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SYNTHESIS OF TETRAFUNCTIONAL CUBANE DERIVATIVES

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Process studies for converting cubane-1,4-dicarboxylic acid to cubane-1,2,4,7-tetracarboxylic acid were carried out. Routes to cubane polyacids without vicinal diacid groups were explored. Fluorination of dimethyl cubane-1,4-dicarbamate failed to give an NF derivative. A high yield of 1,5-di-t-butyl-3,7-dihydroxyoctahydro-1,5-diazocine was obtained form t-butylamine and epichlorohydrin. The compound is a potential intermediate to a difluoramino nitramine target.

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INTRODUCTION

This final report summarizes the work on Contract N00014-89-C-0279, a Phase II SBIR contract in continuation of the work on Phase I contract N00014-88-C-0648. The initial objectives were to develop a practical process for scale-up of the preparation of cubane-1,2,4,7-tetracarboxylic acid, to explore simplified routes to cubane-1,3,5,7-tetracarboxylic acid, and to examine the synthesis of difluoramino derivatives of cubane. Subsequently, the work was redirected to the synthesis of cyclic compounds containing both nitro and difluoramino groups.

DISCUSSION

Preparation of Cubane-1,2,4,7-tetracarboxylic Acid. Propellant formulations with improved performance are required for Strategic Defense Initiative applications. There is a particular need for non-metal containing propellants with increased specific impulse (I_{sp}) for rocket-propelled kinetic energy weapons as higher I_{sp} would reduce the minimum effective mass of the projectiles. An approach that has been taken to meet the I_{sp}-intensive needs of SDI applications is based on the intrinsic energy that would be released during combustion of energetic cubane derivatives. The approach is based on the high thermodynamic strain energy[1] and inherent high density[2] of cubane (known to be greater than 166 Kcal/mole and 1.3 g/cm^3, respectively, for the unsubstituted hydrocarbon). In addition, cubane derivatives have excellent thermal stability making them ideal candidates for incorporation into advanced propellant and explosive formulations.

The most readily accessible starting material for the synthesis of energetic cubanes is cubane-1,4-dicarboxylic acid. Functional group transformations have yielded energetic derivatives, such as 1,4-dinitrocubane[2] and 1,4-bis(N,N-dinitroamino)cubane[3], demonstrating the feasibility of synthesizing stable, energetic cubane compounds. The dinitraminocubane, for example, is stable above 200°C, based on DSC measurements. However, to achieve the performance requirements for SDI applications requires oxygen balance at least to the CO level, and tetrafunctional energetic derivatives are needed. Carboxy groups are generally the most useful precursors to energetic groups on cubanes.

Cubane-1,4-dicarboxylic acid[4] was first prepared by Eaton as a key intermediate in his synthesis of the parent hydrocarbon, cubane. This diacid has been investigated in many laboratories as the synthetic starting point for the application of cubane technology to fuels, energetic materials, binders, and liquid gun propellants. Fluorochem, Inc. has been involved in a program of process development of the multi-step synthesis required to make this starting material.[5] We have supplied this diacid to other laboratories for their research efforts.

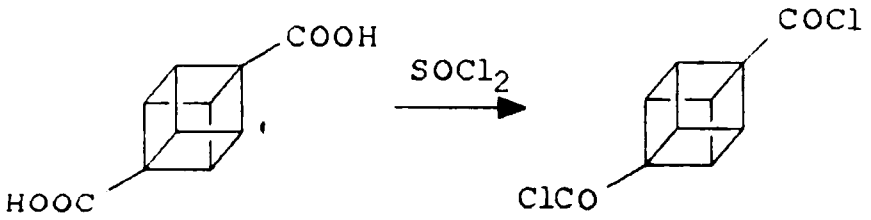
During Phase I of this program, the conversion of cubane-1,4-diacid to cubane-1,2,4,7-tetraacid was explored. Reported methods for this transformation are based on the conversion of the diacid to a diamide, "ortho" lithiation with lithium tetramethylpiperidine (LiTMP), trapping the anions by metal-metal interchange, carboxylation with carbon dioxide, and removal of the amides. Barriers to scale-up included the use of mercury or zinc salts for transmetallation, resulting in serious waste-disposal problems. Amide removal was

carried out by reduction with lithium aluminum hydride and subsequent oxidation with potassium permanganate.

The transmetallation problem was overcome by the use of magnesium bromide in the exchange reaction. Although Grignard reagents alone will not "ortho" metallate the cubyl amides, a mixture of excess LiTMP and magnesium bromide dimetallates the cubane ring quantitatively in less than 60 min at 0°C. Unlike the mercury or zinc procedures, this reaction can be scaled up to gram levels without significant loss in yield. The use of magnesium salts provides no significant environmental problems.

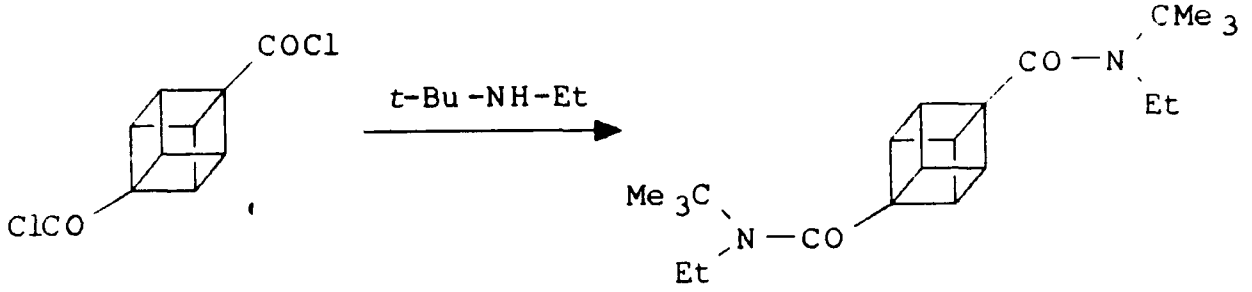
The second problem was overcome by replacing the previously used di-*i*-propylamino groups in the amide with *t*-butylethylamino groups.[6] It is known that *t*-butyl groups can be removed easily by acid catalysis, and this method has proven successful in the cubane system. After metallation and carboxylation of bis(N-*t*-butyl-N-ethyl)cubane-1,4-carboxamide, the amide groups from the intermediate diamide diacid are readily hydrolyzed by nitric acid.

On the present program, additional work was carried out on the scale-up of cubane-1,2,4,7-tetracarboxylic acid. In the first step of the preparation of the tetraacid, cubane 1,4-dicarboxylic acid is converted to the acid chloride. Better results were obtained using thionyl chloride rather than phosphorous pentachloride as the chlorinating agent. A 97% yield of the acid chloride was obtained using 100 g of the diacid as the starting material. An excess of thionyl chloride was used as the solvent.



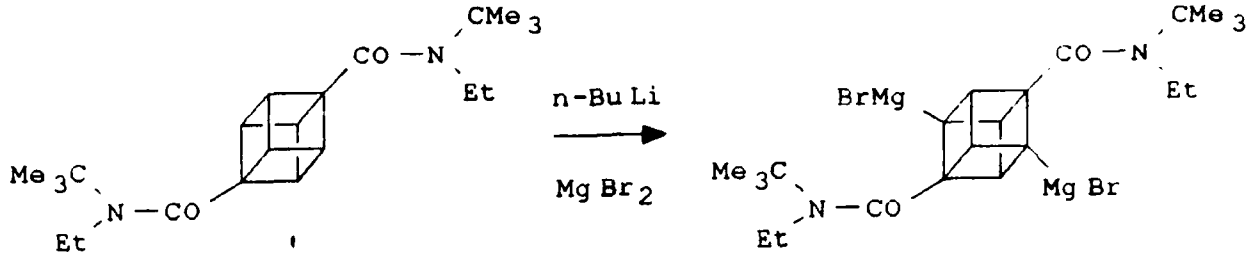
Bis(N-*t*-butyl-N-ethyl)cubane-1,4-diamide is then prepared from *t*-butylethylamine and cubane-1,4-acid chloride. *t*-Butylethylamine is not commercially available, and has been prepared previously in 50% yield from *t*-butylamine and ethyl bromide.[7] The material prepared in this manner was contaminated with *t*-butylamine which could not be removed by distillation. The presence of unreacted *t*-butylamine leads to the formation of *t*-butylamides thus lowering the yield of the bis(t-butylethylamide). We have developed an alternative high yield preparation of *t*-butylethylamine by the reaction of t-butylamine with diethyl sulfate in aqueous sodium hydroxide. The crude amine was stirred over solid potassium hydroxide for 24 h and then distilled. This procedure gave pure amine from inexpensive starting materials.

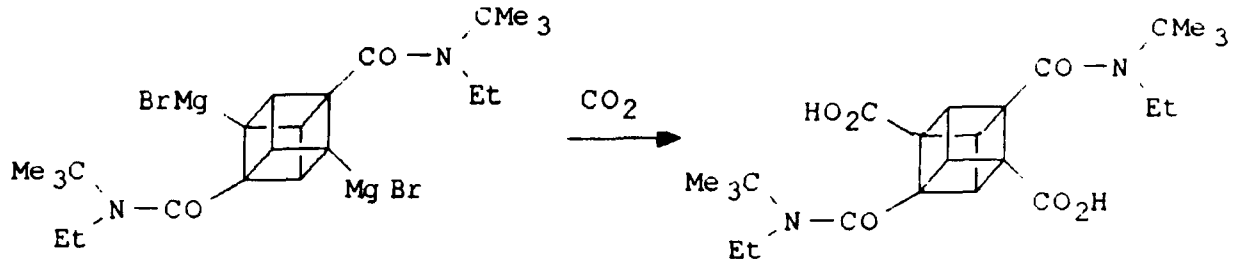
The reaction of *t*-butylethylamine with cubane diacid chloride in methylene chloride gave the bisamide in 98% yield. An equivalent amount of triethylamine was used to remove the hydrogen chloride formed. The work-up was simplified by removing the solvent under vacuum and washing the product with water and acetone.



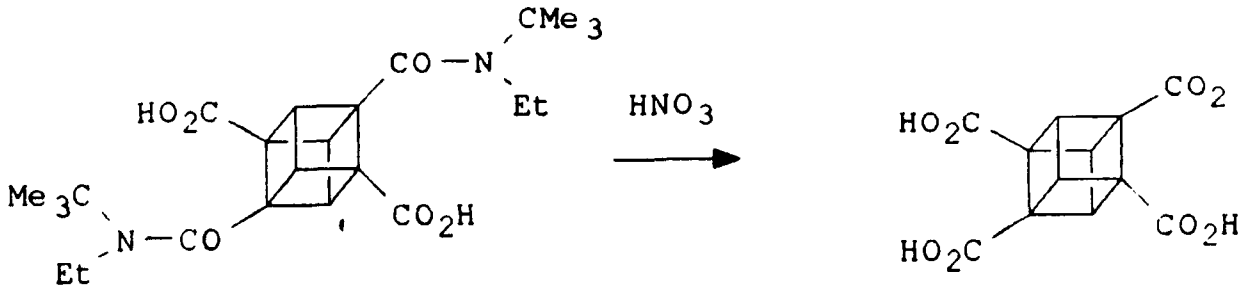
Subsequently, the diamide is lithiated and transmetallated. Unlike other metal salts previously investigated for the transmetallation of lithiated cubane derivatives, the magnesium salts do not precipitate from solution. Difficulties from heterogenicity, often encountered in scale up of organometallic reactions, are thus avoided. The metal transfer reagent used in the metallation reaction in large excess is 2,2,6,6-tetramethylpiperidine (TMP). This material is expensive and its commercial availability from Aldrich Chemical Co is limited. We have developed procedures to synthesize TMP on the multi-kg scale from inexpensive phorone and ammonium hydroxide followed by Wolff-Kischner reduction.[8]

TMP was reacted with butyl lithium in THF at -78 °C to -50 °C in tetrahydrofuran to give a solution of the lithium salt (LiTMP). Cubane-1,4-bis(N-*t*-butyl-N-ethylcarboxamide) and magnesium bromide etherate were then added to this solution at 0°C and the solution was allowed to stand at -15°C for 48 h. Quenching of this Grignard reagent with carbon dioxide, followed by aqueous work-up, gave a 60% yield of cubane-1,4-bis(N-*t*-butyl-N-ethylcarboxamide)-2,7-dicarboxylic acid.

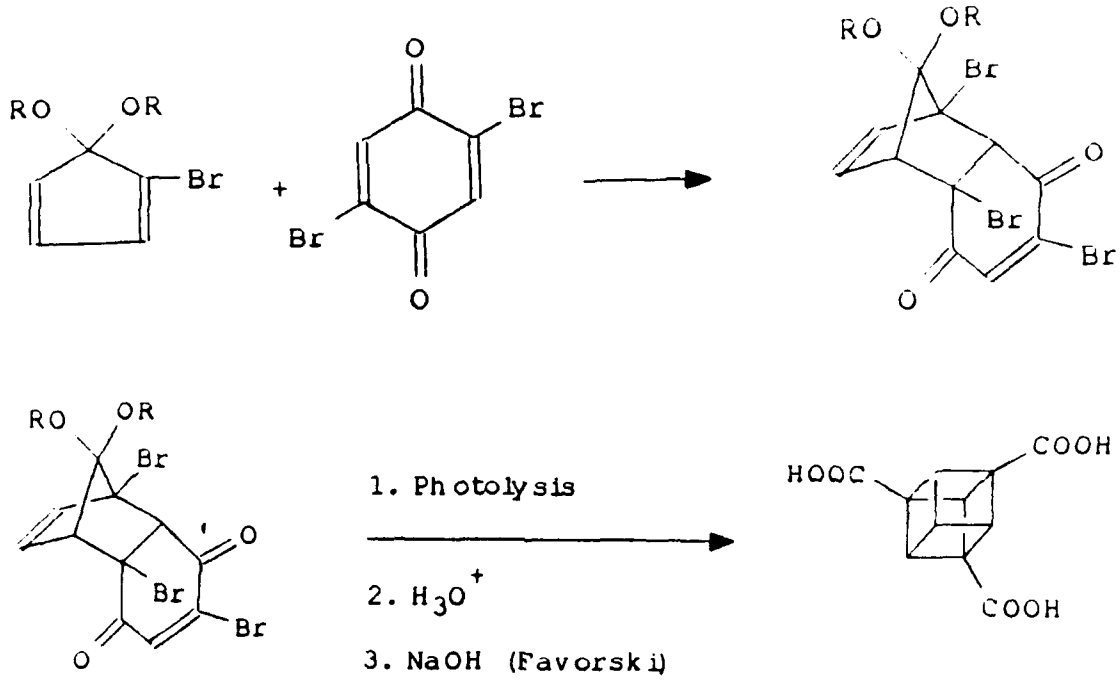




Acid hydrolysis of the diamide diacid intermediate gave pure cubane tetracarboxylic acid. Previously, the acid hydrolysis was done with 90% nitric acid, but it was found that concentrated acid performs similarly. The reagents were mixed at 0°C and the solution was then refluxed for 12 h. The resulting solids were washed with acetonitrile to give of cubane-1,2,4,7-tetracarboxylic acid in 68% yield. A run was also made in which cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide) was metallated, carboxylated and hydrolyzed, all without purifying intermediates. A 46% yield of cubane-1,2,4,7-tetracarboxylic acid was obtained.

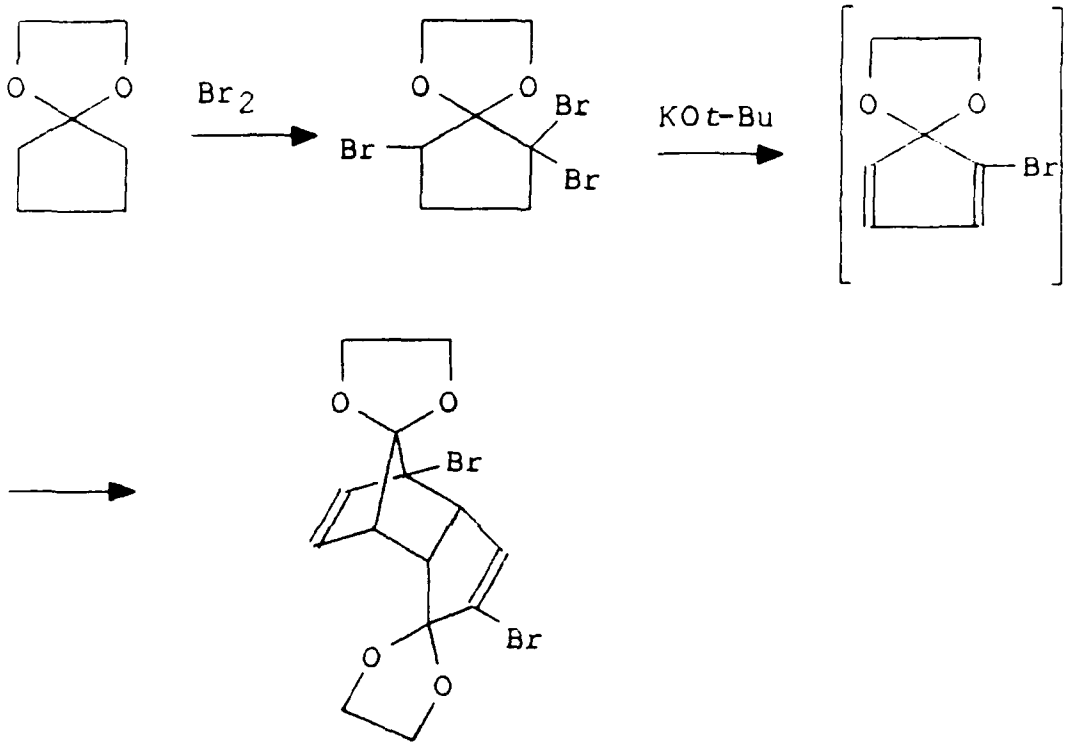


Approaches to Cubane-1,3,5,7-tetracarboxylic Acid. A route to avoiding the multistep metallation sequence previously used is desired. This "all 1-3-" isomer is expected to give more stable energetic derivatives than the more readily available isomer with vicinal carboxy groups. As an approach to "all 1-3" cubane polycarboxylic acids, the Diels-Alder reaction of ketals of 2-bromocyclopentadienone with 2,5-dibromo-1,4-benzoquinone was investigated. The products would be expected to have the required geometry for conversion to cubane-1,3,5-tricarboxylic acid after hydrolysis of the ketal and a triple Favorski reaction.



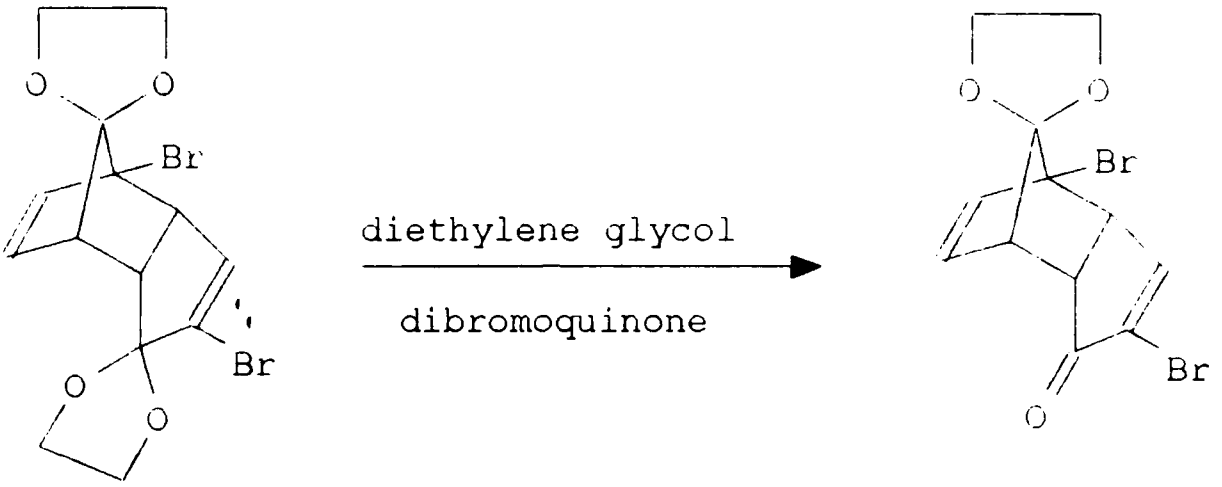
The preparation of the ethylene ketal of 2-bromocyclopentadienone was undertaken for this purpose. The ethylene ketal of 2,5,5-tribromocyclopentanone is an intermediate in the preparation of cubane 1,4-dicarboxylic acid and is prepared by the selective bromination of the cyclopentanone ketal. Dehydrobromination of this ketal was studied under a variety of conditions. The

use of a slight excess of potassium *t*-butoxide in DMSO at room temperature gave the Diels-Alder dimer of the desired diene selectively. Because potassium *t*-butoxide reacts with 2,5-dibromo-1,4-benzoquinone, dehydrobromination in the presence of this dienophile could not be used to give the desired adduct.

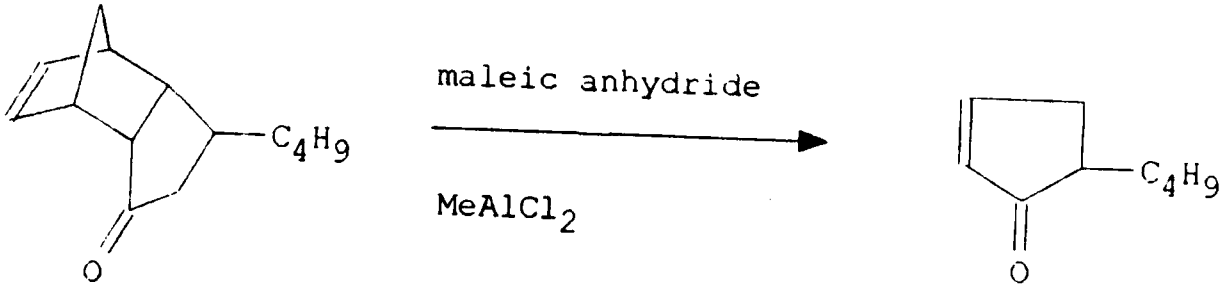


Dehydrohalogenation with the non-nucleophilic base, 1,8-diazabicylo-[5.4.0]undec-7-ene (DBU), resulted in mono-elimination to give the ethylene ketal of 2,5-dibromocyclopent-2-enone. Further dehalogenation took place when this solution was heated to 75 °C, but only the dimer of the dienone was obtained. Attempts to use 2,5-dibromo-1,4-benzoquinone as an *in situ* diene trap were also unsuccessful. Even DBU was found to decompose 2,5-dibromo-1,4-benzoquinone more rapidly than it could react with the diene. Subsequently, attempts were made to reverse the dimerization thermally in the presence of the quinone. When the bis-ketal was heated at 132 °C in chloro-

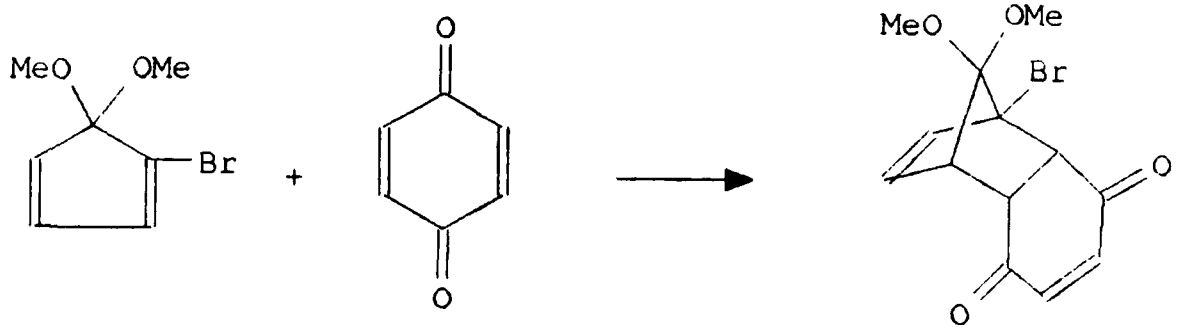
benzene for 1 h with 2,5-dibromobenzoquinone no cracking was observed and the mixture was unchanged. When this reaction was carried out in diethylene glycol at 200 °C, only conversion of the bis-ketal to the mono-ketal was noted.



It has been reported[9] that a retrograde Diels-Alder reaction of the norbornenyl derivative shown below takes place under mild conditions (55 °C) in the presence of $MeAlCl_2$ or triflic acid[10] and maleic anhydride, whereas with the absence of catalyst high temperatures are required. When the above mono-ketal was treated with an excess of maleic anhydride in the presence of aluminum chloride or triflic acid, no reaction was observed.



In 1965, Eaton and Hudson reported an interesting difference in reactivity of the ketals of cyclopentadienone.[11] They observed that the ethylene ketal of cyclopentadienone dimerized at a rate nearly 500,000 times faster than cyclopentadiene. The relative rates of dimerization of the dimethyl ketal, diethyl ketal, trimethylene ketal and the ethylene ketal were 1.7, 1.0, 14 and 1070. Furthermore, these authors[11] reported that the dimethyl ketal of 2-bromocyclopentadiene gave a Diels-Alder reaction with benzoquinone.



Efforts were therefore shifted to less reactive ketals. An attempt to effect transketalization of the ethylene ketal of 2,2,5-tribromocyclopentanone was carried out by stirring the ketal in ethanol with H_2SO4 catalyst, but no reaction was observed. Preparation of the ketal from cyclopentanone was then studied. Cyclopentanone was treated with triethyl orthoformate under acid catalysis to give the diethyl ketal in 71% yield. However the product was contaminated by some triethyl orthoformate which was not easily separated using fractional distillation. The diethyl ketal was also prepared by stirring cyclopentanone with an excess of triethyl orthoformate and 3A molecular sieves. Distillation afforded a 90% yield of 1,1-diethoxycyclopentane.

Brominations of the diethyl ketal were conducted in CH_2Cl_2 using bromine and dioxane. When the ketal was treated with 3.2 eq. of dioxane and 3.1 eq.

of bromine at 20 °C the major product was 2,5-dibromo-2-cyclopentenone accompanied by a smaller amount of the tribromide. It is not clear whether bromide ion or possibly water from the solvent and HBr is responsible for the deketalization. A bromination at 0 °C gave similar results.

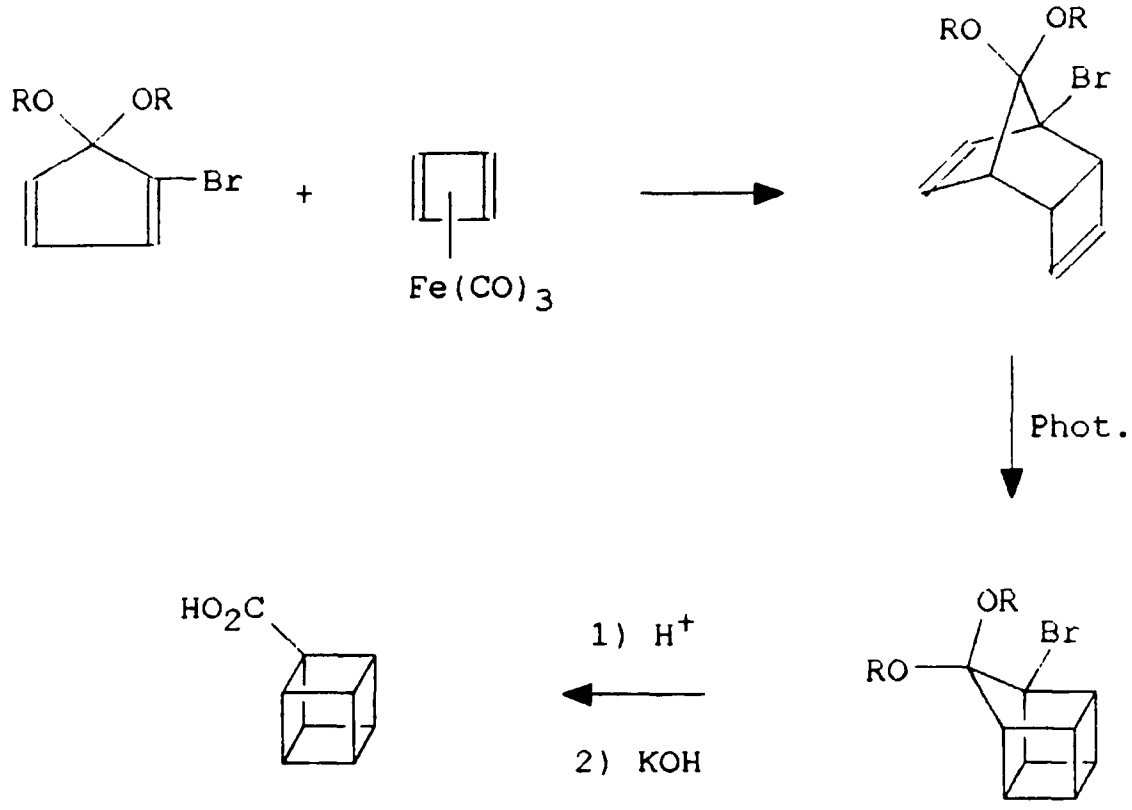
Brominations of this type have been carried out previously on the dimethyl ketal of cyclopentanone by Eaton and Hudson but pyridinium bromide perbromide was used as the brominating agent.2 In 1982, Dong and Edward also prepared this tribromide by using pyridinium bromide perbromide in methanol and obtained a 74% yield[10] When a solution of 1,1-diethoxycyclopentane in methanol was treated with 3.1 equiv. of bromine at 0 °C with dioxane present a colorless oil was obtained which was found to be a complex mixture by ^{1}H NMR. A bromination with 3.1 equiv. of pyridinium bromide perbromide in methanol at 0 °C proceeded similarly. However, Addition of 2 equiv. of pyridinium bromide perbromide at 0 °C to a methanolic solution of the ketal gave 1,3-dibromo-2,2-diethoxycyclopentane in 84% yield.

The trimethylene ketal of cyclopentanone was prepared by treatment of cyclopentanone with 1,3-propanediol using p-toluenesulfonic acid as catalyst. Water was removed azeotropically and distillation afforded the desired ketal in 53% yield. An attempt to brominate the trimethylene ketal of cyclopentanone using bromine/dioxane in CH2Cl2 at 0 °C also produced a complex mixture.

Work was also undertaken to prepare the dimethyl ketal of cyclopentanone. Treatment of cyclopentanone in methanol with trimethyl orthoformate and p-toluenesulfonic acid afforded 1,1-dimethoxycyclopentane in 79% yield. Bromination attempts were not carried out.

Cubane monocarboxylic acid has been made by decarboxylation of the 1-4 diacid, and work was conducted briefly on an economical direct synthesis.

The anticipated route was based on the Diels-Alder reaction of cyclobutadiene-iron tricarbonyl complex with 2-bromocyclopentadienone ketal with cyclobutadiene, followed by photolytic ring closure and a Favorski reaction.



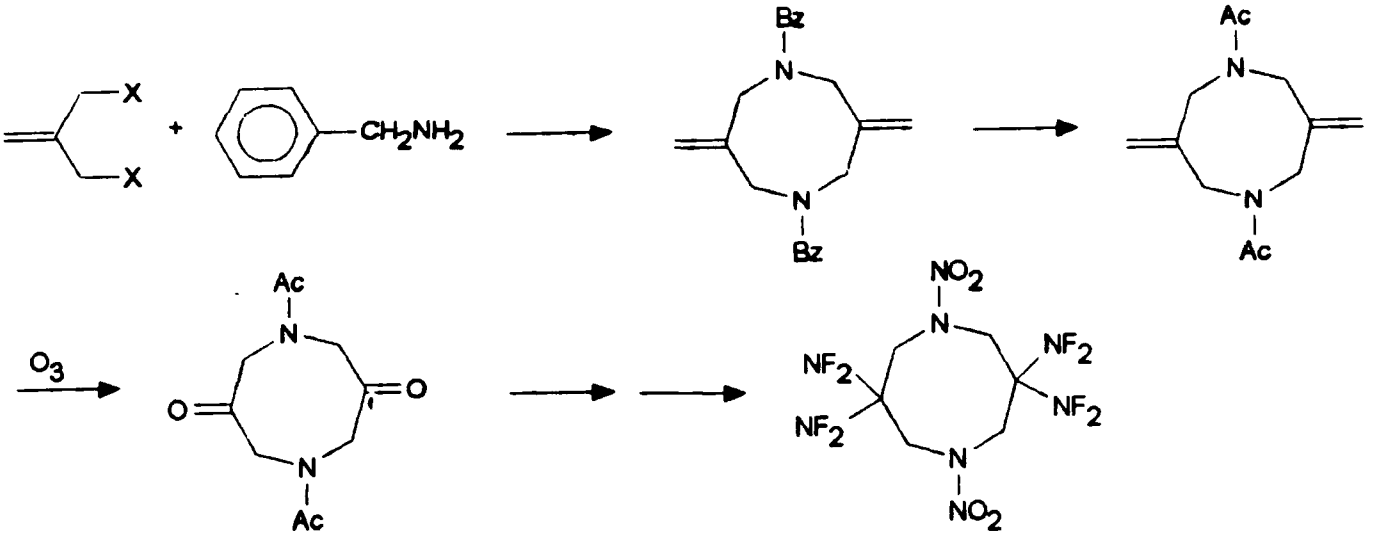
Although the cyclobutadiene-iron tricarbonyl complex was at one time a low-cost commercial product, it is not currently available at reasonable cost. The preparation of 3,4-dichlorocyclobutene as a functional equivalent of cyclobutadiene was investigated. The photoreaction of 1,2-dichloroethylene with 2,3-dichloromaleic anhydride was expected to give the [2+2] product which could then be hydrolyzed to the diacid and then decarboxylated to the 3,4-dichlorocyclobutene with $Pb(OAc)_4$. When a solution of dichloromaleic anhy-

dride with a three-fold excess of 1,2-dichloroethylene was irradiated for 32 h, analysis by ^{1}H NMR indicated that the reaction was 75% complete. Further work on this reaction may also provide a useful route to cubane mono-acid.

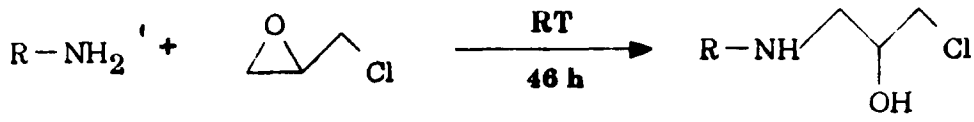
Difluoramino Derivatives of Cubane. Difluoramino derivatives of cubane have not been reported, and these materials are expected to meet the energy requirements of this program. Aqueous fluorination of carbamates is a known route to difluoramino compounds.[12] Fluorination of a suspension of dimethyl cubane-1,4-dicarbamate in water at 0°C gave no NF-containing material, based on NMR, and the starting material was recovered. Under the same conditions, methyl N-cyclohexylcarbamate gave difluoraminocyclohexane. Similarly, no reaction was observed when a suspension of dimethyl cubane-1,4-dicarbamate in Freon 113 was fluorinated at 0°C. When a solution of dimethyl cubane-1,4-dicarbamate in acetonitrile was fluorinated at -20 °C, no reaction was observed, but when the reaction was carried out at -8 °C, ^{19}F NMR analysis of the crude product showed more than 50 absorbances in the region of +20 to +30 ppm. When the oil was triturated with water, a brown intractable tar resulted.

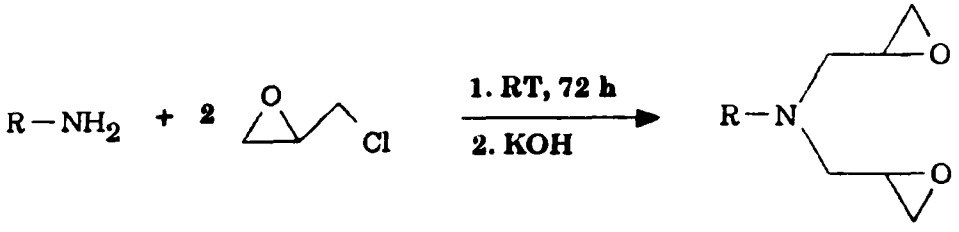
Difluoramino-Nitro Compounds. Research at Fluorochem, Inc. under Contract N00014-88-C-0536 has been aimed at the synthesis of cyclic compounds containing both difluoramino and nitro groups.[13] One objective was 3,3,7,7-tetrakis(difluoramino)-1,5-dinitrooctahydro-1,5-diazocine, calculated to provide high performance for both propellant and explosives applications. The compound was obtained in low yield by a multistep route based on the alkylation of benzylamine with 3-halo-3-halomethylpropenes, debenzylation and

acetylation of the amino groups, ozonolysis, and stepwise difluoramination and nitration. In the final difluoramination step, instability of nitramine groups in the strongly acidic medium resulted in low yields.



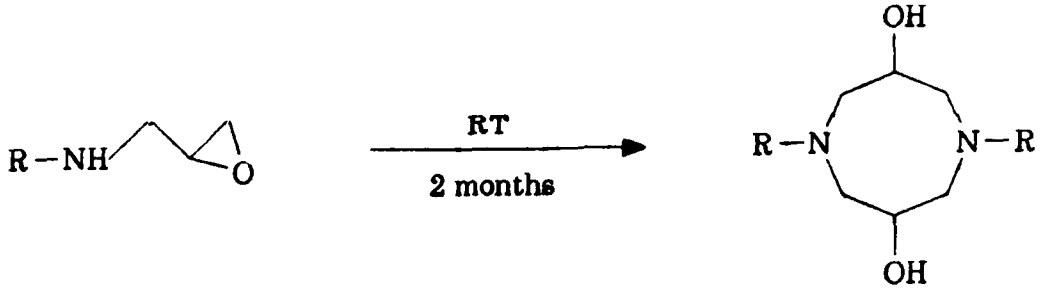
On the present program, a more efficient route to this structure was sought. Gaertner[14] reported that *t*-alkylamines react slowly with one or two equivalents of epichlorohydrin in methanol at room temperature to give the respective adducts which can be dehydrohalogenated to give *t*-alkylglycidylamines (58-66% yield) and *t*-alkyl-N,N-diglycidylamines (40% yield).

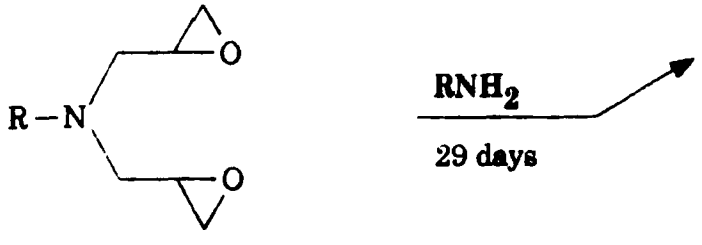




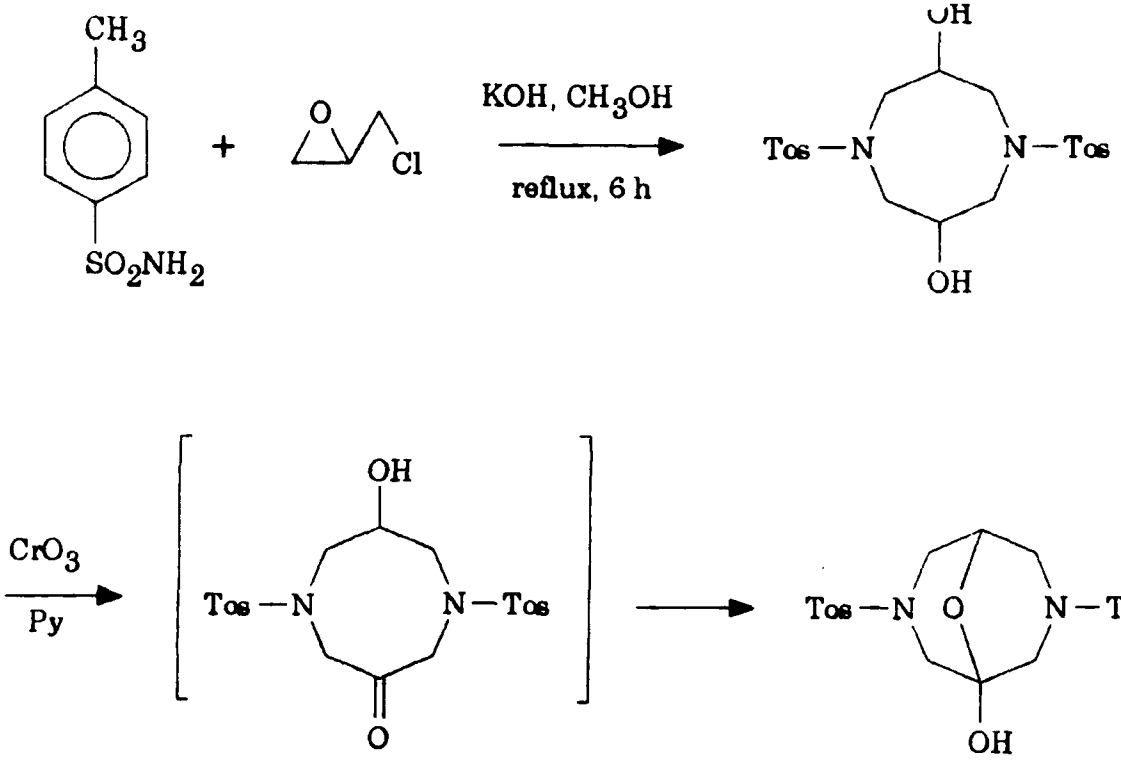
R = *t*-butyl, benzyl

The dimerization of *t*-butylglycidylamine took place in methanol at room temperature to give a 15% yield of 1,5-di-*t*-butyl-3,7-dihydroxyoctahydro-1,5-diazocine, but a two month reaction period was required. The diazocine was also obtained in ca. 28% yield from *t*-butyl-N,N-diglycidylamine and one equivalent of *t*-butylamine in 33 days.[14].





Similarly,[15] 1,5-bis(p-toluenesulfonyl)3,7-dihydroxyoctahydro-1,5-diazocine was obtained in 12% yield in 6 hours from p-tolunesulfonamide. Oxidation of this diol to the corresponding diketone was attempted with CrO3/Pyridine, but only the hemiketal of the monoketone was obtained.



On the present program, reactions of benzylamine as well as *t*-butylamine with epichlorohydrin were studied under various reaction conditions. The reactions were carried out either at room temperature or at reflux, and the results of screening experiments are presented in Table 1 and Table 2.

Table 1. Reaction of Benzylamine with Epichlorohydrin.

Run	Amine/ECH #ratio	Time (hr)	Temp ^{0} C	Solvent	Product(s)
1	1:5	24	RT	Hexanes	mono + di
2	1:5	72	RT	Hexanes	mono + di
3	1:5	24	Reflux	Hexanes	mono + di
4	1:5	48	RT	CH3OH	mono + di
5	1:5	48	50	CH3OH	mono + di
6	1:2.1	72	RT	CH3CN	mono + di
7	1:2.1	48	Reflux	CH3CN	mono + di
8	1:2.1	72	RT	CH2Cl2	mono + di
9	1:2.1	0.5	RT	Neat	Decomposition

Table 2. Reaction of *t*-Butylamine with Epichlorohydrin.

Run #	Amine/ECH ratio	Time (hr)	Temp ^{0} C	Solvent	Product(s)
1	1:5	24	RT	Hexanes	mono + di
2	1:5	72	RT	Hexanes	mono + di
3	1:5	24	Reflux	Hexanes	mono + di
4	1:5	48	RT	CH3OH	mono + di
5	1:5	48	50	CH3OH	mono + di
6	1:2.1	72	RT	CH3CN	mono + di
7	1:2.1	48	Reflux	CH3CN	mono + di
8	1:2.1	72	RT	CH2Cl2	mono + di
9	1:2.1	>7 days	RT	Neat	di

Efforts to obtain the 1:2 adduct of benzylamine cleanly were unsuccessful, and GC analysis also showed higher oligomers that were difficult to characterize. However, in the reaction of *t*-butylamine with epichlorohydrin without solvent at room temperature (table 2, entry 9) after 7 days, only one peak in GC was observed which was identified by NMR as the 2:1 adduct, *t*-butyl-N,N-bis-(3-chloro-2-hydroxypropyl)amine. Dehydrohalogenation gave the diglycidylamine.

The reaction of *t*-butyl-N,N-diglycidylamine with another equivalent of *t*-butylamine to obtain the diazocine was carried out. As mentioned above,

Gaertner's procedure requires 33 days to carry out this reaction. Higher reaction temperatures were tried with the objective of accelerating this reaction. Reactions at 50 ^{0}C for 15 hours were carried out in methanol, hexanes, and acetonitrile, and the solutions were was monitored by GC and NMR analysis. No diazocine was isolated, and only higher oligomers were observed.

Another reaction was carried out in methanol at room temperature. After 30 days, a 50% yield of 1,5-di-(*t*-butyl)-3,7-dihydroxyoctahydro-1,5-diazocine was observed by GC (lit. yield[14] 28%), and after two months, all the starting material was consumed and GC indicated quantitative conversion to the diazocine. Solvent removal and trituration with ether resulted in a 60% isolated yield of the crystalline diazocine. Improvements in the isolation procedure are anticipated.

Since 1,5-bis(p-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine was prepared in a relatively short reaction time (6 hr) in refluxing methanol, its reactions were explored. Paudler[15] has reported a yield of only ~12 % of the diazocine. However, when a mixture of p-toluenesulfonamide, potassium hydroxide and epichlorohydrin was refluxed in methanol under high dilution conditions for 12-15 hours, work-up gave the desired diazocine in 28 % crude yield. A similar reaction using benzamide gave only recovered starting material.

The oxidation of ditosyldiazocine was studied. Previously, oxidation with CrO_3/pyridine resulted in the formation of hemiketal. Recently, pyridinium chlorochromate (PCC) in dichloromethane[16] and pyridinium dichromate (PDC) in dichloromethane[17] have been developed as oxidation reagents, with the advantage that excess reagent is not needed. Typically 1.1 equivalent of PCC or

PDC per hydroxy group is needed for the reaction and over oxidation or decomposition of the product is avoided. Both the PCC/CH_2Cl_2 and PDC/CH_2Cl_2 systems are mild oxidation reagents and can be used with acid-sensitive substrates. However, when 1,5-bis(p-toluenesulfonyl)-3,7-dihydroxy-1,5-diazocine was reacted with PCC in CH_2Cl_2 at 0°C, a product with a complex proton NMR was obtained, but with no C=O carbon in the ^{13}C NMR. The oxidation of another dihydroxy compound, also prone to hemiketal formation, to diketone was reported by Gilbert[18] PDC as an oxidant. The oxidation of 1,5-bis(p-toluenesulfonyl)-3,7-diazocine by PDC/CH_2Cl_2 was therefore carried out for 18 hr. Again, no C=O signal in the ^{13}C NMR spectrum was observed. These studies are being continued on another program.

EXPERIMENTAL

Elemental analyses were obtained from Galbraith Labs. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Brucker AC 200 spectrometer and chemical shifts are in parts per million from TMS. IR spectra were obtained in CH_2Cl_2 on a Perkin-Elmer 700 spectrometer. DSC and TGA analysis were performed on a Dupont 9900 Thermoanalyzer.

Cubane-1,4-dicarboxylic Acid from the Favorskii Mixture. A mixture of crude cubane-1,4-diacid and salt (800 g) (obtained from the filtration of an acidified Favorskii reaction mixture resulting from 1 kg of cage dione) was stirred with 10% aqueous NaOH (600 mL) for .5 h and filtered. The filtrate was acidified by dropwise addition of conc HCl. The solid was filtered, and

washed with cold water (3 x 50 mL) and cold acetone (3 x 50 mL), and dried at ambient temperature *in vacuo* (0.5 torr) to give 175 g (30% based on cage dione) of 95% pure cubane-1,4-dicarboxylic acid (by titration with standard NaOH) as a white powder, mp 225°C: ^{1}H NMR (DMSO-d6) δ 4.09 (s).

Cubane-1,4-diacid Chloride. A mixture of cubane-1,4-dicarboxylic acid (100 g, 0.52 mol) and freshly distilled $SOCl_2$ (326 g, 2.7 mol) was refluxed under N_2 for 14 h to give a homogeneous solution. The excess thionyl chloride was removed under reduced pressure. The residue was extracted sequentially with toluene (50 mL) and CCl_4 (50 mL), filtered and dried to give 116 g (97%) of cubane-1,4-diacid chloride, as a white solid, mp 135°C: δ ^{1}H NMR ($CDCl_3$) 4.48.

Cubane-1,4-bis(N-*t*-butyl-N-ethylcarboxamide) (Bisamide). A solution of cubane-1,4-dicarboxylic acid chloride (114 g, 0.49 mol) in methylene chloride (1000 mL) was cooled to 0°C and a mixture of triethylamine (121 g, 1.3 mol) and *t*-butylethylamine (121 g, 1.2 mol) was added dropwise. This mixture was stirred at room temperature for 48 h and the solvent was removed *in vacuo*. The residue was extracted with water (3 x 100 mL) and acetone (3 x 80 mL) and dried to give 178 g (98%) of cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide), as a white solid, mp 185°C: IR (KBr) 3050, 1620, 1400, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.27 (s), 3.14 (q), 1.55 (s), 1.22 (t); ^{13}C NMR δ 171, 59.7, 56.6, 40.7, 30.1, 20.09, 18.7. Anal. Calcd for $C_{22}H_{34}N_2O_2$: C, 73.7; H, 9.49. Found: C, 73.39; H, 9.48.

Cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide)-2,7-dicarboxylic acid (Bisacid Bisamide). A solution of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was prepared by the dropwise addition under N_2 of n-butyl lithium in hexane (111 mL, 0.26 mol) to a stirred solution of 2,2,6,6-tetramethylpiperidine (39 g, 0.277 mol) in THF (500 mL, freshly distilled from sodium benzophenone ketal) at a rate such that the internal temperature did not exceed -50°C. This solution was warmed to 0°C and was stirred for 3 h with cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide) (9.5 g, 26.5 mmol) and magnesium bromide etherate (35 g, 139 mmol) and then allowed to stand at -15°C for 48 h. Carbon dioxide gas was passed through the cooled solution for 5 h during which time the temperature rose to ambient. The solvent was evaporated in vacuo at 40°C and the residue was suspended in water (500 mL) at 0°C and conc. HCl (100 mL) was added in 5 portions resulting in a pH of 3. The precipitate was removed by filtration, washed with water (2 x 10 mL), and dried at ambient temperature (0.1 torr) to give 7.5 g (60%) of cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide)-2,7-dicarboxylic acid as an off-white solid, mp 241°C: IR (KBr) 3050, 1725, 1550, 1490, 1200, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57 (s, 4 H), 3.7 (q, J = 7 Hz, 4 H), 1.48 (s, 18 H), 1.28 (t, J = 7 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 172.0, 171.0, 61.2, 59.1, 56.7, 51.1, 39.8, 28.2, 18.4. Anal. Calcd for $C_{24}H_{34}N_2O_6$: C, 64.59; H, 7.16; N, 6.28. Found: C, 64.28; H, 7.47; N, 6.21.

Cubane-1,2,4,7-tetracarboxylic Acid from Bisamide. A solution of LiTMP (1.05 mol) in THF (1.6 L) (prepared as described above) cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide) (50 g, 138 mmol) and magnesium bromide etherate (143 g, 570 mmol) was stirred under N_2 at 0°C for 2 h. Carbon dioxide was passed through the solution for 3 h and the temperature was allowed to rise

to ambient. The solvent was evaporated, the residue suspended in an ice-water mixture (1.5 kg), and a pH of 3 attained by addition of conc HCl (160 mL). The mixture was filtered and the crude solid dissolved in cold conc HNO_3 (120 mL, 70%). The acid solution was refluxed for 5 h, cooled and filtered. The solid was washed with acetonitrile (3 x 10 mL) to give 17.5 g (46%) of cubane-1,2,4,7-tetracarboxylic acid as a white solid, mp 265°C (dec): IR (KBr) 3200 (br), 1740, 1600, 1460, 1300, 1230, 1205, 1120, 880 cm^{-1}; ^1H NMR (DMSO-d6) δ 4.27 (s) ^{13}C NMR (acetone-d6, D_2O) δ 173, 56.13, 47.78.

Cubane-1,2,4,7-tetracarboxylic Acid from Bisacid Bisamide. Solid cubane-1,4-bis(N-*t*-butyl-N-ethylcarboxamide)-2,7-dicarboxylic acid (1.4 g, 3.14 mmol) was added to conc HNO_3 (30 mL, 70%) at 0°C and the solution was then heated to reflux for 12 h. The resulting mixture was cooled, filtered and the solids washed with acetonitrile (2 x 10 mL) to give 0.6 g (68%) of cubane-1,2,4,7-tetracarboxylic acid as a white solid, mp 265°C (dec) identical to that prepared above.

Cubane-1,2,4,7-tetracarboxylic Acid Chloride. A mixture of cubane-1,2,4,7-tetracarboxylic acid (1.0 g, 3.6 mmoles) and freshly distilled thionyl chloride (25 mL) was stirred and refluxed for 6 h to give a homogeneous solution. The thionyl chloride was removed *in vacuo* (0.5 torr) and the residue was recrystallized from dry toluene to give 1.2 g (95%) of cubane-1,2,4,7-tetracarboxylic acid chloride, mp 132°C (DSC): ^1H NMR ($CDCl_3$) δ 4.8. Anal. Calcd for $C_{16}H_4Cl_4O_4$: C, 40.7; H, 1.13; Cl, 40.06. Found: C, 49.79; H, 1.31; Cl, 38.84.

t-Butylethylamine. A mixture of 50% KOH (475 mL), water (200 mL) and t-butylamine (431 g, 5.89 moles) was cooled to 0°C and diethyl sulfate (1000 g, 6.48 moles) was added with rapid stirring over 1 h. The organic layer was separated, stirred over solid KOH for 16 h, filtered and distilled from CaH_2 to give 390 g (66%) of t-butylethylamine, b.p. 81-85°C, ^1H NMR: 2.6 (q, J = 7 Hz, 2 H); 1.1 (s, 9 H); 1.15 (t, J = 7 Hz, 3 H).

2,2,6,6-Tetramethylpiperidine. Ammonia gas (1400 g, 82 mol) was dissolved in a stirred suspension of acetone (12.5 kg, 215 mol) and calcium chloride (4 kg) over 48 hours at a rate such that the temperature was maintained below 40°C. The solvent was removed at 30-40°C (30 torr) and a 10% aqueous NaOH solution (5 L) was added. The organic layer was decanted and the water extracted with CH_2Cl_2 (3 x 2 L). The organic materials were combined and solvent evaporated to give 8.5 kg of crude triacetone amine.

A solution of the crude triacetone amine (8.5 kg), hydrazine hydrate (10 kg), KOH (9.3 kg) in polyethylene glycol (carbowax 400, 80 L) was heated at 135°C for two hours and then the temperature was slowly increased to 180°C. The two-phased distillate was extracted with CH_2Cl_2 (2 x 2 L), separated, and the organic layer was dried (Na_2SO_4). This solution contained 3.4 kg (31%) of essentially pure 2,2,6,6-tetramethylpiperidine, by nmr assay, and was stored in solution. The solvent was evaporated from a 200 mL aliquot and the crude product stirred for 24 h over solid KOH, filtered and distilled to give 2,2,6,6-tetramethylpiperdine, bp 151-152°C.

Tetramethyl Cubane-1,2,4,7-tetracarboxylate. A suspension of cubane-1,2,4,7-tetracarboxylic acid (7.6 g, 27 mmoles) in methanol (150 mL) and

trifluoromethanesulfonic acid (1.0 g, 6.7 mmol) was refluxed for 4 h until a homogenous solution formed. The cooled solution was diluted with a saturated $NaHCO_3$ solution (150 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried (Na_2SO_4), evaporated and the residue recrystallized from CH_2Cl_2/hexane (1:4.5) to give 6.0 g (68%) of tetramethyl cubane-1,2,4,7-tetracarboxylate as a white solid, mp 180°C: IR (KBr) 3050, 1720, 1450, 1320, 1220, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.47 (s, 4 H), 3.8 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 168.45, 55.89, 51.97, 47.39.

Tetraethyl Cubane-1,2,4,7-tetracarboxylate. A suspension of cubane-1,2,4,7-tetracarboxylic acid (0.7 g, 2.5 mmoles) in ethanol (20 mL) and trifluoromethanesulfonic acid (1 drop) was refluxed for 5 h. The solvent was remove *in vacuo* and the residue dissolved in CH_2Cl_2 (20 mL), and washed with water (2 x 15 mL). The organic layer was dried (Na_2SO_4) and evaporated to give 1.0 g (98%) of tetraethyl cubane-1,2,4,7-tetracarboxylate as a white solid, mp 86°C: IR (KBr) 3050, 1720, 1320, 1220, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (s, 4 H), 4.18 (q, J = 7 Hz, 8 H), 1.27 (t, J = 7 Hz, 12 H). Analysis pending.

Cubane-1,2,4,7-tetracarboxylic Acid from Cubane Tetramethyl Tetracarboxylate. Tetraester (4.0 g, 14.7 mmol) in 12N HCl was stirred at 60°C for 4 h. All volatiles were removed under vacuum as quickly as possible at 50°C. The white solid was filtered to give 3.0 g (90%) of cubane-1,2,4,7-tetraacid as white solid: mp 257 (dec.) ^1H NMR (D_2O) δ 4.3 ppm (s, 4 H). IR (KBr) 3200-2500 br, 1240, 1800, 1300, 1230.

Cubane-1,2,4,7-tetracarboxamide. Cubane-1,2,4,7-tetraacid chloride (1.1 g, 3 mmol) was dissolved in dry ethanol free chloroform (50 mL) and cooled to -40°C (dry ice/methanol). Liquid ammonia was then added to the stirred solution for about 1 h. and allowed to warm up to room temperature. The solvent was removed and the residue was washed with cold chloroform to give 1.0 g (97%) cubane-1,2,4,7-tetracarboxamide as light yellow solid. Mp 226°C (dec, DSC). ^{1}H NMR (DMSO) δ 7321 (8 H, 4 x $CONH_2$). and 4.19 (s, 4 H, C_8H_4).

Attempted Preparation of 2-Bromocyclopentadienone Ethylene Ketal. A mixture of 2,2,5-tribromocyclopentanone ethylene ketal (1.035 g, 2.84 mmol) in DMSO (40 mL) was treated with potassium t-butoxide (0.797 g, 7.10 mmol) at 25 °C. An aliquot was removed after 0.5 h and examined by ^{1}H NMR which showed that the bis ketal dimer had formed and that the reaction had not gone to completion. Reexamination (NMR) after 22 h showed no remaining starting material and the bis-ketal as the major product.

1,1-Diethoxycyclopentane. Method A. A solution of cylopentanone (12.0 mL, 136 mmol), triethyl orthoformate (68.0 mL, 408 mmol) and concentrated sulfuric acid (0.5 mL) in ethanol (100 mL) was stirred overnight and then poured into 5% $NaHCO_3$. The product was extracted with methylene chloride (4 x 100 mL) and the combined methylene chloride solution was washed with saturated sodium chloride solution and dried over potassium carbonate. Distillation gave 17 g of 90% pure 1,1-diethoxycyclopentane, contaminated with triethyl orthoformate (estimated yield 70%).

Method B. A solution of cyclopentanone (10.0 mL, 113 mmol) and sulfuric acid (1.0 mL) in 120 mL of ethanol was stirred over 3A molecular sieves for 72

h. The mixture was filtered through celite and added to a 5% $NaHCO_3$ solution. The product was extracted with methylene chloride (4 X 100 mL), dried over potassium carbonate and distilled to give 16.1 g of a colorless oil (90% yield) of pure which was essentially pure 1,1-diethoxycyclopentane. ^1H NMR d 1.20 (t, 6 H), 1.60-1.80 (m, 8 H), 3.48 (q, 4 H) ppm.

Bromination of 1,1-Diethoxycyclopentane. A solution of 1,1-diethoxycyclopentane (14.8 g, 93.8 mmol) in 1,4-dioxane (25.6 mL) and methylene chloride (350 mL) was treated dropwise with bromine (15.45 mL, 300 mmol) at 20 °C. The mixture stirred at ambient temperature overnight. ^1H NMR indicated that the product consisted mainly of 2,5-dibromocyclopentenone [δ7.79 (broad t, 1 H) and 5.17 (broadened t, 1 H)], with 1,1,3-tribromo-2,2-diethoxycyclopentane as a minor product [δ5.52 (d, 1 H), 4.27 (q, 2 H), 4.16 (q, 2 H), 3.55-2.90 (m, 4 H), 1.48 (t, 6 H) ppm].

1,3-Dibromo-2,2-diethoxycyclopentane. To a methanol (20 ml) solution of 1,1-diethoxycyclopentane (1.582 g, 10.0 mmol) at 0 °C was added pyridinium bromide perbromide (technical grade, 90%, 11.73 g, 33.0 mmol) and the mixture was stirred for 2 h. The solution was then neutralized with 5% potassium carbonate and extracted with methylene chloride (4 x 40 mL). The combined organic solutions were washed with brine and dried over Na_2SO_4. Evaporation of the solvent in vacuo afforded 3.32 g of a colorless oil. ^1H NMR d 1.10-1.26 (m, 6 H), 2.20-2.70 (m, 4 H), 3.47-3.74 (m, 4 H), 4.40-4.55 (m, 1 H) ppm.

Cyclopentanone Trimethylene Ketal. A mixture of cyclopentanone (50.0 mL, 0.565 mol), 1,3-propanediol (75.0 mL, 1.038 mol), toluene (125 mL), and p-

toluenesulfonic acid (0.70 g) was refluxed and water was removed azeotropically with a Dean-Stark trap. Distillation gave 42.66 g (53%) of cyclopentanone trimethylene ketal, bp 108-110 °C (25 mm) as a clear colorless liquid; ^{1}H NMR d 1.60-1.75 (m, 6 H), 1.85-1.95 (m, 4 H), 3.90 (t, 4 H, J = 6 Hz).

1,1-Dimethoxycylopentane. A mixture of cyclopentanone (50.0 mL, 0.565 mol), methanol (225 mL, 5.65 mol), trimethyl orthoformate (86.5 mL, 0.791 mol), and p-toluenesulfonic acid (0.70 g) was stirred at room temperature for 48 h. The methanol removed by distillation at atmospheric pressure. A small amount of the trimethyl orthoformate was removed at reduced pressure followed by 58.5 g (79%) of 1,1-dimethoxycyclopentane (78-81 °C, 45 mm); 1 H NMR d 1.58-1.67 (m, 4 H), 1.80-1.90 (m, 4 H), 3.24 (s, 6 H).

Fluorination of Dimethyl Cubane-1,4-dicarbamate. A suspension of dimethyl cubane-1,4-dicarbamate (1.0 g, 4.0 mmol) in water (200 mL) was cooled to 0°C in an ice bath and the mixture was reacted with fluorine (0.5 L, 22 mmol) diluted to 20% with nitrogen over 40 min. The solution was filtered to give 1.0 g of unreacted starting material. No absorbances indicative of N-F groups were detected by ^{19}F NMR analysis of the water solution or the organic solid. The same results were obtained using Freon 113 as the solvent.

A solution of dimethyl cubane-1,4-dicarbamate (1.0 g, 4.0 mmol) in acetonitrile (200 mL) was cooled to -20 °C in an ice-methanol bath. Precipitation of solids was observed. The mixture was reacted with fluorine (0.4 L, 18 mmol) diluted to 20% with nitrogen over 55 min. The solution was warmed to room temperature and no absorbances indicative of N-F groups were detected by ^{19}F NMR analysis of the homogenous solution. The solution was diluted with

additional acetonitrile (100 mL) and was cooled to -8°C. This homogenous solution was reacted with fluorine (0.4 L, 18 mmol) diluted to 20% with nitrogen over 40 minutes. The solvent was removed at 30-40°C under high vacuum during which the clear solution became dark brown. ^{19}F NMR analysis of the crude oil showed >50 absorbances in the region of +20 to +30 ppm. When the oil was triturated with water, a brown intractable tar resulted.

General Procedure for Reaction of Amine with Excess Epichlorohydrin. Typically 0.1 mole of benzylamine or t-butylamine was dissolved in 100 ml of solvent and 5 eq of epichlorohydrin was added. In the neat reaction, the reactants were mixed in a 1:2.1 amine to epichlorohydrin mole ratio and the mixture was stirred at room temperature. A homogeneous solution was obtained. The mixture was stirred at room temperature for 3 days under nitrogen. The benzylamine reaction mixture became cloudy which upon standing at room temperature without stirring and separated into two layers. The heavier layer consisted of mono and di-adducts and epichlorohydrin.

***t*-Butyl-N,N-diglycidylamine.** *t*-Butylamine (73.1 g, 1.00 mol) was added dropwise to a solution of epichlorohydrin (191.0 g, 2.06 mol) in 100 mL of methanol, and the mixture was stirred at room temperature for 4 days. Solvent was removed (25-50 0°C, 25 mm Hg), and the residue was stirred with 50 mL of DMSO and 200 g of 40% aqueous sodium hydroxide. The organic layer was separated and dried. Distillation gave a forerun (13.6 g) of impure product and 77.1 g (42%) of *t*-butyl-N,N-diglycidylamine, bp 87-88 0°C (1.0 mm); ^{13}C NMR ($CDCl_3$) 52.9, 52.6, 52.4, 45.9, 27.2, 27.0; ^{1}H NMR δ 2.5-3.3 (m, 10

H), 1.1 (s, 9 H). GC: 30 m SE-54 capillary column, 100 °C (hold 2 min), increase 10°C/min to 240°C, hold 30 min, retention time 9.6 min.

1,5-Bis(*t*-butyl)-3,7-dihydroxyoctahydro-1,5-diazocine. A solution of *t*-butyl-N,N-diglycidylamine (18.5 g, 0.100 mol) and *t*-butylamine (7.3 g, 0.100 mol) in methanol (120 mL) was kept at room temperature with stirring for 30 days. After 30 days, GC analysis indicated a 48% product yield. The methanol was removed with a rotary evaporator and the product distilled to give 3.9 g (15 %) of oil, bp 180-220 (2 mm). Loss of product by decomposition during the distillation was evident. The reaction was repeated on the same scale and the reaction time was extended to 2 months. At the end of this period, GC showed that all the starting material was consumed and the yield was quantitative. The solvent was removed by rotary evaporation and the resulting oily residue was triturated with ether to obtain a white precipitate (15.6 g, 60%): ^{1}H NMR δ 2.5-3.5 (br m, 12 H), 1.0 (s, 18 H); GC: 30 m SE-54 capillary column, 60 °C (hold 2 min), increase 10°C/min to 240°C, rt 15.8 and 15.9 min (cis, trans).

1,5-Bis(p-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine. A mixture p-toluenesulfonamide (171 g, 1.0 mole), potassium hydroxide (56.0 g, 1.0 mole) and methanol (3 L) was warmed slightly to effect dissolution and epichlorohydrin (100 g, 1.1 mole) was added in one portion with vigorous stirring. The mixture was heated under reflux with stirring overnight to give a neutral solution. The precipitated potassium chloride was filtered and methanol was removed with a rotary evaporator. The resulting oily residue was mixed with 500 ml of ether and a white solid precipitated. The solid was filtered and washed with 300 ml of ether. The combined ether washing were

dried over magnesium sulfate and ether was removed by rotary evaporation. The resulting viscous residue was dissolved in a minimum quantity of ethanol and water was added to precipitate more product. A total of 67 g (28%) of diazocinediol was obtained, mp 200-202 ^{0}C (lit. 198-200 ^{0}C).

Oxidation of 1,5-Bis(p-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine by Pyridinium Chlorochromate (PCC). A solution of the dihydroxydiazocine (0.05 mole) in 20 mL of dichloromethane was then added in one portion to a magnetically stirred suspension of pyridinium chlorochromate (32.3 g, 0.15 mole) in 200 mL of dichloromethane. After 18 h, 200 mL of diethyl ether was added and the mixture was filtered through a short florisil column and the solvent removed. The crude product obtained was analyzed by GC and NMR. The GC analysis shows the presence of unreacted diol along with several new products. The carbon NMR shows absence of any peaks in the region 160-220 ppm where a carbonyl carbon will generally show.

REFERENCES

1. Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724.
2. Eaton, P. E.; Shankar, B. K. R.; Price, G. D.; Plath, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185.
3. Willer, R., Workshop on Energetic Materials, Great Oak Landing, Md, August 1988.
4. Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964** *86*, 962.
5. Fluorochem, Inc., Report SDI-2-1 (Final), Cubane Derivatives for Propellant Applications, Contract N00014-87-C-0076, July 1989.

6. Schmidt, R., Botaro, J. Workshop on Energetic Materials, Great Oak Landing, Md, August 1988.

7. Bortnick, N.; Luskin, L. S.; Hurtwitz, M. D.; Craig, W. E.; Exner, L. J.; Mirza, J. *J. Am. Chem. Soc.* **1956**, *78*, 4039.

8. Leonard, N. J.; Nommensen, E. W. *J. Am. Chem. Soc.* **1949**, *71*, 2808.

9. Grieco, P. A.; Abood, N. *J. Org. Chem.* **1989**, *54*, 6008.

10. Dong, D. C.; Edward, J. T. *Chem. Eng. Data* **1982**, *27*, 211.

11. Eaton, P. E.; Hudson, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 2789.

12. Grakauskas, V.; Baum, K. *J. Org. Chem.* **1972**, *37*, 334.

13 Fluorochem, Inc. Report ONR-7-1, "Research in Energetic Compounds", Contract N00014-88-C-0536, September 1991.

14 a) Gaertner, V. R., *Tet. Lett.*, **1964**, 141. b) Gaertner, V. R., *Tetrahedron*, **1967**, *23*, 2123.

15 Paudler, W. W., Gapski, G. R. and Barton, J. M., *J. Org. Chem.*, **1966**, *31*, 277.

16 Piamcatelli, G.; Scettri, A. and D'Auria, M.; *Synthesis*, **1982**, 245.

17 Corey, E.J. and Schmidt, G.; *Tet. Lett.*, **1979**, 399.

18 Zalikowski, J.A.; Gilbert, K.E. and Borden, W.T.; *J. Org. Chem.* **1980**, *45*, 346.