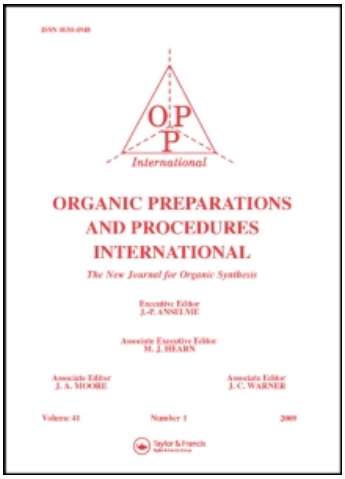

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THE SYNTHESIS AND REACTIONS OF PRISMANES. RECENT DEVELOPMENTS

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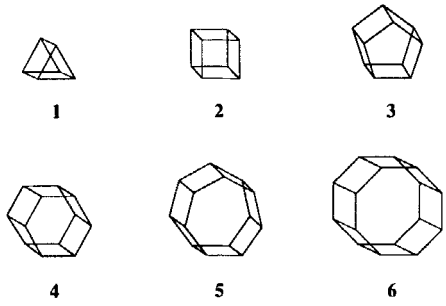
INTRODUCTION

With their high degree of symmetry and aesthetically pleasing molecular architecture, polycyclic "cage" hydrocarbons have long fascinated a wide range of organic chemists. Synthetic organic chemists are attracted by the highly symmetric molecular structure as well as the formidable synthetic challenge that these molecules pose. Physical organic chemists are drawn to the unique structural features, especially unusual carbon-carbon bond lengths and angles, and the novel chemical reactivity which these molecules often exhibit. Finally, the high degree of symmetry and rigidity of these molecules make them attractive to theoreticians for testing concepts of bonding, structure, and reactivity. Indeed, our understanding of these concepts has been enhanced by the synthesis and study of these molecules.

One class of polycyclic cage hydrocarbons that has attracted a great deal of attention over the past thirty years is the [n]-prismanes (Figure 1). The [n]-prismanes are highly symmetrical $(CH)_{2n}$ polyhedranes possessing D_{nh} symmetry and are composed of two n-membered rings and n-four membered rings connected in a *cis, syn* fashion. The compact carbocyclic framework of the [n]-prismanes thus possesses considerable strain energy and poses a formidable challenge to the synthetic chemist.

In response to this synthetic challenge, creative and ingenious strategies have been developed to circumvent, or at least mitigate, the deleterious effects of the strain inherent in these systems, resulting in the synthesis of the first three members of the [n]-prismane family. The synthesis of [4]-prismane (cubane) (**2**) was completed in 1964 through the pioneering efforts of Eaton and Cole.[1] In 1973, Katz and Acton reported the first synthesis of [3]-prismane (prismane) (**1**),[2] the smallest member of the prismane family, and in 1981 Eaton and Or reported the synthesis of [5]-prismane (pentaprismane) (**3**).[3] However, despite extensive effort and considerable progress in some cases, all higher order prismanes (n>5), including [6]-prismane (hexaprismane) (**4**) and [7]-prismane (heptaprismane) (**5**), remain unknown. Herein, we describe some of the recent results in the synthesis and reactions of prismanes[4] including our synthetic efforts toward **3**, **4**, and **5**.

Figure 1



1 2 3 4 5 6

I. [3]-PRISMANE

The first member of the [n]-prismane family, and the second to succumb to total synthesis, is [3]-prismane (**1**) (Ladenberg's benzene, prismane). Along with being a member of the [n]-prismane family, prismane (**1**) is also a member of the isomeric $(CH)_6$ family of benzene valence isomers.[5] Other members of this family include benzvalene (tricyclo[3.1.0.0^{2,6}]hex-3-ene) (**7**),[6] which also serves as a precursor to **1**, and Dewar benzene (bicyclo[2.2.0]hexa-2,5-diene) (**8**). Prismane (**1**) was also the first of the prismanic structures to be conceptualized, as Ladenberg postulated that benzene might have the prismane structure.[7] Despite this early inception, prismane (**1**) was not successfully synthesized until Katz and Acton completed the task in 1973.[2]

Figure 2

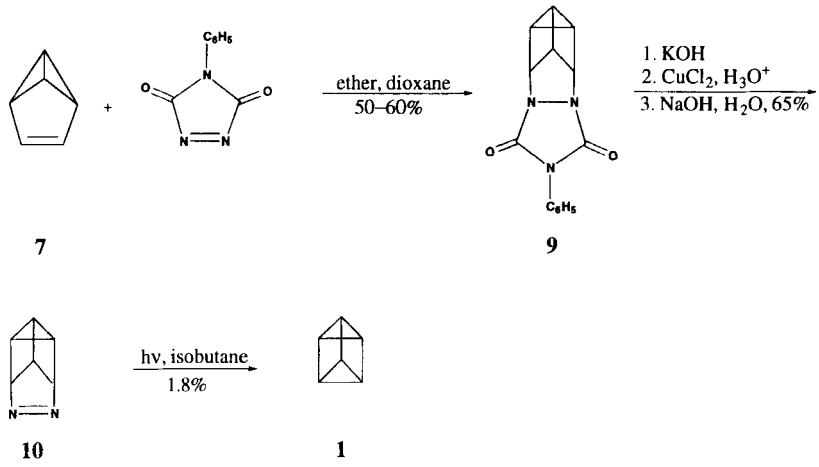
7 8

Katz and Acton found that combining benzvalene (**7**) in ether-dioxane with 4-phenyltriazolinedione for one hour gave 50-60% yield of the 1:1 adduct **9** after silica gel chromatography. Hydrolysis and oxidation afforded azoalkane **10** in 65% yield. Photolysis of a 0.19 M solution of **10** in isobutane at 35° gave a complex mixture of products from which prismane (**1**) was isolated in 1.8% yield as a colorless explosive liquid (Scheme 1).

Two years earlier, Trost prepared **10** independently *via* a different route but did not report successful denitrogenation to prismane (**1**).[8] The extreme reluctance of azoalkane **10** to lose nitrogen, as observed by Katz and Trost, is characteristic of six-membered ring azo compounds, particularly those residing in a bicyclo[2.2.2] framework. Turro and Engel have uncovered the origin of this phenomenon,[9] (vide infra) and slightly improved yields of **1** may now be obtained.[10]

Despite the fact that its synthesis was first completed over twenty years ago, the chemistry and reactivity of prismane remains relatively unexplored. Undoubtedly this paucity of studies is a reflection of the synthetic inaccessibility of **1**, and a new, more efficient synthesis is needed.

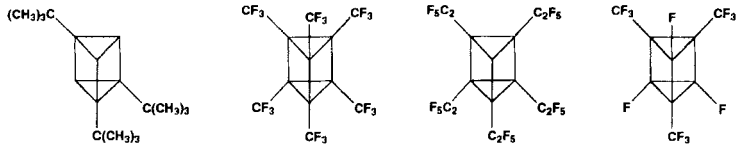
Scheme 1



7 **9**

10 **1**

Figure 3



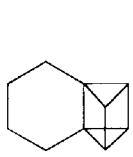
11 **12** **13** **14**

The most rational and direct route to **1** is through photochemical valence isomerization of benzene but such attempts have not been successful. It has been possible, however, to prepare several sterically encumbered prismane derivatives *via* irradiation of the corresponding benzene precursors. Although in many cases complex product mixtures containing other benzene valence isomers are obtained, this method has proven very useful for preparing a variety of substituted prismanes. For example, tri-*t*-butylprismane (**11**),[11] hexakis(trifluoromethyl)prismane (**12**),[12] hexakis(pentafluoroethyl)prismane (**13**),[12b,c] and perfluoro-1,3,5-trimethylprismane(**14**)[13] have all been prepared *via* this route.

The direct irradiation of Dewar benzene isomers has also proven to be a reliable method for the preparation of [3]-prismanes. In fact, the parent hydrocarbon **1** has been prepared in 15% yield through direct irradiation of Dewar benzene (**8**).[14] A variety of other sterically encumbered prismane derivatives may also be prepared in this fashion, and the interested reader is referred to these studies.[15]

It is also interesting to note that several bridged prismanes have recently been prepared. For example, **15-19** are available *via* irradiation of their corresponding Dewar isomers.[16] Pentakis(pentafluoroethyl)-1-azaprismane (**20**) has been prepared through irradiation of pentakis(pentafluoroethyl)-1-azabicyclo[2.2.0]hexa-2,5-diene,[17] and 1,2,3-tri-*t*-butyltrifluoro-prismane may be produced *via* oligomerization of *t*-butylfluoroacetylene.[18]

Figure 4



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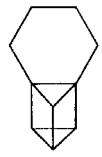

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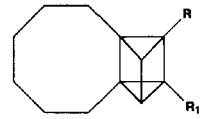
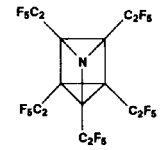


17: R, R_1=$CH_2OCONHC_6H_{11}$
18: R=H, R_1=CO_2CH_3
19: R, R_1=$CO_2CH_2CH_3$



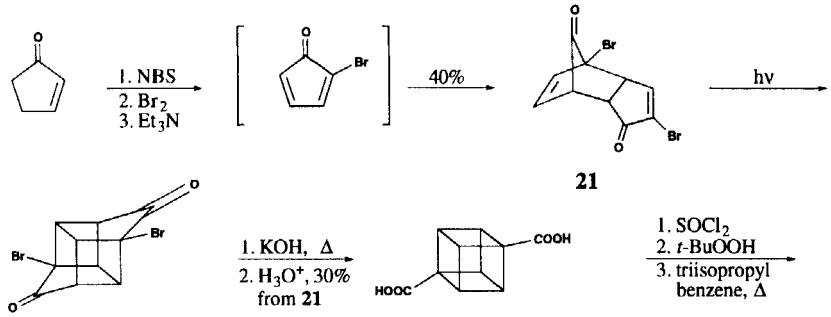
20

II. [4]-PRISMANE

In 1964 Eaton and Cole reported the synthesis of cubane-1,4-dicarboxylic acid,[19] the first organic compound to possess a prismanic skeleton, and shortly thereafter the synthesis of the parent hydrocarbon, [4]-prismane (cubane) (**2**),[1] appeared. With its aesthetic appeal, remarkable synthetic accessibility, and extraordinary kinetic stability, cubane (**2**) has been the most studied of the [n]-prismanes thus far. Today, nearly thirty years after its initial preparation, cubane remains the subject of intense research.

The synthesis of cubane (**2**) by Eaton and Cole is remarkable not only in its brevity but also in its simplicity. Although several steps including the preparation of the bromocyclopentadienone ketal,[20] the Favorskii rearrangement[21] and the decarboxylation[22] have undergone refinement, the foundation of the original synthetic scheme remains intact. Today, ten gram lots of this fascinating hydrocarbon may be prepared in about a month. The original cubane synthesis is shown in Scheme 2.

Scheme 2

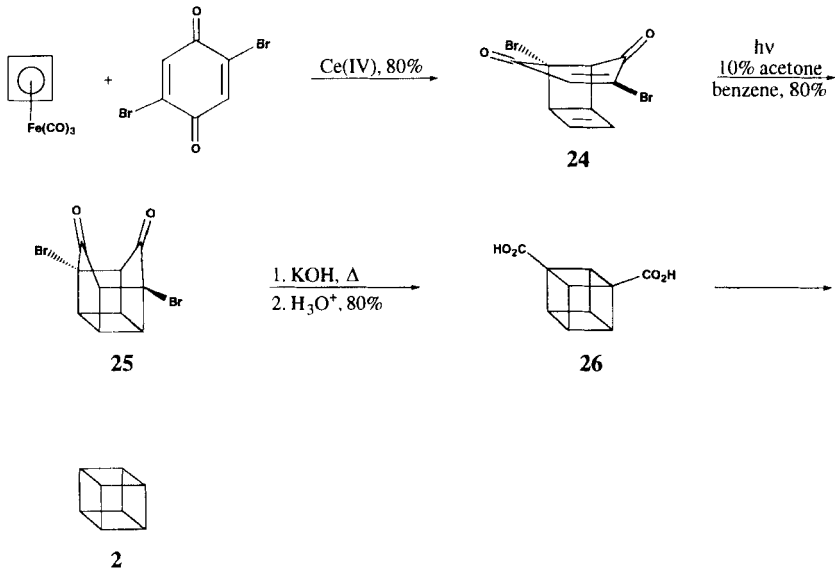


While the cubane synthesis is now a familiar one to organic chemists, a few comments are merited. First, the key step in the cubane synthesis is a double Favorskii ring contraction of dibromo

diketone **22**. While the Favorskii reaction was well known prior to the cubane synthesis, Eaton's utilization of this reaction propelled it into widespread use in the synthesis of strained ring compounds. Today, a variety of strained polycycles have been prepared utilizing this reaction. Second, the product of the two-fold Favorskii ring contraction, cubane 1,4-dicarboxylic acid (**23**), has proven to be a versatile intermediate, and a variety of substituted cubane derivatives are now available due to this intermediate diacid (vide infra).

Shortly after the Eaton synthesis of cubane (**2**), Pettit reported an alternative cubane synthesis.[23] Oxidative decomposition of cyclobutadiene iron tricarbonyl in the presence of 2,5-dibromobenzoquinone afforded the endo Diels-Alder adduct (**24**) in 80% yield. Irradiation of a benzene solution of **24** produced dibromo-1,2-bishomocubanedione (**25**) in 80% yield. Heating the dibromodione in aqueous potassium hydroxide at 100°, followed by acidification, yielded 1,3-cubanedicarboxylic acid (**26**). Repeating Eaton's decarboxylation steps then yielded cubane (**2**) (Scheme 3).

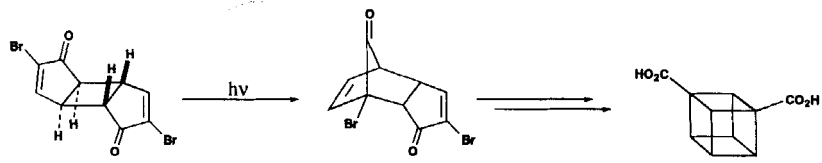
Scheme 3



An alternative approach to cubane-1,3-dicarboxylic acid, and thus a formal synthesis of **2**, has also been reported by Eaton and Cole.[24] This sequence is based on the photochemical rearrangement of *cis,anti,cis*-4,9-dibromotricyclo[5.3.0.$0^{2,6}$]deca-4,9-diene-3,8-dione (**27**) to dibromodiketone **28**. Note that **28** is a positional isomer of **21** which was utilized by Eaton in the original cubane synthesis. Conversion of **28** to cubane-1,3-dicarboxylic acid (**26**) was accomplished by employing the same series of steps as in the original synthesis (Scheme 4).

An additional formal synthesis of cubane was reported by Masamune and co-workers several years later.[25] In the Masamune synthesis, basketene is converted into cubanecarboxylic acid. The interested reader is referred to this work.

Scheme 4

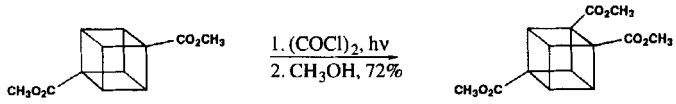


27 **28** **26**

A review of the physical properties and reactions of cubane is too voluminous to do justice to here. Moreover, several excellent reviews have recently appeared.[26] It is suffice to say that much of the renaissance in cubane chemistry can be traced to Eaton's observation that the cubane skeleton may be directly metalated.[27] As a result of this work, which is now well established and documented, a wide variety of substituted cubanes are now available. The potential applications of these substituted cubanes range from high energy explosives and propellants to building blocks for rational drug design.

Recently, new methodology for the functionalization of the cubane skeleton has been developed. Hashemi has shown that the cubane skeleton may be directly carboxylated through irradiation in oxalyl chloride.[28] For example, sun lamp irradiation of 1,4-cubane dicarboxylic acid dimethylester (**29**) and oxalyl chloride for 6 hours produced 1,2,4-cubane tricarboxylic acid trimethylester (**30**) in 72% yield (Scheme 5). Extension of the irradiation time led to tetra- and pentacarboxylated cubanes. Hashemi noted that this method is complementary to the metalation sequence of Eaton because carboxylation takes place at more remote sites on the cubane skeleton. Moreover, this simple procedure affords carboxylated cubanes directly whereas Eaton's metalation requires multiple synthetic steps.

Scheme 5



29 **30**

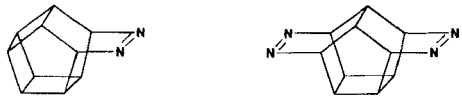
III. [5]-PRISMANE

Pentaprismane (**3**) was the third member of the [n]-prismane family to succumb to total synthesis, having first been prepared in Eaton's laboratories in 1981.[3] It has also proven to be much more difficult to prepare than either cubane (**2**) or prismane (**1**). In fact, aside from the Eaton synthesis, and later a formal synthesis by Dauben,[29] no other pentaprismane syntheses have been reported despite the intense synthetic effort directed toward this endeavor in the middle 1970's.

Most of the effort toward the construction of this ring system relied on methodology that had been successful in the synthesis of other polycyclic cage compounds. For example, the extrusion of nitrogen from appropriate azo compounds has proven to be a very valuable method for making polycyclic hydrocarbons.[30] In fact, as we have seen, prismane (**1**) was prepared, albeit in low yield, *via* this denitrogenation method (Scheme 1). Shen[31] and Allred and Beck[32] independently prepared **31**

and **32**, ostensibly appropriate azo precursors to pentaprismane (**3**), but could not generate **3** through photolysis or thermolysis.

Figure 5

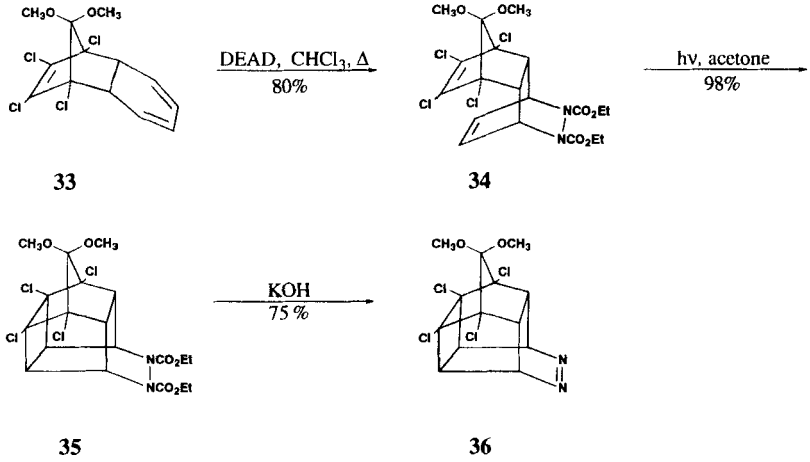


31 **32**

As noted previously, six-membered ring azoalkanes, particularly those residing in a bicyclo[2.2.2] framework, lose nitrogen with a low quantum yield (Φ_r), and more forcing conditions, if successful, often result in substantial fragmentation. Such was the case for azo compounds **31** and **32**. In recent years, there have been many other examples of these six-membered ring azo alkanes that failed to denitrogenate, and Engel and Turro performed experiments to uncover the origin of this effect.[9] They found that [2.2.2]bicycloazoalkanes have very high fluorescence quantum yields, which directly diminishes the quantum yield of decomposition. To circumvent this problem, Engel reported that Φ_r can be enhanced by raising the temperature of photolysis, conducting the photolysis in the gas-phase or modifying the azo structures to make them more thermally labile. As we have seen, Katz performed the successful denitrogenation of **16** to yield prismane at high temperature.

More recently, the chlorinated azo compound **36** has been prepared independently by Chou[33] and Forman.[34] The syntheses are very similar and both emanate from diene **33**. We had previously prepared **33** in conjunction with our synthetic efforts toward **4** and **5** (vide infra). The Diels-Alder addition of ethylazodicarboxylate to **33** followed by intramolecular [2+2]photocycloaddition afforded **35** in 78% yield. One pot hydrolysis and oxidation afforded azo alkane **36**. However, in our hands as well as Chou's, **36** proved to be resistant to denitrogenation (Scheme 6).

Scheme 6

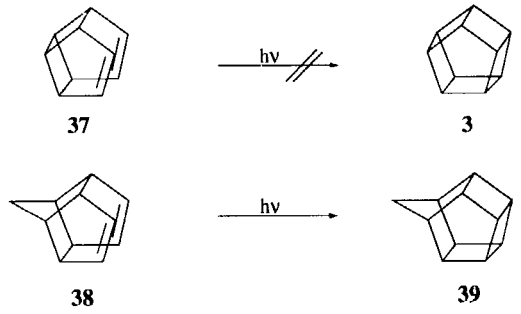


33 **34**

35 **36**

Hypostrophene (**37**) was thought to be an ideal photochemical precursor to pentaprismane (**3**), particularly in light of the successful photoclosure of homohypostrophene (**38**) to homopentaprismane (**39**).[35] Given this precedent, three research groups[36] independently prepared **37** but were unable to effect intramolecular [2+2]photocycloaddition to pentaprismane (**3**) (Scheme 7).

Scheme 7



37 **3**

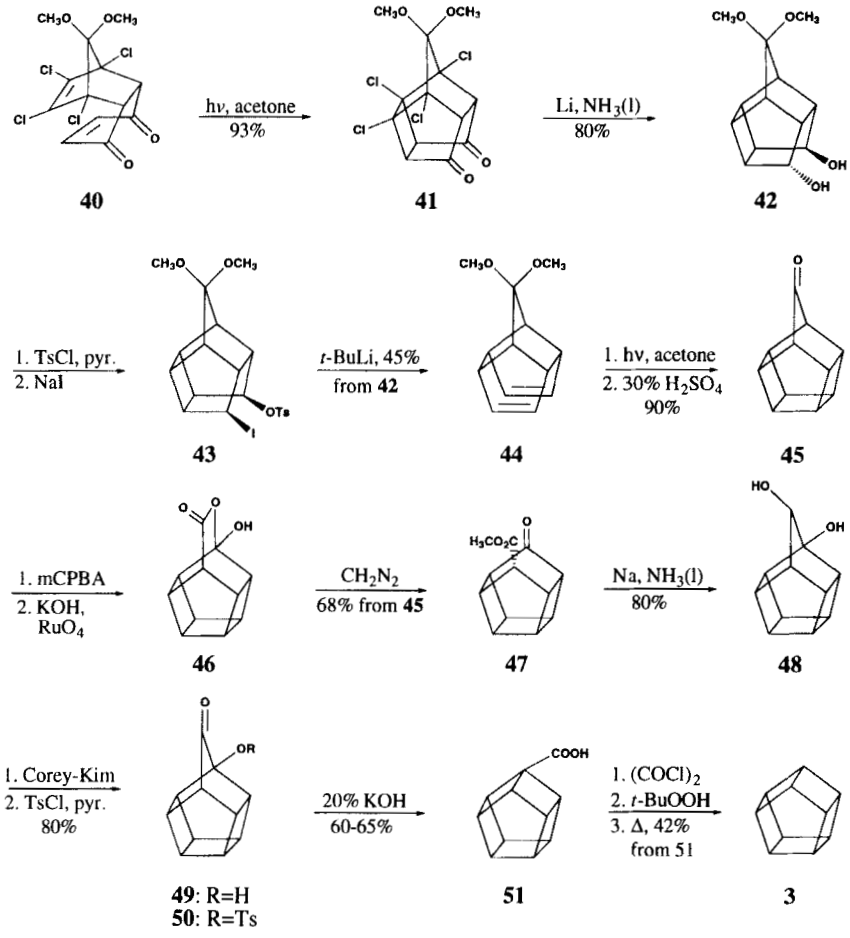
38 **39**

The failure of hypostrophene (**37**) to undergo intramolecular [2+2]photocycloaddition to pentaprismane (**3**) has been rationalized in two ways. Schmidt and Wilkins have proposed that extensive through-bond coupling of the two π orbitals with an exceptionally high lying σ level overrides the through-space interaction. This inverts the level ordering and converts a symmetry allowed $2_\pi+2_\pi$ reaction into a symmetry forbidden one.[37] Alternatively, Osawa asserts that intramolecular $[2_\pi+2_\pi]$ photoclosures are influenced by three factors: r (the midpoint distance between double bonds), θ (the dihedral angle between the two planes containing the four unsaturated carbon atoms), and ΔSE (the difference in strain energy between the starting diene and product). Using empirical force field calculations, Osawa was able to estimate these values and provide rationalizations for many successful and unsuccessful [2+2]photocycloadditions.[38] In the attempted closure of hypostrophene (**37**), both r and θ fall within the acceptable ranges for photoclosure. However, the predicted ΔSE of 110.87 kcal/mol far exceeds the threshold value of 70 kcal/mol put forth by Osawa. In the case of homohypostrophene (**38**), the ΔSE is 70 kcal/mol, still very high, but apparently close enough for successful closure.

Prompted by the observation that the homopentaprismane system can be prepared by direct photoclosure whereas pentaprismane cannot, Eaton developed the idea of contracting a homopentaprismane into a pentaprismane.[3] The successful realization of this approach occurred in 1981 with the first total synthesis of pentaprismane (**3**). Eaton began the synthesis with the readily available Diels-Alder adduct **40** of *p*-benzoquinone and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene.[39] Irradiation in acetone followed by dissolving metal reduction with sodium in ammonia yielded the dechlorinated diol **42**. Conversion of the hydroxyl groups to tosylates and reaction with sodium iodide furnished iodotosylate **43**. Grob-type fragmentation with *t*-butyllithium produced dimethoxyhomohypostrophene (**44**). Irradiation of acetone solutions of **44** followed by acid hydrolysis produced homopentaprismanone (**45**) in 30% overall yield from **41** (Scheme 8). Homopentaprismanone (**45**)

had previously been prepared by Pettit *via* a different route;[40] however, despite the novelty of the Pettit approach, ample quantities of **45** could not be obtained to complete the synthesis.

Scheme 8

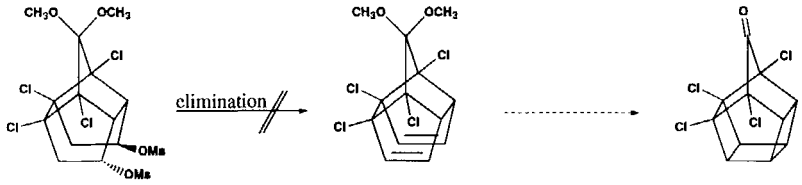


To contract homopentaprismanone (**45**) to a pentaprismane system, Eaton again chose the reliable Favorskii ring contraction which was utilized with success in the cubane synthesis. However, Favorskii ring contraction required introduction of a leaving group at the bridgehead position of **45**, a rather formidable task. Baeyer-Villager oxidation of **45** followed by further oxidation with ruthenate ion generated **46** which gave keto-ester **47** on treatment with diazomethane. Adding dilute ether solutions of **47** to sodium in ammonia facilitated intramolecular acyloin coupling to give diol **48** in 83% yield. Careful oxidation of **48** *via* the Corey-Kim protocol furnished ketone **49** in 77-85% yield. Recently it has been shown that this tricky oxidation may be effected in quantitative yield using methyl(trifluoromethyl)dioxirane.[41] Conversion of **49** to **50** was accomplished by treatment with tosyl

chloride in pyridine. Heating **50** in 20% aqueous KOH furnished the ring-contracted pentaprismane carboxylic acid **51**. Decarboxylation then afforded the parent hydrocarbon, pentaprismane (**3**).

Functionalization of the bridgehead of **45** required 5 steps and was accomplished in 44% overall yield. The advantages of preparing **45** with appropriate functionality intact at the bridgehead are obvious. Toward this end, Singh and co-workers recently reported the synthesis of dimesylate **52**.[42] It was envisioned that elimination of the mesylate groups would furnish **53**, a homohypostrophene derivative. Intramolecular [2+2]photocycloaddition would then furnish **54**. However, treatment of **52** with aluminum oxide or potassium-*t*-butoxide did not give the desired diene **53**. Moreover, **52** proved inert to substitution with sodium iodide, a result consistent with previous attempts at substitution on this type of chlorinated ring system (Scheme 9).[3b]

Scheme 9

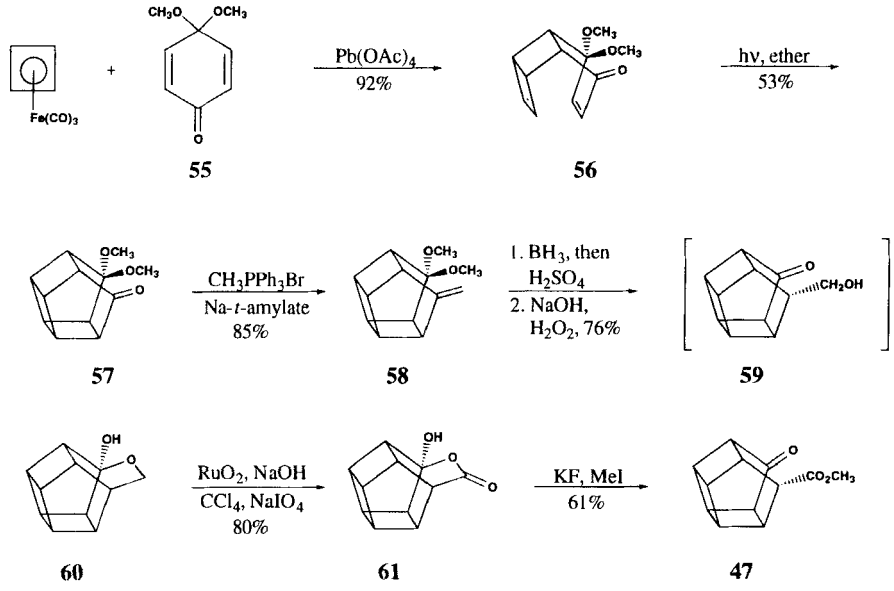


52 **53** **54**

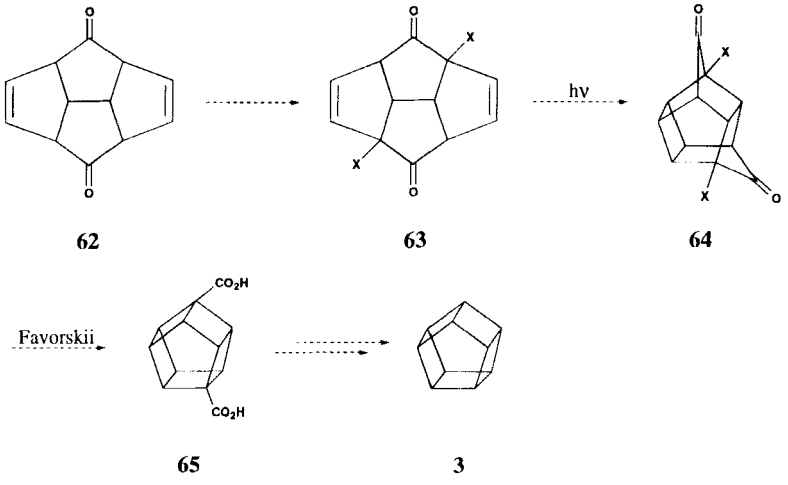
An alternative method for the preparation of keto-ester **47** and thus a formal synthesis of pentaprismane (**3**) was reported by Dauben and Cunningham in 1983.[29] Diels-Alder reaction of cyclobutadiene with 4,4-dimethoxycyclohexa-2,5-dien-1-one (**55**) furnished adduct **56**, which was subsequently irradiated in ether to yield **57**. Wittig methylenation followed by hydroboration gave hemiketal **60**. Oxidation of **60** followed by treatment with KF and methyl iodide yielded keto-ester **47**, a common intermediate in the Eaton synthesis (Scheme 10).

To date, the Eaton and Dauben methods remain the only routes to pentaprismane (**3**). The lack of physical and reactivity studies on pentaprismane (**3**) is indicative of the difficulty in the preparation of this hydrocarbon. Clearly, alternative synthetic approaches capable of producing larger quantities of **3** are desirable.

Scheme 10



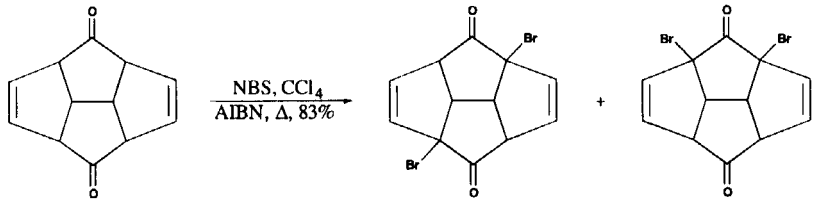
Scheme 11



In view of the successful application of Favorskii ring contractions in the synthesis of strained polycycles (including other members of the [n]-prismane family), we considered the two-fold Favorskii ring-contraction of a bishomopentaprismanone as an attractive approach to pentaprismane (**3**). Diene **62**, prepared independently by Prinzbach,[43] Mehta,[44] and Paquette,[45] was utilized as a precursor to a substituted bishomopentaprismanone. We surmised that functionalization of **62**, followed by [2+2]photocycloaddition, should yield an appropriately functionalized bishomopentaprismanone **64** ripe for Favorskii ring-contraction. The resulting pentaprismane dicarboxylic acid (**65**), also an unknown compound, could then be decarboxylated to pentaprismane (**3**) (Scheme 11).

Thus, refluxing **62** with 2.1 equivalents of NBS and AIBN as an initiator furnished a 2:1 mixture of isomeric dibromides **66** and **67**.[34] Separation of the isomers followed by sensitized irradiation of **66** furnished only decomposed material, a result which was not surprising considering the proximity of the bromines to the ketones and double bonds (Scheme 12).

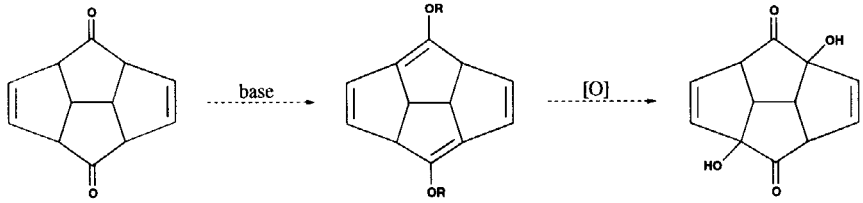
Scheme 12



62 **66** **67**

Given Eaton's success in preparing pentaprismane (**3**) from the homopentaprismanone tosylate, we next attempted to introduce oxygens alpha to the ketones of **62**. However, preliminary attempts at oxygenating enolate **68** with Davis' oxaziridine have been unsuccessful. Moreover, attempts at preparing silyl enol ether **69** have to this point been unsuccessful (Scheme 13).[34] Our work in this area continues.

Scheme 13



62 **68**: R=Li, K, Na **70**
69: R=TMS

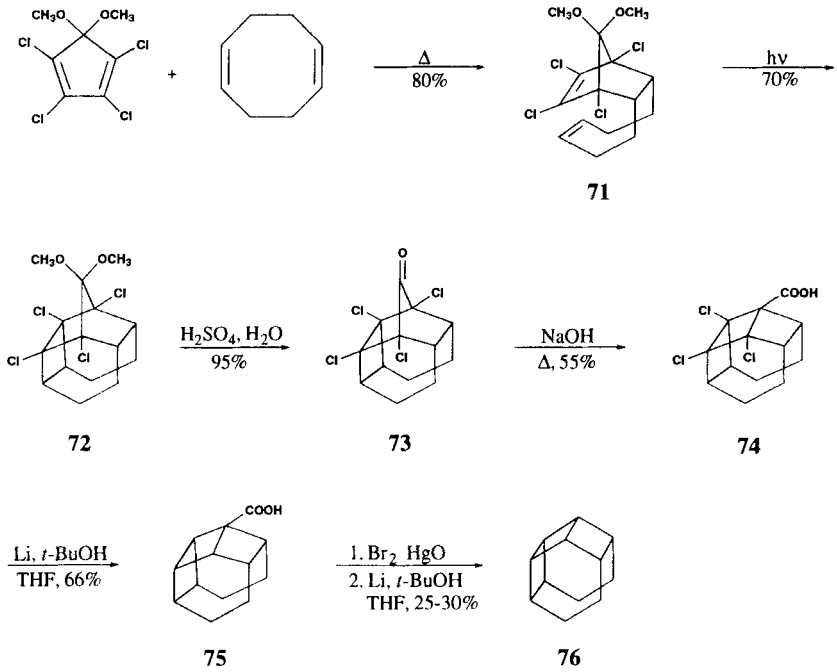
IV. TOWARD [6]-PRISMANE

The successful preparation of prismane (**1**), cubane (**2**), and pentaprismane (**3**) has shifted the focus to the next higher homolog, hexaprismane (**4**). Formally, the face-to-face dimer of benzene, hexaprismane (**4**) has attracted widespread interest and numerous synthetic strategies have been advanced. Despite this, hexaprismane (**4**) remains unconquered. In this section we will discuss those approaches, including our own, which have made the furthest headway toward the synthesis of this elusive hydrocarbon. Other groups have recently reported attempts at synthesizing **4** and hexaprismane analogs. For these approaches, the interested reader is referred to the literature.[46,47,48,49]

Eaton was the first to report significant progress toward the synthesis of hexaprismane (**4**) as the synthesis of bis-seco-[6]-prismane (**76**) was accomplished in 1978.[50] Diels-Alder reaction of 5,5-

dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with 1,5-cyclooctadiene afforded **71** which gave the cage isomer **72** upon irradiation in dilute acetone. Acid catalyzed hydrolysis to ketone **73** followed by Favorskii ring-contraction in sodium hydroxide/toluene gave carboxylic acid **74** after acidification. Dechlorination and decarboxylation then afforded bis-seco-[6]-prismane (**76**) (Scheme 14).

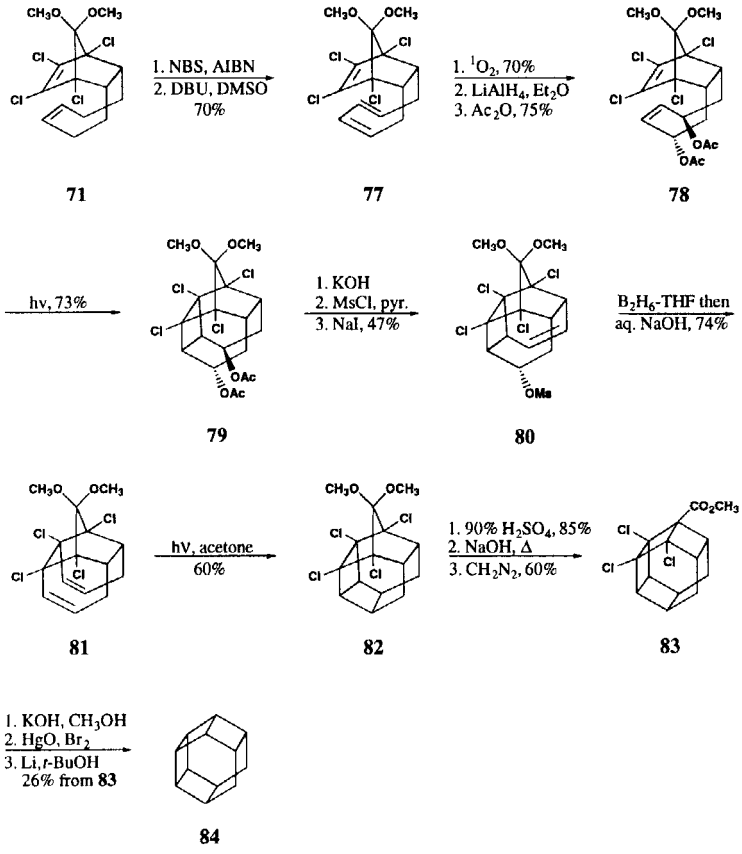
Scheme 14



Although Eaton noted that modification of the sequence shown in Scheme 14 should lead to hexaprismane (**4**), subsequent alterations of this sequence did not originate from his group. Instead, Mehta and Padma exploited the Eaton strategy and developed a synthesis of secohexaprismane (**84**), the closest one-bond-away secolog of **4** (Scheme 15).[51]

Bromination of **71** followed by dehydrobromination furnished the diene **77** which gave the exo endoperoxide upon reaction with singlet oxygen. Lithium aluminum hydride reduction of the endoperoxide followed by acetylation of the resultant diol gave **78**. Acetophenone sensitized irradiation of **78** in benzene produced the caged diacetate **79** in 73% yield. Careful functional group manipulations afforded the olefinic monomesylate **80** which underwent fragmentation to diene **81** upon treatment with diborane followed by aqueous sodium hydroxide. Irradiation of **81** in dilute acetone then afforded photoadduct **82** in 42% yield from **80**. Favorskii ring contraction and dehalogenation yielded secohexaprismane (**84**).

Scheme 15



71 **77** **78**

79 **80**

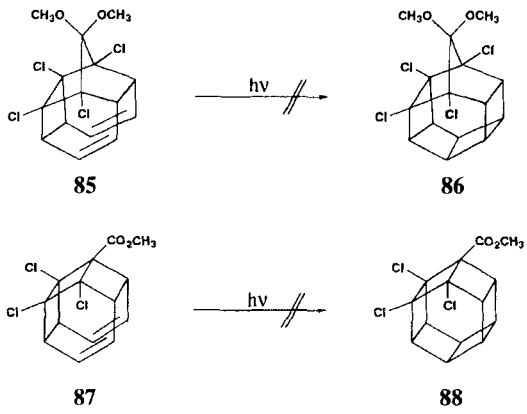
81 **82** **83**

84

Through modifications of the synthetic sequence shown in Scheme 15, Mehta and Padma also prepared dienes **85** and **87**, seemingly ideal precursors to **4**. However, the requisite intramolecular [2+2] photocycloadditions were unsuccessful, a result Mehta has attributed to a strain energy increase above the previously established threshold value of 55 kcal/mol obtained using the MM2 forcefield[52] (Scheme 16).

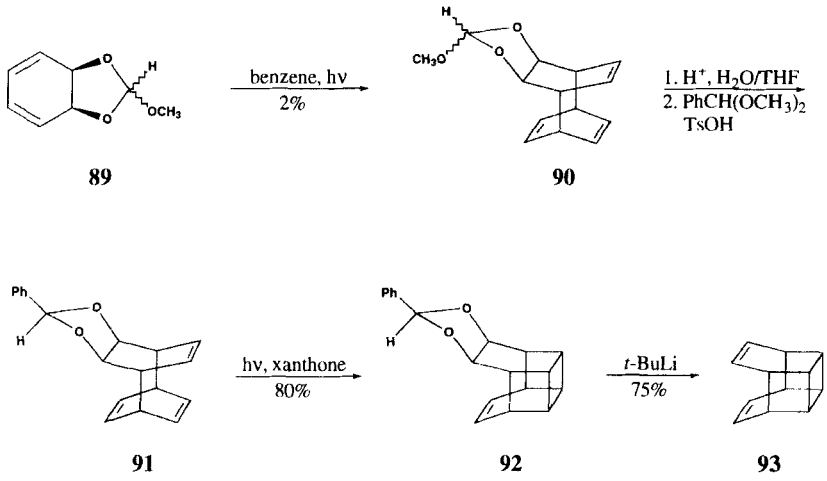
Diene **93**, the parent hydrocarbon of **87**, has also been prepared independently by Yang and co-workers[53] (Scheme 17). In their approach, irradiation of a benzene solution of cyclohexadiene **89** produced the desired [4+4] adduct **90**, albeit in only 2% yield. Hydrolysis to the diol followed by reprotection furnished acetal **91**. Xanthone sensitized irradiation of acetal **91** produced the cage isomer **92** in 90% yield. Finally, treatment of the cage acetal **92** with *t*-butyl lithium produced diene **93** in 75% yield. Although Yang has not reported results of the intramolecular [2+2]photocycloaddition of **93**, it is presumed that, as was the case for **87**, this photocycloaddition failed.

Scheme 16



85 **86** **87** **88**

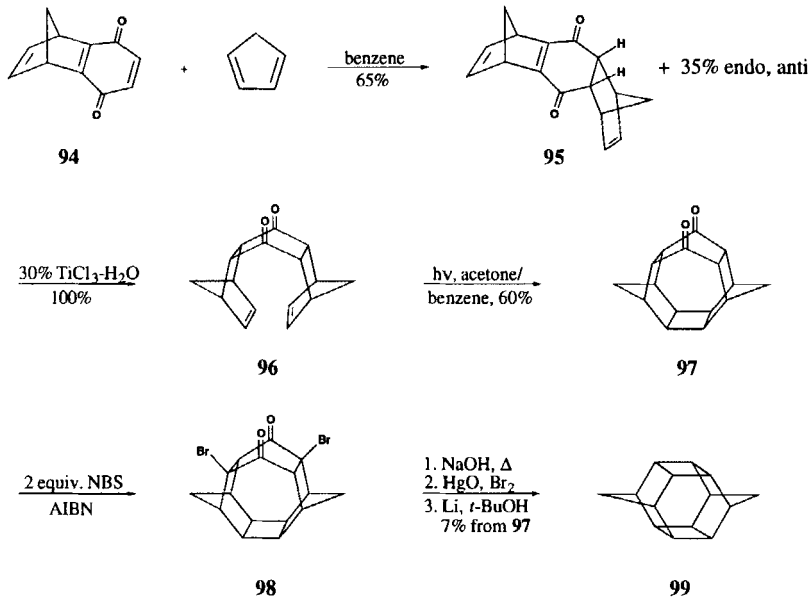
Scheme 17



89 **90** **91** **92** **93**

Shortly after reporting the preparation of **84**, Mehta revealed the synthesis of 1,4-bishomohexaprismane (**99**), formally the face-to-face dimer of norbornadiene.[54] Reaction of the previously prepared quinone **94** with cyclopentadiene furnished a 65% yield of the endo,syn adduct **95** and 35% of the undesired endo,anti adduct. Despite the modest selectivity, the isomers were separated by column chromatagraphy and the enedione moiety of **95** reduced with $TiCl_3$-H_2O to give the endo,syn,endo adduct **96** in 100% yield. Acetone sensitized irradiation of **96** produced 1,4-bishomo-6-seco-[7]-prismane **97** in 60% yield. Conversion of dione **97** to **99** required two ring-contractions and again the Favorskii ring-contraction was employed. Radical α-bromination of **97** with NBS followed by Favorskii reaction and decarboxylation furnished 1,4-bishomohexaprismane (**99**) in 7% yield from **97** (Scheme 18).

Scheme 18



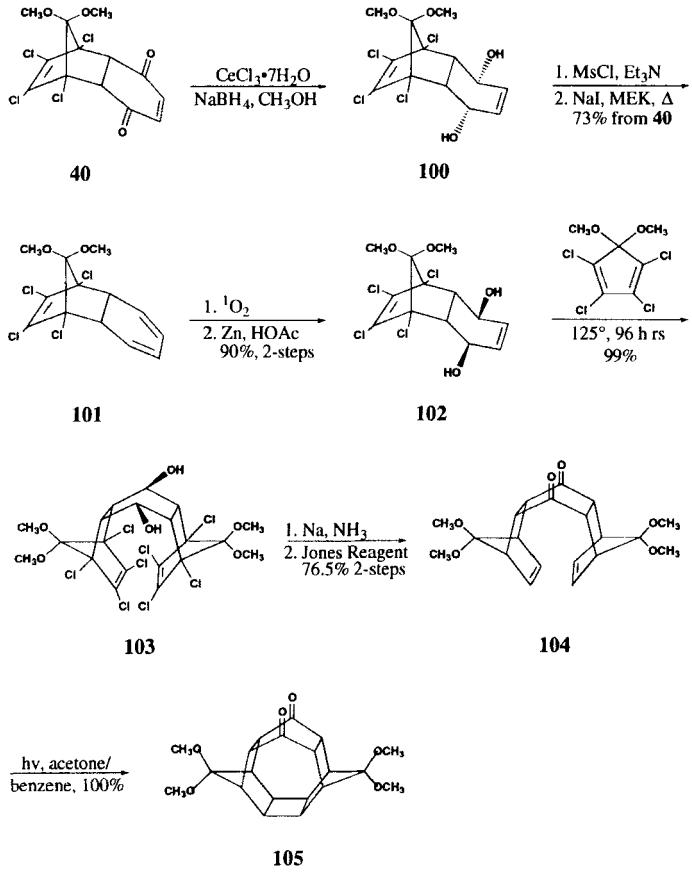
Concurrent with Mehta's synthesis of **97**, and ultimately **99**, we had been independently working on a synthesis of a 1,4-bishomo-6-seco-[7]-prismane ring system of our own, the results of which have recently appeared in print (Scheme 19).[55] We began our synthesis with the readily available Diels-Alder adduct **40** of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and p-benzoquinone. Cerium-mediated borohydride reduction of **40**, as described by Marchand,[56] furnished the endo,endo diol **100**. Conversion of **100** to the diene **101** was accomplished *via* a modification of the literature method of Chou and co-workers.[33] Addition of singlet oxygen to **101** followed by immediate endoperoxide cleavage furnished the desired exo,exo diol **102** in 90% yield from diene **101**. Diels-Alder reaction of **102** with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene cleanly afforded only the endo,syn,endo adduct **103** in 99% yield. Dechlorination of **103** followed by Jones oxidation yielded diketone **104** which cleanly underwent intramolecular [2+2]photocycloaddition to **105** in quantitative yield.

The synthesis of **105** *via* the route shown in Scheme 19 offers several advantages over the Mehta synthesis of **97**. First, the 1,4-methano bridges of **105** possesses ketal groups whereas the methano bridges of **97** are devoid of such functionality. Mehta and Padma have been unable to extend their methodology to **105** or similarly functionalized derivatives.[54b] Second, the synthesis of **105** may be accomplished in 45% overall yield starting with the abundantly available Diels-Alder adduct **40**. Thus, ten gram lots of **105** are available in about two weeks in an extremely efficacious manner.[34]

For ring-contraction of **105** to a bishomo-[6]-prismane ring system, we had also hoped to rely on the Favorskii ring-contraction. However, despite using conditions similar to those reported by Mehta, we were unable to effect the required α-brominations. We reasoned that this was due to the proximity of the methano ketals and that acid catalyzed deketalization would alleviate this problem.

However, despite utilizing a wide range of reaction conditions, we were unable to carry out this deprotection.[34]

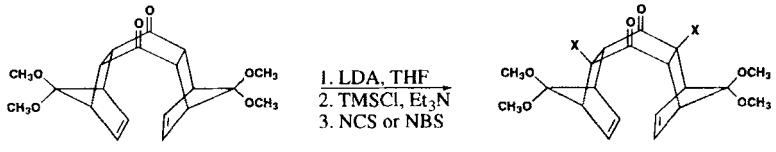
Scheme 19



40 **100** **101** **102** **103** **104** **105**

A potential solution to the α-keto bridgehead functionalization problem of **105** lies with functionalization (of **104**) prior to intramolecular [2+2]photocycloaddition. Thus, adducts **106** and **107** were prepared *via* trapping the bis-enolate form of **104** with trimethylsilylchloride and treating the resultant silylenolether with either N-chlorosuccinimide or N-bromosuccinimide. Unfortunately, irradiation of **106** or **107** in 10% acetone/benzene gave only complex mixtures of products and in the case of **107** significant decomposition (Scheme 20).

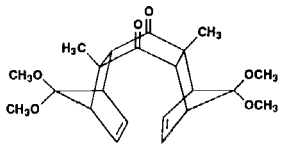
Scheme 20



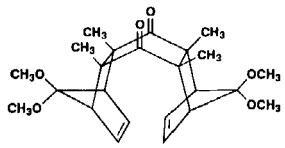
104 **106**: X=Cl **107**: X=Br

The surprising failure of these halogenated derivatives to undergo photoaddition prompted us to prepare the simple di- and tetramethylated derivatives **108** and **109**. Upon irradiation, however, these methylated derivatives gave only complex product mixtures which contained none of the desired photoadduct. The sensitivity of this photoaddition appears to preclude functionalization prior to photocycloaddition, and thus, new strategies must be developed. Our progress in this area continues.

Figure 6



108

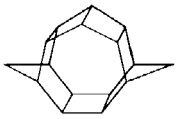


109

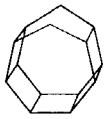
V. TOWARD [7]-PRISMANE

Like its lower homolog hexaprismane (**4**), heptaprismane (**5**) remains an unknown compound. Unlike **4**, however, there has been little synthetic attention paid to **5** or its various analogs. In fact, the literature is devoid of a direct synthetic assault on **5**. Instead, most of the synthetic effort has been directed toward the synthesis of various homologs and secologs of **5**, and once again the furthest inroads have been made by the Mehta group. In this section, we will summarize the recent progress in the synthesis of heptaprismane analogs such as 1,4-bishomo-[7]-prismane (**110**) and seco-[7]-prismane (**111**) (Figure 7).

Figure 7



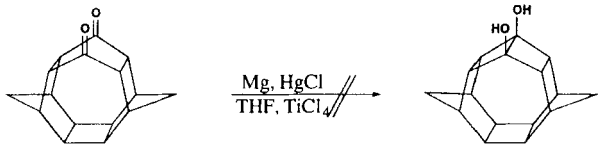
110



111

Pinacolic coupling of the carbonyls in **97** or **105** offers a potentially direct route to the 1,4-bishomo-[7]-prismane ring system. However, such coupling is not feasible due to the large strain energy increase accompanying this transformation as well as the unfavorable dihedral angle between the carbonyl groups as predicted by molecular mechanics.[57] Indeed, Mehta has reported unsuccessful attempts at coupling the carbonyls of **97** (Scheme 21).[4a,57]

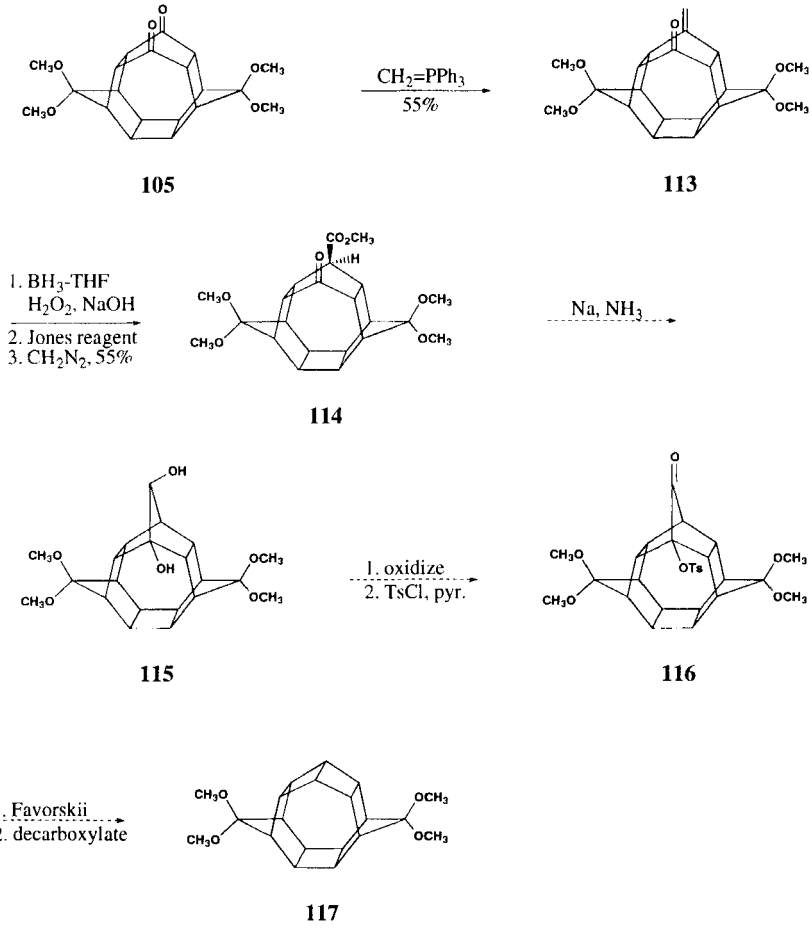
Scheme 21



97 **112**

Although direct carbonyl coupling methods have thus far been unsuccessful, the indirect methods described by Dauben[29] and Marchand[58] may prove to be more fruitful. Accordingly, we have prepared the keto-ester **114**, which is ideally suited for intramolecular acyloin reaction.[59] Attempts at acyloin coupling of **114** to **115**, the first compound with the 1,3,5-trishomo-[7-]prismane ring system, have thus far been met with failure (Scheme 22).

Scheme 22



105 **113**

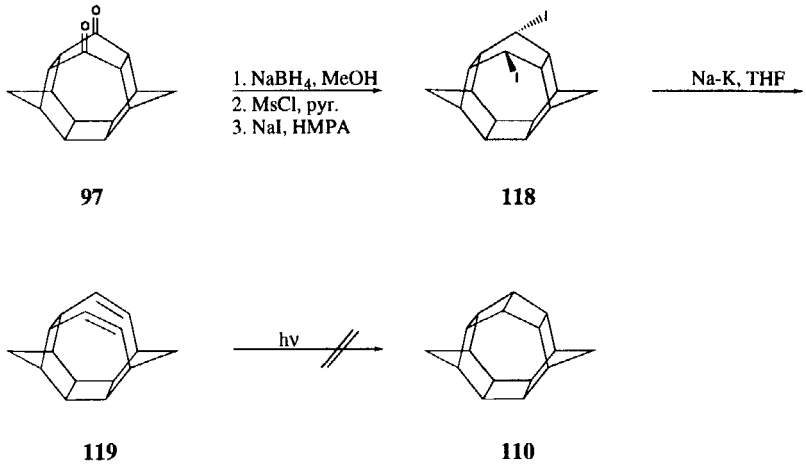
114

115 **116**

117

An alternative attempt to gain entry into the 1,4-bishomo-[7]-prismane ring system has been described by Mehta.[60] Dione **97** was converted into **119** *via* the four step sequence shown below. However, the intramolecular [2+2]photocycloaddition of **119** to 1,4-bishomo-[7]-prismane **110** was not successful, probably due to the large increase in strain energy.[60]

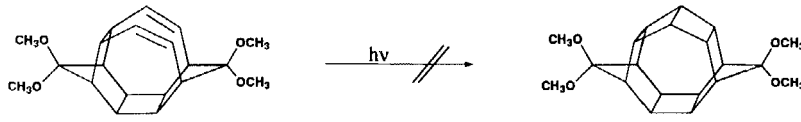
Scheme 23



97 **118** **119** **110**

Incidentally, we have prepared the analogous diene **120** *via* a similar synthetic sequence. Not surprisingly, **120** also resists closure upon sensitized irradiation[61] (Scheme 24).

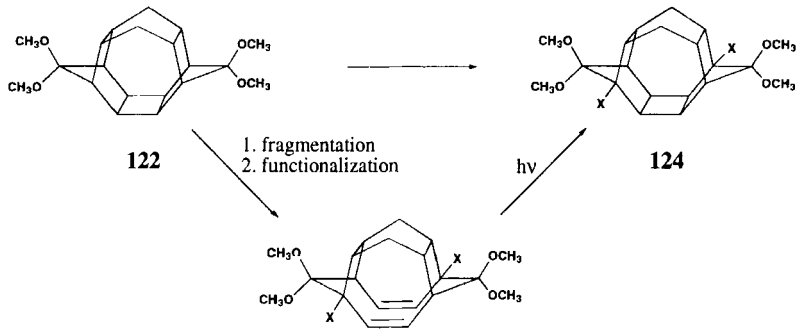
Scheme 24



120 **121**

Thus far, there have been no reported attempts at synthesizing seco-[7]-prismane (**111**), the closest one-bond-away homolog of **5**. The conversion of **97** or **105** to seco-[7]-prismane (**111**) requires ring-contraction of the two methano bridges. In the case of **105**, this is possible *via* Favorskii reaction if leaving groups can be introduced at the norbornane-type bridgehead positions, a rather formidable task. We envisioned introduction of leaving groups X *via* the route shown in Scheme 25. Thermal cyclobutane fragmentation followed by functionalization and reclosure offers an attractive method for this functionalization. Forman has demonstrated the successful photochemical closure of **126** (**123**: X=H) back to **122**,[34] and Mehta has shown the analogous closure works on a relative of **126**[60] which was devoid of the methyl ketal functionality.

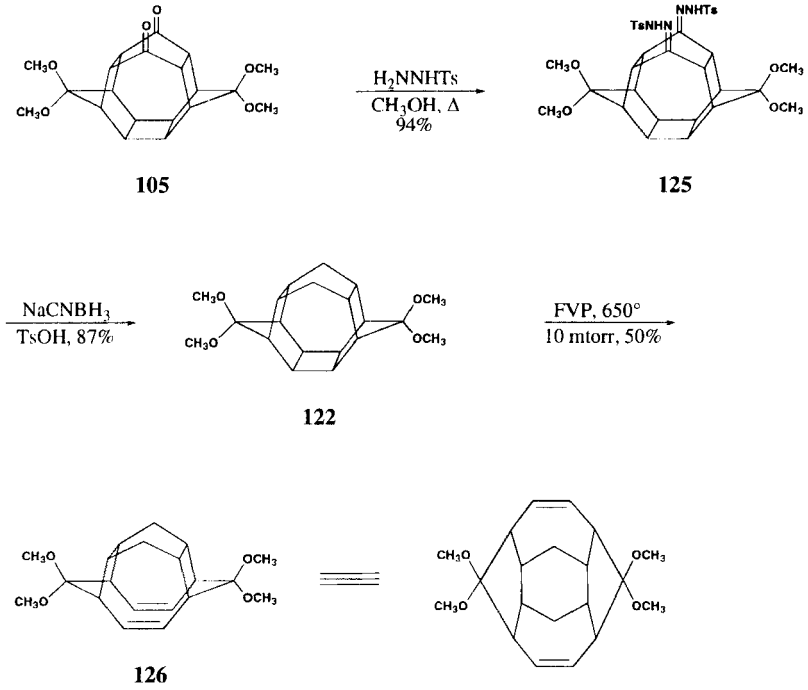
Scheme 25



122 **123** **124**

In practice, the ketone groups of **105** were reductively removed *via* sodium cyanoborohydride reduction of bistosylhydrazone **125** to yield **122**. Sublimation at 10 mtorr of **122** through a quartz tube at 650° furnished a 50% yield of diene **126** (Scheme 26).

Scheme 26

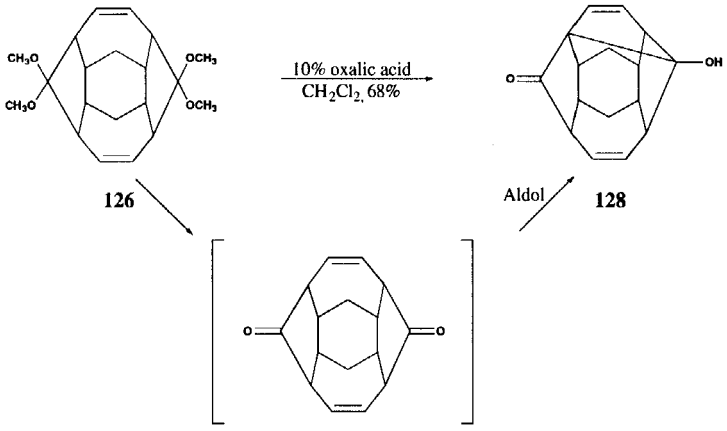


105 **125** **122** **126**

Initially, we attempted to introduce the bromine atoms (**123**: X=Br) *via* radical bromination with NBS. However, only decomposed material was recovered. Alternatively, allylic hydroxylation of **126** (**123**: X=OH) would also afford a precursor appropriately functionalized for eventual reclosure and Favorskii ring-contraction. To carry out the hydroxylation, we envisioned trapping the bis-enolate

form of diketone **127** with an appropriate oxygen electrophile. However, acid-catalyzed hydrolysis of **126** gave not diketone **127** but instead the intramolecular aldol adduct **128**, the identity of which was confirmed *via* single-crystal x-ray analysis. Attempts to reverse this process by treatment with base were not successful (Scheme 27).[34]

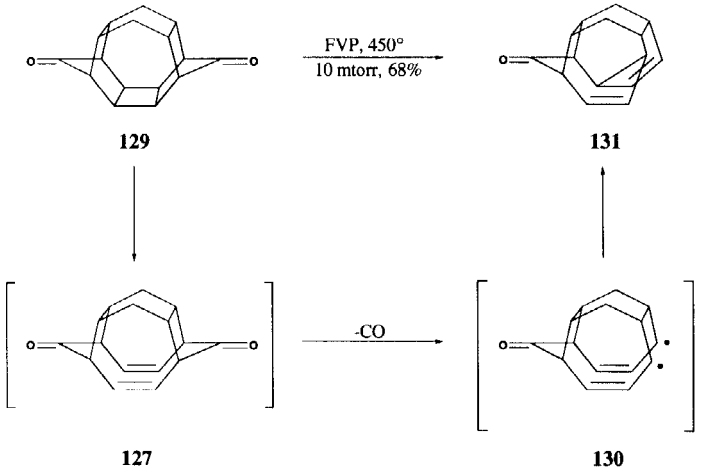
Scheme 27



127

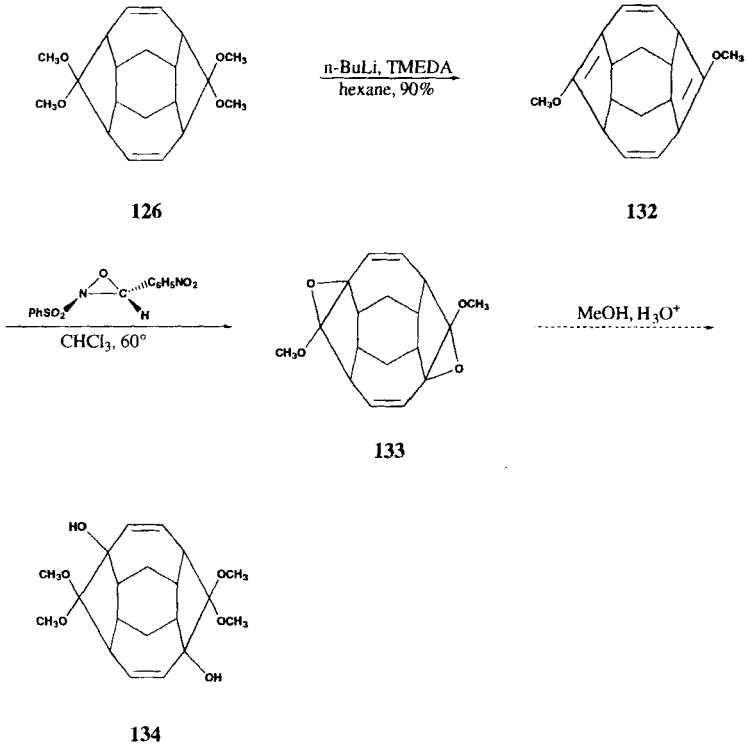
In order to circumvent the problems presented by the propensity of **127** to undergo acid-catalyzed aldol reaction, we decided to prepare **127** *via* flash vacuum thermolysis of diketone **129**. In this manner, **127** could be prepared without exposure to acid or even basic conditions. However, sublimation of **129** through a quartz tube heated to 450° did not furnish the desired diene diketone **127** but rather ketone **131**. Ketone **131** must emanate from loss of carbon monoxide and recombination of the putative diradical in a 1,3-sense (Scheme 28).

Scheme 28



As a final attempt at introducing oxygen at the bridgehead positions of **126**, we attempted to form the allyl anion and trap it with an appropriate electrophile. Accordingly, diene **126** was treated with *n*-butyl lithium-TMEDA complex in THF and, as a test of this approach, methyl iodide was added after several hours. We did not detect any of the methylated product; instead, we obtained the novel tetra-ene **132** which results from elimination of two moles of methoxide from diene **126**. Although not the expected product, we quickly realized that **132** is amenable to transformation to **134** (**123**: X=OH) as shown in Scheme 29. Thus, epoxidation of **132** with Davis' 2-benzenesulfonyl-3-(*p*-nitrophenyl) oxaziridine[62] in acid-free chloroform at 60° yielded bis-epoxide **133**, identified thus far solely by its ^{1}H NMR spectrum.[34] We are currently investigating the transformation of **133** to **134** and anticipate the conversion of **134** into secoheptaprismane (**111**).

Scheme 29



VI. HIGHER ORDER PRISMANES AND OUTLOOK

At the time of this review, there have been no reported direct attempts at the synthesis of the next higher prismane, [8]-prismane (**6**). Moreover, there has been only one reported attempt at an [8]-prismane analog, as dione **97** was resistant to ring expansion with diazo compounds. It is interesting to note, however, that [8]-prismane is the first member of the [n]-prismane family which lacks at least D_{nh} symmetry, for ab initio calculations by Disch and Schulman indicate that [8]-prismane has E_u symmetry.[63] In contrast, MM2 calculations of Jemmis suggest that [8]-prismane prefers a crown-like

D_{4d} structure.[64] These predictions await experimental verification. In any event, it now appears that [8]-prismane will, for the time being, remain a theoretical curiosity.

Progress toward the synthesis of the unknown [n]-prismanes (n>5) has been painstakingly slow. The fact that since the pentaprismane synthesis in 1981 no other higher order prismanes have been synthesized is a reflection upon the Herculean task that these molecules pose. Although the progress reported by Mehta and us has been significant, much remains to be done to accomplish the synthesis of hexaprismane (**4**) and heptaprismane (**5**). Although the future holds promise for the synthesis of these unknown higher order prismanes, clearly new synthetic strategies are desired and welcomed. Perhaps such new strategies will lead not only to the synthesis of unknown prismanes but also to new, more efficient syntheses of known synthetically inaccessible prismanes such as pentaprismane (**3**).

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