Synthesis of High Energy Density Materials Based on Strained Ring Chemistry

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Final Report

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NOTICE

FOREWORD

This Final Technical Report was prepared by the Department of Chemistry at the University of Pennsylvania, Philadelphia, PA, under Contract F04611-94-K-0056, for the Air Force Research Laboratory (formerly OL-AC Phillips Laboratory), Edwards AFB, CA. The project manager for AFRL/PRSP was Capt Jessica Harper.

Due to a severe cut in the funding that was originally anticipated for this program, it was necessary to abruptly stop work under the contract. No final technical report was required of the contractor due to the lack of funds to pay for the effort. Despite this, the contract's principal investigator provided the following report on his own initiative, wanting to bring closure to the project. Results from the research carried out before the contract schedule modification are described in this report.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF Form 298.

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13. ABSTRACT (MAXIMUM 200 WORDS)

Several new cyclopropenes were synthesized and evaluated as new High Energy Density Material (HEDM) candidates. An optimized synthetic route to [1.1.1]propellane was developed and several bicyclo[1.1.1]pentanes were prepared and evaluated as HEDM materials. Preliminary work toward the preparation and study of bicyclo[1.1.1]pentyl carbenes under inert gas matrix isolation conditions was undertaken. Several new prismane derviatives were prepared and their stuctures determined by X-ray crystallography.

14. SUBJECT TERMS
high energy density materials; strained ring; cyclopropenes; matrix isolation; hydrocarbons; bicyclo[1.1.1]pentanes; [1.1.1]propellane; bicyclo[1.1.1]pentylcarbenes; prismanes

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GLOSSARY

1H	proton
Ac_2O	acetic anhydride
AcO	acetate
Br_2	bromine
Bu_3SnH	tributyltin hydride
CH_2Br_2	methylene bromide
CH_2Cl_2	methylene chloride
CH_2OH	hydroxymethyl
CH_3	methyl
CH_3Li	methyl lithium
CH_3O	methoxy
$CHBr_3$	bromoform
CO_2	carbon dioxide
H_2O	water
HCl	hydrogen chloride
HEDM	high energy density materials
HgO	mercuric oxide
$h\nu$	light
HNO_3	nitric acid
HO-	hydroxide
I_{sp}	specific impulse
$KMnO_4$	potassium permanganate
MCSCF	multiconfiguration self-consistent-field
MEK	methyl ethyl ketone
MnO_2	manganese oxide
Ms	methanesulfonyl
MsCl	methanesulfonyl chloride
N_2	dinitrogen
Na/K	sodium/potassium alloy
$NaBH_4$	sodium borohydride
NaI	sodium iodide
$NaIO_4$	sodium periodate
NaOH	sodium hydroxide
NCS	N-chlorosuccinimide
NH_2NH_2	hydrazine
NMO	N-morpholine oxide
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OsO_4	osmium tetroxide
PBr_3	phosphorus tribromide
RO	alkoxy
$SOCl_2$	thionyl chloride
t-BuLi	tertiary butyl lithium
t-BuOH	tertiary butanol

TEBA	tetraethylbenzylammonium chloride
THF	tetrahydrofuran
$TiCl_4$	titanium tetrachloride
VT	variable temperature
Zn	zinc
ΔHf	enthalpy of formation

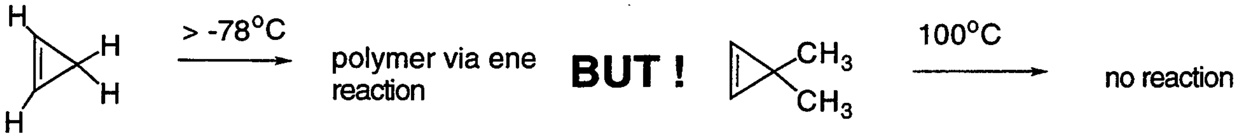
Introduction

This final technical report covers work from September 1, 1994 to August 31, 1997 that was sponsored under F04611-94-K-0056 through the Air Force Research Laboratory (AFRL) Propulsion Directorate Edwards Site (formerly Operating Location-AC Phillips Laboratory), at Edwards AFB, CA. The objectives of this work were to 1) synthesize and study the properties of strained-ring cyclopropenes for potential application as high energy density materials (HEDM), 2) synthesize and study the properties of bicyclo[1.1.1]pentanes derived from [1.1.1]propellane, and 3) study carbene rearrangements of bicyclo[1.1.1]pentyl carbenes under matrix isolation conditions. In spite of severe funding cuts in years two and three of the contract all of these objectives were still met. Because of this work, several novel molecules are under development as promising high energy fuels.

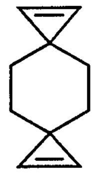
This report will be divided into several sections. The first part will concentrate on the synthetic work with cyclopropenes and their potential as high energy density compounds. The second section will focus on efforts in the preparation of bicyclo[1.1.1]pentanes derived from [1.1.1]propellane. The third section will describe the computational and experimental results in the study of bicyclo[1.1.1]pentylcarbenes. The final section will detail results in the area of prismanes.

Synthesis of Novel Cyclopropenes as Potential HEDM

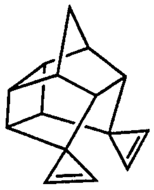
On a per carbon basis, cyclopropene is one of the most energetic hydrocarbons that can be synthesized and manipulated. Cyclopropene itself has $\Delta H_f = 66$ kcal/mol and a strain energy of 55 kcal/mol. The parent compound and substituted derivatives which have fewer than two substituents on the methylene carbon tend to be unstable. They undergo polymerization via an ene reaction. However, cyclopropenes that have two groups at the methylene carbon can be quite robust. For instance, 3,3-dimethylcyclopropene can be heated to 100°C for extended periods without decomposition. These compounds are being investigated as potential high energy fuels and fuel additives.



Two of the new compounds that were prepared in this study are shown in Schemes 1 and 2.

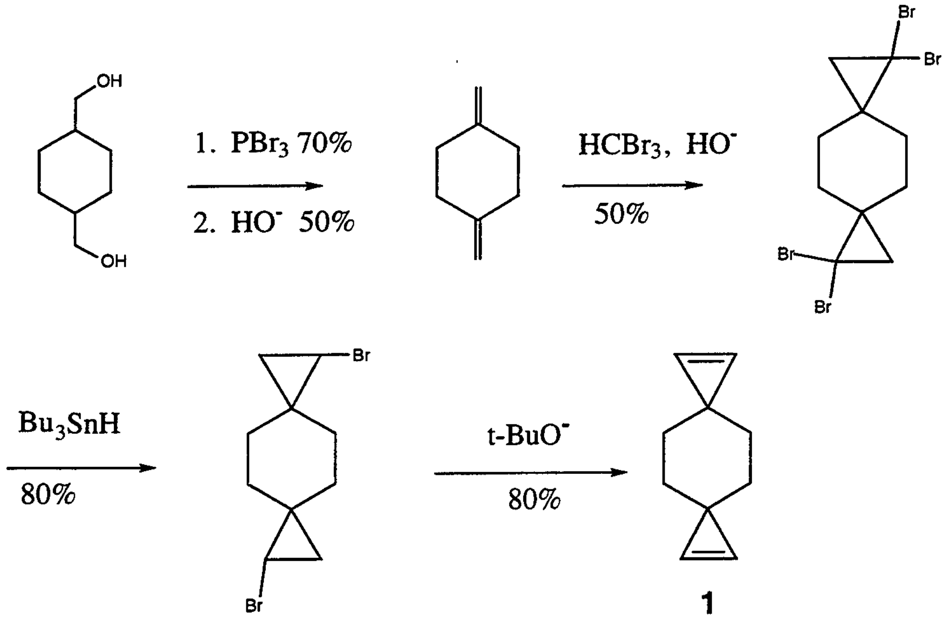


1
$\Delta H_f = 120$ kcal/mol
$I_{sp} = 310.2$ sec
Scheme 1



2
$\Delta H_f = 184$ kcal/mol
$I_{sp} = 306.3$ sec
Scheme 2

The synthesis of **1** is shown in Scheme 3. The bisdiene was prepared using modifications of literature preparations. Addition of dibromocarbene using phase transfer conditions produced the bis(dibromocyclopropane). Tin hydride reduction followed by base induced elimination produced the biscyclopropene **1** in good overall yield. The compound is a liquid at room temperature and is moderately sensitive to oxygen or Lewis acids.



Scheme 3

A conformational study of **1** was undertaken by dynamic ^{1}H nuclear magnetic resonance (NMR). At room temperature the ^{1}H NMR for **1** consists of 2 sharp peaks. Upon cooling, each of these peaks broadens and resharpens into two peaks. At 500 MHz, the coalescence temperature for the methylene protons was -70°C. The spectra are shown in Figure 1.

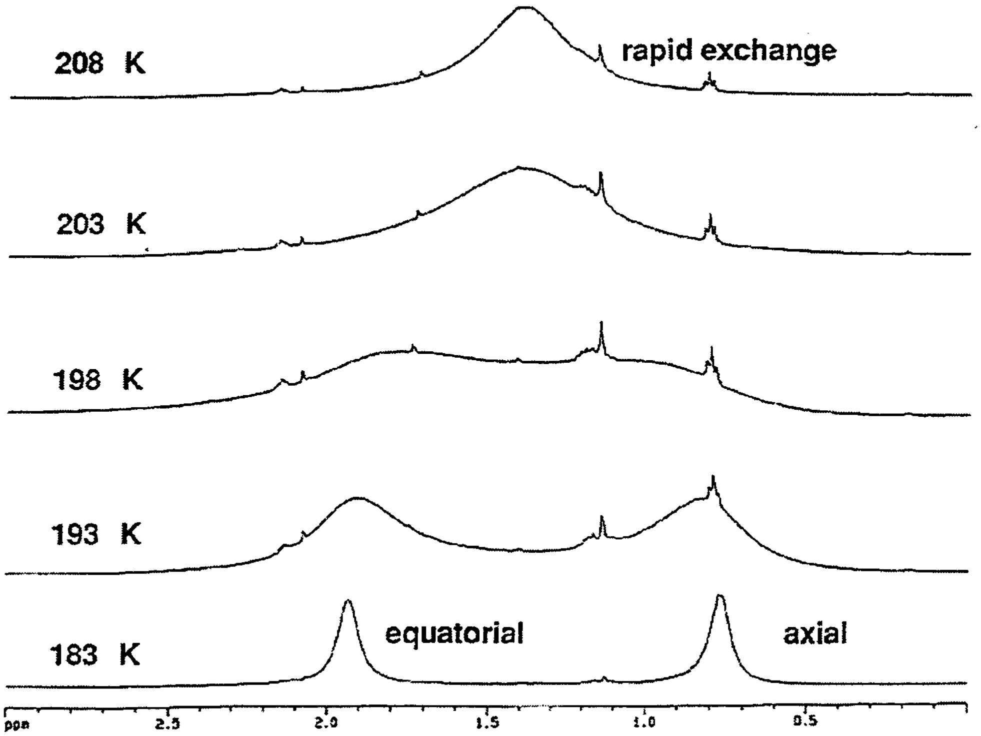


Figure 1. VT-NMR Experiment

The free energy of activation for the site exchange process in **1** is 8.8 kcal/mol. This can be compared with cyclohexane (10.8 kcal/mol) and 1,1,4,4-tetramethylcyclohexane (11.4 kcal/mol). The transition structure for conversion of the chair form of cyclohexane to give the twist boat form, the half twist chair form, was located using HF/6-31G* calculations. The barrier is calculated to be 12.2 kcal/mol. In a similar manner, the analogous transition structure was calculated for the biscyclopropene **1**. The barrier is calculated to be 9.8 kcal/mol, in good agreement with the value derived from dynamic NMR measurements. A diagrammatic representation of this process is shown in Figure 2.

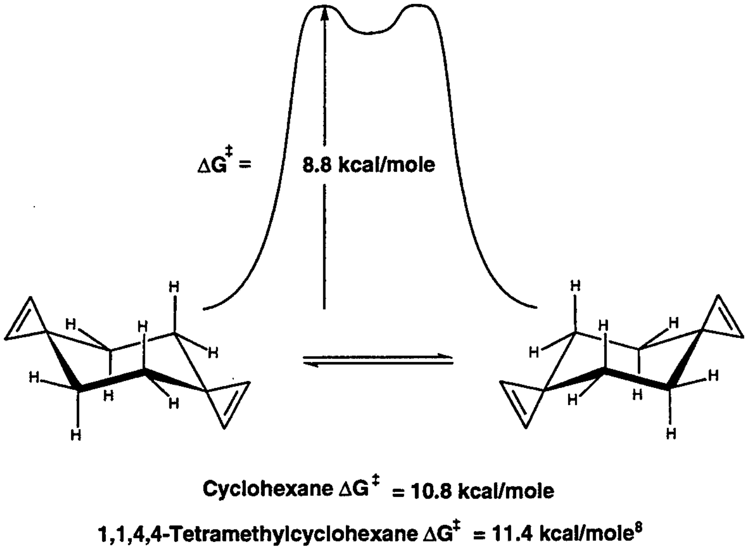
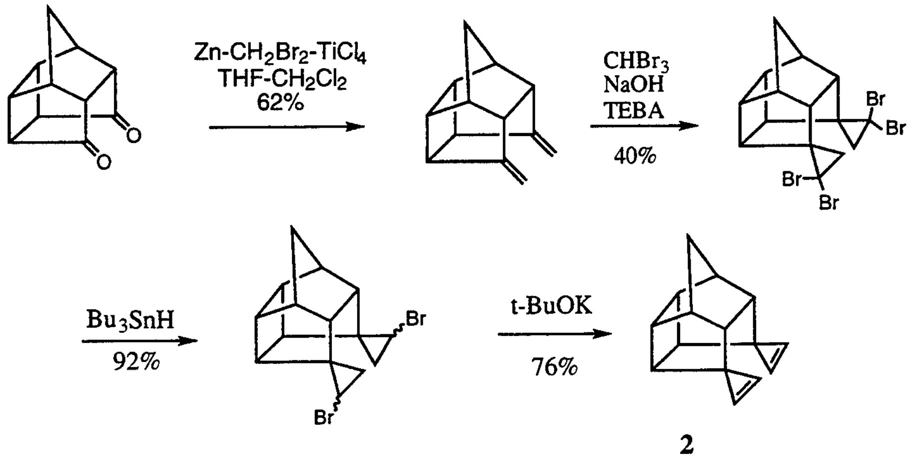


Figure 2. Free Energy Coordinate Diagram of Chair Interconversion

The caged-ring compound **2** was prepared in a manner similar to that of **1**. Investigators found that the precursor diene could be prepared much more easily using the Lombardo reagent than the literature method (3 steps, 52% yield). Dibromocarbene addition followed by reduction and base induced elimination produced the biscyclopropene **2**, which was a crystalline solid with mp 44-46°C. This biscyclopropene was much more sensitive to oxygen than compound **1**. (See Scheme 4).



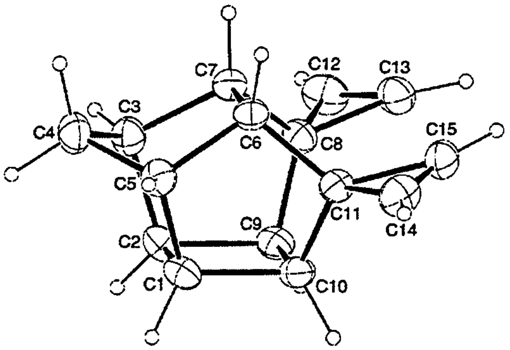
2

Scheme 4

The structure of **2** was confirmed by single crystal X-ray analysis. An ORTEP[1] is shown in Scheme 5. A comparison of the experimental and HF/6-31G* calculated structure is included in Table 1. The agreement is outstanding. The calculated density is 1.26 g/cc.

Table 1. Comparison of Selected Bond Lengths in 2

Bond	**X-ray(Å)**	**HF/6-31G***
C1- C2	1.554	1.553
C9-C10	1.567	1.568
C11-C14	1.505	1.494
C14-C15	1.273	1.281
C11-C15	1.488	1.488



Scheme 5

Synthesis of Bicyclo[1.1.1]pentanes Derived from [1.1.1]propellane

A second area of study concerns the conversion of [1.1.1] to stable high energy materials. A number of bicyclo[1.1.1]pentanes are shown in Schemes 6–10, along with their calculated performance values.

$\Delta H_f = 83$ kcal/mol

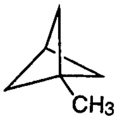
$I_{sp} = 316.6$

Scheme 6

$\Delta H_f = 51$ kcal/mol

$I_{sp} = 313.9$ sec

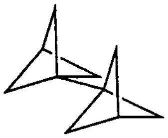
Scheme 7



$\Delta H_f = 45$ kcal/mol

$I_{sp} = 311.2$

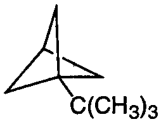
Scheme 8



$\Delta H_f = 95$ kcal/mol

$I_{sp} = 309.9$

Scheme 9

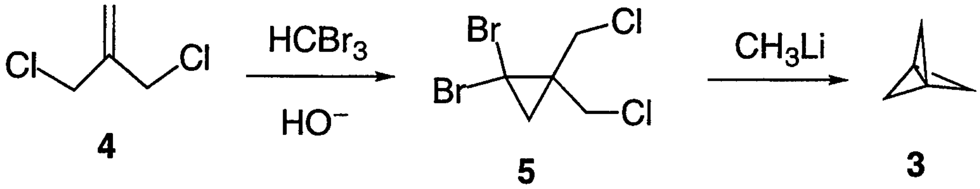


$\Delta H_f = 26$ kcal/mol

$I_{sp} = 308.0$

Scheme 10

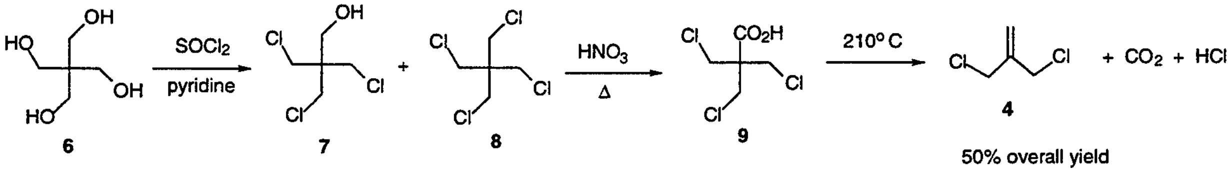
The remarkably direct Szeimies synthesis[2] of [1.1.1]propellane (**3**) has allowed the investigation of many reactions of this compound on a preparative scale. The Szeimies method involves addition of dibromocarbene, formed by based induced dehydrobromination of bromoform, to commercially available 3-chloro-2-(chloromethyl)-1-propene (**4**) followed by methyl lithium induced ring closure of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (**5**). (See Scheme 11).



Scheme 11

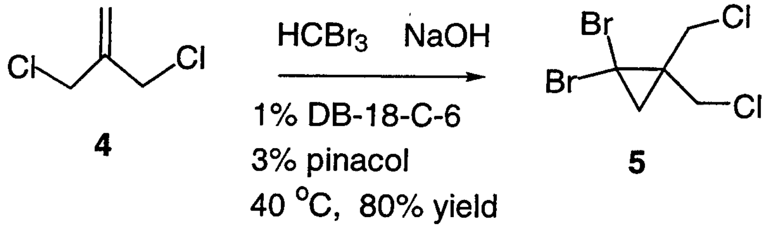
While this method is brief, literature yields for the dibromocarbene addition reaction are modest (30% of recrystallized material), and the work-up is time-consuming due to emulsions. Additionally, 3-chloro-2-(chloromethyl)-1-propene is expensive. Procedures have been developed[3] that allow the preparation of large quantities of **4** and **5** in good yields.

The synthesis of 3-chloro-2-(chloromethyl)-1-propene (**4**) can be accomplished by the direct chlorination of methallyl chloride, but the yields are low and purification involves a tedious spinning band distillation. A much more satisfactory method is described in a recent report[3] starting with pentaerythritol (**6**). Pentaerythritol is converted to a 2.8:1 mixture of trichloride 7 and tetrachloride **8** using 3.08 equivalents each of pyridine and thionyl chloride. Without purification, the crude mixture of chlorides is oxidized with hot nitric acid. Unreacted tetrachloride **8** may be recovered unchanged from the oxidation while the trichloride 7 is converted to the carboxylic acid **9**. The overall yield of crude acid **9** is 55% from **6**. Heating the crude acid **9** to 210°C allows for smooth decarboxylation and elimination of HCl and gives a virtually quantitative yield of pure alkene **4**. (See Scheme 12.)



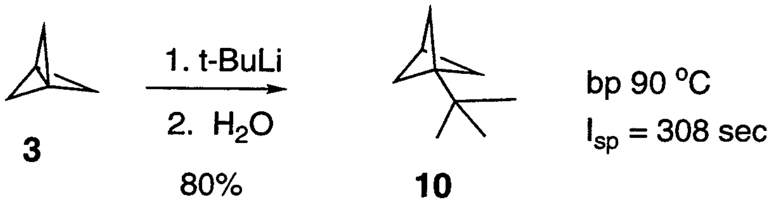
Scheme 12

Optimization of the conditions for the dibromocarbene addition to alkene **4** required many trials. Finally a set of conditions was found that afforded high yields of **5** with easy workup[3]. These conditions involve the combination of a catalytic amount of pinacol and dibenzo-18-crown-6 together with bromoform and 50% aqueous sodium hydroxide solution at 40°C. In this way, pure crystalline cyclopropane can be obtained in yields of up to 80%. (See Scheme 13.)



Scheme 13

While [1.1.1]propellane shows modest stability, it is sensitive to Lewis acids, strong bases and moderate temperatures. Investigators are interested in developing methods that will allow the conversion of the high energy [1.1.1]propellane system to more kinetically stable species that still have high energy. These will be useful as high energy fuel candidates. Cleaving the central carbon-carbon bond in [1.1.1]propellane produces bicyclo[1.1.1]pentanes which are kinetically very stable, yet have 68 kcal/mol of strain energy. One attractive candidate as a high energy fuel additive is 1-t-butylbicylo[1.1.1]pentane (**10**), which is available by reaction of propellane with t-butyl lithium followed by protonolysis.[4] This molecule is a liquid at room temperature and has a boiling point of 90°C. It is a very stable compound that is unaffected by moderate temperatures or acids or bases. Geometry optimized *ab initio* calculations at the 6-31G* level predict a heat of formation of 26 kcal/mol. This translates to an I_{sp} of 308 sec when combusted with liquid oxygen. Investigators are in the process of optimizing conditions for the preparation of 1-t-butylbicyclo[1.1.1]pentane so that substantial amounts can easily be prepared. A great advantage of this preparation is that it does not involve any photochemistry and only requires three synthetic steps from commercially available material.

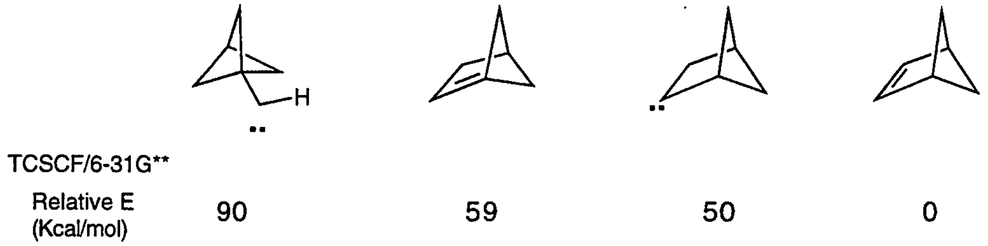


Scheme 14

Synthesis and Study of Bicyclo[1.1.1]pentylcarbenes

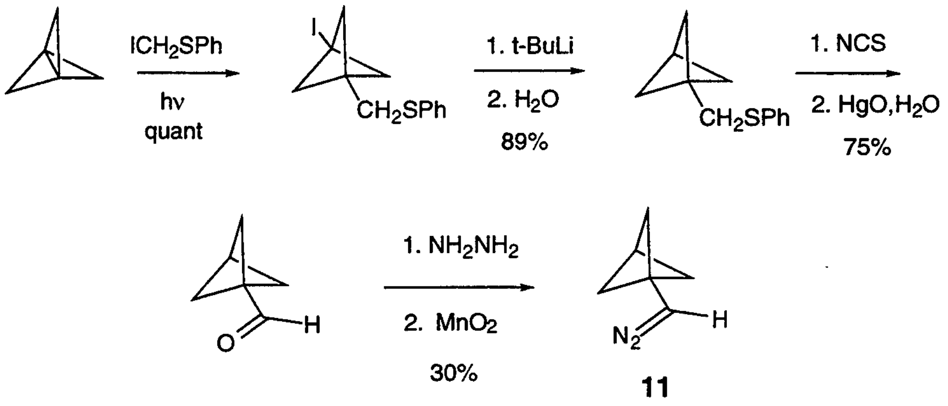
A third area of study during the funding period was bicyclo[1.1.1]pentylcarbenes. There is interest in studying these systems in order to determine whether they will be stable under cryogenic inert gas matrix isolation conditions or will rearrange to strained alkenes. In many ways the bicyclo[1.1.1]pentylcarbene system is similar to the cubylcarbene-homocubene system that has received considerable study.

As a starting point, the energies and structures for singlet bicyclo[1.1.1]pentylcarbene have been determined, along with some possible rearrangment products. The computational method employed was a three configuration multiconfiguration self-consistent-field (MCSCF) wavefunction using the 6-31G* basis set. The results are shown below.



Scheme 15

It was desirable to investigate the parent carbene, so a route to the corresponding diazo compound **11** was developed. This route is shown below in Scheme 16.



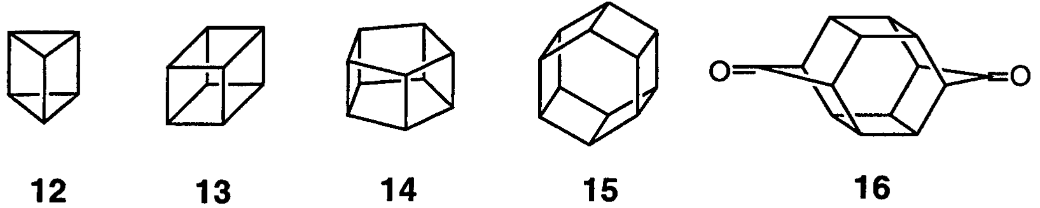
Scheme 16

Initial investigations of the matrix isolation photochemistry of diazo compound **11** have indicated that there be a carbene intermediate. Unfortunately, funding cutbacks in years two and three of the contract required that this area be abandoned. With the groundwork thus laid, future work in this area is guaranteed to generate exciting results.

Synthesis of Prismane Derivatives

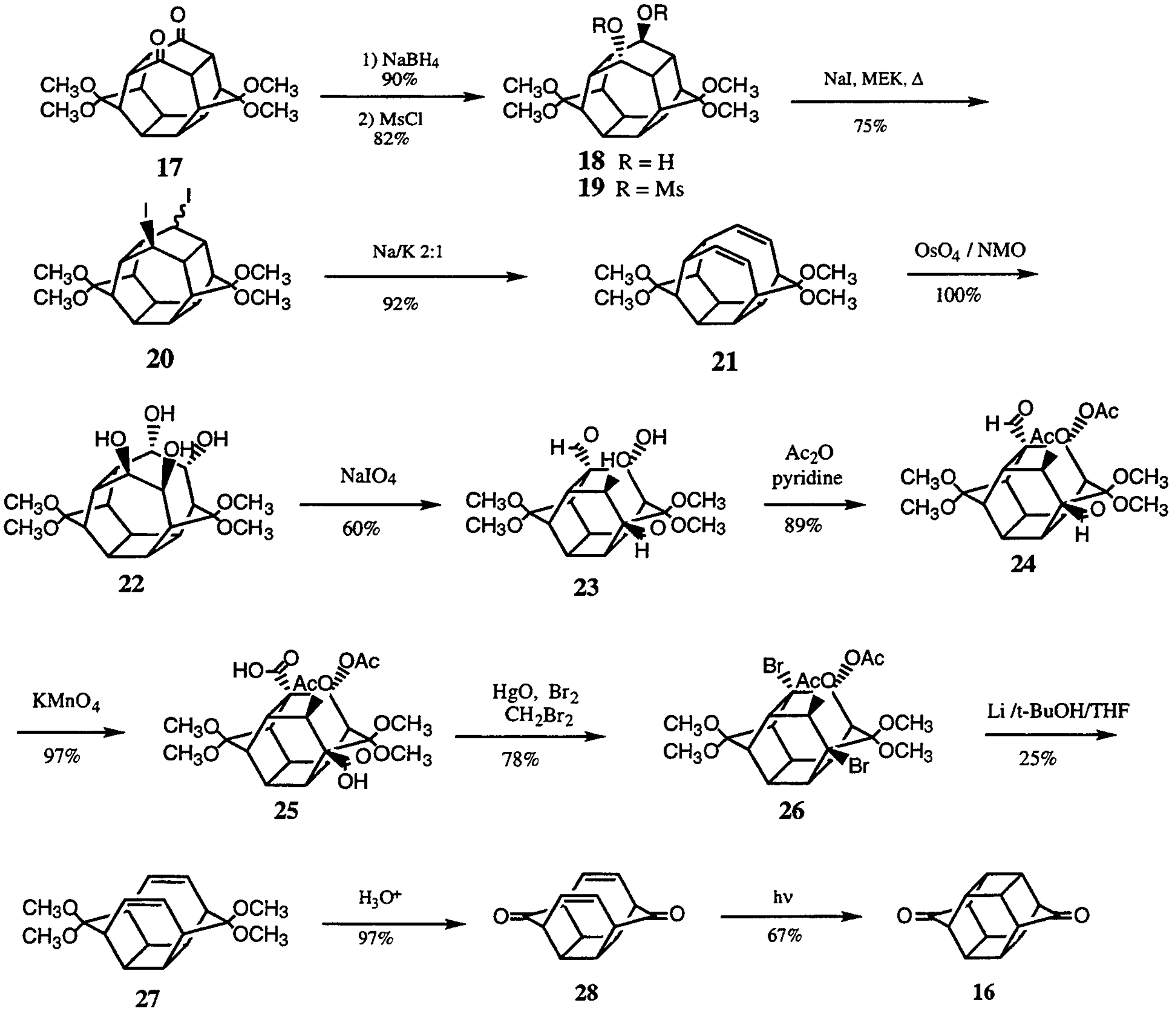
Prismanes are a class of polyhedranes composed of fused four-membered rings. The three smallest prismanes, [3]prismane, [4]prismane (cubane), and [5]prismane (pentaprismane) have been synthesized using a wide variety of synthetic methods.

During this study, efforts in this area have been directed toward the preparation of an unknown prismane, hexaprismane (**15**), a formal face-to-face dimer of benzene. Hexaprismane is predicted to have 175 kcal/mol of strain energy and a calculated I_{sp} of 313 sec. Good progress has been made toward the synthesis of hexaprismane and bishomohexaprismanedione (**16**) has been prepared.[5] Hexaprismane can be prepared using similar chemistry.



Scheme 17

The starting point for the synthesis of **16** was bishomosecoheptaprismanedione **17**, which is conveniently available in eight steps[6] and without resort to any chromatography starting with the Diels-Alder adduct between 5,5-dimethoxycyclopentadiene and benzoquinone. Conversion of the bishomosecoheptaprismane system of **17** to the bishomohexaprismane system was accomplished in the following manner. Dione **17** was converted to diol **18** using $NaBH_4$, and this was converted to dimesylate **19**. Dimesylate **19** was converted to diiodide **20** as a mixture of diastereomers which, when treated with Na/K alloy, produced diene **21** in good yield via Grob fragmentation. Diene **21** was converted to the highly water soluble tetraol **22** in quantitative crude yield using catalytic OsO_4. Treatment of crude tetraol **22** with periodic acid leads to formation of **23**, the doubly ring contracted product, in 60% yield. The hydroxyl groups in **23** were protected as the acetates to give **24**, and the aldehyde groups were oxidized with $KMnO_4$ to produce diacid **25**. The carboxylic acid groups were converted to bromides via Hunsdiecker reaction to give **26**. Treatment of **26** with lithium dispersion in *t*-BuOH/THF solution resulted not only in reductive debromination, as anticipated, but also reductive fragmentation to form diene **27** in 25% overall yield. Hydrolysis of **27** produced dienedione **28**, which also underwent photochemical ring closure to the highly sought-after norbornadienone dimer **16**. (See Scheme 18.)

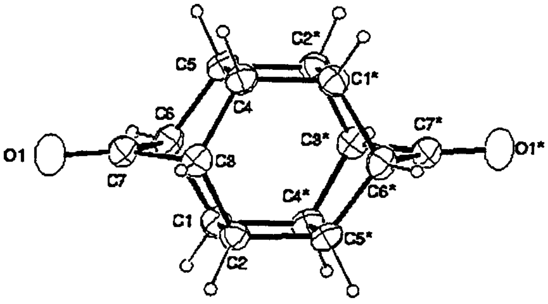


Scheme 18

The structure of **16** was determined by single crystal X-ray analysis, and some of the results are compared with those obtained from geometry optimized *ab initio* calculations at the HF/6-31G* level (Table 2). The agreement is outstanding. (See Scheme 19.)

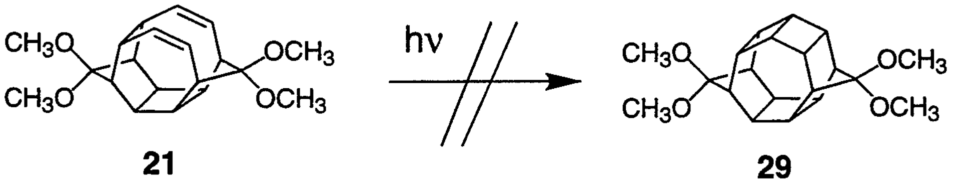
Table 2. Comparison of Bond Lengths in 16

Bond	**X-ray(Å)**	**HF/6-31G***
C1*- C4	1.546	1.546
C3-C4	1.530	1.538
C3-C7	1.535	1.536
C4-C5	1.574	1.569
C7-O1	1.206	1.183



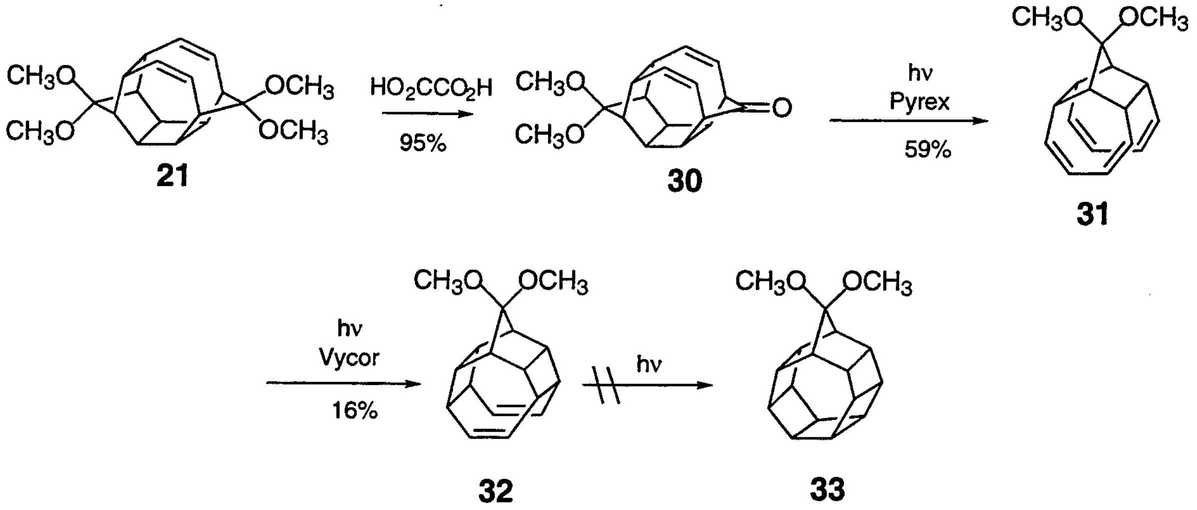
Scheme 19

In an effort to synthesize a bishomoheptaprismane derivative, investigators attempted the photochemical ring closure of **21** to **29**. However, the reaction failed under all conditions attempted. This failure was attributed to the 80 kcal/mol increase in strain energy that accompanies the transformation of **21** to **29**. This value is above the 55 kcal/mol threshold suggested as the maximum increase in strain energy tolerated in the photoreaction. Therefore, other methods were sought to access this unknown ring system.



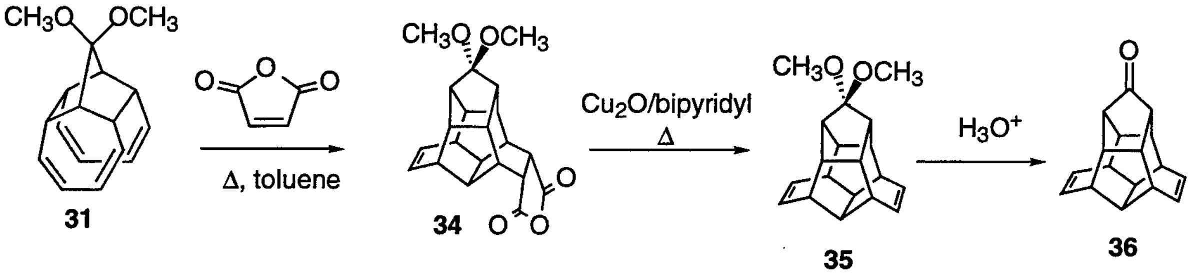
Scheme 20

Mild hydrolysis of **21** using aqueous oxalic acid gave a high yield of ketone **30**. When irradiated using a medium pressure mercury arc through Pyrex^{TM}, **30** smoothly underwent decarbonylation/fragmention to produce tetraene **31** in 60% yield. Further direct irradiation ($\lambda > 220$ nm) of tetraene **31** produced the [4+4]cycloadduct **32** in low yield. The identity of **32** was determined by analysis of the ^1H and ^{13}C NMR spectra which revealed the symmetrical nature of the compound. Diene **32** was resistant to further photochemical ring closure and yielded no traces of the homoheptaprismane ring system of **33**.



Scheme 21

Investigators were intrigued by the possibility of performing tandem Diels-Alder reactions[7] with tetraene **31**. By analogy to the pagodane synthesis, the reaction of **31** with maleic anhydride was investigated, and it was found that the reaction proceeds in excellent yield to give **34**, the domino Diels-Alder adduct. Analysis of the crude reaction mixture by ^{1}H NMR produced no evidence for any other isomer in the reaction. The stereochemistry of the product was confirmed by single crystal X-ray analysis, although the R factor was poor. Diene **35** was produced in modest yield via an oxidative decarboxylation. Hydrolysis of **35** gave ketone **36**, which was subjected to single crystal X-ray analysis.[8]

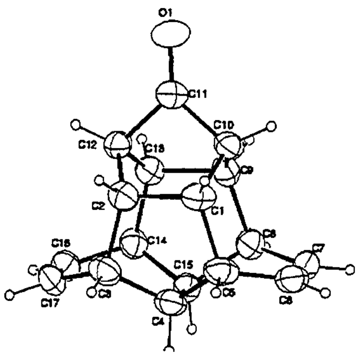


Scheme 22

For comparison, the structure of **36** was calculated using *ab initio* molecular orbital theory at the HF/6-31G* level, and a comparison of some selected bond lengths are shown in Table 3. The agreement is quite satisfactory.

Table 3. Experimental and Calculated Bond Lengths in 36

Bond	X-ray(Å)	HF/6-31G*
C1-C2	1.568	1.571
C1-C5	1.548	1.545
C4-C5	1.544	1.545
C5-C6	1.482	1.507
C6-C7	1.305	1.319
C4-C15	1.536	1.551
C10-C11	1.528	1.523
C11-O1	1.208	1.186



Scheme 23

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