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THE SYNTHESIS OF PENTAPRISMANE†

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Abstract—The first synthesis of pentaprismane, hexacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]decane, is presented with full experimental details. A new and practical synthesis for homopentaprismanone is developed as is methodology for the functionalization of a bridgehead position α to the carbonyl group of this cage compound. The latter uses a mixed acyloin reductive coupling. Favorskii contraction of the bridgehead functionalized homopentaprismanone is employed to enter the pentaprismane ring system. A brief discussion is given of the geometry of pentaprismane, of its behavior relative to cubane, and of the future of prismane chemistry.

Pentaprismane (1) is the hexacyclic, saturated hydrocarbon $(CH)_{10}$ in which the methine units are disposed equally at the corners of a regular pentagonal prism. The compound is a member of the prismane family, an infinite class of organic compounds with empirical formula $(CH)_n$. All prismanes consist of two identical $n/2$-membered rings held together by $n/2$ C—C bonds between them. This arrangement leads necessarily to $n/2$ 4-membered rings. The first member of the series is triprismane, also known as prismane or Landenburg's benzene. It is a known, stable molecule, but it has been little studied.[1] Substituted triprismanes have been implicated numerously in the photoisomerizations of various benzenes.[2] The next higher "prismalogue" is tetraprismane, alias cubane, first made in this laboratory in 1964.[3,4] It has been studied extensively.[5] The first synthesis of pentaprismane, the next prismane in the set, was accomplished here in 1981 and is the subject of this paper.[6]

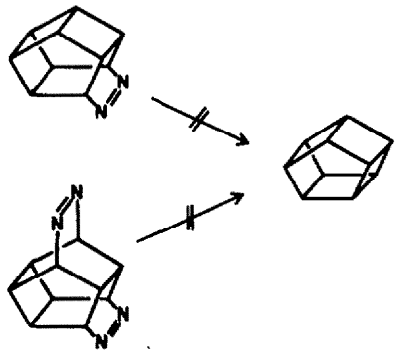
1

Molecular mechanics calculations predict D_{5h} symmetry for pentaprismane in the lowest energy arrangement.[7] There is little opportunity for conformational flexibility within this rigid prismatic skeleton. Each face is planar, and the hydrogens on each are coplanar and completely eclipsed by their immediate neighbors. Pentaprismane is significantly strained Empirical force field calculations (MM2) give a strain energy of about 140 kcal mol^{-1}, about 25 kcal mol^{-1} less than that of cubane, but still very strained. Like its lower relatives, pentaprismane is expected to be isolable, there being no "allowed" pathways to its destruction.

Early approaches

Pentaprismane has resisted numerous rational synthetic efforts both here and elsewhere. It is worthwhile considering these briefly.

The extrusion of dinitrogen from cyclic azo compounds has often proven to be a valuable method for making unusual small rings and polycyclic structures. Indeed, the synthesis by Katz and Acton of triprismane depends on just such a reaction.[1] However, the method is not particularly reliable. Shen[8a] and Allred and Beck[8b] independently tried to take seemingly appropriate azo precursors to pentaprismane (Eq. 1), but were without success.[9]



(1)

One of the obviously attractive approaches to pentaprismane is analogous to the photoclosure of homohypostrophene 2 to homopentaprismane 3 (Eq. 2).[10] However, even under the onslaught of three separate research groups,[11] each of which had prepared it independently, hypostrophene 4 unrelentingly resisted photoclosure (Eq. 3). The fact that hypostrophene cannot be closed photochemically to

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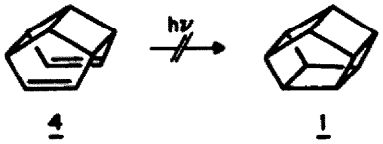


4 1 (3)

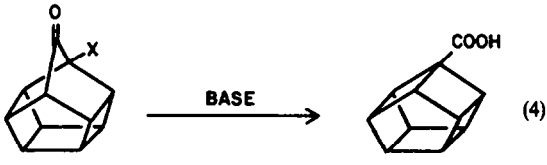
pentaprismane has been rationalized by Schmidt and Wilkins in terms of extensive through-bond coupling between a high lying σ level and the π-orbitals,

† Taken in part from the Ph.D. thesis of Yat Sun Or, University of Chicago (1981).

overriding the direct through-space interaction of the systems, inverting the level ordering, and converting the usually allowed $\pi_{2s}+\pi_{2s}$ photocyclization into a symmetry-forbidden reaction.[12] Osawa *et al.* offered another explanation, proposing that the (calculated) strain increase of about 78 kcal mol^{-1} that would accompany the formation of pentaprismane from hypostrophene is too large to be accommodated by the energetics of the photoclosure.[13] Another possibility is that novel (and perhaps degenerate) photorearrangements, or -cleavages are available to the *cis*-divinylcyclobutane subsystem in hypostrophene but not to the other divinyl systems to which it has been compared. The matter merits further investigation. To the best of our knowledge there is no well-documented example of a successful photoclosure of a *cis*-divinylcyclobutane hydrocarbon.[14]

Idea: contract homopentaprismane

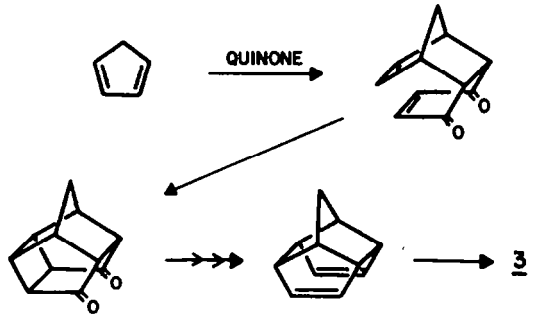
Given that the homopentaprismane system can be synthesized by direct photoclosure, but pentaprismane cannot, we developed the idea of contracting a homopentaprismane into a pentaprismane. Given previous experience,[3a,15] we decided to use the Favorskii contraction.[16] The synthetic problem then reduces to the preparation of a homopentaprismanone with a halide α to the carbonyl group, in the expectation of the contraction shown in Eq. (4).



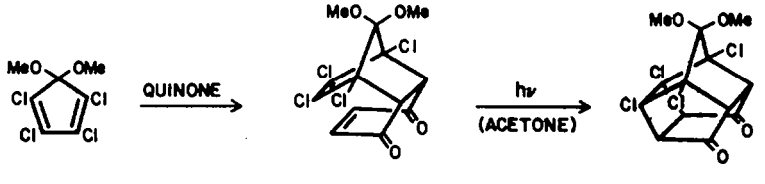
(4)

If one examines the various synthetic routes to homopentaprismane (Scheme 1) they all can be seen to trace back to the Diels–Alder adduct of cyclopentadiene to *p*-benzoquinone.[10] The methylene group of cyclopentadiene becomes the methylene group in homopentaprismane. On paper, it seems then the synthesis of an α-halohomopentaprismanone might be done by substituting an α-halocyclopentadienone for cyclopentadiene in the first step. However, cyclopentadienones and halocyclopentadienones dimerize with notorious ease, even at low temperature, and cannot otherwise be trapped effectively. We showed some years ago that this problem can be ameliorated by using cyclopentadienone ketals rather than the free ketones.[17] Certain of these can be trapped usefully with reactive dienophiles. We were even able to extend this chemistry to the preparation of the Diels–Alder adduct of the dimethyl ketal of 2-bromocyclopentadienone to quinone, a compound perfect for the plan at hand. However, as it turned out, the preparation of the necessary intermediate, 1,1-dimethoxy-2,2,5-tribromocyclopentane, was not amenable to scale-up, nor was it particularly reproducible.[18] The project had a brief rebirth when Chapman *et al.* discovered that the bromine–dioxane complex reacted readily with the ethylene ketal of cyclopentanone to produce the corresponding 2,2,5-tribromo material which could be dehydrobrominated to α-bromocyclopentadienone ethylene ketal.[4c] Unfortunately (but usefully in other contexts), this ketal dimerizes before it can be trapped. Our attempts to extend this bromination methodology to the dimethyl or diethyl ketals were not successful.

We had to go further afield to find the proper masked α-halocyclopentadienone. 1,1-Dimethoxy-2,3,4,5-tetrachlorocyclopentadiene (**5**) is easily made stable toward dimerization, but yet quite reactive toward dienophiles such as quinone.[19] Although use of this diene would carry into the projected sequence more halogen substituents than the one necessary for the Favorskii closure, these can be removed reductively after the contraction as we did, for example, in our synthesis of octahydro[2,2]paracyclophane.[15d] Thus we thought the tetracyclic diketone **6**, readily available in mole amounts in two steps (Eq. 5) from



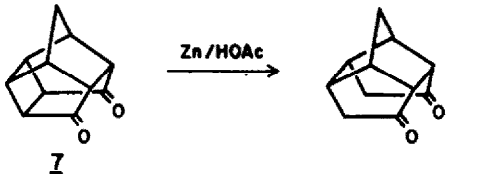
Scheme 1.



5 **6**

(5)

5,[20] would be a useful α-halohomopentaprismanone precursor. As it turned out, the four chlorine substituents so altered the reactivity of the ring system that much of what had been learned earlier about the chemistry of homopentaprismane precursors was no longer applicable. For example, whereas treatment of ketone 7 with zinc/acetic acid gives cleanly reductive cleavage of the cyclobutane bond adjacent to the two carbonyl groups (Eq. 6),[21] identical treatment of the tetrachloro analogue 6 goes entirely differently (Eq. 7).



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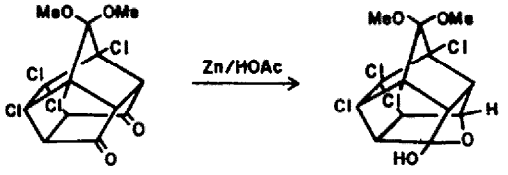

(7)

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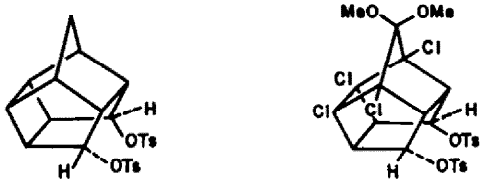
Another example is the quite different behavior of the ditosylates 8 and 9 towards sodium iodide in



8 9

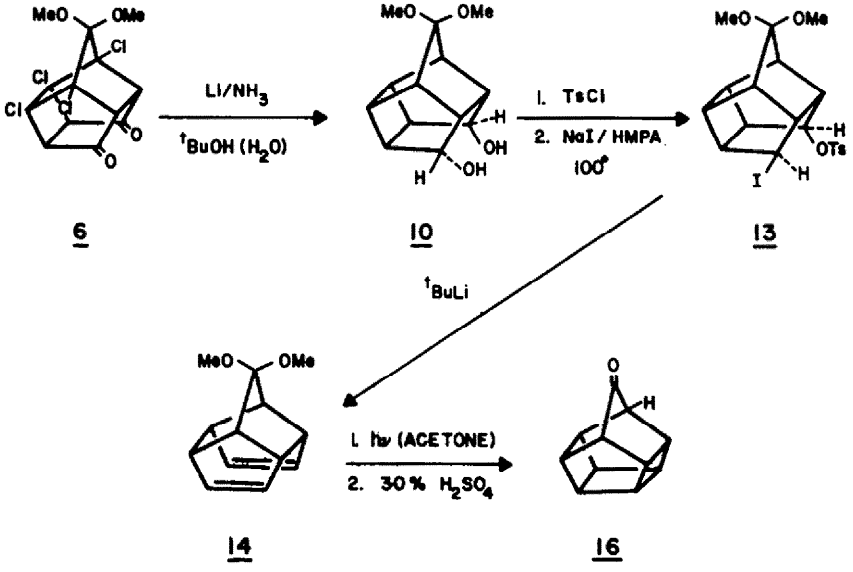
hexamethylphosphoramide. The tosylate groups of 8 are easily replaced by iodide,[22] but those of 9 are inert to such displacements.

Once it became clear that the chlorine substituents on 6 hopelessly modified the reactivity of the ring system, the tactical decision was made to proceed without them. This decision to proceed into the synthesis without any substituent α to the carbonyl group (or the ketal at this point) carried with it a severe penalty: later in the synthesis it would be necessary to develop methodology for the introduction of a leaving group at the carbonyl bridgehead of homopentaprismanone. This seemed a worthwhile challenge.

Homopentaprismanone

Dechlorination of 6 was carried out in refluxing liquid ammonia with excess lithium and t-butanol in wet tetrahydrofuran.[23] Concomitantly the ketone groups were reduced (Scheme 2). The *endo–endo* diol 10 was obtained in 78–86% yield. Reaction with tosyl chloride in pyridine gave the ditosylate 11 in 90% yield. This was heated with sodium iodide in hexamethylphosphoramide at 110° to achieve substitution of iodide for tosylate.[24] It proved best to stop this reaction when the starting material had completely disappeared, but before conversion to the diiodide was complete. Thus, we would usually obtain a mixture of about 1:3 of diodide 12 and iodotosylate 13. Both compounds proved suitable, together or alone, in the next step. In the ^{1}H-NMR spectrum of 12 the single sharp singlet at δ 4.55 ppm due to 2 × HCI is consistent with the *exo–exo* stereochemistry as expected for S_N2 displacement of the tosylate groups and consistent with the 8-line proton decoupled CMR spectrum of 12. In the iodotosylate 13 the singlet in the ^{1}H-NMR spectrum at δ 5.08 ($W_{1/2} \simeq 2$ Hz) and the triplet at δ 4.46 ppm (J = 3.5 Hz) were assigned respectively to HCI and HCOTs, the coupling constants reflecting appropriately the dihedral angles of these protons to their respective neighbors.

In previous hypostrophene and homohypostrophene syntheses it had been shown that treatment of diiodides from, e.g. 8 with metals or alkyl lithiums resulted in Grob-like fragmentation.[10b,c,11b,e] With t-butyllithium this works splendidly *both* on



6 10 13

14 16

Scheme 2.

diiodide **12** and iodotosylate **13** to give dimethoxyhomohypostrophene **14** in good yield. Purification was accomplished by way of the crystalline silver nitrate complex. Overall, pure **14** was obtained as colorless needles in 50% yield from ditosylate **11**. The ^{1}H-NMR spectrum of diene **10** is enlighteningly simple and fully consistent with the C_{2v} symmetry of the molecule, as is its fully decoupled ^{13}C-NMR spectrum in which there are just five resonances for the 13 carbons.

Dimethoxyhomohypostrophene could be photocyclized easily, indeed in rather higher yield than ever observed for the photocyclization of its unsubstituted relative **3**. Irradiation in acetone (vycor filter) or in benzene containing xanthone as sensitizer (Pyrex filter) gave a 92% yield of dimethoxyhomopentaprismane (**15**). The C_{2v} symmetry of the system was as obvious from its ^{1}H- and ^{13}C-NMR spectra as it was for the precursor. Hydrolysis of the ketal to homopentaprismanone (**16**) was achieved in 95% yield by treatment with 30% aqueous sulfuric acid at room temperature.

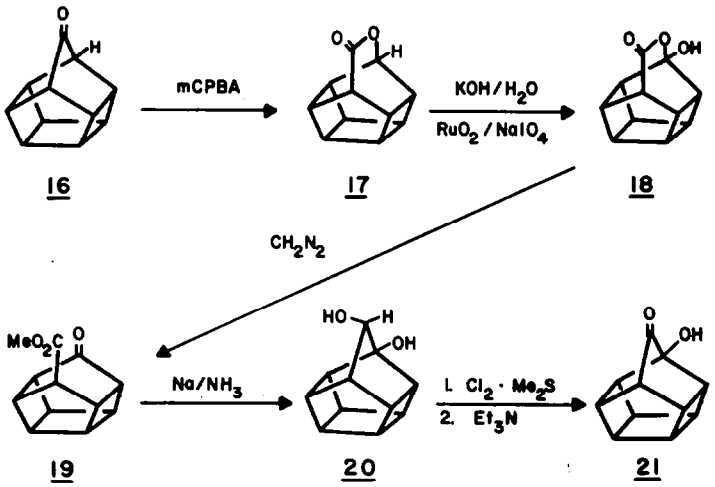
Homopentaprismanone **16** was in fact already known prior to this work, Ward and Pettit having made it in 1971.[25] Their approach was conceptually extraordinary, but the overall yield was uselessly low (0.25% from cyclooctatetraene). The synthetic scheme described here is practical, producing homopentaprismanone in 30% overall yield in six steps from the very readily available compound **6**. We have prepared homopentaprismanone frequently in greater than 10 g lots.

Bridgehead substitution

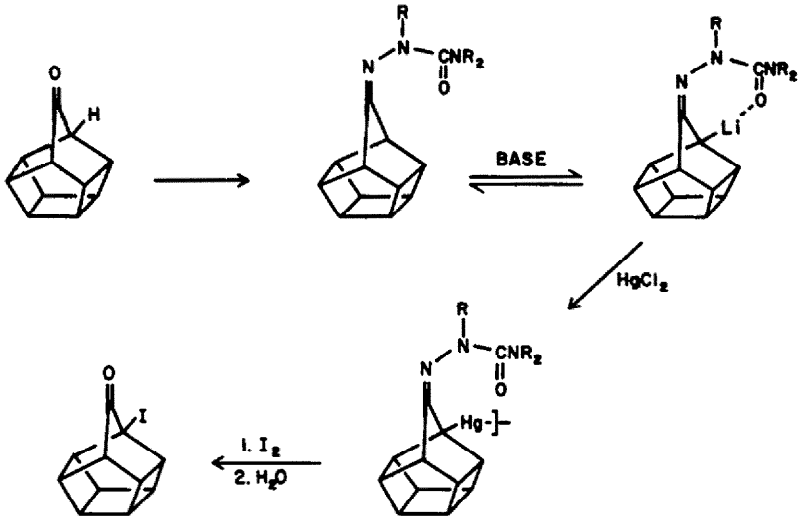
Now there is more difficult work to be done: homopentaprismanone must be readied for Favorskii contraction into the pentaprismane system. This requires that a leaving group be introduced α to the bridging carbonyl group. Simple kinds of α substitution that proceed via the enol or enolate ion are of course inapplicable as they violate Bredt's rule, even in the most modern relaxation of this stricture. Although we believe it will ultimately be possible to effect controlled bridgehead substitution directly (*vide infra*), such invasions are not yet known. Perforce, a more indirect route was developed.

The basic idea of our approach (Scheme 3) is oxidative decoupling of the bond between the carbonyl carbon and an adjacent bridgehead carbon to be followed by a less severe reductive recoupling that leaves both carbons with oxygen functionality. Baeyer–Villiger oxidation of homopentaprismanone to lactone **17** was accomplished smoothly in 90% yield using *m*-chloroperbenzoic acid. Further oxidation of the lactone via its opened salt was done with ruthenate anion generated (and regenerated) from the reaction of a catalytic amount of ruthenium dioxide with excess sodium periodate in aqueous potassium hydroxide.[26] The desired keto-acid, as the corresponding lactol **18**, was formed in 75–80% yield. Reaction of **18** with diazomethane in ether gave the keto-ester **19**,[27] there being sufficient keto-acid in equilibrium with the lactol to allow this reaction to proceed. The *endo* configuration of the ester group was assigned based on the 3.8 Hz splitting in the triplet at δ 2.75 ppm (C<u>H</u>COOMe) in the ^{1}H-NMR spectrum of **19** caused by coupling of this proton to those adjacent. Were the configuration reversed, the splitting would have been fairly small as the dihedral angle between the coupled protons would then have been close to 90°.

Keto-ester **19** is in the right oxidation state for acyloin-like coupling to a bridgehead substituted homopentaprismanone. Although the acyloin reaction has been known for many years, it has been used extensively only for the reductive coupling of like esters and, in related versions, for the reductive coupling of ketones or of aldehydes. For obvious reasons, little use has been made of mixed couplings. Only a few examples of this type appear in the literature. In one, Cook and Knox reported in 1970 the construction of the C–D ring of steveol by an acyloin-like intramolecular condensation of a keto-ester, but the product mixture was very complex.[28,29] In our case, however, the rigidity of the system and the *endo* configuration of the ester group confine the ester and ketone groups in close proximity to one another. This should favor the desired intramolecular C—C bond formation. Only one stereoisomer can result. The most likely side reaction, dimerization, can be minimized by paying appropriate attention to experimental detail. Indeed, at the bench,



Scheme 3.



Scheme 4.

intramolecular coupling was achieved in 83% yield by adding a dilute ether solution of **19** dropwise into a solution of excess sodium metal in liquid ammonia. Incidental to the coupling reaction the expected product, α-ketal **21**, was reduced further to diol **20**, the isolated product. It was (and remains) a fair nuisance to oxidize this diol back to hydroxyhomopentaprismanone **21**. Most oxidations of secondary–tertiary 1,2-diols result in C—C bond cleavage, that of **21** is no exception; most oxidants gave the lactol **18**. However, the 1973 Corey oxidation using the complex of dimethylsulfide with chlorine gave **21** in 77–85% yield.[30]

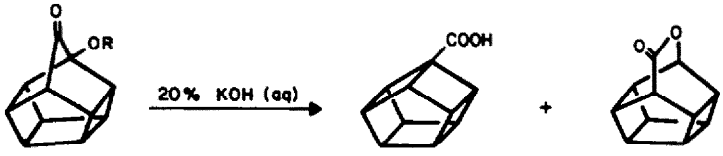
In summation, Scheme 3 provides for functionalization of a bridgehead position of homopentaprismanone simply in five steps in approximately 44% overall yield. Such methodology should be generally applicable for the functionalization of the bridgehead position of 7-ketonorbornanone subunits contained within other cage systems. If so, this opens one way for the synthesis of higher prismalogues.

This is an appropriate point to speculate on another, quite different approach to functionalization of bridgehead positions. Recently, we showed that amide activation for *o*-lithiation, a method widely used in aromatic synthesis, can be extended to special "saturated" systems such as cubane.[31] We suggest that direct substitution at the bridgehead of appropriately activated homopentaprismanone derivatives might be possible using modifications of this discovery. "Appropriate activation" remains to be defined, but the methodology is to be based on stabilized lithiation followed by transmetalation as was used profitably in the cubane system. Scheme 4 is presented as "paper chemistry" illustrative of the possibilities we are now examining.

Favorskii contraction

Only halogens have been used as leaving groups in previously reported examples of Favorskii contractions for the synthesis of strained polycycles.[15,16] Conversion of the bridgehead hydroxyl group of **20** into a halogen is not a trivial matter. Fortunately, it was unnecessary; other good leaving groups suffice. Treatment of the mesylate **22** with 20% aqueous potassium hydroxide solution at 80° for 30 min gave pentaprismane carboxylic acid **24** and lactone **17** in about a 3 : 1 ratio after acidification (Eq. 8). Formation of the lactone must have its origins in Haller–Bauer ring cleavage, a familiar competitive reaction in similar Favorskii contractions.[15a,d] Although the mechanistic details of neither the Haller–Bauer cleavage nor the Favorskii contraction are well understood, it is clear that the choice of base and solvent can affect profoundly the yield and ratio of products. However, no base–solvent combination appears to be generally superior. The 20% aqueous potassium hydroxide used was the best of those we tried. Powdered sodium hydroxide in refluxing toluene or in tetrahydrofuran at room temperature, for example, gave only the Haller–Bauer product. It was soon found that the choice of leaving group affected the yield and direction of the reaction very significantly. Changing from mesylate **22** to tosylate **23** doubled the isolated yield of pentaprismane carboxylic acid from 30 to 60% (overall from **21**), and only traces of lactone **17** were formed. The effect of the leaving group on the preferred mechanistic pathway is not understood. It is clear that hydrolysis back to **21** is not a significant competing reaction. The matter is under investigation.

A pure sample of pentaprismane carboxylic acid, the first compound to be made in the pentaprismane series, was obtained by crystallization from chloroform as



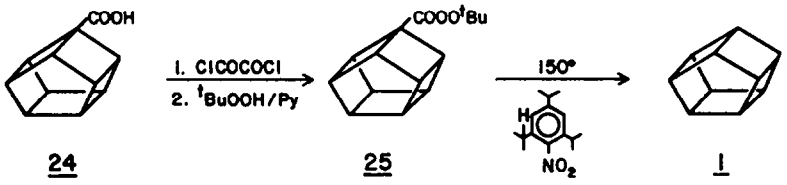
22, R = Ms
23, R = Ts
24
17

(8)

white prisms, m.p. 158.5–159.5°. The NMR data are completely consistent with the assigned structure. The 500 MHz ^{1}H-NMR spectrum is reproduced in Fig. 1. In accord with the compound's symmetry, only seven different carbon resonances appear in the decoupled CMR spectrum for the 11 carbon atoms.

Pentaprismane

No synthesis of a new ring system can be considered complete until the parent hydrocarbon has been prepared and characterized. As we did for the conversion of cubane carboxylic acid into cubane,[3] we used the method invented earlier by Wiberg *et al.*[32] for decarboxylation: thermal decomposition of the t-butylperoxyester in the presence of a hydrogen atom donor. Pentaprismane carboxylic acid was first converted to its acid chloride and this was treated with dry t-butylhydroperoxide and pyridine in dry ether to get the perester **25**. Anhydrous reaction conditions are absolutely essential for good yields, otherwise substantial quantities of the acid chloride are converted to pentaprismane carboxylic acid anhydride. Thermal decompositions of a perester are usually done in boiling cumene or *sym*-triisopropylbenzene as hydrogen atom sources. When the hydrocarbon product is easily volatile, it can be isolated by sweeping it in a nitrogen steam into a cold trap. Usually it is contaminated with a small amount of the aromatic. This can be a nuisance. Della and Patney solved this problem ingeniously by using the less volatile and more polar 2,4,6-triisopropylnitrobenzene as the hydrogen atom source; any trace of this can be removed by simple column chromatography over silica gel.[33] When the t-butyl perester of pentaprismane carboxylic acid was heated in 2,4,6-triisopropylnitrobenzene at 150° decomposition proceeded smoothly (Eq. 9). The yield of purified pentaprismane was 42% overall from the carboxylic acid.



24 25 1 (9)

Pentaprismane condenses from the gas phase as glistening crystals, m.p. 127.5–128.5°. Its electron impact mass spectrum is reproduced in Fig. 2. As in cubane, the most intense fragment in the spectrum is at m/e P − 1. In accord with its symmetry pentaprismane shows only a single line in its ^{1}H-NMR and in its proton decoupled ^{13}C-NMR spectra. The ^{13}C—H coupling constant is 148 Hz, corresponding to approximately 30% s character in the C—H bond.† This implies, as of course was expected, substantial rehybridization of the carbons in the pentaprismane frame away from tetrahedral geometry with its four similar sp^3 bonding orbitals. Instead, there is an increase in p character in the C—C bonds and an increase in s character in the C—H bonds made to adjust to the geometric demands of the skeleton.

† Calculated as $J_{^{13}C-H}/5$.

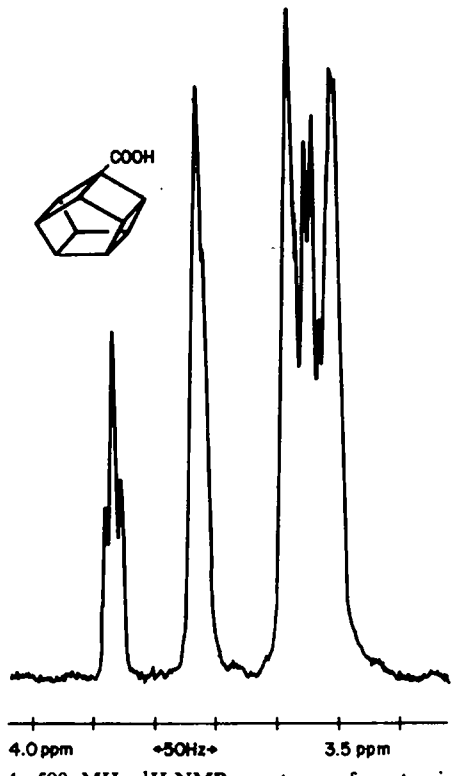


Fig. 1. 500 MHz ^{1}H-NMR spectrum of pentaprismane carboxylic acid.

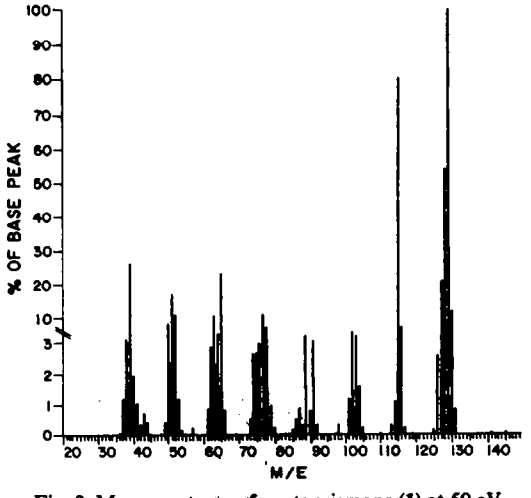


Fig. 2. Mass spectrum of pentaprismane (1) at 50 eV.

The geometry of pentaprismane

A satisfactory single crystal of pentaprismane for X-ray analysis could not be obtained. Possibly this is due to the D_{5h} symmetry of pentaprismane, which is not compatible with any space group symmetry. Instead, the crystal and molecular structure of pentaprismane carboxylic acid was determined (R = 0.049) in collaboration with Engel *et al.* at the University of Bern. The details have been published elsewhere[34] and need not be repeated here, except for a few summary comments. The skeleton is only slightly distorted by the carboxylic acid group and exhibits, with the exception of that group, almost perfect D_{5h} symmetry. The seven faces are planar within the precision of the measurements. The mean C—C bond length within the 5-membered rings is 1.548(8) Å, whereas the bonds that connect the two 5-membered rings are significantly longer with a mean distance of 1.565(4) Å. The average bond angle in the 5-membered rings is 108.0(3)° and 90.0(3)° in the 4-membered ring, exactly the values of the geometric ideals.

The very significant difference in lengths between the two kinds of pentaprismane C—C bonds, 1.548 and 1.565 Å, are of particular interest. These values bracket the average C—C bond length of 1.551 Å in cubane (tetraprismane). We have already published with Allinger of the University of Georgia a rationalization of these differences derived from MM2 valence force field calculations.[35] One way of briefly verbalizing the results of these calculations is as follows: two carbons bonded to a common carbon in a small ring are rather closer together than they would be in an open chain. If the system is rigid, as it is in pentaprismane, these atoms cannot move apart by angle bending. The bonds then stretch to diminish the repulsion. This is the "stretch–bend" interaction in MM2. When this is brought into play on pentaprismane, and the necessary balances and compromises struck around the system, there results a significant lengthening of the bonds shared by *two* 4-membered rings relative to those in the less awkward situation of being shared between *one* 4- and *one* 5-membered ring.

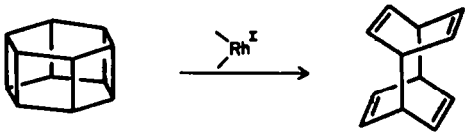
The electronic structure of pentaprismane as disclosed by its photoelectron spectrum and *ab initio* STO-3G calculations has been examined in collaboration with Heilbronner and Honegger of the University of Basel, particularly vis-à-vis a comparison with cubane. The results have been presented in detail elsewhere.[36]

Pentaprismane vs cubane

Pentaprismane is the "prismalogue" of cubane. It is rather more difficult to make, and behaves differently in interesting ways. Qualitative observations indicate it is significantly more fragile thermally than cubane, but it is more stable to reactions with strong acid. Whereas cubane is rearranged very rapidly by silver ion,[37] pentaprismane is very stable towards silver ion even under much more drastic conditions.[10a] Cubane and pentaprismane are cleaved easily by rhodium(I) complexes: the first, to *syn*-tricyclooctadiene;[38] the other, to hypostrophene. Cubane reacts more rapidly by about a factor of two. The rhodium(I) cleavage of substituted pentaprismanes opens the way to substituted hypostrophenes, otherwise unknown. We shall expand on each of these observations and others in more detail elsewhere.

For the future

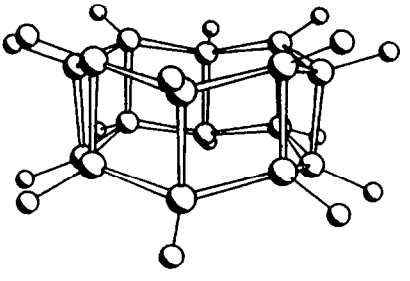
Pentaprismane is the third of the great family of prismanes to be synthesized and examined. There is an infinite number of prismanes ahead. They all offer exceptional challenges, for there is not yet any really general synthetic approach available. New thoughts about the construction of such systems are needed. There are special reasons to attempt the synthesis and characterization of the next few members of the family. Hexaprismane (**26**) is predicted by molecular mechanics calculations to have static D_{6h} symmetry in which each 6- and 4-membered face is planar.[35] Under this circumstance the flat 6-membered rings would have C—C—C angles of 120°, significantly above the normal tetrahedral angle. Saturated, tetravalent carbon atoms with such angles are very rare and worth detailed consideration.[39] MM2 calculations predict exceptionally long C—C bond lengths (1.571 Å) between the 6-membered rings and exceptionally short lengths within them (1.532 Å). Hexaprismane is, in a formal sense, a dimer of benzene. Extension of the rhodium(I) catalyzed openings of cubane and pentaprismane leads to the prediction that hexaprismane would be opened to the otherwise unknown tetraene **27** (Eq. 10).



(10)

26 **27**

Heptaprismane will probably be rather like hexaprismane, but with yet an increase in the bond length difference. Octaprismane (**28**) is predicted to be the first of the prismane systems to be puckered.[40] The dynamics of this phenomenon and understanding its role in the structure and reactivity and spectroscopy of such a prismane are a challenge for the future.



(11)

28

EXPERIMENTAL

^{1}H-NMR spectra were taken usually in the Fourier transform mode on a Bruker HS-270 spectrometer at 270 MHz on solns in $CDCl_3$ containing $CHCl_3$ (7.26 ppm) as internal standard. For convenience, the spectra were recorded on a compressed scale (3 Hz/mm); thus chemical shifts and coupling constants are reported only to a precision of ±0.02 ppm or ±1 Hz, respectively, sufficient for the purpose. ^{13}C-NMR spectra of $CDCl_3$ solns (or otherwise specified) were run at 22.63 MHz on a Bruker HX-90 spectrometer interfaced to a

Nicolet Instrument Corporation 1080 Series Acquisition System operating in the pulsed-Fourier transform mode. $CDCl_3$ (δ[center-line] = 77.30 ppm) was used as internal standard.

High resolution mass spectra were recorded at 50 eV and resolution 10,000 using an Associated Electrical Industries MS-902 spectrometer equipped with an on-line Digital Equipment Corporation PDP-8/I computer for data collection and manipulation. Perfluorokerosene was used as internal reference.

IR spectra of solns in $CHCl_3$ (unless otherwise mentioned) were obtained on a Perkin 283 spectrophotometer using the 1602 cm^{-1} band of polystyrene for calibration. Absorptions of interest are reported ± 5 cm^{-1}.

Analytical vapor phase chromatography was performed either on glass, 6 ft × 2 mm columns of 2% OV-225 on 80–100 mesh Gas Chrom Q, or 5% carbowax 20 M on 80–100 mesh Gas Chrom Q in a Hewlett–Packard 5830A dual column gas chromatograph equipped with flame ionization detectors and a 18850A terminal. A Varian Aerograph 1700 dual column gas chromatograph with 5 ft × 1/4 in stainless steel columns containing 10% OV-17 on 80–100 mesh Gas Chrom Q or 15% OV-17 on 60–80 mesh Gas Chrom Q was used for preparative vapor phase chromatography.

Analytical TLC was done on 4 × 8 cm plates precoated with 0.25 mm thick silica gel with fluorescent indicator (Sil G-$25U_{254}$) from Brinkmann Instruments; similar, but thicker (1 mm, 10 × 20 cm) glass plates were used for preparative purposes. Visualization was accomplished with a 7% soln of phosphomolybdic acid in 95% EtOH, or with iodine vapor, or with short wavelength UV light in a Ultra Violet Products, Chromato-Vue Model CC-20. Silica gel powder, 60–200 mesh, supplied by J. T. Baker was used for open column chromatography.

M.ps were determined on a Hoover Unimelt apparatus and are uncorrected. Removal of solvent *in vacuo* refers to the evaporation of solvent at aspirator pressure on a Büchi Rotavapor R. Organic solvents were reagent grade solvents and used without purification, except as mentioned. Organic extracts were dried over anhyd Na_2SO_4.

4,4 - *Dimethoxypentacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane* - endo,endo - 8,11 - *diol* (**10**)

Liquid ammonia (2.5 l) was condensed from the gaseous phase (Union Carbide Corp., Linde Division) into a 3-necked, 5 l, round-bottomed flask equipped with a Vibromixer and dry ice condenser. A soln of **6** (70 g, 0.188 mol)[20] and t-BuOH (168 g, 2.26 mol) and water (5 g) in THF (400 ml, distilled from LAH) was added slowly to the liquid ammonia kept cool with a dry ice–EtOH bath. Li wire (36 g, 5.19 g-atom, high or low Na content, Lithium Corporation of America) was added in short portions into the stirred soln. The rate of addition was adjusted to keep the mixture at gentle reflux. The soln was allowed to reflux for 2 h after the addition of Li was completed (1 h) and then quenched with granular NH_4Cl (200 g). Sometimes hand stirring was necessary as the mixture became viscous in the quenching process. After standing at room temp overnight, the mixture was heated on the steam bath to drive off most of the ammonia and THF. Water (600 ml) and $CHCl_3$ (300 ml) were added and the mixture heated on a steam bath to dissolve the solids. The aqueous layer was extracted thoroughly with $CHCl_3$ (4 × 100 ml). The combined organic phase was washed once with water (100 ml), dried, and the solvent was removed *in vacuo* to leave 46 g of crude solid. Crystallization from CCl_4–CH_2Cl_2 gave **10** as white needles (36 g, 80%): m.p. 182–183°; IR ν 3600, 3500–3100, 2980 and 1080 cm^{-1}; ^{1}H-NMR δ 5.67 (2H, br, OH, exchangeable with D_2O), 3.79 (2H, brs, $W_{1/2}$ = 6 Hz, O—CH), 3.32 (3H, s, CH_3O), 3.19 (3H, s, CH_3O), 2.78 (2H, brs), 2.73 (2H, brs), 2.65 (2H, brs) and 2.26 ppm (2H, brm); ^{13}C-NMR 113.5, 71.8, 51.1, 50.8, 44.9, 44.0 and 38.3 ppm; MS *m/e* calc for $C_{13}H_{18}O_4$ (P^+): 238.1205; found: 238.1207; calc for $C_{13}H_{16}O_3$ ($P^+ - H_2O$): 220.1099; found: 220.1083; calc for $C_{12}H_{15}O_3$ ($P^+ - OCH_3$): 207.1020; found: 207.1205.

The reaction has been repeated on four times the scale with similar results.

4,4 - *Dimethoxypentacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane* - endo,endo - 8,11 - *ditosylate* (**11**)

Diol **10** (128 g, 0.54 mol) and toluenesulfonyl chloride (250 g, 1.35 mol, m.p. 67–68°) were dissolved in dry pyridine (785 ml, distilled from BaO), and the soln was refrigerated at 0° for 24 h. The mixture was then poured slowly into ice–water (3.6 l). The ppt was collected and washed copiously with water (8 l). The crude, white, air-dried product (283 g, 96%, m.p. 152–154°) could be used directly in the next step. Crystallization from hexanes–CCl_4 gave **11** as white needles (264 g, 90%): m.p. 153.7–154.5°; ^{1}H-NMR δ 7.86 (4H, d, J = 8 Hz, ArH), 7.32 (4H, d, J = 8 Hz, ArH), 4.39 (2H, brs, $W_{1/2}$ = 7.5 Hz, CH—O), 3.23 (3H, s, CH_3O), 3.12 (3H, s, CH_3O), 2.71 (2H, brs), 2.60 (4H, brs), 2.44 (6H, s, Ar—CH_3) and 2.20 ppm (2H, brs); MS *m/e* calc for $C_{20}H_{23}SO_5$ ($P^+ - C_7H_7SO_3$): 377.1264; found: 375.1308.

4,4 - *Dimethoxypentacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane* - exo,exo - 8,11 - *diiodide* (**12**) *and* 4,4 - *dimethoxypentacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane* - exo - 8 - *iodo*, endo - 11 - *tosylate* (**13**)

A mechanically stirred mixture of **11** (66 g, 0.12 mol), NaI (144 g, 0.96 mol) and hexamethylphosphoramide (288 ml, distilled from CaH_2) was heated at 100° under N_2 for 48 h by which time TLC analysis (ether) showed complete reaction of starting material. The mixture was cooled to room temp. Water (300 ml) and ether (500 ml) were added; the mixture was hand-stirred until all the solids had dissolved. The water layer was extracted with ether (3 × 150 ml). The combined organic phase was cooled to 0° in an ice–water bath, then washed with ice-cold conc HCl (2 × 75 ml), then sat $NaHCO_3$ aq 15% aq sodium thiosulfate soln. The soln was dried and the solvent removed *in vacuo* leaving a white solid (55 g), normally this was used directly in the next step.

A small portion of the crude solid (2 g) was chromatographed through silica gel (10 g, hexanes–ether, 10:1 v/v) to give pure **12** (0.46 g) and pure **13** (1.5 g). Diiodide **12**: m.p. 132.5–133°; ^{1}H-NMR δ 4.55 (2H, s, $W_{1/2}$ = 2 Hz, CH—I), 3.36 (3H, s, CH_3O), 3.33 (2H, brs), 3.30 (3H, s, CH_3O), 3.03 (4H, brs) and 2.87 ppm (2H, brs); ^{13}C-NMR 111.2, 52.7, 51.4, 51.2, 51.1, 50.1, 40.4 and 30.3 ppm; MS *m/e* calc for $C_{12}H_{13}I_2O$ ($P^+ - OCH_3$): 426.9059; found: 426.9046. Iodotosylate **13**: m.p. 143–145°; ^{1}H-NMR δ 7.89 (2H, d, J = 8 Hz, ArH), 7.37 (2H, d, J = 8 Hz, ArH), 5.08 (1H, s, $W_{1/2}$ = 2 Hz, CH—I), 4.46 (1H, brt, J = 3.5 Hz, CH—O), 3.29 (3H, s, CH_3O), 3.21 (3H, s, CH_3O), 3.16–2.84 (4H, m), 2.63–2.61 (3H, brm), 2.47 (3H, s, Ar—CH_3) and 2.43 ppm (1H, br); MS *m/e* calc for $C_{20}H_{23}SO_5$ ($P^+ - I$): 377.1223 (4%), 375.1264 (100%); found: 377.1210 (13%), 375.1220 (97%).

10,10 - *Dimethoxytetracyclo*[6.3.0.0^{4,11}.0^{5,9}]*undecane* - 2,6 - *diene* (**14**)

Ether (400 ml) was distilled from LAH directly into a crude mixture (53 g) containing **12** and **13** prepared as described. The mixture was stirred at room temp until the solids were finely suspended. t-BuLi (2 M in pentane, Aldrich, 130 ml) was added dropwise into the stirred ether suspension kept under N_2. The reaction temp was kept below 30° by external cooling. The progress of the reaction was monitored by following the disappearance of **12** and **13** by TLC (ether eluant). After it had been stirred at room temp for 1 h, the mixture was cooled in an ice–water bath. Water (150 ml) was added cautiously, the layers separated, and the aqueous layer extracted with ether (3 × 80 ml). The combined ether soln was concentrated to about 50 ml on the steam bath. $AgNO_3$ aq (16.7 g in 50 ml water) was added and the whole stirred for 30 min. The precipitated $AgNO_3$ complex was collected by filtration, washed with dry ether and air dried. The complex was then stirred with NH_4OH (150 ml) and the mixture then extracted with pentane (4 × 70 ml). The extract was washed once with brine (80 ml), dried ($MgSO_4$) and the solvent removed by distillation at

atmospheric pressure to give diene **14** as colorless needles (12 g, 50% overall from **11**): m.p. 70.5–73°; IR ν 3050, 2960, 1590 and 1070 cm^{-1}; ^{1}H-NMR δ 5.92 (4H, olefinic H), 3.36 (6H, s, CH_3O), 3.20–3.08 (2H, m, bridgehead H) and 2.60 ppm (4H, brs, methine H); ^{13}C-NMR 136.5, 107.9, 65.0, 50.7 and 46.9 ppm; MS *m/e* calc for $C_{13}H_{16}O_2$ (P^+): 204.1150; found: 204.1162 (100%).

4,4 - *Dimethoxyhexacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*undecane* (**15**)

An acetone soln (100 ml) of **14** (12 g) in a quartz cell was irradiated using a 400 W Hanovia medium pressure lamp shielded with a vycor 7910 filter. During the irradiation a slow stream of N_2 was bubbled through the soln. The reaction was followed by VPC (2% OV-225) and took 45 min to complete. The acetone was then removed by distillation on a steam bath. The solid residue was crystallized from cold ether (dry ice–EtOH bath) as colorless plates (10.8 g). The mother liquor was chromatographed through silica gel with pentane to give additional pure **15** (0.3 g), for a total yield of 92%; m.p. 64–66°; ^{1}H-NMR δ 3.32 (6H, s, CH_3O), 3.21 (4H, brs), 3.15–3.03 (4H, brm) and 2.66–2.56 ppm (2H, m, bridgehead H); ^{13}C-NMR δ 120.1, 53.4, 51.1, 47.1 and 43.9 ppm.

Hexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*undecane* - 4 - *one*. *Homopentaprismanone* (**16**)

A soln of **15** (6.00 g) in ether (50 ml) was stirred with 30 wt% H_2SO_4 at room temp overnight. The aqueous layer was extracted with ether (3 × 20 ml). The extract was washed with sat NH_4Cl aq (10 ml), dried, and the solvent distilled on the steam bath to leave crude, solid homopentaprismanone (4.50 g, 95%) used usually without further purification.

A pure sample of **16** was obtained by preparative VPC (15% OV-17) followed by crystallization from a small volume of ether: m.p. 154.8–155.2° (lit.[25] 154–155°); IR ν 1765 cm^{-1}; ^{1}H-NMR δ 3.43 (4H, brs), 3.37–3.26 (4H, m) and 2.40–2.26 ppm (2H, m, bridgehead H); ^{13}C-NMR 212.9, 52.5, 47.4, and 43.5 ppm; MS *m/e* calc for $C_{11}H_{10}O$ (P^+): 158.0731; found: 158.0765; calc for $C_{10}H_{10}$ ($P^+ - CO$): 130.0782; found: 130.0748 (100%).

4 - *Oxo* - 5 - *oxahexacyclo*[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]*dodecane* (**17**)

A soln of *m*-chloroperbenzoic acid (3.5 g, 70% titre, 14.2 mmol) and **16** (1.9 g, 12 mmol) in CH_2Cl_2 (35 ml) was stirred at room temp overnight. The initial reaction was exothermic; external cooling was necessary. Excess oxidizing agent was destroyed by washing once with 15% Na_2SO_3 aq (10 ml). The aqueous portion was back extracted with CH_2Cl_2 (30 ml). The combined organic phase was washed quickly with sat $NaHCO_3$ aq (10 ml) and then dried. The solvent was evaporated *in vacuo* to leave the lactone as a white solid (1.9 g, 90%), sufficiently clean for use in the next step without further purification. Larger scale runs behaved similarly. A pure sample was obtained by crystallization from ether: m.p. 150° (dec.); IR ν 1750 cm^{-1}; ^{1}H-NMR δ 5.03 (1H, t, J = 5.3 Hz, CH—O), 3.40–3.28 (4H, m), 3.28–3.10 (4H, m) and 2.85 ppm (1H, t, J = 4.5 Hz).

4 - *Oxo* - 5 - *oxa* - 6 - *hydroxyhexacyclo* - [6.4.0.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]*dodecane* (**18**)

A catalytic amount of ruthenium dioxide (20 mg) was added to a fine suspension of **17** (1.90 g, 10.9 mmol) in 1 M KOH aq (40 ml) and the mixture magnetically stirred. Sodium metaperiodate (3.85 g, 18 mmol, 60% excess) in water (20 ml) was added dropwise. After the mixture was stirred at room temp overnight, the excess oxidizing agent was destroyed with 30% Na_2SO_3 aq testing against KI–starch paper. The soln was then acidified with cold 4 N HCl and extracted with $CHCl_3$ (3 × 80 ml). The extract was washed with sodium thiosulfate, dried, and the solvent was evaporated *in vacuo* to leave **18** as a white solid (1.9 g, 90%). The crude material was crystallized from CH_2Cl_2–ether to give pure **18** as colorless plates (1.69 g, 81%): m.p. 214° (dec.); IR ν 3560, 3500–3100, 1740 and 1730 cm^{-1}; ^{1}H-NMR δ 3.67 (1H, br, OH), 3.43–3.28 (6H, m), 3.03–2.92 (2H, m) and 2.91 ppm (1H, t, J = 2.4 Hz); MS *m/e* calc for $C_{11}H_{10}O_3$ (P^+): 190.0629; found: 190.0631.

Larger scale oxidations (10 ×) gave less satisfactory results; yields averaged 60–70%. In retrospect, the problem is probably with insufficient extraction of the aqueous reaction mixture.

endo - 7 - *Carbomethoxypentacyclo*[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*decane* - 10 - *one* (**19**)

A soln of **18** (1.0 g) in CH_2Cl_2 (75 ml) was cooled to 0–5° and treated dropwise with diazomethane in diethyl ether until an excess was evident (yellow color). The excess was removed on a steam bath (titration with AcOH would probably have been better), and the remaining soln was dried, decolorized with Norit, and the solvent removed *in vacuo* to leave crystalline **19** (1.3 g, 96%). Larger scale (4–11 g) preparations afforded 93–95% isolated yields of high quality material.

A pure sample of **19** was obtained by crystallization from a small volume of ether: colorless prisms; m.p. 93–95°; IR ν 1730 cm^{-1}; ^{1}H-NMR δ 3.82–3.66 (2H, m), 3.66 (3H, s, CH_3O), 3.56–3.44 (2H, m), 3.40–3.30 (2H, m), 3.06 (2H, d of t, J = 2.5, 3.8 Hz) and 2.75 ppm (1H, t, J = 3.8 Hz); ^{13}C-NMR δ 219.3, 170.7, 52.0, 51.5, 46.2, 44.5, 42.7 and 35.6 ppm; MS *m/e* calc for $C_{12}H_{12}O_3$ (P^+): 204.0785; found: 204.0766; calc for $C_{11}H_{12}O_2$ ($P^+ - CO$): 176.0837; found: 176.0842; calc for $C_{11}H_9O_2$ ($P^+ - OCH_3$): 173.0602; found: 173.0599.

3,4 - *Dihydroxyhexacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*undecane* (**20**)

A soln of **19** (0.714 g, 3.5 mmol) in ether (160 ml, dried and distilled from LAH) was added dropwise into a magnetically stirred soln of Na (1 g, 43.5 mg-atom) in refluxing liquid ammonia (150 ml, dried and distilled from Na). The mixture was allowed to reflux for 30 min after the addition was completed. Excess Na was destroyed by slow addition of granular NH_4Cl. The mixture was stirred at room temp overnight, the ammonia and ether being allowed to evaporate. The solid left was dissolved by adding in $CHCl_3$ (50 ml) and water (20 ml); the aqueous portion was saturated with NH_4Cl and extracted with hot $CHCl_3$ (4 × 30 ml). The combined organic portion was dried, and the solvent evaporated on a steam bath to a crude solid that was crystallized from ether–CH_2Cl_2 to give a pale yellow, granular solid (510 mg, 83%): m.p. 200° (dec.); ^{1}H-NMR δ 4.20 (1H, d, J = 1.9 Hz), 3.58–3.44 (1H, m), 3.27 (2H, br), 3.12 (4H, br), 3.01–2.90 (1H, m), 2.80 (2H, br, OH) and 2.49 ppm (1H, d of t, J = 1.9, 6 Hz); ^{13}C-NMR (methanol-d_4, center line = 49.0 ppm) δ 98.3, 83.0, 54.0, 51.7, 51.1, 49.9, 45.1, 44.9, 44.1 and 43.3 ppm; MS *m/e* calc for $C_{11}H_{12}O_2$ (P^+): 176.0837; found: 176.0839; calc for $C_{11}H_{10}O$ ($P^+ - H_2O$): 158.0731; found: 158.0737. Runs on 9 times the scale gave equivalent results.

3 - *Hydroxyhexacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*undecane* - 4 - *one* (**21**)

A soln of Me_2S–Cl_2 complex was prepared by adding Me_2S (5.3 g, 85 mmol) dropwise into a soln of Cl_2 (2.8 g, 40 mmol) in CH_2Cl_2 (50 ml, dried and distilled from P_2O_5) cooled in dry ice–CCl_4 bath. The soln was then stirred at ice bath temp for 10 min to ensure complete complex formation and put back into the dry ice–CCl_4 bath afterwards. Powdered diol **20** (900 mg, 5.1 mmol) was added and washed down with a bit of CH_2Cl_2. The mixture was stirred at −25° for 3 h. (The mixture became homogeneous after the first 30 min.) Et_3N (8.5 g, 80 mmol, distilled from KOH) in CH_2Cl_2 (50 ml, distilled from P_2O_5) was then added dropwise to the mixture at −25°, and the whole was stirred for 10 min. The resulting mixture was allowed to warm to room temp and then poured into anhyd ether (200 ml) and the ppt filtered off. (Occasionally, small amounts of product were occluded in the ppt which should be checked therefore by TLC before discarding.) The clear pale yellow soln was concentrated on the steam bath and the concentrate chromatographed on silica gel (40 g, CH_2Cl_2) to give **21** (750 mg, 4.3 mmol, 84%), which was used without

further purification. The yields of the oxidation were 77–85% on smaller scales, and could not be improved substantially on larger scale.

A pure sample of **21** was obtained by crystallization from cold ether as colorless prisms: m.p. 75.5–76.5°; IR ν 3540, 2980, 1765 and 1055 cm^{-1}; ^{1}H-NMR δ 3.65–3.41 (4H, m), 3.41–3.24 (2H, m), 3.24–3.10 (2H, m), 2.44 (1H, t, J = 5.5 Hz) and 2.20 ppm (1H, OH); ^{13}C-NMR δ 212.13, 88.88, 48.83, 47.50, 47.46, 46.93 and 43.38 ppm; MS *m/e* calc for $C_{11}H_{10}O_2$ (P^+): 174.0680; found: 174.0704; calc for $C_{10}H_{10}O$ ($P^+ - CO$): 146.0731; found: 146.0728.

Hexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*undecane - 4 - one - 3 - tosylate* (**23**)

A mixture of **21** (700 mg, 4 mmol) and toluenesulfonyl chloride (1.15 g, 6 mmol) in dry pyridine (700 μl, distilled from KOH) was heated on the steam bath for 30 min and then refrigerated at 0° overnight. The whole mixture was then dissolved in CH_2Cl_2 (20 ml) and washed with ice-cold 10 wt% H_2SO_4, then sat $(NH_4)_2SO_4$, and dried. The solvent was evaporated *in vacuo*. The residue consisted of keto tosylate **23** and unreacted tosyl chloride, but was generally used in the next step without further purification.

A pure sample of **23** was obtained by column chromatography on silica gel (CH_2Cl_2) and was crystallized from hexanes as pale tan needles: m.p. 118.5–119.5°; ^{1}H-NMR δ 7.74 (2H, d, J = 8.3 Hz, ArH), 7.31 (2H, d, J = 8.3 Hz, ArH), 3.53 and 3.52 (6H, overlapping singlets), 3.28 (2H, brs), 2.44 (3H, s, Ar—CH_3) and 2.41 ppm (1H, brs); MS *m/e* calc for $C_{11}H_9O_2$ ($P^+ - C_7H_7SO_2$): 173.0602; found: 173.0614.

Hexacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]*decane - 1 - carboxylic acid. Pentaprismane carboxylic acid* (**24**)

Finely powdered crude **23** (from 700 mg of **21**, contaminated with tosyl chloride) was added in portions into a preheated 20% KOH aq (20 ml, 110°) and washed in with another 20 ml of the base soln. The resulting mixture was refluxed rapidly with good stirring for 5 h and became homogeneous. The soln was allowed to cool down after work-up of an aliquot showed (^{1}H-NMR) total disappearance of starting material. $CHCl_3$ (50 ml) was added; the mixture was cooled to 0–5° and then acidified, keeping it cold, with ice-cold 50 wt% H_2SO_4. The insoluble material formed was filtered using glass wool and extracted many times with $CHCl_3$. The aqueous phase was further extracted with $CHCl_3$ (4 × 20 ml). The combined organic extract was washed once with sat $(NH_4)_2SO_4$ aq soln (40 ml) and dried. The solvent was removed *in vacuo* to leave 470 mg of pale yellow solid. Purification via chromatography on silica gel (CH_2Cl_2) gave **24** (426 g, 61% overall from **21**), m.p. 156–158°. In other runs the yields ranged up to 90%.

A pure sample of **24** was obtained by crystallization from a small volume of $CHCl_3$ as prisms: m.p. 158.5–159.5°; IR ν 3400–2450 and 1690 cm^{-1}; ^{1}H-NMR δ 12.6 (1H, br, COOH), 3.87 (1H, br, t, J = 4 Hz), 3.82–3.70 (2H, m), 3.70–3.44 (6H, m); ^{13}C-NMR δ 180.6, 60.5, 52.6, 50.9, 49.1, 48.2 and 46.4 ppm; MS *m/e* calc for $C_{11}H_{10}O_2$ (P^+): 174.0680; found: 174.0676; calc for $C_{11}H_8O$ ($P^+ - H_2O$): 156.0575; found: 154.0571; calc for $C_{10}H_9$ ($P^+ - COOH$): 129.0704; found: 129.0681.

Hexacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]*decane - 1 - carboxylic acid, t - butylperester* (**25**)

Pentaprismane carboxylic acid **24** (230 mg) was refluxed with excess oxalyl chloride (9 ml) for 1 h, then the excess oxalyl chloride was removed under reduced pressure. Anhyd ether (10 ml) was distilled from LAH directly onto the colorless acid chloride. The soln was cooled in an ice–water bath and stirred. Anhyd[41] t-butyl hydroperoxide (405 mg, m.p. 0–5°) and pyridine (250 μl, distilled from KOH) were added in that order. Stirring was continued overnight at room temp. The white solid was filtered and washed with anhyd ether. The excess pyridine in the combined ether soln was precipitated by adding oxalyl chloride with a microsyringe. The ppt was removed, and the ether soln was washed once with sat $(NH_4)_2SO_4$, dried, and the solvent evaporated on a steam bath. The crude perester was obtained as a pale yellow solid (320 mg), m.p. 105–110°, which was used without further purification: IR ν 1740 cm^{-1}; ^{1}H-NMR δ 3.88 (1H, t, J = 4 Hz), 3.78–3.70 (2H, m), 3.62–3.47 (6H, m) and 3.51 ppm (9H, t-butyl H).

Hexacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]*decane. Pentaprismane* (**1**)

2,4,6-Triisopropylnitrobenzene (810 mg) was mixed with **25** (320 mg) in a round-bottomed flask equipped with a cold finger cooled by ice-cold water. The mixture was heated under N_2 in an oil bath; the solvent melted at 72°, and the soln was then stirred magnetically. Vigorous gas evolution started at 120° and persisted to 150°. The mixture was held at 150° for 1 h. Pale yellow needles collected on the cold finger. These were dissolved in pentane and chromatographed on silica gel (pentane) to give pure pentaprismane (45 mg). The mixture was heated for a further 6 h at 150°; more pentaprismane collected on the cold finger and it was purified as before (29 mg). The total yield of pentaprismane was 42% overall from acid **24**.

A pure sample of **1** was obtained by condensation from the gas phase as colorless prisms: m.p. 127.5–128.5° (sealed tube); IR (KBr) ν 2973, 1273, 1231, 1069, 875 and 768 $\pm$ 3 cm^{-1}; ^{1}H-NMR δ 3.48 ppm; ^{13}C-NMR δ 48.63 ppm (d, J = 148.1 $\pm$ 0.3 Hz); MS *m/e* calc for $C_{10}H_{10}$ (P^+): 130.0782; found: 130.0762; calc for $C_{10}H_9$ ($P^+ - H$): 129.0700; found: 129.0695.

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