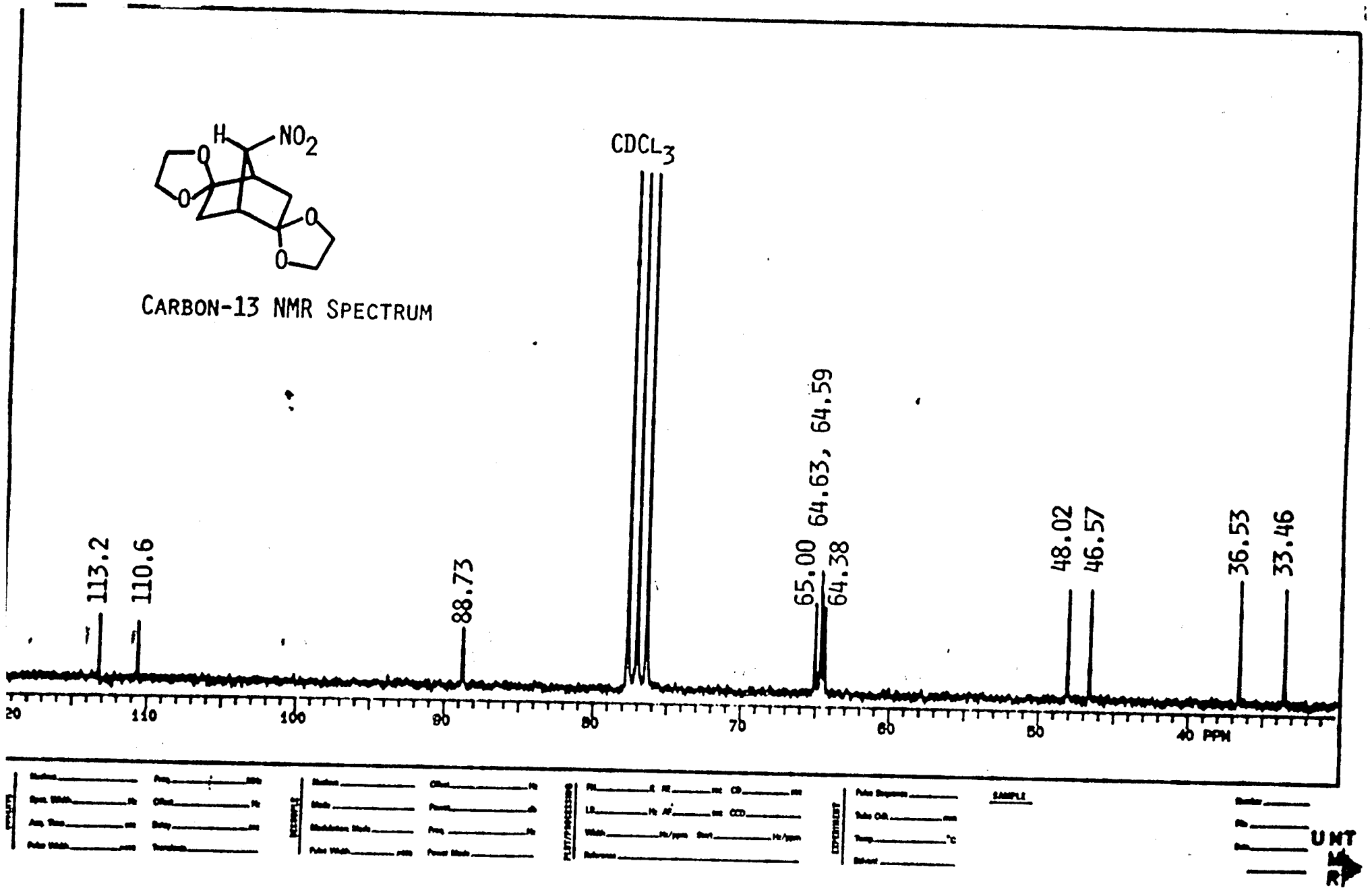

H
NO2
O
O
O
O
CARBON-13 NMR SPECTRUM
CDCL3
113.2
110.6
88.73
65.00
64.63, 64.59
64.38
48.02
46.57
36.53
33.46
20
110
100
90
80
70
60
50
40 PPM
UNT

Figure 28

SYNTHESES OF SUITABLE PRECURSORS TO NEW ENERGETIC POLYNITROPOLYCYCLIC COMPOUNDS

Principal Investigator: Dr. Alan P. Marchand

Postdoctoral Research Associates: Drs. V. R. Gadgil, R. Sharma, and U. R. Zope

Department of Chemistry, University of North Texas, Denton, TX 76203-0068

Contract Number DAAA21-89-C-0012, Reference: GC-1853-89-003

FINAL REPORT: Covers period January 7, 1991 through June 30, 1992

ACKNOWLEDGMENTS

U. S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER PICATINNY ARSENAL, NEW JERSEY (CONTRACT NO. DAAA21-89-C-0012)

GEO-CENTERS, INC.

THE ROBERT A. WELCH FOUNDATION (GRANT B-963)

Figure 29.

TASK 6:

ANALYTICAL CHEMISTRY

Objective 1:

Synthesis of Polynitrobicyclo[1.1.1]pentanes

(Prof. Kenneth B. Wiberg)
(Yale University)

Final Report

Geo-Centers, Inc.

Dec, 1991

Synthesis of Polynitrobicyclo[1.1.1]pentanes

Contract No. GC-1853-89-004

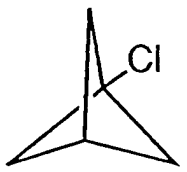
Kenneth B. Wiberg

Department of Chemistry

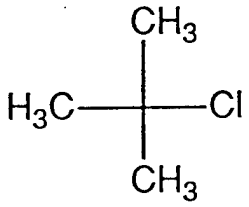
Yale University

New Haven, CT 06511

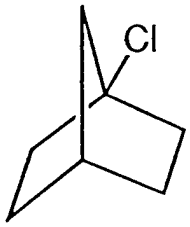
We have shown that 1-chlorobicyclo[1.1.1]pentane is three times as reactive in solvolysis than is t-butyl chloride. This high reactivity is surprizing since 1-chloronorbornane is 10^{14} less reactive than t-butyl chloride. There are two possible explanations: 1. participation by the C2-C3 bond occurs leading to relief of strain as part of the reaction, and 2. internal stabilization in a fashion as has been found for the cyclobutyl cation. We have explored this question via ab initiō mo calculations. We find that in the cation, the 1-3 distance decreases to 1.54Å - a normal bond length. The ion may best be described as a protonated [1.1.1]propellane.



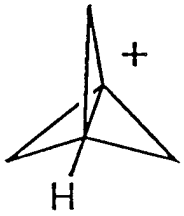
3



1



10^{-14}

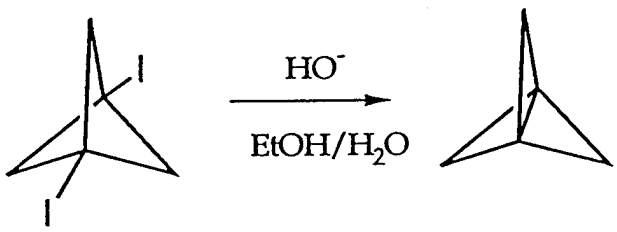


C1-C3 = 1.54Å

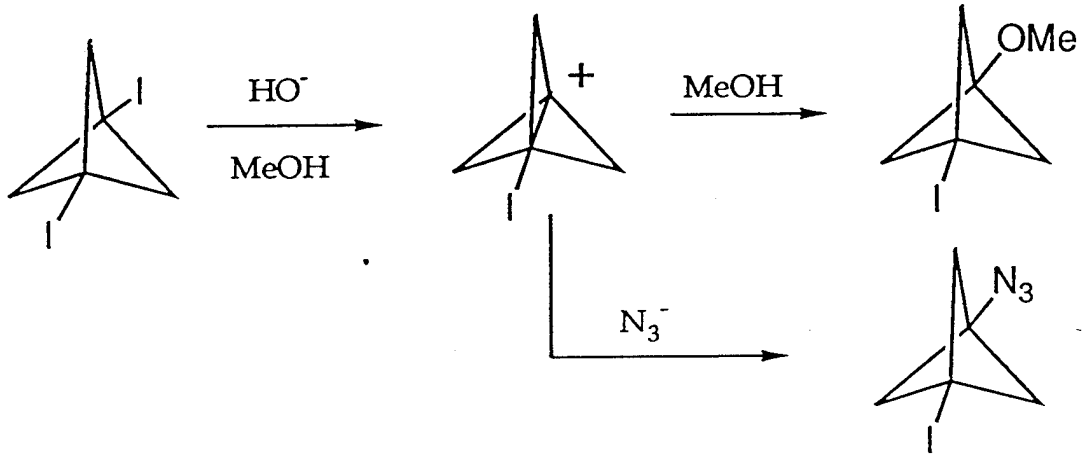
In order to see if this was a reasonable possibility, we have examined the solvolysis of bicyclo[1.1.1]pentane-1,3-diiodide, which formed by the addition of iodine to the propellane. An iodine in the 3-position should destabilize the interaction shown above. In accord with this prediction, the solvolysis in 80% ethanol was at first very slow, but as some HI was formed, the reaction became somewhat more rapid. In order to avoid acid catalyzed, sodium hydroxide was added to the solution to remove the acid as it was formed. We were surprized to find that the reaction now became more rapid, and was in fact first order in base.

An examination of the products showed that [1.1.1]propellane was formed in quantitative yield. Thus, the reaction was a nucleophilic displacement on iodine! We have examined other 1,3-dihalides such as 1,3-diiodopropane and 3-chloro-1-iodobutane, but they

do not undergo this reaction. Among "normal" compounds, only 1,2-diiodides appear to undergo this type of reaction.



When the reaction was carried out in methanol, the course was different, and though some propellane was formed, the major product was 3-methoxybicyclo[1.1.1]pentyl-1 iodide, apparently formed by the addition of MeOI to the propellane. This should proceed via the 3-iodo-1-cation as an intermediate. Evidence for this species was obtained by running the reaction in the presence of azide ion. Now, a considerable amount of 3-iodobicyclo[1.1.1]pentyl1-azide was formed, indicating that the cation was captured by the very good nucleophile, N_3^-.



We were now interested in seeing if we can observe the ion via nmr spectroscopy. The diiodide was treated with antimony pentafluoride in SO_2ClF solution, and the ^{13}C spectrum was taken. The results were promising, but the solubility of the diiodide was so low that the signal to noise ratio was poor. It was clearly necessary to obtain a derivative having a lower melting point and greater solubility.

We have shown that it is possible to convert iodides into bromides via treatment with bromine, presumably via some $RIBr_2$ species. This reaction was tried with the bicyclopentane diiodide, and it was possible to isolate the bromoiodide. Although it did have a somewhat lower melting point, its solubility was not great, and further work needs to be done. We also have examined the preparation of the dichloride via reaction of the propellane with $PhICl_2$. Although the yield is low, it was possible to obtain enough of the dichloride to study it. The reaction with antimony pentafluoride appears to have been successful, and signals due to a cation were found.

Calculations also have been carried out for the bridgehead radical, and again a shortening of the 1,3-distance was found. Thus, the interactions in the cation and radical appear to be similar, but different in magnitude. We have begun calculations of the effect of substituents on the energies of the bridgehead cation and anion. We also have started a series of IGLO calculations in order to estimate the ^{13}C chemical shifts of the compounds of interest.

The work we have carried out on 2-substituted bicyclo[1.1.1]pentanes has been written up for publication, and a preprint of the paper is attached.

2-Substituted Bicyclo[1.1.1]pentanes

Kenneth B. Wiberg,* Brenda S. Ross,† John J. Isbell and Neil McMurdie

Department of Chemistry, Yale University

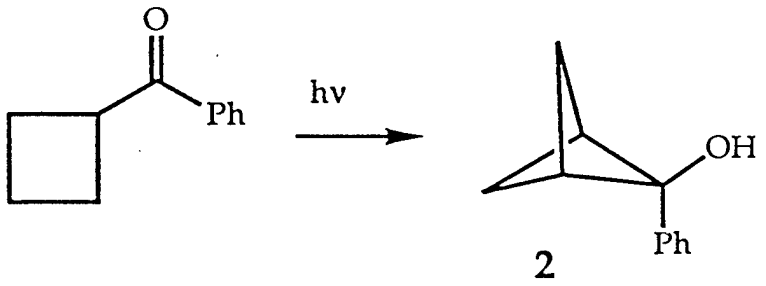
New Haven, Connecticut 06511

Abstract: A simple procedure has been developed for the conversion of 2-phenylbicyclo[1.1.1]pentan-2-ol to 2-phenyl-bicyclo[1.1.1]pentane. Oxidation gives bicyclo[1.1.1]pentane-2-carboxylic acid which may be converted to the amine, the nitro derivative, and the phenyl ketone. The pK_a values for the carboxylic acid and related acids were determined, and the pK_a's of the amine hydrochloride and related compounds also were studied. The pK_a's of the amines were approximately linearly related to the %s character determined from the nmr ^1H-C coupling constants. The pK_a of the nitro derivative was determined, and the kinetic acidity of the phenyl ketone also was measured. The relationship of the differences in energy to the changes in strain energy is discussed. In an effort to prepare a compound with substituents at both the 1 and 2 positions, the reaction of 1,3-dinitrobicyclo[1.1.1]pentane with oxalyl chloride was examined. The reaction had a surprising course, leading to 2,2-dichloro-1,3-dinitrobicyclo[1.1.1]pentane.

† Present address: Department of Chemistry, Southwest Missouri State University, Springfield, MO 65804.

The bicyclo[1.1.1]pentane (1) ring system is of special interest with regard to substituent effects. The short bridgehead-bridgehead distance (1.85Å)[1] and the short distance between methylene groups (2.14Å) should lead to unusually large non-bonded interactions. Some of these effects have been studied by Applequist for 3-substituted bicyclo[1.1.1]pentane-1-carboxylic acids.[2] We[3] and others[4] have developed efficient procedures for preparing a variety of 1,3-disubstituted bicyclo[1.1.1]pentanes via free radical additions to [1.1.1]propellane, allowing a detailed examination of these compounds.[5]

The 2-substituted derivatives are not so easily obtained. Although free radical substitution reactions on 1 will give some 2-substituted compounds,[6] the only effective method of placing a substituent at this position is the photolysis of cyclobutyl phenyl ketone.[7]



2

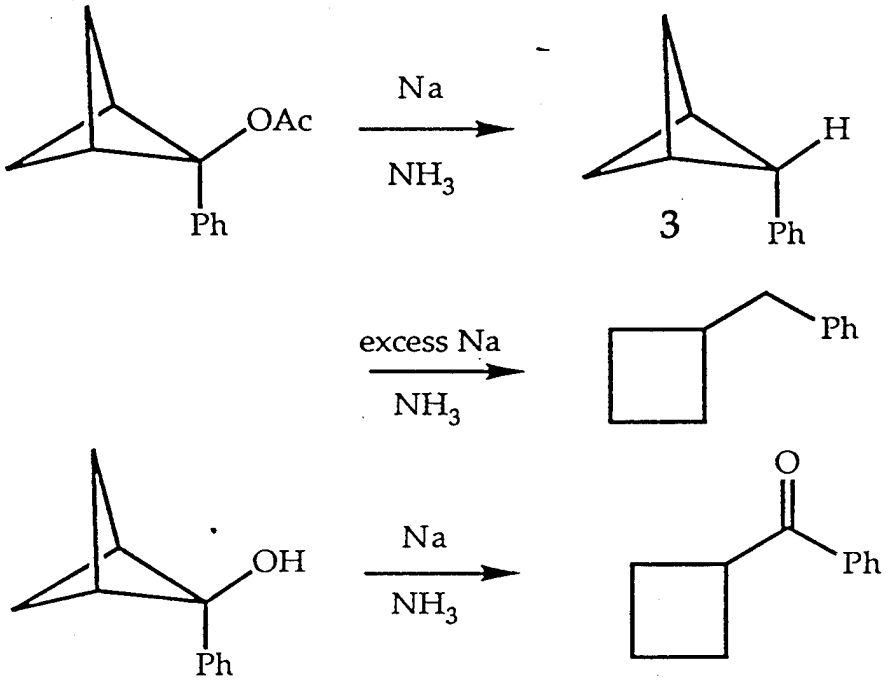
The hydroxy group has been removed via a long series of reactions involving formation of the mandelic acid ester, photolysis, oxidation and a Haller-Bauer cleavage.[8] Direct oxidation has given bicyclo[1.1.1]pentan-2-one in low yield.[9]

Phenyl is not an ideal substituent because it is relatively difficult to convert it to other groups. Several other substituents were examined for the photolysis reaction including o, m and p-anisyl, 2-furyl and vinyl, but they did not yield a significant amount of the cyclized product. One major problem is that these substituents lead to a red shift of the π–π^* transition, and makes the relatively weak n-π^* photochemically ineffective.

It was important to find a simple way in which to remove the hydroxy group. The reaction of 2 with mild halogenating agents such as triphenylphosphine and bromine or triphenylphosphine and N-bromosuccinimide[10] led to rearrangement and the formation of olefinic products. Similarly, an attempted direct reduction to the hydrocarbon using triethylsilane and boron trifluoride etherate[11] again led to rearranged products. It was clear that reactions which might proceed via a carbocation

were not suitable. The acid catalyzed rearrangement of 2 to 3-phenyl-3-cyclopenten-2-ol has previously been reported.[7]

It is known that benzyl alcohols undergo hydrogenolysis under Birch reduction conditions.[12] The reaction of 2 with sodium and ammonia led only to reversion to the ketone, presumably via a base catalyzed process. However, the acetate derived from 2 did undergo reduction under these conditions (-78°C) giving 2-phenylbicyclo[1.1.1]pentane (3) in 80% yield. The reaction must be controlled because an excess of reducing agent causes cleavage of the bicyclic ring giving benzylcyclobutane. Some of this product also was obtained using one equivalent of sodium at -33° (the boiling point of ammonia). It is interesting that the bicyclopentane ring is more easily reduced than the benzene ring.



The ready availability of 3 allowed a number of transformations to be effected (Scheme 1). Oxidation using ruthenium tetroxide gave the carboxylic acid (4). The use of the Schmidt reaction led to the conversion of 4 to bicyclo[1.1.1]pentyl-2-amine (5). Oxidation of 5 with m-chloroperbenzoic acid gave the 2-nitro derivative (6). The acid (4) also was converted to the phenyl ketone with phenyllithium.

The oxidation of the amine (5) presented some difficulties. Oxidation with m-chloroperbenzoic acid in methylene chloride at reflux gave no reaction. The use of chloroform at reflux gave a 25-40%

yield of 6 as determined by analytical gc. However, the isolated yield was lower. If the oxidation were carried out in 1,2-dichloroethane as the solvent, loss of the bicyclic ring was noted. The use of peracetic acid was not successful.

We have previously reported the effect of some small ring structures on the acidity of carboxylic acids in order to examine the effect of hybridization on changes in acidity.[6] As an extension of the previous study, the pK_a values for 4 and several related acids were determined and are given in Table I. The first four acids have been studied previously,[6] but were redetermined so that any systematic error should cancel. The pK values follow roughly the trend expected from the %s character determined from the nmr ^{1}H-C coupling constants.[13] However, the range of pK is quite small, and cyclopropanecarboxylic acid was considerably less acidic than expected. One problem with interpreting the acidity of acids is that in aqueous solution they have maximum pK_a values near 25°C.[14] Thus, it is possible that the relative acidities of a pair of acids may invert on changing temperature.

The acidities of the corresponding amine hydrochlorides are of more interest because the charge is developed at an atom closer to the cyclic rings, and larger effects should be found. The pK_a values were determined for several hydrochlorides in 50% ethanol-water giving the data in Table II. Here, there was a much better relationship between the pK_a values and the %s character (Figure 2).

2-Nitrobicyclo[1.1.1]pentane was interesting in that it would not dissolve in 1 *M* sodium hydroxide solution, whereas nitrocyclohexane is readily soluble.[15] This indicates that the pK_a has been significantly increased as a result of the angle strain at the 2-position. A similar observation has been reported for nitrocyclopropane.[16] In order to obtain more quantitative data, we have determined the pK_a values for some nitrocycloalkanes[17], and they are recorded in Table III. The data for the nitrocycloalkanes were in good agreement with those reported by Bordwell, et. al.[16] Nitrocyclopentane was the most acidic, and here, conversion to the anion will relieve some of the eclipsing strain in the cyclopentane ring. Nitrocyclobutane and nitrocyclohexane were significantly less acidic, and in both cases the formation of the anion with its larger normal bond angles will lead to some increase in strain. The least acidic of the nitro compounds was 2-nitrobicyclo[1.1.1]pentane. Here, the formation of an

anion stabilized by the nitro group will be very difficult since the bond angle is so small. The extreme of this behavior is, of course, nitrocyclopropane.

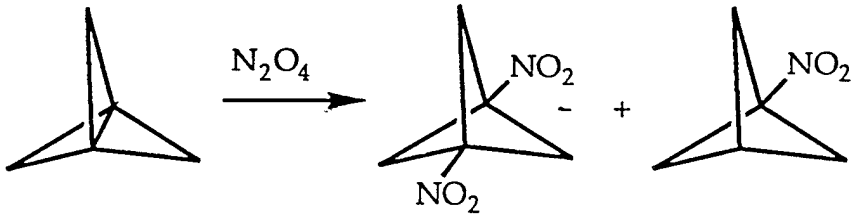
It might be expected that the free energy change on ionization would be related to the difference in strain energy between the parent ring system and one in which a trigonal center has been introduced. The best comparison might be with the heats of reduction of ketones, and the available data are summarized in Table IV. Taking the strain energy change for acetone as zero, the strain energy changes for the other compounds may be obtained. It can be seen that nitrocyclopentane has the largest acidity and a negative change in strain energy, whereas bicyclo[1.1.1]pentan-2-one has the lowest acidity and the largest increase in strain. The other compounds have intermediate values. Thus, there is a rough correlation with the change in stain energy.

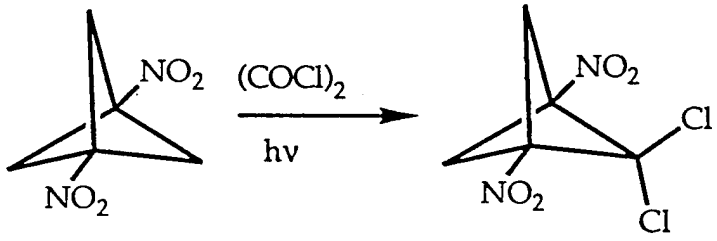
We have attempted to convert 6 to 2,2-dinitrobicyclo[1.1.1]pentane via a procedure which is quite effective for converting nitrocyclopentane to its dinitro derivative.[15] Whereas the latter is formed in good yield, only traces of the dinitro compound was found with 6. The low acidity is presumably a major factor causing the difficulty in this reaction.

The kinetic acidity also was of interest, but with the difference in behavior of the nitro compounds, it was not convenient to study them. Therefore, we have examined the kinetic acidity of the corresponding phenyl ketones via the measurement of the rate of deuterium exchange in the presence of base. The results are shown in Table V. Here, cyclobutyl phenyl ketone and cyclopentyl phenyl ketone had comparable reactivities. Phenyl bicyclo[1.1.1]pentyl-2 ketone was less reactive by a factor of 10^3, and less than 10 times more reactive than cyclopropyl phenyl ketone. The relative rates are roughly correlated with the change in strain energy on going from a tetrahedral to a trigonal center (Table IV). Here, cyclobutane and cyclopentane have a small change in strain energy, bicyclo[1.1.1]pentane has an intermediate value, and cyclopropane has the largest increase in strain.

We were also interested in having bicyclo[1.1.1]pentane derivatives with functional groups at both the 1 and 2 positions. Some compounds of this type have been prepared by the direct chlorination of 1,3-disubstituted bicyclo[1.1.1]pentanes.[18]The photochemically induced reaction of bicyclo[1.1.1]pentane with oxalyl chloride has been found to give substitution of a chlorocarbonyl group

at both the 1- and 2-positions.[6] 1,3-Dinitrobicyclo[1.1.1]pentane may be prepared by the reaction of [1.1.1]propellane with N_2O_4[3] and it appeared to be a promising substrate for functionalization at the 2-position. The procedure for the preparation of the dinitro derivative was developed for preparative use, and it was found that 1-nitro-bicyclo[1.1.1]pentane was a major byproduct when the reaction was carried out in ether. The reaction of the dinitro derivative with oxalyl chloride was carried out in excess oxalyl chloride. On workup with methanol, the major product was found to be 2,2-dichloro-1,3-dinitrobicyclo[1.1.1]pentane, and only a trace (gcms) of the methyl ester that would be formed from the expected acid chloride was found.





The formation of the chloride rather than the acyl chloride is surprising, as well as the observation that the dichloride rather than monochloride was the major product.

Conclusions: It is possible to prepare a variety of 2-substituted bicyclo[1.1.1]pentane from the photochemical closure product, **2**. The properties of the 2-substituted bicyclo[1.1.1]pentanes appear to be largely determined by a combination of hybridization and angle strain. The acidities of a series of cycloalkylammonium halides were approximately related to the %s character as determined from their ^{13}C-H nmr coupling constants. Both the equilibrium acidities of nitrocycloalkanes and the kinetic acidities of phenyl cycloalkyl ketones were found to be approximately related to the change in strain energy on going from a tetrahedral to a trigonal center.

Acknowledgment: This investigation was supported by U. S. Army ARDEC via Geo-Centers, Inc. We thank Dr. Hortensia Sanchez-Martinez, U. C. Torrelaguna, Madrid, for a generous gift of cyclobutyl phenyl ketone.

Experimental section:

Nmr spectra were determined in $CDCl_3$ solutions at 250 MHz for protons and 68 MHz for carbons, and are reported in ppm downfield from TMS. Column chromatography made use of Kieselgel (230-400 mesh) as the solid support.

2-Phenylbicyclo[1.1.1]pentane. To a solution of 12.6 g (0.079 mol) of 2-phenylbicyclo[1.1.1]pentan-2-ol in 65 mL of pyridine at 0°C was added dropwise with stirring, 6.2 mL (0.087 mol) of acetyl chloride. The solution was stirred for 0.5 hr at 0, and for 1 hr at room temperature. The solution was added to ice, and extracted with 300 mL of ether. The ether solution was washed with aqueous sodium bicarbonate solution, and with saturated aqueous copper sulfate solution. After drying over $MgSO_4$ the solution was passed through a 6" florisil column, and concentrated to give 13.0 g (82%) of the acetate. ^1H nmr (ppm): 7.26-7.47 (m, 5H), 3.30 (s, 1H), 2.42 (dd, J=10.3, 2.7 Hz, 1H), 1.94 (s, 3H), 1.80 (d, J=2.7 Hz, 1H), 1.66 (d, J=3.2 Hz, 1H), 1.48 (dd, J=10.4, 3.2 Hz, 1H). ^{13}C nmr: 169.9, 138.0, 128.2, 127.7, 127.6, 95.4, 42.5, 41.6, 41.2, 21.0.

A solution of 27.2 g (0.135 mol) of the acetate in 500 mL of anhydrous ether was placed in a 5L three-necked flask. The flask was cooled to -78° C, and 1.5 L of liquid ammonia was added. Sodium (6.5 g, 0.28 mol) was added in small pieces over a period of 30 min. Stirring was continued until the blue color was discharged. The reaction was quenched by the addition of NH_4Cl, and the solvent was allowed to evaporate overnight. Pentane (200 mL) was added to the residue, and the solution was washed with NaCl soln, dried over $MgSO_4$ and concentrated. Purification via column chromatography (9:1 hexane:ether) gave 2-phenylbicyclo[1.1.1]pentane as a colorless liquid (15.5 g, 80%), bp 43° at 1 torr. ^1H nmr: 7.27-7.40 (m, 5H), 3.53 (d, J=6.9Hz, 1H), 2.85 (s, 2H), 2.26 (dd, J=9.7, 2.6Hz, 1H), 2.00 (d, J=1.9Hz, 1H), 1.90-1.94 (m, 2H). ^{13}C nmr: 141.0, 128.1, 127.9, 125.7, 63.9, 47.7, 47.0, 36.2.

Bicyclo[1.1.1]pentane-2-carboxylic acid. A mixture of 5.0 g (0.035 mol) of 2-phenylbicyclo[1.1.1]pentane, 0.2 g of ruthenium dioxide, 100 g (0.47 mol) of sodium periodate, 310 mL of water, 220 mL of carbon tetrachloride and 220mL of acetonitrile was stirred for two days during which time a gelatinous precipitate formed. Approximately 300 mL of CH_2Cl_2 was added to the mixture, and the solids were removed by filtration. The organic layer was separated and the aqueous

layer was washed with ether. The combined organic solution was concentrated. Ether (250 mL) was added to precipitate ruthenium salts. After standing overnight, the solution was filtered through Celite, dried over Na_2SO_4 and evaporated to dryness. The product was dissolved in aqueous NaOH and extracted with ether. Flash chromatography (9:1 pentane:ether followed by 4:1) and evaporation of the solvent gave the acid as a white solid (2.2 g, 56%). It could be further purified by sublimation at 50° C and 0.2 torr, and had mp 40-41°. ^1H nmr: 2.92 (d, J=7.3 Hz, 1H), 2.77 (s, 2H), 2.45 (dd, J=10.4, 3.2Hz, 1H), 1.88 (dd, J=7.3, 3.2 Hz, 1H), 1.72-1.76 (m, 2H). ^{13}C nmr: 178.8, 61.5, 48.2, 47.9, 36.7.

Bicyclo[1.1.1]pentyl-2-amine hydrochloride. To as 500 mL three necked flask equipped with a mechanical stirrer and reflux condenser was added 100 mL of chloroform, 1.04 g (9.7 mmol) of bicyclo[1.1.1]pentane-2-carboxylic acid and 4.0 mL of conc. sulfuric acid.. Sodium azide (1.2 g., 18.5 mmol) was added in portions to minimize heating and bubbling due to release of nitrogen. The mixture was heated at 50° C for 30 min, then cooled and diluted with ice. Slow addition of aqueous KOH to pH 12-13 gave the free amine. The amine, along with water and chloroform, was distilled into a cooled flask containing dilute hydrochloric acid. Concentration of the acidic solution gave the hydrochloride (83%) which could be purified by recrystallized from ether-n-propanol, mp 177-187° C. ^1H nmr (D_2O): 3.38 (d, J=6.6 Hz, 1H), 2.54 (s, 2H), 2.31 (dd, 10.3, 4.8 Hz, 1H), 1.90 (dd, J=6.4, 4.9, 1H), 1.79 (d, J=2.8Hz, 1H), 1.50 (dd, J=10.3, 3.0Hz, 1H). Anal, calc for $C_5H_{10}NCl$: C, 50.2; H, 8.4. Found: C, 49.8; H, 8.6.

2-Nitrobicyclo[1.1.1]pentane (6). A solution of 7.3 g of m-chloroperbenzoic acid in 150 mL of chloroform was heated to reflux and 2-bicyclo[1.1.1]pentylamine from 1.0 g of the hydrochloride in 10 mL of chloroform was added. After stirring for 16 hr at reflux, the solution was cooled to room temperature and 2 mL of dimethyl sulfide was added to remove excess oxidant. The reaction mixture was separated by column chromatography with chloroform as the eluent. The nitro compound eluted immediately after dimethyl sulfide. The solvent was removed by distillation through a 4" glass bead column giving 0.23 g (24%) of **6**. ^1H nmr: 4.48 (d, J=7.0Hz, 1H), 3.01 (s, 2H), 2.35 (dd, J=10.2 Hz, 4.0 Hz, 1H), 1.97 (dd, J-7.0, 4.0 Hz), 1.77 (d, J=3.1 Hz, 1H), 1.55 (dd, J=10.2, 3.1 Hz, 1H). ^{13}C nmr: 91.8, 46.5, 39.4, 38.5. MS (CI): calc for $C_5H_8NO_2$ (p+1): 114.0555; found, 114.0546.

2-Benzoylbicyclo[1.1.1]pentane. A solution of 210 mg (1.8 mmol) of bicyclo[1.1.1]pentane-2-carboxylic acid in 20 mL of dry ether was placed in a 100 mL flask with a reflux condenser. Phenyllithium (2.75 mL, 1.3 M, 3.6 mmol) was added dropwise, and the solution was heated at reflux for 30 min. The solution was treated with 2 mL of 10% sulfuric acid, and the layers were separated. The ether layer was washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (ether-pentane) to give the ketone as a colorless liquid (195 mg, 63%). ^1H nmr: 7.95-7.99 (m, 2H), 7.41-7.56 (m, 3H), 3.51 (d, J=6.8, 1H), 2.96 (s, 2H), 2.27 (dd, J=3.0, 9.8 Hz, 1H), 1.90 (dd, J=2.0,9.8 Hz, 1H), 1.82-1.86 (m, 2H). ^{13}C nmr: 199.3, 136.9, 132.8, 128.4, 128.2, 67.4, 47.7, 46.7, 37.7. Anal, calc for $C_{12}H_{12}O$: C,83.7; H,7.0. found: C, 84.0; H, 7.2.

Determination of Ionization Constants. The pK_a values for the carboxylic acids and the amine hydrochlorides were determined via potentiometric titration as previously described.[6] The pK_a values for the nitro compounds were determined using the procedure described by Bordwell, et. al.[16] The rate of base catalyzed deuterium incorporation into the phenyl cycloalkyl ketones was measured in methanol-d_4 solution at 25°C via nmr spectroscopy. They gave good pseudo-first order kinetics. The rate constants were divided by the base concentration (~ 5×10^{-3} M for the more reactive compounds and ~ 4×10^{-2} M for the less reactive compounds) to give the reported second order rate constants.

Addition of Nitrogen Dioxide (N_2O_4) to [1.1.1]propellane: 1,3-Dinitrobicyclo[1.1.1]pentane, and 1-Nitrobicyclo[1.1.1]pentane. The procedure reported here is based upon that reported by Wiberg and Waddell.[3] During a scaled up synthesis using the original procedure, a detonation of the concentrated reaction mixture occurred. We report a new procedure that safely decomposes the unstable compounds in the reaction mixture before purification.

To a three necked flask equipped with magnetic stirring, cooled in an ice bath, and purged under an argon atmosphere was added 250 mL of dry diethyl ether. Nitrogen dioxide gas (50 mmoles, approximately 4.6 g) was added to the ether through a bubbler. To this solution over 10 minutes was added 72 mL of a 0.28 M solution of [1.1.1]propellane (1.33 gram, 20.2 mmole) in ether prepared as described previously.[18] The reaction mixture was then allowed to stir for an additional 15 min. Then the ice bath was removed and 250 mL of an aqueous 5% NaCl solution was added to hydrolyze

reactive compounds. The biphasic mixture was stirred for 5 min and was then decanted into a separatory funnel and the layers separated. The organic layer was washed 5 times with 125 mL of aqueous saturated sodium bicarbonate. The combined aqueous washes were extracted 3 times with 50 mL of ether. All the organic layers were combined and dried over sodium sulfate. The pale green ether solution was carefully concentrated to approximately one fifth of the original volume. The resultant liquid was filtered to remove a yellow precipitate. The remaining solution was then concentrated to give 2.6 g of a semi-crystalline liquid. This mixture was purified by column chromatography using a 1:1 mixture of hexanes and methylene chloride mixture as eluent. From this was collected 528 mg. (3.34 mmole, 16.5% yield) of crystalline 1,3-dinitrobicyclo[1.1.1]pentane and 198 mg. (1.75 mmole, 8.7% yield) of 1-nitrobicyclo[1.1.1]pentane as a liquid.

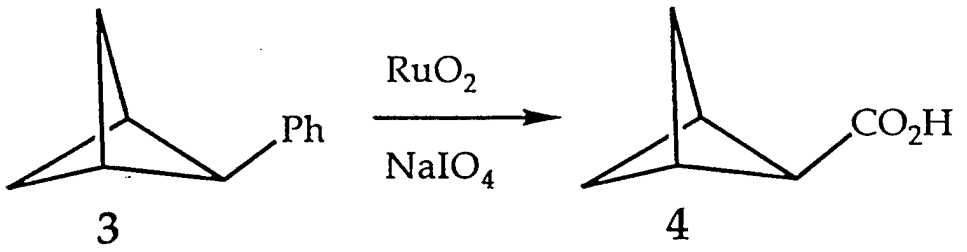
1,3-Dinitrobicyclo[1.1.1]pentane. Subl. 65 ^{o}C/1.0 mm Hg; ^{1}H NMR δ 3.01 (s, 6H); ^{13}C NMR δ 61.7 (C-NO_2), 57.1 (CH_2); FTIR 1549 cm^{-1} (NO_2 stretch); CIMS (isobutane) m/z 159 (M+1); EIMS, m/z 82(7), 66(15), 65(100), 54(28), 39(88); HRMS (CI, Isobutane) calc. for $C_5H_7N_2O_4$ (M+1) : 159.0406 Found 159.0435

1-Nitrobicyclo[1.1.1]pentane. ^{1}H NMR δ 2.34 (s, 6H), 2.61(s, 1H); ^{13}C NMR δ 66.4 (C-NO_2), 53.1 (CH_2) 20.0 (C-H); FTIR 1532 cm^{-1} (NO_2 stretch); CIMS (isobutane) m/z 114 (M+1); EIMS, m/z 67(100), 65(67), 41(67); HRMS (CI, isobutane) calc. for $C_5H_8NO_2$ (M+1) : 114.0555 Found 114.0541.

2,2-Dichloro-1,3-dinitrobicyclo[1.1.1]pentane. Into a quartz tube was placed 90.0 mg (0.569 mmole) of 1,3-dinitrobicyclo[1.1.1]pentane. The tube was sealed with a rubber septum and purged with argon. To this was added 10 mL of freshly distilled oxalyl chloride. The mixture was briefly degassed with argon and allowed to remain attached to a bubbler to prevent pressure build-up. The sample was irradiated in an ice bath with a 250 watt Hanovia medium pressure mercury vapor lamp equipped with a quartz filter for 5 days. After irradiation was complete, oxalyl chloride was removed under reduced pressure on a rotary evaporator. Excess methanol was then added to destroy any acid chlorides which remained. The methanol was removed and the remaining crystalline sample was purified by column chromatography using 3:2 hexanes:methylene chloride as eluent. A total of 6.5 mg of starting material as well as 56.2 mg. of 99.2% pure and 2.7 mg of 95% pure (total of 58.9 mg., 0.260 mmole, 49%

yield based on recovered starting material) 2,2-dichloro-1,3-dinitrobicyclo[1.1.1]pentane was obtained. A white, crystalline, analytical sample was obtained by sublimation at 75°C and 0.9 mm Hg pressure. ^{1}H NMR δ 3.20(dd, J=0.67 Hz, 2H), 3.69(dd, J=0.67 Hz, 2H) ; ^{13}C NMR δ 71.07 (C-NO_2), 53.50 (CH_2), 91.35(CCl_2) ; FTIR 1556 cm^{-1} (NO_2 stretch); CIMS (isobutane) m/z 227, 229 (M+1); EIMS, m/z 134(3), 122(35), 120(37), 99(46), 87(100), 73(83), 63(60); HRMS (CI, Isobutane) calc. for $C_5H_5Cl_2N_2O_4$ (M+1) 226.9626. Found 226.9620 ; Anal. calc. for $C_5H_4Cl_2N_2O_4$: C, 26.46 H, 1.78 Found: C, 26.56 H, 1.81.

Scheme 1



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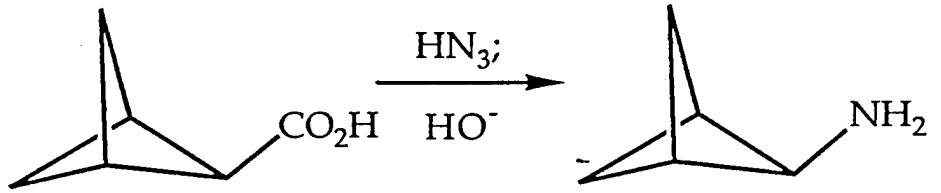

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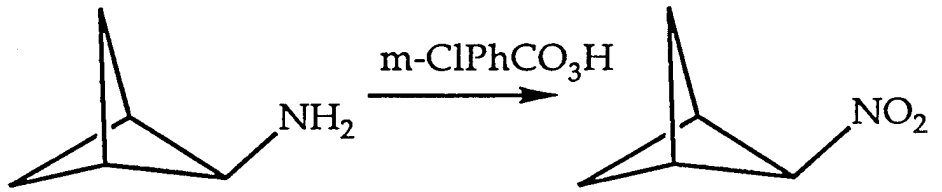

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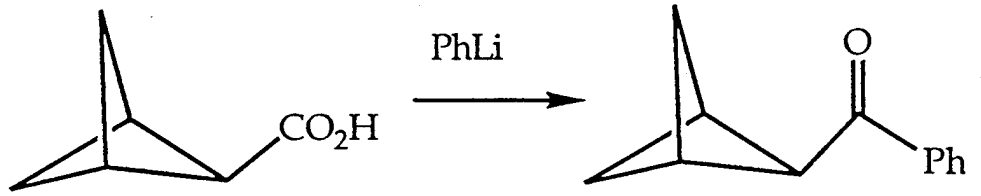

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Table I Acidities of cycloalkane carboxylic acids.

R	pK_a	%s[a]
CH_3	4.85	25
Cyclohexyl	4.84	25
Cyclopentyl	4.87	26
Cyclobutyl	4.66	27
Cyclopropyl	4.65	33
1-Bicyclo[2.1.1]hexyl	4.46	31
2-Bicyclo[1.1.1]pentyl	4.27	29
1-Bicyclo[1.1.1]pentyl	4.09	33

a. The %s values were derived from the ^{13}C-H nmr coupling constants (ref. 13)

Table II. Acidities of cycloalkylamine hydrochlorides

R	pKa,50%EtOH	pKa, H_2O[a]
Cyclohexyl	10.05	
Cyclopentyl	10.16	
Cyclobutyl	9.61	10.04
Cyclopropyl	8.76	
1-Bicyclo[2.1.1]hexyl	[8.9][b]	9.30
2-Bicyclo[1.1.1]pentyl	8.90	
1-Bicyclo[1.1.1]pentyl	[8.2][b]	8.58

a. Ref. 6.

b. Estimated values based on the pK_a in water.

Table III. Equilibrium acidities of nitrocycloalkanes.

R	pKa, 50%MeOH
Cyclobutyl	10.05±0.03
Cyclopentyl	8.19±0.04
Cyclohexyl	10.02±0.05
2-Bicyclo[1.1.1]pentyl	11.20±0.11

Table IV Heats of reduction of cycloalkanones and strain energy changes

Compound	ΔH_{redn} kcal/mol[a]	ΔSE (tet→trig) kcal/mol
Acetone	-13.0	0.0
Cyclopropanone	-31[b]	+18
Cyclobutanone	-12.7	-0.3
Cyclopentanone	-10.9	-2.1
Cyclohexanone	-14.1	1.1
2-Bicyclo[1.1.1]pentane	-18[b]	~ 5

a. Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447..

b . Estimated from ab initio calculations at the RHF/6-31G* level.

Table V. Rates of deuterium exchange for cycloalkyl phenyl ketones, 25°C, methanol-d_4.

Ring	k, min^{-1}
Cyclopropane	1.63×10^{-4}
Cyclobutane	2.11
Cyclopentane	1.06
2-Bicyclo[1.1.1]pentane	2.91×10^{-3}

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Figure captions:

Figure 1. Relationship between the pK_a values for cycloalkanecarboxylic acids and the % s character as determined from the ^{13}C-H nmr coupling constants.

Figure 2. Relationship between the pK_a values for cycloalkylammonium ions amd the % s character.

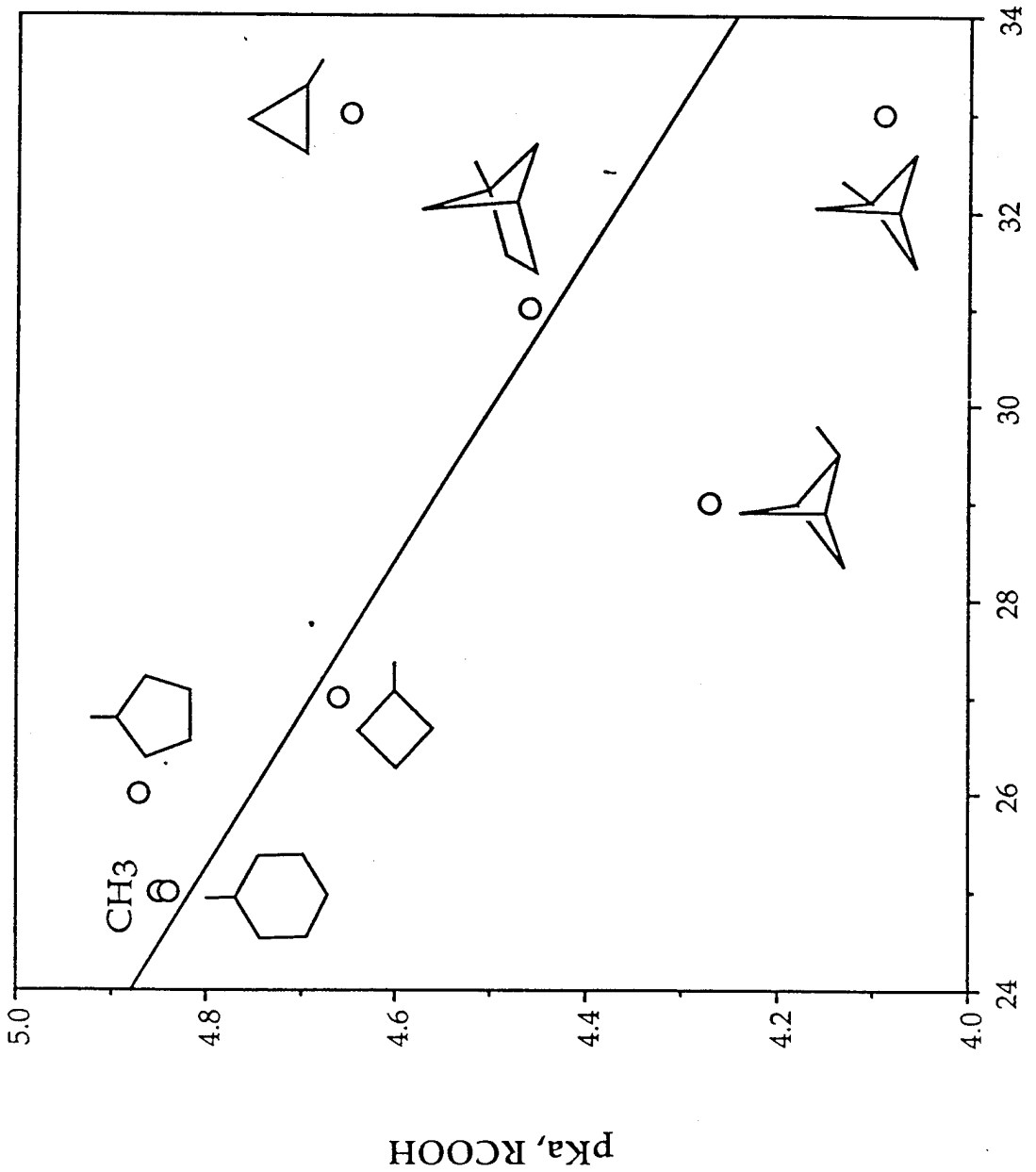

Figure 1

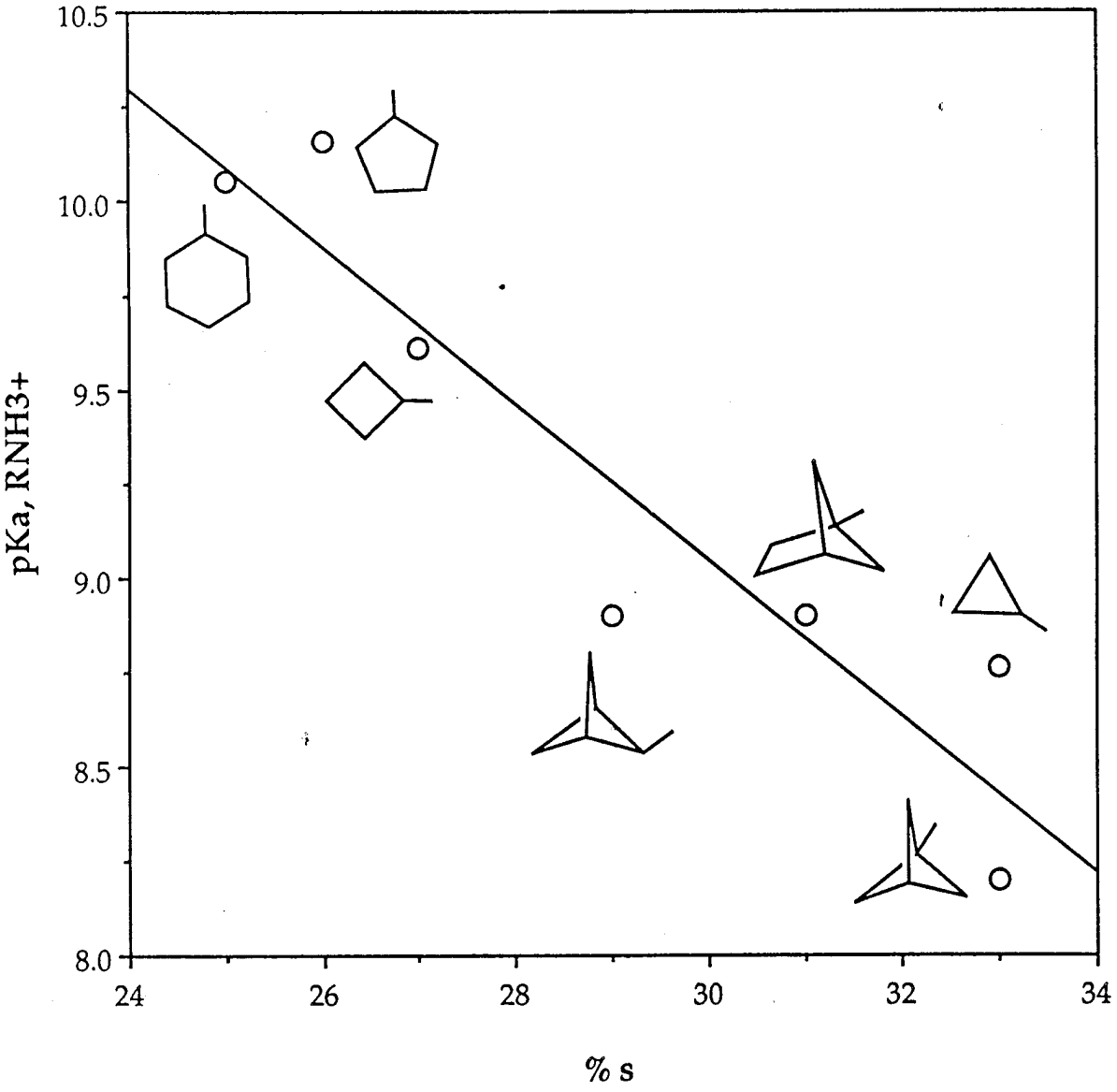

Figure 2

TASK 7:

ELECTROMAGNETIC PULSE EFFECTS

TASK 9:

DECOMPOSITION STUDIES

Objective 1:

Scale-Up Procedures for TNAZ

(Aerojet Propulsion Division)

Note: Information included in Appendix A is on file at the GEO-CENTERS, INC. office and is available for review.

February 22 1993

FINAL REPORT
Covering Period 4 November 1991 to 15 February 1993

SCALE-UP PROCEDURES FOR TNAZ

by

T. G. Archibald and R. P. Carlson

Prepared for:

GEO-CENTERS, INC.
7 Wells Avenue
Newton Upper Falls, MA 02159

From:

AEROJET PROPULSION DIVISION
P.O. Box 13222
Sacramento, CA 95813-6000

Contract No. GC-1853-91-011

Table 3. Phase II Preparation of 1-t-Butyl-3,3-Dinitroazetidine

Batch	Azetidol HCl pounds	Ratio to Phase I	Dinitroazetidine pounds	Yield % based on Phase 1	Yield % based on Azetidol
CH2CL2- Freon 113 Runs					
Phase I (typical)	38	1.0	5.1	100	11.0
3A	56	1.47	7.4	98	10.8
3B	116	3.05	15.3	98	11.0
3C	112	2.94	14.6	97	10.6
Toluene Runs					
3D	60	1.57	8.2	103	11.2
3E	116	3.05	20.0	129	14.0
3F	116	3.05	16.0	103	11.2
3G	112	2.94	14.0	93	10.2
3H	100	2.63	14.9	111	12.1
Total	**734**		**110.0**		**12.2**

Based on information developed in laboratory scale runs, it was found that the nitrite displacement reaction could be run at temperatures from 30-50°C. Under these conditions, the reaction was complete in 4 hours and the yield was improved. Previously, reactions were run at 20°C and required 30 hours to reach completion. In the pilot plant it was found that the nitrite reaction was exothermic. The toluene solution of mesylate was stirred with aqueous sodium nitrite and heated to 30°C. Over an hour, the temperature continued to increase spontaneously to 50°C. For convenience, the mixture was heated at the end of the day and allowed to exotherm and cool overnight. After 16 hours, no mesylate remained, but the reaction was probably complete sooner.

The nitrite solution was removed and the toluene layer extracted with sodium hydroxide for 30 minutes. The water layer was removed and subjected to standard oxidative nitration to give the dinitroamine. All runs in toluene were equal to or superior to the Freon runs in yield. The red tars that were encountered in the interface of the Freon runs were absent in toluene. As a result all separations were cleanly and easily made. In general the solutions were lighter in color.

The use of a single solvent simplified the waste stream, reduced cost of buying chemical solvents, and saved labor costs. The average yield of the dinitroazetidine obtained in greater than 100 pounds scale in methylene chloride-Freon was slightly less than the smaller scale reactions of Phase I (about

98%). The use of Toluene increased the yield to 106% of Phase I scale reactions. This represents an 8% overall increase in yield by using Toluene as the solvent. Based on these improvements, two complete conversions of azetidol hydrochloride to dinitroamine can be completed in one working week. A summary of the amounts of dinitroazetidine prepared are shown in Table 4.

Table 4. Total amounts of dinitroazetidine prepared.

Phase 1	4 runs	20 pounds
Phase 2 (current)	8 runs	110 pounds (12.2%)

Nitrolysis of the dinitroamine to TNAZ presented serious difficulties in the pilot plant. The equipment used was a 50 gallon Pfaudler reactor with remote controls and a video camera. During the time that nitric acid was being added to the organic amine nitrate salt, no operators were permitted in the building and procedures were conducted remotely. The reactor was fitted with a 18" x 3" condenser with an adjustable water supply. There was a thermocouple above this condenser, and a second condenser (30" x 6") equipped with a take-off valve leading to a 15 gallon 316 ss holding tank equipped for handling N_2O_4. Both condensers were equipped with 14°F cooling.

During Phase I, the dinitroamine products from the four batches were placed in the 50 gallon Pfaudler to give a combined volume of 20 gallons. Then, 98% nitric acid was added such that the temperature was maintained below 85° F. After approximately 8 pound of nitric acid had been added, the exotherm ceased and the nitric acid addition was discontinued. The methylene chloride was removed at 70° F and 28 inches of vacuum for 24 hours. Nitric acid was added to a total of 288 pound (23 gal), and the mixture was kept at 40°F for 24 hours. The reaction mixture was then heated at 185° F (85° C) for 6 hours and then cooled to ambient temperature. During this heating approximately 1.5 gallon of dinitrogen tetroxide was removed by the top condenser. The cooling rate in the bottom condenser was adjusted such that no nitric acid was removed in the distillation. Analysis of the mixture showed than no TNAZ had been produced and that only starting material was present.

The reaction mixture was kept at 38° F overnight. Then, 5 gallons of 98% nitric acid was added and the mixture was heated for two hours without the

removal of N_2O_4. The temperature in the reactor dropped from 185° F to 172° F, and no TNAZ was formed. The reflux take off was opened and the reactor was heated at maximum heat of 220° F such that the internal temperature of the reactor reached 197° F for 1 hour. The reaction mixture was cooled, and TNAZ was found to be present.

The filtrate was found to contain starting amine by NMR and glc analysis. The reaction mixture was held at 32°F overnight and heated to 197-199°F for 1 additional hour, cooled and quenched into 60 gallons of ice water such that the temperature did not exceed 20°C.

The quenched water slurry of TNAZ was cooled to 1°C, filtered and washed four times with water to give 12 pound (7% based on t-butyl amine) of TNAZ. The product exhibited a melting point of 212°F (100°C) by DSC and was pure by NMR and FTIR analysis.

The product had a light blue color and was dissolved in acetone, filtered and reprecipitated from water to give 8 pounds of purified TNAZ. The descripancy in weight was unexplained during Phase I, but appears to be due to the presence of t-butyl nitrate in the crude material. The yield based on starting dinitroamine was 45%. Seven pounds of this material was shipped to Eglind Air Force Base and the remainder was held for ARDEC.

During Phase II, the 110 pounds of 1-t-butyl-3,3-dinitroazetidine was converted to the nitrate salt and nitrolyzed in four batches (Batches 4a, 4b, 4c, and 4d) following a nitrolysis procedure obtained from Geo-Centers.

In Batch 4a, 20 pounds of the diamine in methylene chloride solution was converted to the nitrate salt and the methylene chloride evaporated under 20" vacuum at 100° F for 16 hours. Then, 20 gallons of 98% nitric acid and 5 pounds of water (to prepare 95% nitric acid) was added and the mixture was heated to reflux (approximately 200°F) for eight hours. NMR analysis of the reaction mixture showed the reaction was 34% complete. The reaction mixture was heated for 8 hours each day for three more days during which time the conversion of the dinitro salt to TNAZ reached 55% and then appeared to drop to 50%. As the reaction mixture was heated N2O4 was evolved and approximately 8 gallons was collected. It appears that the solvent (nitric acid) had become reduced in volume to such an extent that TNAZ was crystallizing out in the reactor.

Batch 4a was then added to 20 gallons of water at 20-30°C and the resulting mixture cooled to -4°C and filtered. This material was highly

lachramatory and evolved oxides of nitrogen over several days in water. It was determined that this material (crude "dry" weight of 19 pounds) contained about 30% of t-butyl nitrate, 2% of unreacted nitrate salt and 2% of 2,4-dinitrotoluene. The presence of nitrotoluenes resulted from trace contamination of toluene in the nitrate salt. This problem has been overcome by isolation of the nitrate salt rather than evaporation of the methylene chloride in the reactor.

In Batch 4b, 30pound of dinitroazetidine was reacted with nitric acid in methylene chloride. The nitrate salt was isolated by filtration, washed with fresh methylene chloride, and dried to remove residual methylene chloride and toluene. The dry salt was placed in the reactor and 98% nitric acid (300pound) was added. This run was heated for 6-8 hours each day for 5 days. Approximately 12 gallons of N2O4 was evolved, and the presence of solid TNAZ was noted in the nitric acid when samples were taken for analysis. The reaction was cooled and 30 gallons of water was added. The mixture was cooled to -4°C and filtered to give a highly lachramatory solid containing TNAZ, t-butyl nitrate and starting nitrate salt (10%). Inspection of the reactor showed a shinny football size piece of TNAZ indicating that there was liquid TNAZ formed as a separate phase during the reaction. The crude TNAZ was resuspended in 7 gallons of water and heated to 35°C for 4 hours and purged with air under 10 " of vacuum to remove the t-butyl nitrate. The mixture was cooled, filtered, and air dried to give 21 pounds of TNAZ (approximately 70% yield). This material contained no dinitrotoluenes or nitrate salt. The water layers were extracted with methylene chloride to give approximately 0.5 pounds of TNAZ. The water layers were then neutralized with caustic and extracted to give 2 pounds of dinitroamine.

The remaining dinitroamine (60 pounds) was neutralized with 17 pounds of nitric acid and the salt was filtered, washed with methylene chloride dried and divided into two portions (Batch 4c and 4d). The nitrolysis of Batches 4c and 4d were run under identical conditions. The reactor was charged with 1 drum (350 pounds) of 98% nitric acid and the salt added portionwise. The reactor was heated at 130°F overnight to remove any residual volatile materials. The next day the mixture was heated continuously for 14-15 hours at 198-204°F, cooled overnight and analyzed. Batch 4c was 72% done and Batch 4d was 78% done. The mixtures were heated for an additional 8 hours and cooled overnight. In these reactions the amount of N2O4 evolved (7-8 gallons each run) was smaller and the reaction appeared faster than was observed in the earlier runs.

The reason for the faster reaction is unknown. All of the TNAZ appeared to remained in the nitric acid solution during the reaction although solid TNAZ precipitated upon cooling.

The reactions were quenched with 30 gallons of water, cooled and filtered. The lachramatory solids from Batch 4c and 4d were combined and stirred with 14 gallons of water. Each run gave similar amounts of material to run Batch 4b.

Removal of the t-butyl nitrate continues to be a problem. The crude TNAZ was suspended in 10 gallons of water and heated to 110°F for two hours. The water was cooled to 32°F and filtered. The solid TNAZ was air dried for 16 hours. NMR analysis showed the TNAZ to be pure (>99.5%) and to contain approximately 5% of water. However, the solid still had a slight smell and lachramatory aspect indicating the presence of residual nitrate impurity.

Batch 4a that contained dinitrotoluene impurity was suspended in 5 gallons of water and 0.5 gallons of toluene and treated in the manner described above. After evaporation of the toluene, approximately 10 pounds of TNAZ (53%) was obtained. The dinitrotoluene impurity had been reduced from 3% to 1.5% by weight.

Batch 4b (21 pounds) and part of Batches 4c and 4d (9 pounds) was shipped water wet to Eglind Air Force Base. Batch 4a (10 pounds) and the remainder of Batches 4c and 4d (27 pounds) was packaged and awaits shipment to ARDEC.

Table 1. Nitrolysis of 3,3-Dinitroazetidine to TNAZ

BATCH	Dinitroamine pounds	TNAZ pounds	YIELD %
Phase I	20	8	45
Phase II			
4a	20	10	53
4b	30	21	73
4c+d*	60	36	63
Total	130	77	62

Weights and yields corrected by NMR analysis for water content

*Runs 4c&d were combined after nitrolysis and isolated together

The dilute nitric acid layers from the nitrolysis of TNAZ were each extracted twice with approximately 5 gallons of methylene chloride. The extracts from batch 4a were highly contaminated with nitro and dinitro toluene and were discarded. The extracts from the remaining batches were combined with 7 gallons of water and the methylene chloride was removed by distillation under reduced pressure. The residual oil was isolated by decantation of the water and was found to be a mixture of t-butylnitrate and TNAZ. This mixture was allowed to stand for a month in water without significant improvement. Purification of this material may not be feasible.

The dilute nitric acid layers from batches 4b, 4c, and 4d were neutralized and extracted to recover unreacted 3,3-dinitroazetidine. The extracts contained a red - tarry material that caused emulsions to form. Only about a pound of dinitro compound was obtained and it appears that this procedure is not cost effective.

In previous work at ARDEC and during the course of the first phase of this program, a slight bluish color in the TNAZ had been noticed. The source of the blue color in the TNAZ prepared previously was identified. Trace amounts of potassium ferricyanide in the water remain in the methylene chloride after the dinitroazetidine is extracted. Filtration of the methylene chloride solutions through a drying agent such as alumina removes the iron compounds with the water. During Phase II, all the methylene chloride solutions of the dinitroazetidine were combined and dried prior to nitrate salt formation.

Supporting spectral data for Phase I is found in the interim report. Spectral data for Phase II is found in Appendix A.

Task 3: Safety Data on TNAZ.

Aerojet Propulsion Division obtained standard Line 5 safety data on TNAZ from materials prepared in the pilot plant scale reactions during this program. Water wet TNAZ showed a Bureau of Mines impact of > 100 cm (2.5 Kg weight) , DTA onset of 428°F, rotary friction of > 4000 gm at 2000 RPM, and spark of > 1.0 Joules. Dry TNAZ showed a Bureau of Mines impact of 66 cm (2.5 Kg weight).

Task 4 MSDS.

A Material Safety Data Sheet (MSDS) for TNAZ was provided to Aerojet Propulsion Division by ARDEC. This MSDS will serve as the basis of identifying manufacturing problems that could impact the safety of personnel, disable equipment, or degrade the usefulness of facilities. No information was obtained under this program which would modify the existing MSDS. Time did not permit specific health or safety studies, and an Aerojet Propulsion Division Failure Errors Mode/Effects Analysis (FEMA) would be part of a follow-on program.

Task 5. REPORTING REQUIREMENTS

TASK 5.1 Aerojet Propulsion Division provided a monthly letter report detailing work accomplished, problems encountered, and work planned for the next reporting period.

TASK 5.2 This document constitutes a final report for the program.

TASK 5.3 The Material Safety Data Sheet for TNAZ is currently available from ARDEC and will serve as a basis for any MSDS reporting requirements.

TASK 5.4 Although a Manufacturing Safety Checklist based on an Aerojet Propulsion Division FEMA was outside the scope of this program (See TASK 4), a first draft of procedures and FEMAs were prepared. In anticipation of a follow-on program, an independent critical review (CER) is planned for the near future. All pertinent data obtained during the course of this program regarding manufacturing problems affecting safety are included as part of this final report.

RECOMMENDATIONS.

This program has shown the feasibility of moderate scale preparations of TNAZ. Significant progress has been made in material handling, scale and yields of all steps. Further investigations should be directed at improving the synthesis of 3-nitroazetidine and at the reduction of the large amount of waste that this process generates.

References:

Archibald, T. G.; Baum, K. "Research in Energetic Compounds" Fluorochem Report, February 1984.

Archibald, T. G.; Tzeng, D. D.; Bonsu, F.O.; Baum, K. "Studies of the Preparation of Trinitroazetidine" Contract DAAK10-85-C-0076, March 1986.

Archibald, T. G.; Harding, S. A.; Bonsu, F. O.; Baum, K "Energetic Small Ring Compounds" Contract DAA21-86-C-0101, November 1989.

Archibald, T. G.; Gilardi, R.; Baum, K.; George, C. *J. Org. Chem.* **1990**, *55*, 2921. Synthesis and X-ray Crystal Structure of 1,3,3-Trinitroazetidine.

Archibald, T. G; Carlson, R. P "Scale-up Procedures for TNAZ" Areojet Interm Report, April 1992.

Iyer, S.; Eng, Y. S.; Joyce, M.; Perez, R.; Alster, J.; Stec. D. *Defense Preparedness Meeting* 1991 (San Diego)

TASK 10:

FUEL-AIR EXPLOSIVES

Objective 1:

Sensitized Solid Fuels for Fuel-Air Explosives

(Mr. James L. Austing)
(Dr. Allen J. Tulis)
(IIT Research Institute)

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616-3799
312 567-4000

since 1936

October 31, 1989

GEO-CENTERS, INC.
P.O. Box 428
Newton Upper Falls, MA 02164

Attention: Maridee N. Kirwin

Subject: Quarterly Progress Report No. 2
July 8 through September 30, 1989

Reference: **Sensitized Solid Fuels for Fuel-Air Explosives**
Contract No. DAAA-89-C-0012
Subcontract No. GC-1853-89-005
IITRI Project No. C06694

Gentlemen:

This report represents the status of the referenced program for the above period of time. The period quoted has been adjusted to coincide with the IITRI cost accounting system, which is based on thirteen 4-week periods per year. Thus, this report covers the adjusted second quarter period of the program.

1. TECHNICAL ACCOMPLISHMENTS IN THIS PERIOD

During this report period, the major technical effort involved preparation for and conduct of a major demonstration of the bimodal concept for mine neutralization at Fort A.P. Hill, Virginia. This demonstration was conducted on September 28, 1989.

1.1 BACKGROUND

Previous efforts conducted under the Bimodal Program and IITRI Internal Research and Development established that the high explosive main charge of an unfuzed M-15 Anti-Tank Mine could be initiated by a detonating pre-deposited powder layer, which was initiated by a detonating dispersed explosive cloud.

In the bimodal concept, the ground layer would consist of relatively coarse particles, and the cloud of relatively fine particles, such that upon dissemination the coarse powder would gravitate or be driven to the ground while the fine powder would remain aloft and provide detonation coupling to the coarse powder. The pre-depositing of the coarse powder is an experimental expedient until dissemination methodology can be developed to accomplish this dispersal dynamically.

The initial ground layer that was used was a mixture of coarse and fine powders containing 30 percent flaked aluminum by weight, and the area mass coverage of this layer was 2.2 kg/m^2. However, a large number of tests had not been conducted, and thus a prime objective of the effort in the current Bimodal program being conducted by IITRI for BRDEC (Contract No. DAAK70-89-C-0060) was to replicate the previous results or to determine conditions under which the main charge explosive of the target land mines could be reliably initiated by means of the bimodal technology. These results would have a direct bearing on the experimental test plan for the Fort A.P. Hill demonstration.

By way of summary, the testing effort in that program involved the use of pre-deposited powder layers having an area coverage of either 2.2 kg/m^2 or 3.3 kg/m^2. The coupling cloud in all the tests was provided by a 4.536-kg charge of fine powder containing 30 percent flaked aluminum; this powder was dispersed to a cloud radius of 1.83 m in 50 ms, at which time the cloud was detonated. In addition to effort with M-15 Anti-Tank Mines, alternative mines were also evaluated. Initial tests were conducted using ground layers at 2.2 kg/m^2 and containing 30 percent aluminum, but in several instances the detonating cloud did not couple to these layers. It was determined that 30 percent aluminum in the ground layer was too great, and had an adverse effect upon detonation coupling from the cloud detonation. Subsequent testing results using ground layers containing 10 percent aluminum, but an area coverage of 3.3 kg/m^2, were very successful. At these conditions, coupling from the dispersed cloud to the ground layer was achieved, and all of the mines that were evaluated were initiated. These results formed the basis for the technical effort in regard to the demonstration tests at Fort A.P. Hill.

1.2 FORT A.P. HILL DEMONSTRATION

Three mine neutralization demonstration tests were planned and conducted, two of these based on demonstration of the bimodal concept as discussed in the preceding subsection, and the third based on demonstration of a detonation of a relatively dense dispersed explosive cloud without the use of pre-deposited powder ground layers. These tests were identified as the Primary Bimodal Test, the Back-up Bimodal Test, and the Canetip Test; the experimental arrangements for each test are respectively shown in Figures 1, 2, and 3. These drawings are to the scale indicated in each figure. The first two of these tests (Figures 1 and 2) required (a) dissemination cannisters which generated overlapping dispersed explosive clouds, (b) pre-deposited layers of explosives on the ground, (c) five types of unfuzed land mines, and (d) hardened fuzes. The main differences in the set-up of these two tests were with respect to the position of the second event charges and the placement of the hardened fuzes. The third test was similar, except that the mines were fuzed, a greater number of cannisters were used, and no pre-deposited layers were used on the ground.

The pre-deposited layers of explosive on the ground occupied an area of either 0.5625 m^2 (0.75 m by 0.75 m) or 0.45 m^2 (0.3 m by 1.5 m) depending on the configuration of the particular mine being evaluated. The area coverage in the Primary Bimodal Test was 3.3 kg/m^2, and in the Back-up Bimodal Test was 2.2 kg/m^2.

As stated previously, the initiation stimulus for the pre-emplaced ground layers was the detonation of an explosively-disseminated cloud of explosive powder. The so-called dissemination cannister for generating this cloud is depicted schematically in Figure 4. The major components include the 20-g dissemination charge, the flaked aluminum quench charge, and the 4.536-kg explosive charge to be dispersed. In the present effort, this latter charge was a mixture of fine explosive powder/flaked aluminum powder having a weight ratio of 70/30. The dissemination cannister generates a cloud of this powder having a radius of about 1.83 m (6 ft) and a thickness of about 0.7 m (27.5 in.) in 50 ms. The powder mixture has an additive of 3 percent by weight of Tullanox®, a hydrophobic material which improves flowability and reduces agglomeration of powders. These same cannisters were also used for the Canetip Test.

Accordingly, the effort in this report period was dividied into two parts. In the first part, the 46 dissemination cannisters and 6 second event charges that were required were fabricated and loaded, and the explosive powders for the 20 pre-deposited ground layers were weighed and blended. These cannisters and charges were then shipped to A.P. Hill for the demonstration tests, the conduct of which constitutes the second part of the report period. The tests were conducted on September 28. 1989. All three tests were instrumented by high-speed Photec cameras operating at nominally 4000 frames/s. In addition, the Canetip test (Figure 3) was instrumented with four piezoelectric pressure transducers to record the detonation pressure and velocity of the dispersed explosive cloud.

All three tests were successful. In the Primary Bimodal Test, all five mines and all five hardened fuzes were neutralized. In the Back-up Bimodal Test, three of the five mines and four of the five hardened fuzes were neutralized. In the Canetip Test, the cloud detonated and produced pressures and a detonation velocity that were in agreement with previous experimental and analytical data for dispersed explosive systems. A complete (classified) report on the experimental details and results of these tests will be prepared and submitted in the near future.

2. PLANS FOR THE NEXT REPORTING PERIOD

During the next reporting period, work will be begun on a classified technical report covering the experimental details and results of the Fort A.P. Hill demonstration tests. The types of mines evaluated will be identified, and qualitative data, where obtained, will be reported. Recommendations for future experimental effort will be made.

The above classified report together with the present progress report will constitute the final report on this program.

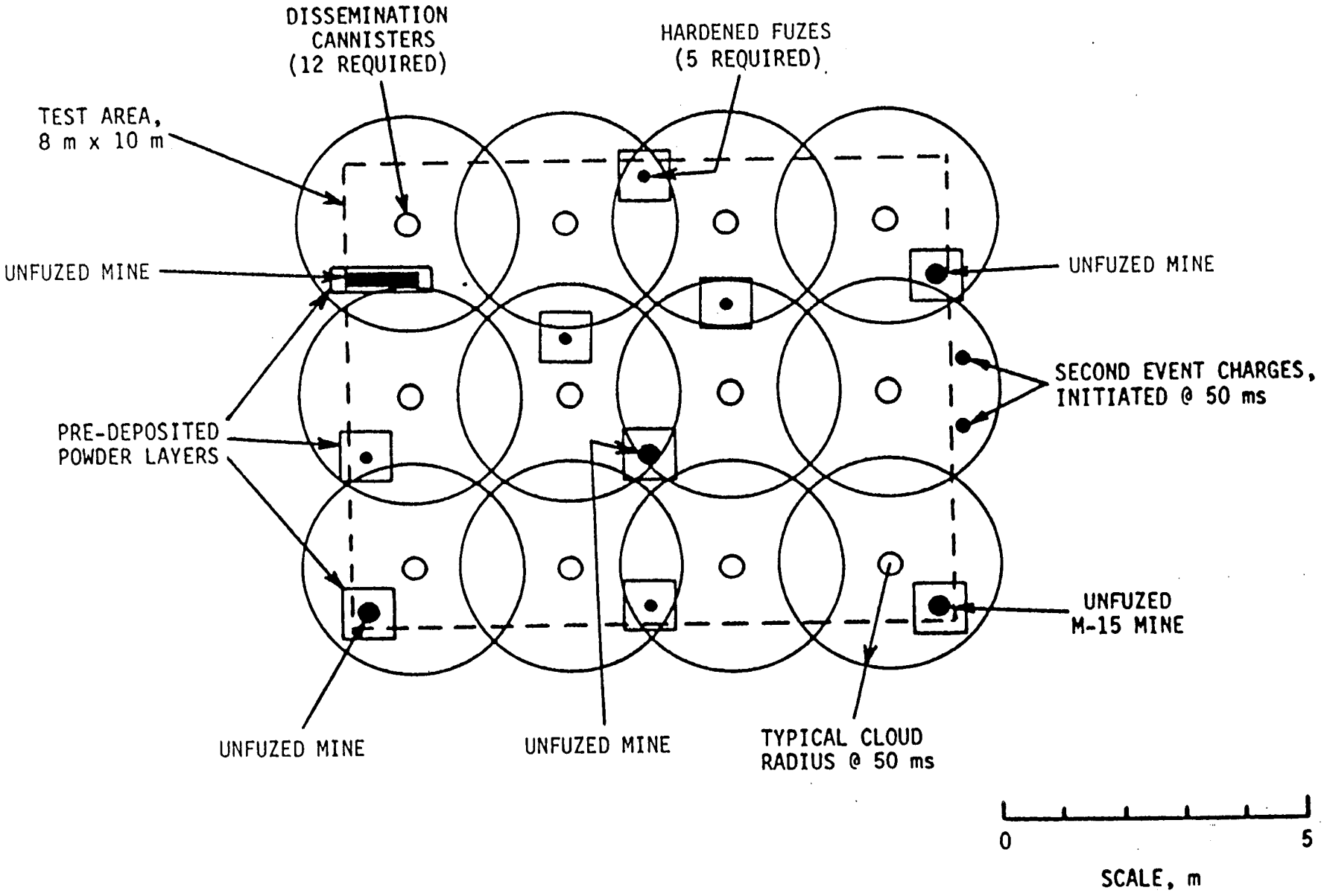

Figure 1. Experimental Arrangement for Primary Bimodal Demonstration Test, as Viewed from Above.

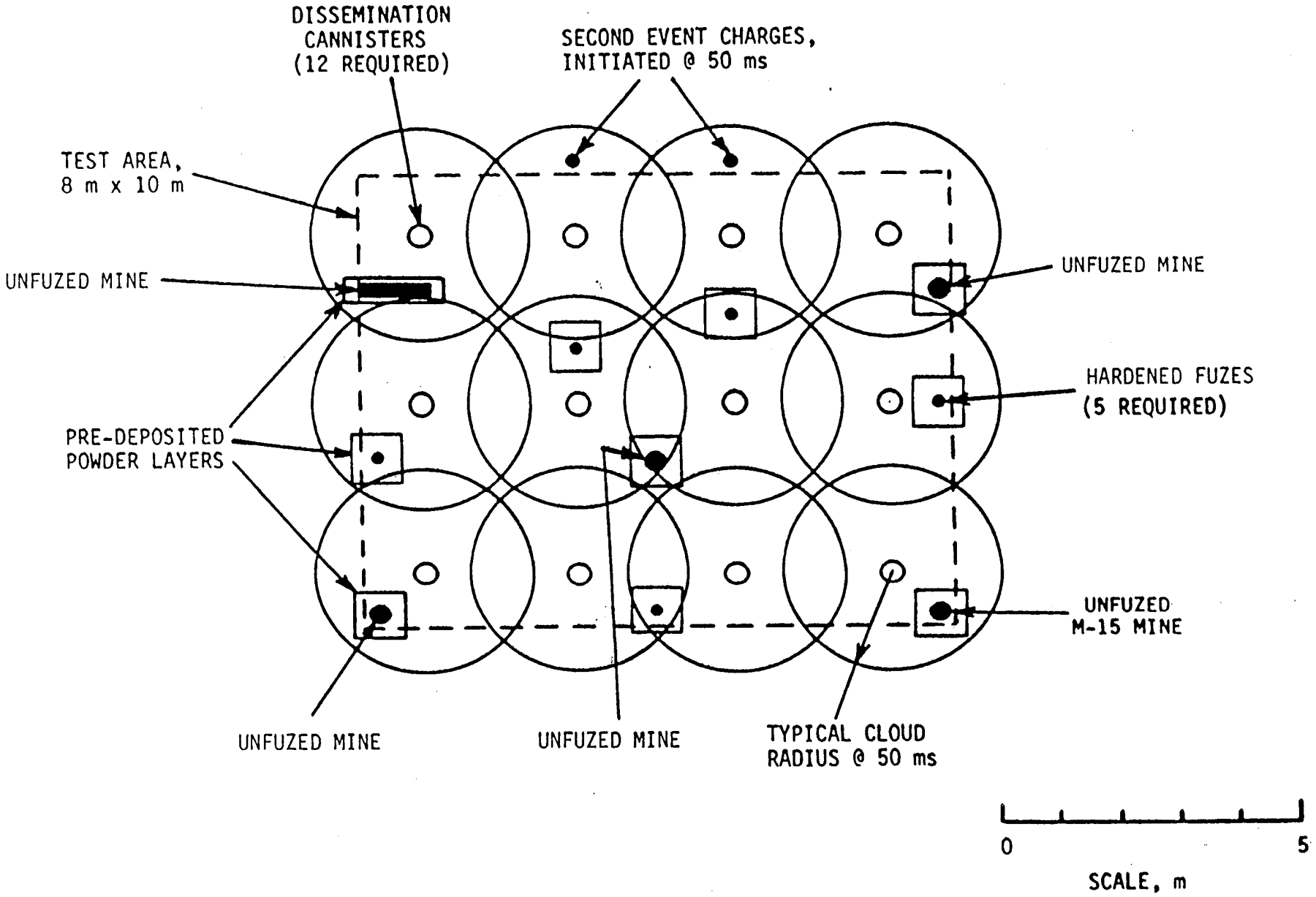

Figure 2. Experimental Arrangement for Back-up Bimodal Demonstration Test, as Viewed from Above.

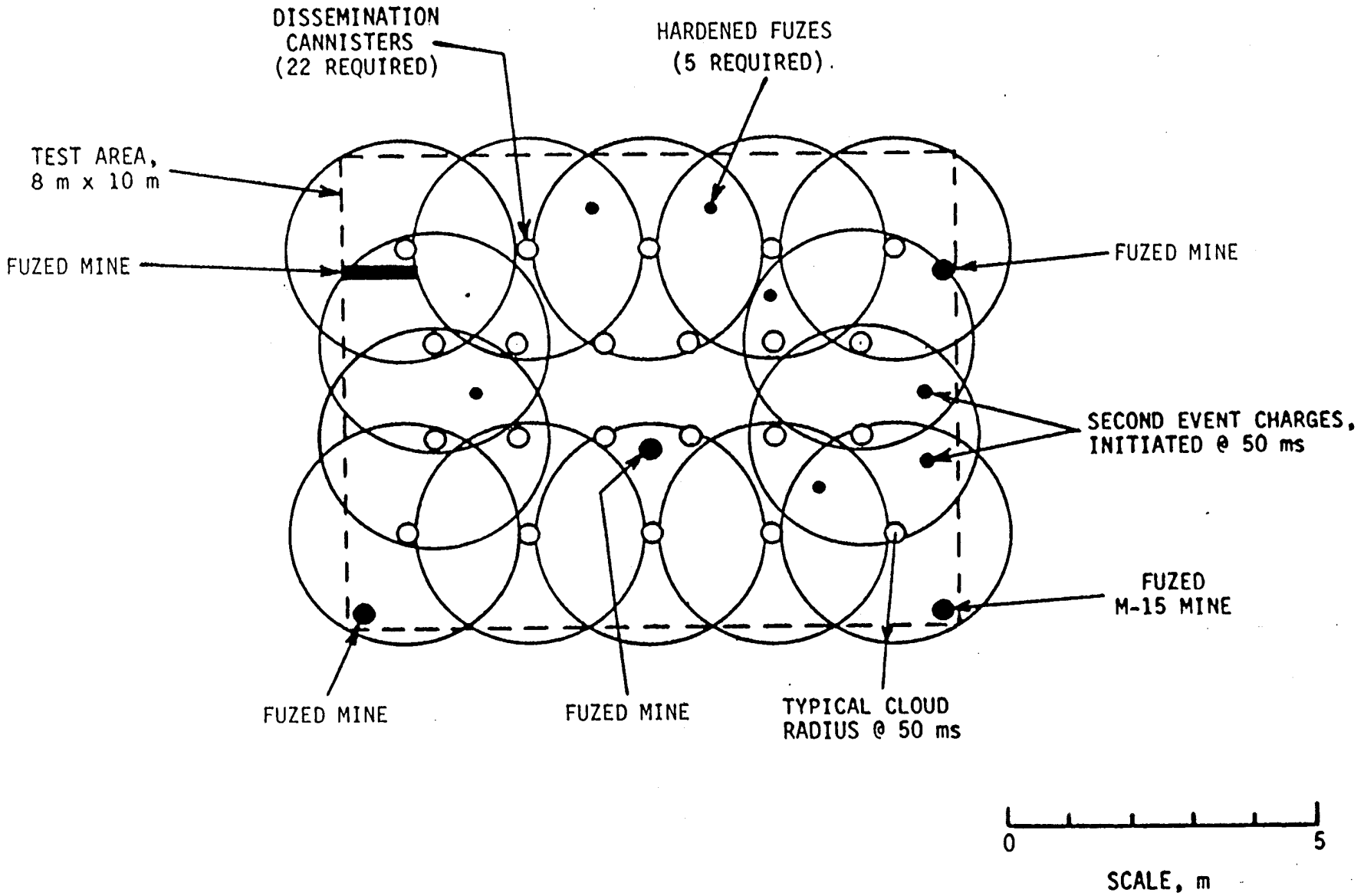

Figure 3. Experimental Arrangement for Cane Tip Demonstration Test, as Viewed from Above. (For purposes of clarity, the eight interior cloud contours are not shown. Total cloud weight per unit area = ∿ 1.247 kg/m^2 (2.75 lb/m^2).)

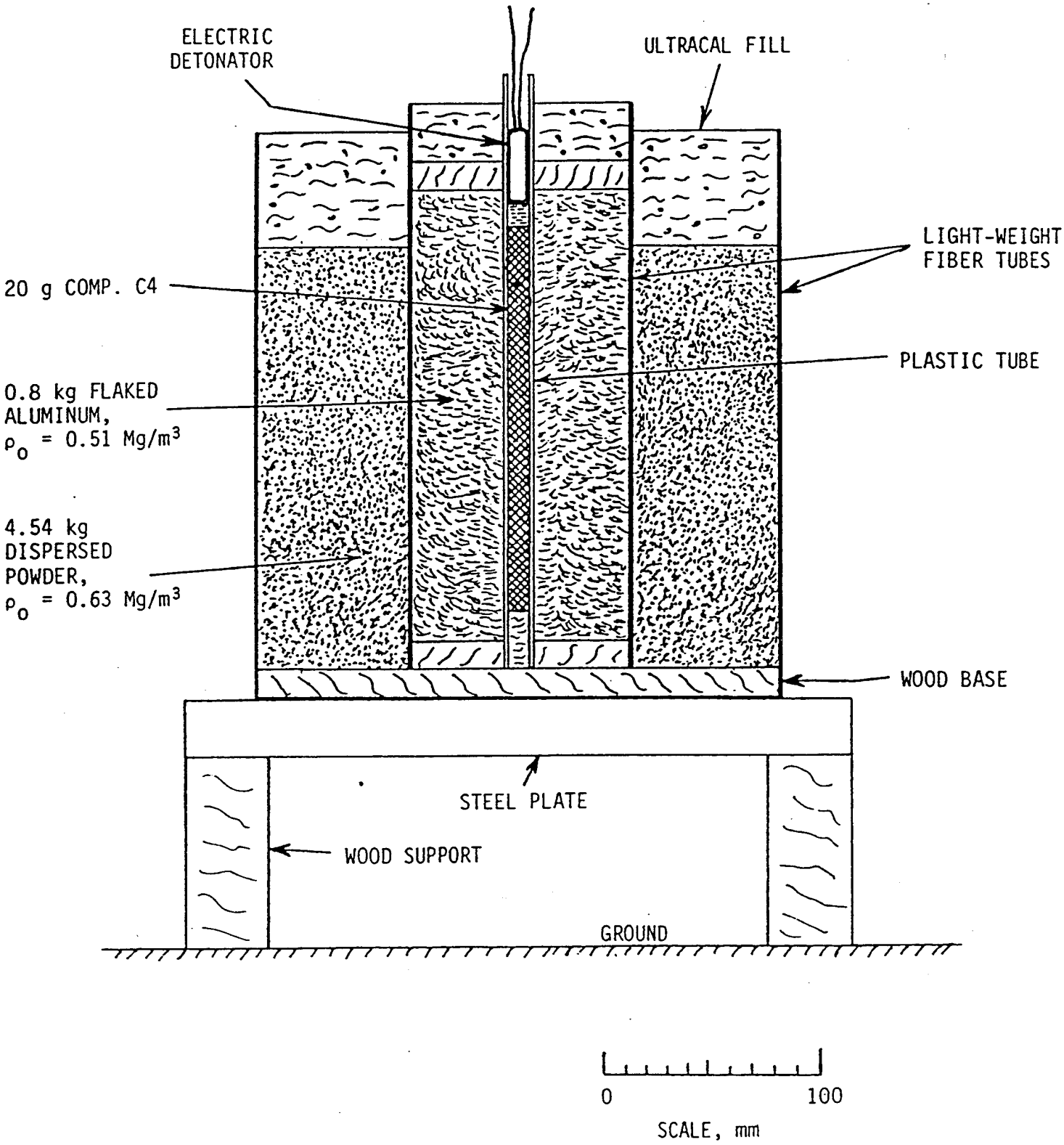

Figure 4. Schematic Drawing of the Dissemination Cannister for Explosively Disseminating Clouds of Dispersed Explosive Powder.

TASK 11:

WORKING GROUP INSTITUTES

Objective 1:

Working Group Institutes

(Dr. Gerald Doyle)

In accordance with the contract, Working Group Meetings were held to provide a forum for presentation and extensive discussion of the state-of-the-art developments in the synthesis and evaluation of new high density energetic materials. Participation was by invitation and included our subcontractors and leading investigators from government, academia, and industry in basic research areas. The meetings were two and a half days in length and the presentations were approximately one half hour in length. Copies of meeting agendas were included in each of the previous annual reports.

The eleventh Annual Working Group Institute was held June 8-11, 1992 at the Concord Hotel, Kiamesha Lake, NY. The meeting was attended by approximately 50 scientists. A complete report which contains a list of attendees, meeting agenda, abstracts of papers and copies of slides or viewgraphs was published. A copy of the agenda is included in this final report.

Eleventh Annual Working Group Institute on Synthesis of High Energy Density Materials

June 8-11, 1992

Final Agenda

Sponsored By

U. S. ARMY ARMAMENT RESEARCH, DEVELOPMENT & ENGINEERING CENTER

Armament Engineering Directorate
Energetics and Warheads Division
Picatinny Arsenal, NJ 07806-5000

Hosted by

GEO-CENTERS, INC.
762 Route 15 South
Lake Hopatcong, NJ 07849

Concord Hotel
Kiamesha Lake
Monticello, NY

GEO-CENTERS, INC.

Monday, June 8, 1992

PM

4:00-5:00	Registration - Lobby	
7:00	Dinner	

Tuesday, June 9

AM

9:00	Call to Order	Dr. S. Iyer, ARDEC
9:05	More Powerful Explosives Overview	Dr. S. Iyer, ARDEC

THEORETICAL PAPERS

CHAIRMAN: Dr. H. Basch

9:30	Beyond Density Prediction to ab Initio Crystal Structure Prediction	Drs. H. Ammon, Z. Du and J. Holden, University of Maryland
10:00	Computational Investigation of New Potential Explosive and Propellant Molecules	Dr. K. Jayasuriya, GEO-CENTERS, INC. at ARDEC
10:30	Coffee Break	
10:45	A Method for Correlating the Composition Properties and Structure of all C,N,O & H Explosives	Dr. L. Allen, Princeton University
11:15	Homolysis of Nitromethane: Theoretical Studies and Synthetic Implications	Drs. S. Hoz and H. Basch Bar-Ilan Univ.; M. Goldberg, R&D Directorate Ministry of Defense Israel

ENERGETIC CAGE COMPOUNDS

CHAIRMAN: Dr. P. Eaton

11:45	Approaches Toward the Synthesis of Cage Vicinal Dinitro Compounds	Drs. W. Zajac Jr. T. R. Walters and J. L. Gagnon, Villanova University
PM		
12:15	Synthetic Transformation of Iodo Cubane	Dr. A. Rodriguez Clark Atlanta University
12:45	Discussion of Papers	
1:00	Lunch	
2:30	Octanitro Cubane: The Optimist vs. the Pessimist	Dr. P. Eaton, University of Chicago
3:15	Functionalization of Substituted Cubanes	Dr. A. Bashir-Hashemi, GEO-CENTERS, INC. at ARDEC
3:45	Nitrocubanes - Progress to Date	Drs. R. Damavarapu, S. Iyer, ARDEC
4:15	Coffee Break	
4:30	Polynitroadamantanes	Dr. P. Dave, GEO-CENTERS, INC. at ARDEC
5:00	Discussion of Papers	

Wednesday, June 10

AM

9:00	Welcome by Sponsor	Mr. B.W. Bushey, Director AED, ARDEC

A New Process For The Benchmark Explosive

CHAIRMAN: Dr. J. Alster

9:10	The GARDEC HMX Process Update	Messrs. W. Lukasavage, GEO-CENTERS, INC. at ARDEC and S. Nicolich, ARDEC

Energetic Systems And Diagnostics

CHAIRMAN: Dr. T. H. Chen

9:40	Synthesis of Novel Nitroamino Derivatives of Cyclotriphosphazene	Drs. F. Farohar and P. Dave, GEO-CENTERS, INC. at ARDEC; T. Axenrod, City College of The City University of NY; C. Bedford, Naval Surface Warfare Center Silver Springs, MD
10:10	Preparation of Polymers Containing RDX & HMX-like Units for Use as Energetic Binders	Drs. J. R. Hardee and P. Dave. GEO-CENTERS, INC. at ARDEC
10:40	Coffee Break	
11:00	Detonation Reactions Frozen by Free Expansion and Analyzed by Mass Spectrometry	Drs. N. R. Greiner, Herbert Fry and Normand C. Blais Los Alamos National Laboratory

11:30	Identification, Conformation and Quantitation of Energetic and Other Intermediates	Drs. T. H. Chen, E. Hochberg and Mr. C. Campbell, ARDEC; Mr. R. Croom, GEO-CENTERS, INC. at ARDEC

PM

12:15	Discussion of Papers	
1:00	Lunch	

TNAZ RESEARCH AND DEVELOPMENT

CHAIRMAN: Dr. S. IYER

2:30	TNAZ Program Overview	Dr. S. Iyer, ARDEC
3:00	Coffee Break	
3:30	Synthesis Improvements and Characterization of 1,3,3-Trinitro-azetidine (TNAZ)	Drs. M. D. Coburn, G. A. Buntain, B. W. Harris, K.-Y. Lee and M. M Stinecipher, Los Alamos National Laboratory
4:00	A Simplified Solventless Process for TNAZ	Mr. W. Lukasavage, GEO-CENTERS, INC. at ARDEC
4:30	TNAZ Particle Modification and Processability	Dr. D. Stec III, GEO-CENTERS, INC. at ARDEC; Mr. R. Perez, ARDEC
6:00	Reception	

Thursday, June 11

TNAZ, OTHER MORE POWERFUL EXPLOSIVES

CHAIRMAN: Dr. H. SCHECTER

AM

9:10	Scale-Up OF TNAZ	Dr. T. Archibald, Aerojet General Corp. Propulsion Division
9:40	New Approaches to TNAZ Synthesis	Drs. H. Schecter, P. Sharma, Ohio State University
10:10	Coffee Break	
10:30	Proposed New Methods for TNAZ	Dr. T. Axenrod, City College of the City University of NY
10:45	The Use of Benzotriazole as a Synthetic Auxiliary in Studies Towards the Preparation of 1,3,3-Trinitroazetidine (TNAZ)	Drs. A. Katritzky and D. Cundy, University of Florida
11:15	TNAZ Based Composition C-4 Development	Dr. S. Iyer, ARDEC
11:45	Nitroimidazoles-New Class of Powerful Explosives	Dr. R. Damavarapu, ARDEC
12:15	Discussion of Papers	
12:45	Concluding Remarks	
1:00	Lunch	

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