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Synthetic Studies Towards Prismanes: Seco-[6]-Prismane

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Key Words: Seco-[6]-prismane; pentacyclic dimer of benzene; photooxygenation; intramolecular 2+2-photocycloaddition; boronate fragmentation.

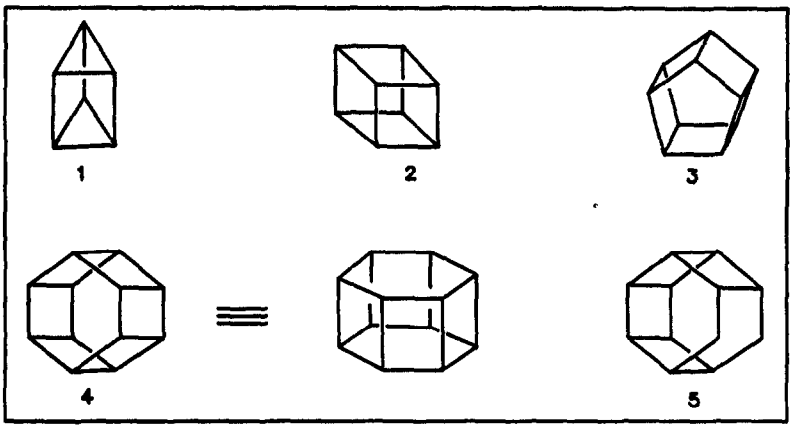
Abstract: The first synthesis of seco-[6]-prismane 5, the closest, one-bond-away secologue of [6]-prismane 4, from the readily available Diels-Alder adduct of 1,5-cyclooctadiene and dimethoxytetrachlorocyclopentadiene is described. The key chemical operations in the 17 step sequence are (i) 4+2-cycloaddition of singlet oxygen 20 ⟶ 22, (ii) boron mediated fragmentation 47 ⟶ 14 and (iii) intramolecular 2+2-photocycloaddition 14 ⟶ 49. The methodology outlined here offers opportunities for further elaboration to [6]-prismane as well as several of its homo- and secologues.

Introduction

[n]-Prismanes constitute an enchanting class of polycyclic hydrocarbons, made-up of even number of methine units of general formula $(CH)_{2n}$ and D_{nh} symmetry, whose synthetic appeal emanates from their compact, aesthetically pleasing shape and the prediction and expectancy of novel structural characteristics and unusual chemical reactivity.[1] Conceptually, prismanes were introduced over a century ago as Ladenburg's structure for benzene but the first practical realisation of a prismane was achieved only in 1964 by Eaton and Cole through their seminal efforts culminating in the synthesis of [4]-prismane (2, cubane).[2] Since then, [3]-prismane 1[3] and [5]-prismane 3[4] have been synthesised in 1973 and 1981, respectively. Thus, in each of the preceding three decades one prismane has been synthesised, and by extrapolation [6]-prismane 4, the next in line, is due for the nineties! To meet the deadline, we initiated efforts in quest for 4, well in advance, and this and the following reports[5a,b] reveal the strategies that have been pursued and the progress achieved so far.

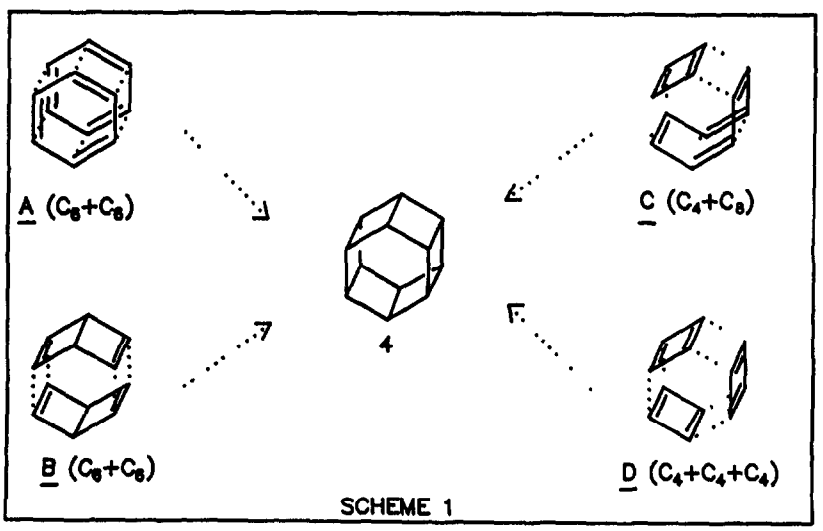
Hexaprismane 4 is composed of twelve identical methine units $(CH)_{12}$, arranged at the corners of a regular hexagonal prism and thus the two parallel 6-membered rings are cojoined by six 4-membered rings. It is formally a face-to-face dimer of benzene. Molecular mechanics[6a-c] and <u>ab initio</u>[6d-h] calculations predict D_{6h} symmetry for hexaprismane in the lowest energy arrangement with a steric energy of ~164 Kcal/mol.[6b] Furthermore, 4 is the first [n]-prismane in the series in which carbon atoms have C-$\hat{C}$-C bond angles, both less than (90°) and greater than (120°) the normal tetrahedral angle.[6i] The synthetic creation of heptacyclic 4 requires a unique assemblage of six cyclobutane rings, all fused in a <u>cis, syn</u>-manner and poses a synthetic challenge of high magnitude that has enticed many synthetic groups around the world. However, only limited

success towards the synthesis of hexaprismane has been achieved so far.[7] Herein, we report the synthesis of secohexaprismane 5, the closest, one-bond-away secologue of 4.[8]



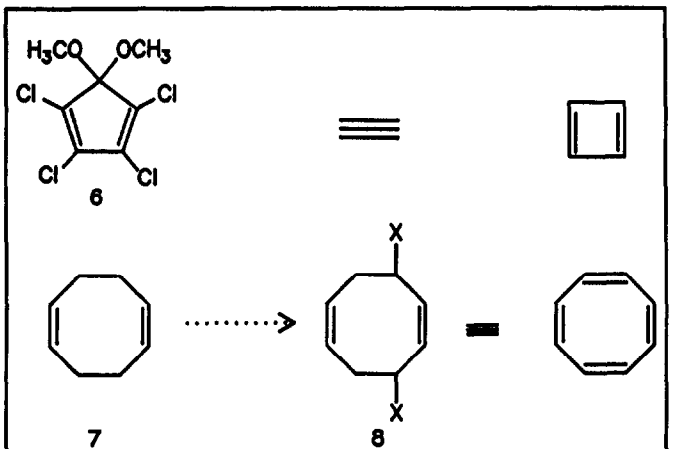
Synthetic Strategy

For the construction of [6]-prismane framework, we opted for a strategy that appeared conceptually simple but involved the arduous task of coaxing the precursors into proper spatial alignment for the multiple cycloadditions. Thus, two face-to-face benzenes A (C_6 + C_6) or two bottom-to-bottom Dewar benzenes B (C_6 + C_6) or a cyclobutadiene over cyclooctatetraene C (C_4 + C_8) or three cyclobutadienes D (C_4 + C_4 + C_4) could eventuate in 4, Scheme 1. While such esoteric approaches look great, they rely heavily on providential forces to succeed! Therefore, a more practical and rational approach would be to deploy readily available chemical equivalents of C_4, C_6 and C_8 fragments and unite them, step-by-step with regio- and stereochemical controls, in a series of logically arranged synthetic operations.



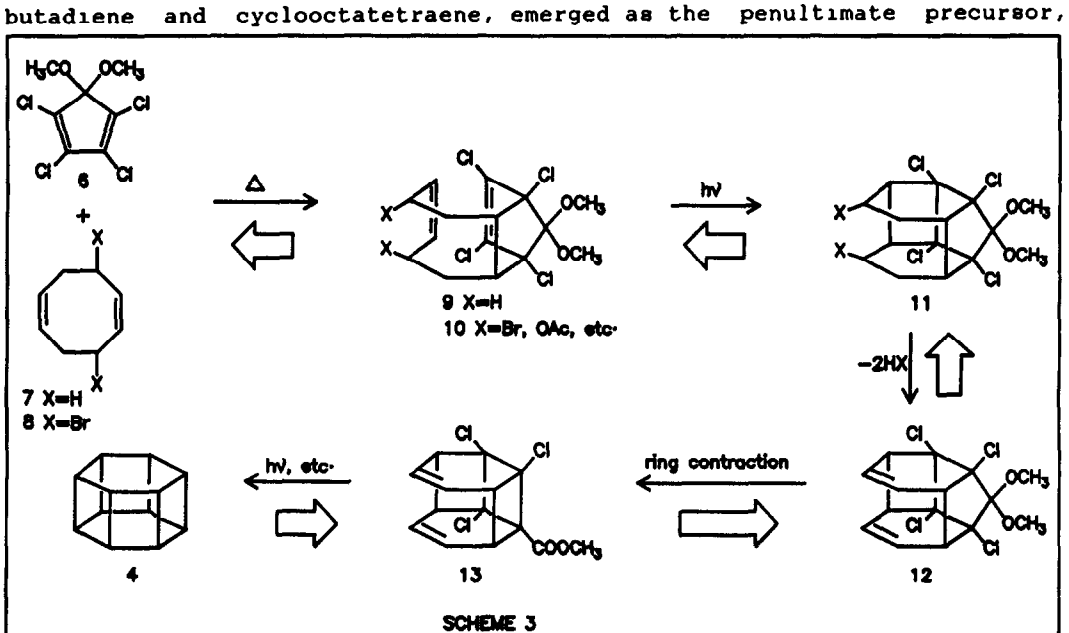
SCHEME 1

Among the possibilities mentioned in Scheme 1, we preferred the C_4 + C_8 approach C to hexaprismane 4 , and, therefore, identified 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene 6 and 1,5-cyclooctadiene 7 via 8 as the chemical equivalent of cyclobutadiene (C_4) and cyclooctatetraene (C_8), respectively, Scheme 2.



SCHEME 2

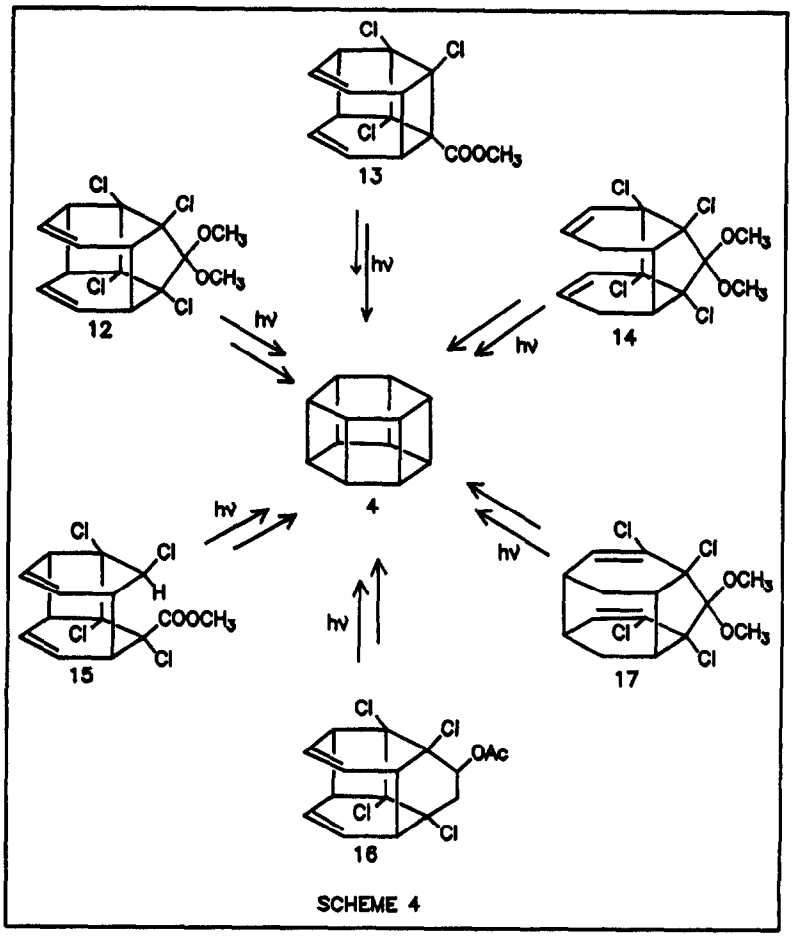
Keeping in view, 6 and 7 or 8 as readily and abundantly available C_4 and C_8 equivalents, a retrosynthetic theme for the projected synthesis of [6]-prismane was delineated, Scheme 3. According to this theme, the pentacyclic dimer of benzene 13, formally a true cycloaddend of cyclobutadiene and cyclooctatetraene, emerged as the penultimate precursor,



SCHEME 3

which on intramolecular 2+2-photocycloaddition would generate [6]-prismane framework. Further down the line, 10 was a pivotal intermediate that required either direct access from 6 and 8 or through 9 via allylic functionalisation. The transformation of 10 to 13 through 11 and 12 appeared to be relatively straight-forward.

To lend a certain degree of flexibility to our strategy, we also targeted some homo- and secologues of 13. These back-up alternatives 12 and 14 ⟶ 17 alongwith 13 are shown in Scheme 4 and each one of them through 2+2-photoclosure and few additional tactical manoeuvres could lead to 4. Access to precursors 12 and 14 ⟶ 17 could be gained within the overall framework of Scheme 3 with minor variations.

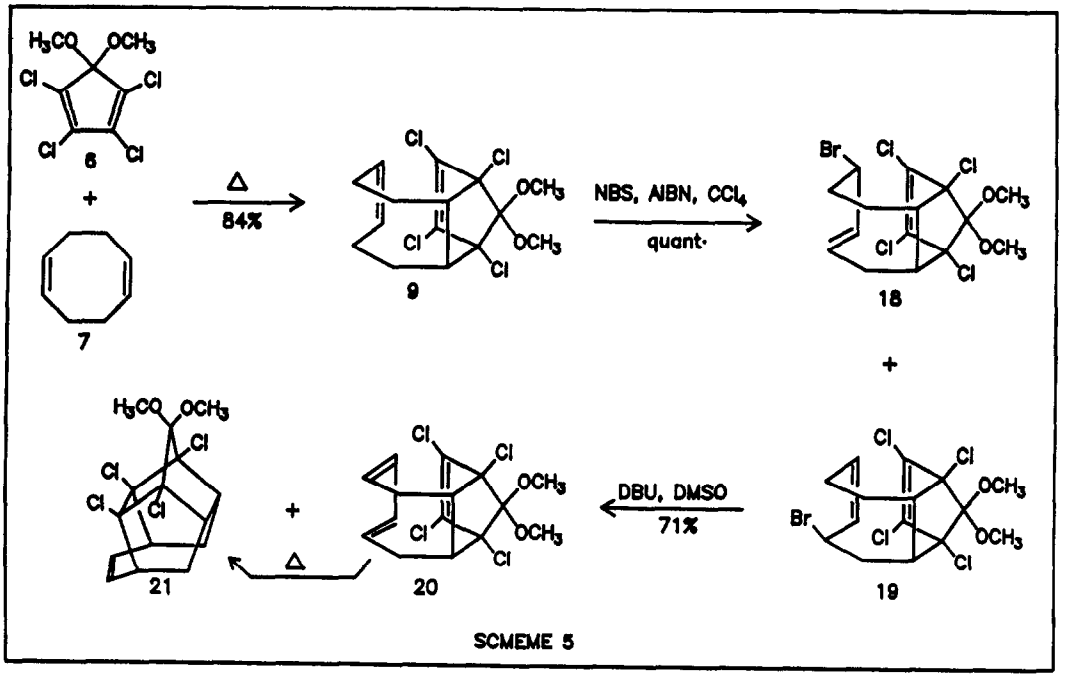


SCHEME 4

Synthetic Studies

To give expression to Scheme 3, 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene 6 and excess 1,5-cyclooctadiene 7 were subjected to Diels-Alder cycloaddition to afford the well characterised endo-adduct 9 in 84% yield, Scheme 5.[9] The next task was to 1,4-difunctionalise the

allylic positions of the cyclooctene moiety in adduct 9, so that the appended functionalities could readily serve as precursors for olefinic bonds of the diene 12. Direct functionalisation of the diene 9 to 10 *via* allylic bromination with N-bromosuccinimide was attempted. It furnished a mixture of allylic mono-bromides 18 and 19 only, and in that too, the double bond shifted isomer 18 predominated.[7b] Since further bromination of 19 to 10 could not be achieved, it was decided to convert the allylic bromide mixture into a symmetrical 1,3-diene and further refunctionalise it through 1,4-addition.

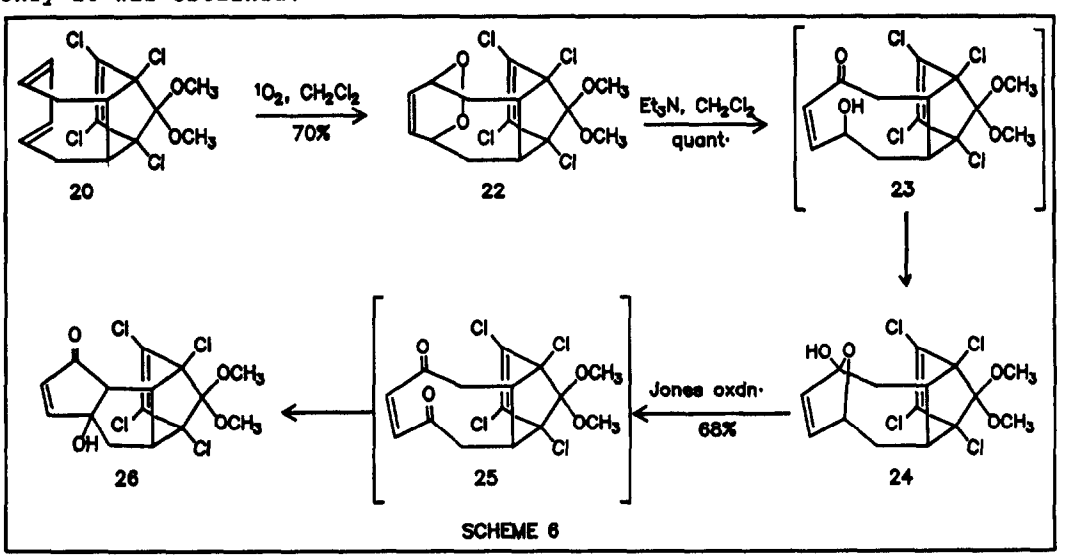


SCHEME 5

Initial attempts at dehydrobromination of 19 led to the formation of 20 in low yield and the major product of the reaction was the intramolecular Diels-Alder adduct 21.[7c] In order to suppress this unwanted product, milder reaction conditions for dehydrobromination were devised and it was found that DBU in DMSO (~20°C) furnished the labile diene 20 in an acceptable 71% yield, Scheme 5. The ^{1}H NMR spectrum of 20 showed a characteristic olefinic proton signal at δ 6.0-5.4 and the ^{13}C NMR spectrum revealed its symmetrical structure.

The next operation was the 1,4-functionalisation of the diene moiety in 20 in a manner that the functionality introduced could be a double bond equivalent to realise the key diene 12. As the initial attempts at 1,4-functionalisation in 20 employing Backvall's palladium chemistry[10] were unsuccessful, recourse was taken to singlet oxygen 4+2-cycloaddition. Irradiation of a solution of 20 using methylene blue as sensitizer at ~15°C led to a single, highly crystalline, stable endoperoxide 22 in 70% yield in a highly stereoselective reaction, Scheme 6.[11] Some quantity of 21 was also formed in the reaction due to competitive intramolecular

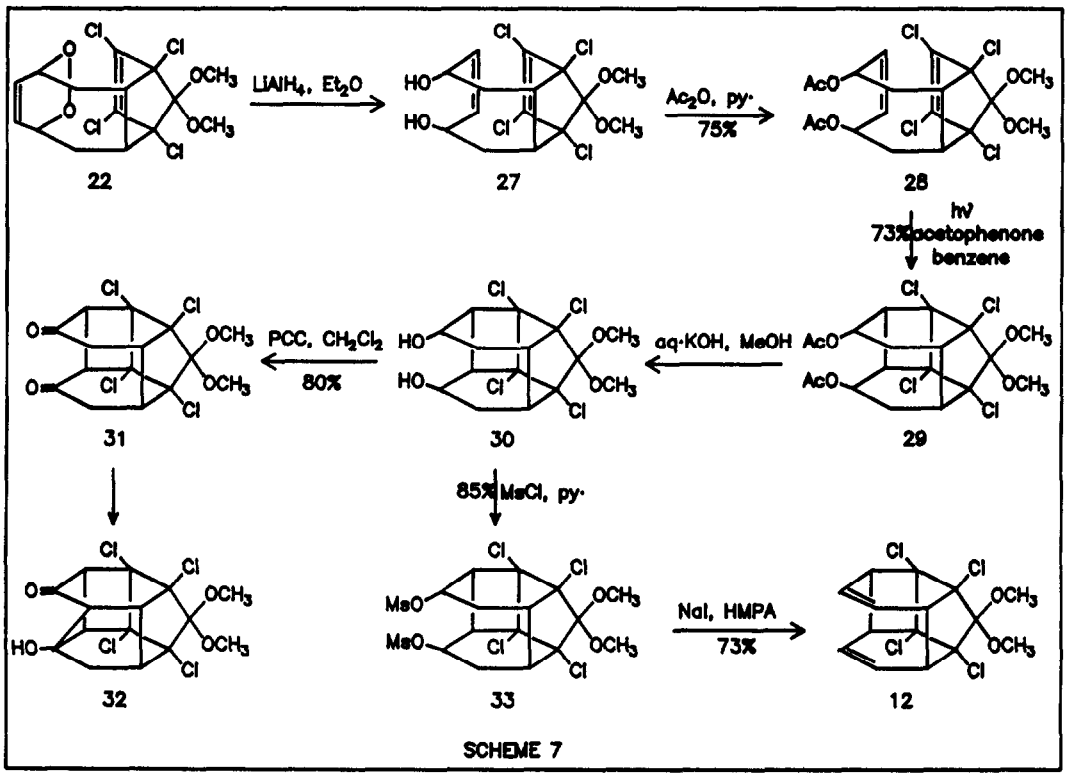
Diels-Alder reaction. While the ^{1}H NMR and ^{13}C NMR spectra of 22 revealed the gross symmetrical structure, its stereostructure was unequivocally established through X-ray crystal structure determination.[12] The addition of $^{1}O_2$ to 20 exhibit remarkable π-facial selectivity and exclusive addition from the etheno-face is observed. This stereoselective addition of $^{1}O_2$ to 20 from the seemingly more hindered face and between the two π-systems indicates that the addition is electronically controlled through secondary orbital stabilisation of the transition state by the etheno π-electrons. As the endoperoxide 22 was not serviceable for the 2+2-photocycloaddition due to the incompatible disposition of the double bonds, it became necessary to cleave the peroxide bridge. Thus, 22 was exposed to Et_3N and the cyclic hemi-acetal 24 was obtained in quantitative yield via the hydroxyketone intermediate 23, Scheme 6. The hemi-acetal was characterised on the basis of the absence of carbonyl absorption in the IR spectrum and presence of a highly deshielded signal at δ 109.4 corresponding to the -O-C-OH moiety in the ^{13}C NMR spectrum. It was subjected to Jones oxidation in the hope of obtaining the enedione 25 as per the literature precedences in similar systems.[13] But, in practice only the intramolecular aldol product 26 having polyquinane structure and derived from 25 was isolated in 68% yield, Scheme 6. Even with milder oxidising agents like PCC and MnO_2, the symmetrical enedione 25 could not be isolated and only 26 was obtained.



SCHEME 6

Since 25 could not be obtained and 26 was not suitable for effecting intramolecular 2+2-cycloaddition, the endoperoxide 22 was reductively opened with $LiAlH_4$ to the diol 27, Scheme 7. The highly polar and insoluble nature of the diol 27 rendered it difficult to characterise and handle, and was therefore, converted to the symmetrical diacetate 28. In 28 we had the masked COT-dimethoxytetrachlorocyclopentadiene adduct (cf. 10) as envisaged in Scheme 3. On UV irradiation, using acetophenone as sensitizer, 28 underwent the desired intramolecular $\pi^2s + \pi^2s$ photocycloaddition to furnish the pentacyclic diacetate 29 in 73% yield, Scheme 7.

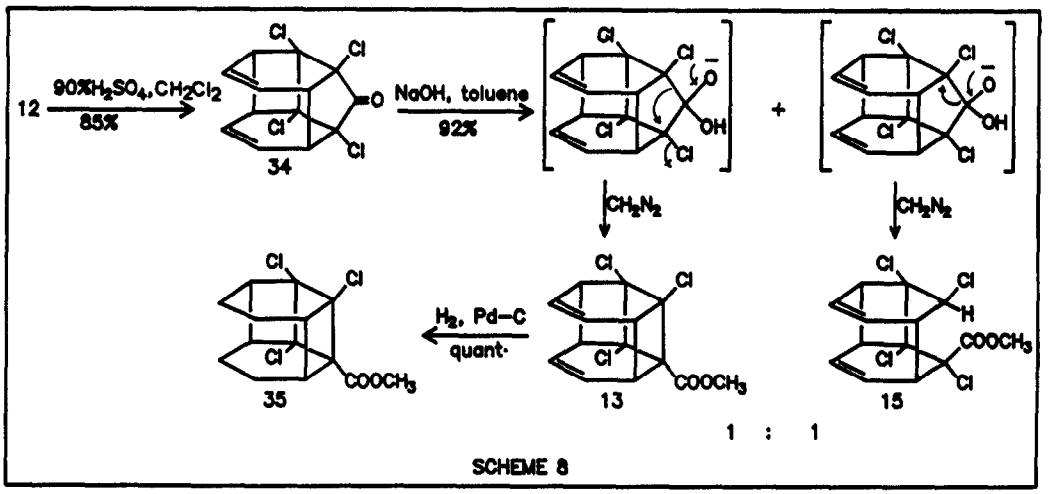
The 1,4-diacetate functionality in 29 now needed to be transformed to the key diene 12. Towards this end, the acetate moieties in 29 were hydrolysed and the resulting endo,endo-diol 30 was oxidised with PCC to the pentacyclic dione 31. However, 31 existed exclusively as the internal aldol 32 and was thus unserviceable for further conversion to 12. It was, therefore, decided to convert the endo,endo-diol 30 to the dimesylate 33 and effect double elimination to the diene 12. However, direct elimination of the mesylate groups in 33 to diene 12 could not be effected. Realising that the endo,endo-stereochemistry of the mesylate groups in 33 was not suited for E_2-type elimination, we opted for a substitution-elimination methodology.[14] Consequently, 33 was treated with NaI in HMPA under high dilution conditions and the much sought-after pentacyclic diene 12 was secured as glistening colourless crystals in 73% yield, Scheme 7. The presence of olefinic proton signals at δ 6.15-6.05 (2H) and δ 5.92-5.82(2H) in the 400 MHz ^{1}H NMR spectrum and a 9 line ^{13}C NMR spectrum with carbon resonances at δ 128.1 and 127.4 established the structure of diene 12. An X-ray crystal structure determination on 12 unambiguously confirmed this formulation.[12]



SCHEME 7

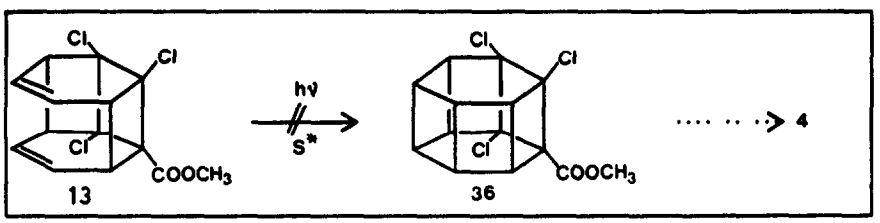
The carbonyl functionality at C_{11} in 12 was unveiled to furnish 34. The keto diene 34 was subjected to the crucial Favorskii ring contraction in toluene containing dry powdered NaOH.[7a,15] The resulting ~1 : 1 mixture of acids was esterified and separated. The less polar ester was

assigned the structure 15 as it exhibited a proton signal at δ 4.34 corresponding to H-C-Cl in the ^{1}H NMR spectrum and a diagnostic 14 line ^{13}C NMR spectrum. The more polar ester 13 turned out to be the required ring contracted diene and exhibited a simplified ^{1}H NMR and a 14 line ^{13}C NMR spectra. The structure of 13 was clinched through catalytic hydrogenation to the known pentacyclic compound 35.[7a] While 13 is formed *via* the expected and desired Favorskii rearrangement, the tetracyclic 15 results from a Haller-Bauer cleavage characteristic of non-enolisable ketones, Scheme 8.[16a] It is known that in many strained ring systems, the Haller-Bauer cleavage competes favourably with Favorskii rearrangement.[7a,16]



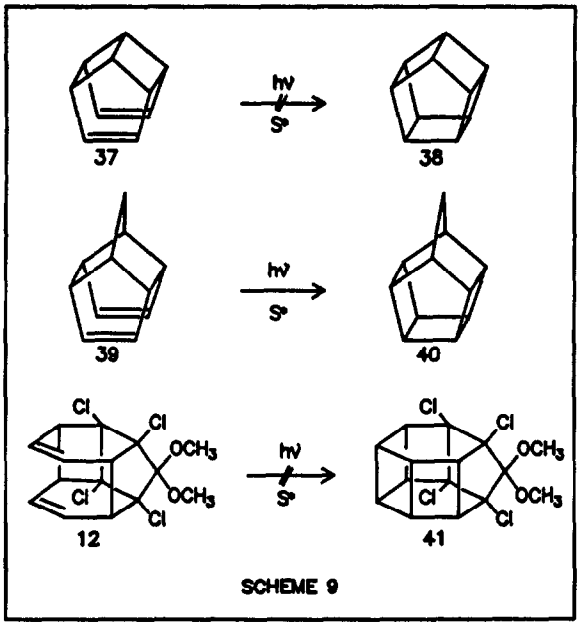
SCHEME 8

With the successful attainment of the penultimate precursor of hexaprismane as contemplated in Schemes 3 and 4, the crucial intramolecular 2+2-photocycloaddition to the [6]-prismane system was attempted. But, disappointingly, 13 could not be induced to undergo 2+2-photocycloaddition to 36 under a variety of conditions employing different solvents and sensitizers. Even recourse to elevated temperatures for irradiation led only to intractable products.



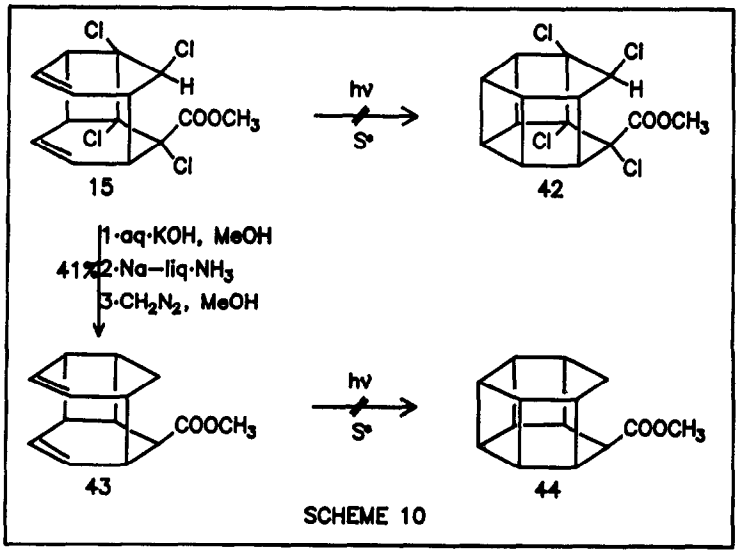
At this stage, we took cognisance of the literature precedence that hypostrophene 37 does not undergo 2+2-photocycloaddition to pentaprismane 38,[17] whereas homohypostrophene 39 undergoes smooth photocycloaddition to homopentaprismane 40,[4b,18] Scheme 9. Consequently, we attempted the intramolecular photocycloaddition in the homologuous diene 12 which is also well suited for conversion to hexaprismane framework *via* ring contraction protocol. However, even 12, whose X-ray crystal structure indicated

that the two double bonds are well within range (2.92 Å) with favourable spatial orientation for an intramolecular $\pi^2s + \pi^2s$ cycloaddition, failed to undergo ring closure to **41**, Scheme 9.



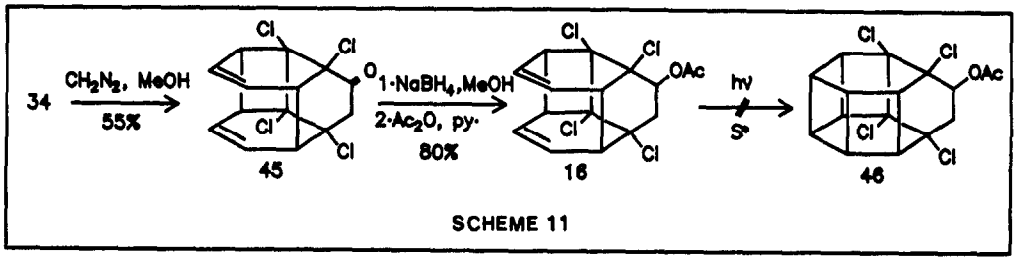
SCHEME 9

An intramolecular 2+2-photocycloaddition on the Haller-Bauer cleavage product **15** was also attempted to gain access to the secohexaprismane framework **42**. However, this reaction also met with failure. In order to overcome possible interference due to chlorine atoms, if any, during photocycloaddition, the ester moiety in **15** was hydrolysed and the acid dehalogenated with Na-liq.NH_3 and reesterified to **43**, Scheme 10. However, **43** also failed to undergo 2+2-photocycloaddition to **44**.



SCHEME 10

At this juncture, attention was turned to the other alternatives indicated in Scheme 11. It appeared reasonable to presume that ring expansion of the norbornane part in 34 to a bicyclo[2.2.2]octane moiety would probably bring the double bonds closer to induce 2+2-photocycloaddition.[19] Hence, 34 was subjected to ring expansion with diazomethane to obtain the keto diene 45. As the direct irradiation of 45 might be complicated due to intervention of Norrish-type reaction, it was reduced with $NaBH_4$ and then converted to the acetate derivative 16. But, 16 also was found to be recalcitrant towards photochemical 2+2-cycloaddition and no evidence for the formation of 46 could be obtained.

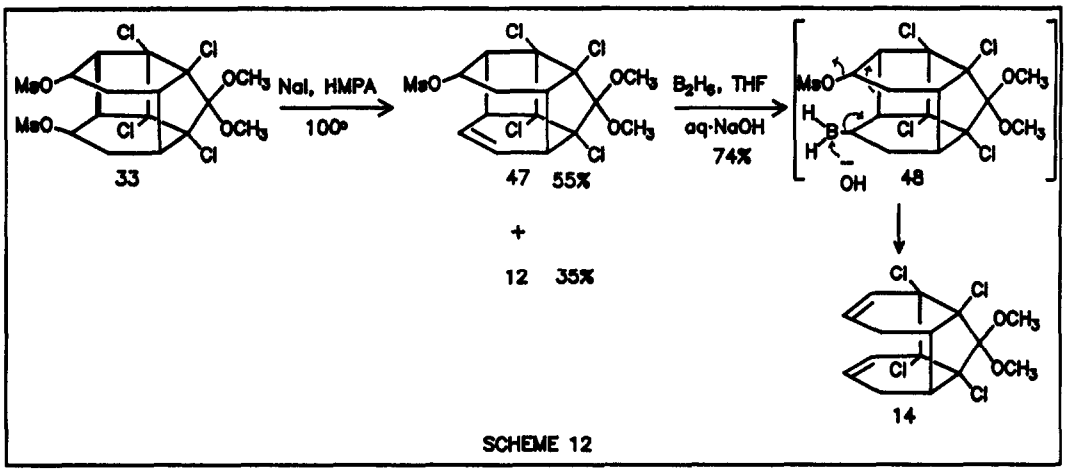


SCHEME 11

The consistent failure of the intramolecular 2+2-cycloadditions in our case, even with double bonds under seemingly favourable spatial disposition, forced us to reassess our options as, such photocyclisations had pivotal role in our scheme of things. A careful scrutiny of the literature revealed that divinylcyclobutane systems do not readily undergo intramolecular 2+2-cycloadditions to furnish multiple fused cyclobutanes due to some stereoelectronic constraints.[4b,20,21] It was therefore decided to employ a diene precursor for the photocyclisation which did not contain the divinylcyclobutane moiety. In Scheme 4, two such precursors 14 and 17 have been identified. However, we recognised the fact that 14 and 17 can only lead to a seco-[6]-prismane system, from which the generation of the target [6]-prismane would be difficult; but given the aberrant behaviour of 12 and 13 towards photoirradiation, settling for 14 appeared to be the best available course.

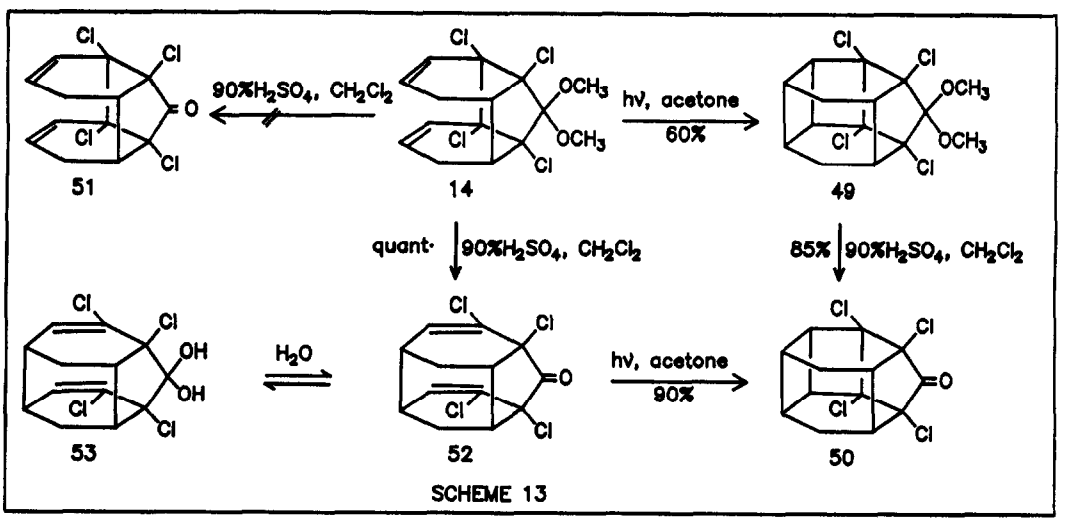
Seco-[6]-Prismane 5

For access to the ring system 5, the tetracyclic precursor 14 had to be prepared (Scheme 4) and this required regioselective removal of one of the cyclobutane bonds in the pentacyclic dimesylate 33 (heavy line, Scheme 12). For this purpose, Marshall's boronate fragmentation strategy[22] appeared to be a promising option. Towards this objective, 33 was first subjected to a controlled NaI-HMPA mediated substitution-elimination reaction and the olefinic monomesylate 47 was readily secured in 55% yield. Next, 47 was sequentially reacted with diborane and aq.NaOH and the reaction took the projected course through 48 to furnish the diene 14 in 74% yield, Scheme 12. The 8 line ^{13}C NMR spectrum of 14 confirmed the restoration of symmetry and the ^1H NMR resonances were fully in consonance with its structure.



Irradiation of a solution of 14 in acetone did take the expected course and the hexacyclic 2+2-cycloadduct 49 was obtained in 60% yield, Scheme 13. The absence of olefinic protons and presence of addition four cyclobutyl protons signal at δ 2.96 in the ^1H NMR and the 9 line ^{13}C NMR spectra were in accordance with its structural formulation. Unmasking of the carbonyl group in 49 led to the hexacyclic ketone 50 (85%) and set the stage for the Favorskii ring contraction protocol.[23]

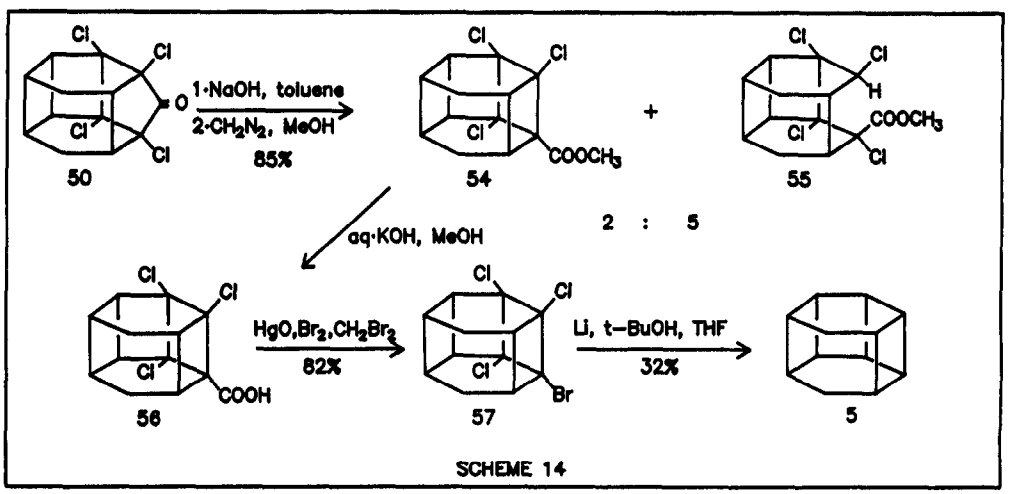
The hexacyclic ketone 50 could also be approached in an alternate way *via* 52 as envisaged in Scheme 13. When 14 was subjected to the carbonyl unveiling operation, a rearranged ketone 52 instead of the expected 51 was obtained in quantitative yield. The ketone 52 showed ready tendency to get hydrated to 53 and the ^{13}C NMR spectrum recorded in DMSO-d_6 indicated the presence of 53. Formation of 52 from 14 involves an extremely facile



[3,3]-sigmatropic transformation (occurring at ~5°C) and can be attributed to the accelerating effect of the remote cationic centre.[24] Intramolecular 2+2-photocycloaddition in 52 proceeded smoothly and the product obtained was identical with 50 obtained earlier.

Favorskii ring contraction of 50 employing the NaOH-dry toluene milieu and esterification furnished a mixture of secohexaprismane ester 54 and the corresponding Haller-Bauer ester 55 in a ~2 : 5 ratio, respectively, in 85% yield, Scheme 14. The 3 line ^{1}H NMR and 14 line ^{13}C NMR spectra of 54 with resonances at δ 168.5, 74.8, 68.6, 66.9, 59.1, 51.9, 44.4, 43.4, 40.0, 31.1, 28.6, 28.2, 17.5, 16.8 were in accordance with its structural formulation. The structure of 55 was established through the presence of a signal at δ 4.38 characteristic of H-C-Cl type functionality in the ^{1}H NMR spectrum and diagnostic ^{13}C NMR resonances.

With the successful attainment of the secohexaprismane framework 54, the next operation was to remove the chloro and ester substituents and acquire the target hydrocarbon 5. This was accomplished in three steps as shown in Scheme 14. The ester group in 54 was hydrolysed to the acid 56 and subjected to modified Hunsdiecker reaction.[25] The resulting tetrahalo compound 57 was subjected to reductive dehalogenation employing Li-t.BuOH-THF[26] to furnish the hexacyclic $C_{12}H_{14}$ hydrocarbon seco-[6]-prismane 5 as a highly volatile waxy solid. Seco-[6]-prismane sublimes readily at ~ 80°C and does not melt till 250°C (sealed tube). The EI and CI mass spectra of 5 did not show a molecular ion peak, but a base peak at m/e 79.0559 corresponding to $M^+/2$ ($C_6H_7^+$) was observed. The 300 MHz ^{1}H NMR spectrum exhibited four resonances at δ 3.12-3.06 (m), 2.90-2.79 (m), 1.78 (d with st., J=14 Hz) and 1.30 (d, J=14Hz) in ratio of 1 : 4 : 1 : 1. The ^{13}C NMR spectrum exhibited four resonances at δ 35.0, 33.8, 29.2 and 20.5 in accordance with its symmetry.



SCHEME 14

In conclusion, we have outlined (Scheme 3 & 4) a novel approach to [6]-prismane involving step-wise, regio- and stereo-controlled, multiple cycloadditions between a cyclobutadiene equivalent and a cyclooctatetraene equivalent. Despite notable success in assembling the pentacyclic precursors 12 and 13 of [6]-prismane, the final target has eluded us due to the unexpected failure of the key 2+2-intramolecular photocycloaddition. However, taking advantage of the built-in flexibility of our approach (Scheme 4), it has been possible to accomplish the synthesis of seco-[6]-prismane 5, the closest possible and one-bond-away, secologue of [6]-prismane.

Experimental

Melting points were recorded on Buchi SMP-20 apparatus and are uncorrected. IR spectra were recorded on Perkin Elmer 297 spectrophotometer and calibrated against the polystyrene absorption at 1601 cm^{-1}. All solid samples were recorded as KBr wafers and liquid samples as thin films between NaCl plates. ^{1}H NMR (100 MHz) and ^{13}C NMR (25.0 MHz) were recorded on JEOL FX-100 spectrometer in $CDCl_3$ solvent. Mass measurements were carried out on JEOL JMS DX-303 spectrometer and Elemental analysis were performed on a Perkin-Elmer 240C-CHN analyser. All reactions were monitored by employing tlc technique using appropriate solvent systems for development. Moisture-sensitive reactions were carried out using standard syringe-septum techniques. Dichloromethane and carbontetrachloride were distilled over P_2O_5. Benzene and toluene were distilled over sodium and stored over pressed sodium wire. Dry ether and dry THF were made by distilling them over sodium-benzophenone ketyl. Pyridine was distilled over potassium hydoxide and stored over potassium hydroxide. All solvent extracts were washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated on a Buchi-EL rotary evaporator. In all gram scale reactions, the yields reported are average yields from a number of experimental runs.

1,10,11,12-Tetrachloro-13,13-dimethoxytricyclo[8.2.1.$0^{2,9}$]trideca-5,11-diene (9):[9] Prepared as per the literature procedure. mp.: 70°C (Lit.[9] 71-72°C); IR:1650, 1608 cm^{-1}; ^{1}H NMR(CCl_4): δ 5.75 (2H, s, -HC=CH-), 3.60 (3H, s, $-OCH_3$), 3.50 (3H, s, $-OCH_3$), 2.88 - 1.28 (10H, m); ^{13}C NMR· δ 131.5, 129.0, 111.8, 79.5, 52.6, 51.5, 50.9, 24.9.

Bromination of 9 (18 and 19):[7b] A mixture of compound 9 (50 g, 0.134 mol), N-bromosuccinimide (24 g, 0.134 mol) and a catalytic amount of AIBN (450 mg) in carbontetrachloride (500 mL) was refluxed for 4h. The reaction mixture was cooled and the floating succinimide filtered off and washed with carbontetrachloride (50 mL). The combined organic layer was washed with 20% HCl (3 x 50 mL), 10% $NaHCO_3$, water and dried. Evaporation of the solvent under reduced pressure furnished a mixture of allylic bromides 18 and 19 (60 g, 100%) as a viscous material which was used as such for the next reaction. IR: 1680, 1655 cm^{-1}. The IR spectrum of the material was found identical to the compound prepared earlier.[7b]

1,10,11,12-Tetrachloro-13,13-dimethoxytricyclo[8.2.1.0^{2,9}]trideca-4,6,11-triene (20):[7c] To a solution of allylic bromide mixture 18 and 19 (30g, 0.066 mmol) in DMSO (150 mL) was added DBU (20g, 0.131 mol) in DMSO (50 mL) dropwise under N_2 atmosphere and the mixture stirred overnight at ~20°C. The reaction mixture was poured into ice-cold water (500 mL) and extracted with ether (4 x 150 mL). The combined ethereal extract was washed with 20% HCl (3 x 50 mL), water and dried. The solvent was removed under vacuum at ~20°C and the residue charged on a silica gel (300 g) column. Elution with 5% ethyl acetate-hexane and evaporation of the solvent under vacuum at ~20°C furnished the triene 20 (17 g, 71%). IR: 1605 cm^{-1}; ^{1}H NMR: δ 6.0-5.4 (4H, m, -HC=CH-), 3.5 (3H, s, -OCH$_3$), 3.45 (3H, s, -OCH$_3$), 2.7 (2H, m, -CH$_2$-CH-), 2.3 (4H, m, -CH$_2$-); ^{13}C NMR: δ 129.6, 129.0, 128.4, 112.2, 79.5, 52.8, 51.5, 47.9, 25.0. Further elution of the column gave the intramolecular 2+2-cycloadduct 21 (4g, 17%) and it was found identical with the sample prepared earlier from our laboratory.[7c] mp.: 177°C (Lit.[7c] 177-178°C)

4,5,6,7-Tetrachloro-15,15-dimethoxy-11,12-dioxatetracyclo[8.2.2.1^{4,7}.0^{3,8}]pentadeca-5,13-diene (22): In a long irradiation vessel fitted with an outer jacket for cold water circulation was placed triene 20 (20 g, 0.054 mol), methylene blue (300 mg) and dichloromethane (350 mL). The solution was irradiated with a 500 W tungsten lamp under a slow stream of bubbling oxygen for 7 days.[11a] The solvent was evaporated off and residue charged on a silica gel (500 g) column. Elution with 10% ethyl acetate-hexane initially furnished the intramolecular Diels-Alder product 21 (5 g, 25%) which was recrystallised from hexane. mp.: 177°C (Lit.[7c] 177-178°C). Further elution of the column with the same solvent furnished the endoperoxide 22 (11 g, 50%) which was recrystallised from dichloromethane-hexane. When the reaction was done on ~ 5 g scale, better yield (~ 70%) of 22 was obtained. mp.: 170°C. IR: 2950, 1600, 1195, 725 cm^{-1}; ^{1}H NMR: δ 6.52-6.4 (2H, m, -HC=CH-), 4.9-4.64 (2H, m, -HC-O-O-), 3.54 (3H, s, -OCH$_3$), 3.52 (3H, s,-OCH$_3$), 2.86-1.9 (6H, series of m). ^{13}C NMR: δ 131.4, 130.0, 111.3, 79.2, 74.6, 52.8, 51.7, 48.3, 32.8. Anal. Calcd. for $C_{15}H_{16}Cl_4O_4$: C, 44.80; H, 4.01. Found· C, 45.04; H, 4.08.

4,5,6,7-Tetrachloro-14,14-dimethoxy-13-oxatetracyclo[8.2.1.1^{4,7}.0^{3,8}]tetradec-5,11-en-1-ol (24): To a solution of endoperoxide 22 (500 mg, 1.24 mmol) in dichloromethane (25 mL) was added Et_3N (250 mg, 2.48 mmol) and the reaction mixture stirred overnight at ~ 25°C.[13] Removal of solvent furnished a residue which was filtered through a silica gel (15 g) column to furnish 24 (500 mg) in quantitative yield. mp.: 141-142°C; IR: 3300, 1610, 1180, 1110, 1030 cm^{-1}; ^{1}H NMR: δ 6.32 (1H, dd, J_1 = 7Hz, J_2 = J_3 = 2Hz, -HC=CH-), 6.12 (1H, d, J = 7Hz, -HC=CH-C-OH), 4.80 (1H, br s,-HC-O-), 3.56 (3H, s, -OCH$_3$), 3.52 (3H, s, -OCH$_3$), 3.10 (1H, s, -O-C-OH), 2.92-1.52 (6H, series of m); ^{13}C NMR: δ 136.0, 134.4, 130.2 (2C), 111.6, 109.4, 79.1, 78.7, 52.7, 51.6, 51.3, 48.4, 46.1, 40.3, 34.0. Anal. Calcd. for $C_{16}H_{16}Cl_4O_4$: C, 44.80; H, 4.01. Found: C, 44.88; H, 4.00. The same product was also obtained when the endoperoxide 22 was stirred with two equivalents of thiourea in methanol.

Oxidation of 24 with Jones reagent: To a solution of compound **24** (100 mg, 0.25 mmol) in acetone (20 mL), Jones reagent was added dropwise (~ 0.5 mL) until tlc (30% ethyl acetate-hexane) indicated the absence of starting material. Acetone was removed under reduced pressure and the residue diluted with water (10 mL). The aqueous phase was extracted with dichloromethane (3 x 10 mL) and the combined organic layer washed with 10% $NaHCO_3$, water and dried. The residue obtained after removal of solvent was charged on a silica gel (5g) column. Elution with 30% ethyl acetate- hexane furnished the intramolecular aldol product **26** (68 mg, 68%) which was recrystallised from dichloromethane- hexane. mp.; 150°C; IR: 3500, 1710, 1610, 1180 cm^{-1}; ^1H NMR: δ 7.42 (1H, d, -HC=CH-C=O), 5.19 (1H, d, -HC=CH-C=O), 3.54 (3H, s, $-OCH_3$), 3.52 (3H, s, $-OCH_3$), 3.2 (2H, m), 2.59 (1H, br s, -HC-C=O), 2.04 (3H, m); ^{13}C NMR: δ 206.7, 164.8, 150.1, 130.6, 130.1, 114.3, 104.9, 91.3, 78.0, 77.5, 59.7, 55.9, 52.5, 51.6, 37.2. Anal. Calcd. for $C_{15}H_{14}Cl_4O_4$: C, 45.01; H, 3.52. Found: C, 44.95; H, 3.65.

1,10,11,12-Tetrachloro-4,7-diacetoxy-13,13-dimethoxytricyclo[8.2.1. $0^{2,9}$]-trideca-5,11-diene (28): In a 500 mL three necked RB flask equipped with a nitrogen inlet and an addition funnel was placed $LiAlH_4$ (2.5 g, 0.065 mol) and ether (100 mL). To this suspension, the endoperoxide **22** (10 g, 0.025 mol) in ether (200 mL) was added dropwise and the reaction mixture stirred for 3h at ~ 25°C. The unreacted $LiAlH_4$ was destroyed by dropwise addition of saturated solution of sodium sulphate. The ethereal layer was separated and the residue extracted with ethyl acetate (3 x 150 mL). The combined organic layer was washed and dried. Removal of solvent gave the crude diol **27** (10 g) which was directly used for the next step. IR: 3500-3250 (br), 1605, 1190 cm^{-1}.

A mixture of the above crude diol **27** (10 g, 0.025 mol), pyridine (80 mL) and acetic anhydride (20 g, 0.196 mol) was stirred at ~ 25°C for 4h. The reaction mixture was poured into ice-cold water (150 mL) and the aqueous layer extracted with ether (3 x 100 mL). The combined ethereal extract was washed thoroughly with 20% HCl (5 x 50 mL), 10% $NaHCO_3$, water and dried. Removal of solvent gave 12 g of crude material which was crystallised from dichloromethane - hexane to furnish the pure diacetate **28** (9 g, 75%). mp.: 171°C; IR: 1750, 1740, 1610, 1245, 1040 cm^{-1}; ^1H NMR: δ 5.68-5.56 (2H, m, -HC=CH-), 5.16-4.96 (2H, m, -HC-O-C(O)-CH_3), 3.62 (3H, s, $-OCH_3$), 3.50 (3H, s, OCH_3), 3.40-3.20 (2H, m, $-CH_2$-CH-), 2.04 (6H, s, -O-C(O)-CH_3), 2.0-1.52 (4H, m, $-CH_2-$); ^{13}C NMR: δ 170.2, 131.3, 128.7, 111.6, 78.8, 72.1, 52.6, 51.7, 50.6, 36.3, 21.1. Anal. Calcd. for $C_{19}H_{22}Cl_4O_6$: C, 46.74; H, 4.54. Found: C, 46.72; H, 4.38.

9,10,12,13-Tetrachloro-11,11-dimethoxypentacyclo[6.5.0.$0^{4,12}$.$0^{5,10}$.$0^{9,13}$] tridecane-2,7-diol, diacetate (29): A solution of the diacetate **28** (8 g, 0.016 mol) and acetophenone (20g) in benzene (800 mL) was purged with nitrogen and irradiated for 8h, using pyrex filter. The solvent was evaporated and acetophenone distilled off at ~ 100°C/1 torr. The residue was

crystallised from dichloromethane-hexane to furnish the pure pentacyclic diacetate 29 (5.8 g, 73%). mp.: 175°C; IR: 1730, 1230, 1010 cm^{-1}; ^1H NMR: δ 5.07 (2H, dd, J_1 = 10Hz, J_2 = 3Hz, -HC-O-C(O)-CH_3), 3.7 (3H, s,-OCH_3), 3.68 (3H, s,-OCH_3), 3.28 (2H, s, cyclobutyl-CH), 3.0 (2H, br s, -HC-CH_2-), 2.56-1.80 (4H, m, -CH_2-), 2.04 (6H, s, -O-C(O)-CH_3); ^{13}C NMR: δ 169.9, 105.1, 72.7, 72.2, 65.2, 51.8, 51.0, 46.8, 41.3, 23.5, 21.0. Anal. Calcd. for $C_{19}H_{22}Cl_4O_6$: C, 46.74; H, 4.54. Found: C, 47.04; H, 4.40.

Hydrolysis of photolysed diacetate 29: The diacetate 29 (5 g, 0.01 mol) was taken in methanol (50 mL) and aq.KOH (1.15 g, 0.02 mol in 5 mL water) was added to it and stirred for 2h at ~ 25°C. Methanol was evaporated off at 50°C in vacuo and the residue was diluted with water (25 mL). The aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic extract was washed with 5% HCl, water and dried. Removal of solvent furnished the crude diol 30 (4g) which was used for the next step without purification. IR: 3500-3100 (br), 1220, 910 cm^{-1};

9,10,12,13-Tetrachloro-11,11-dimethoxy-7-hydroxyhexacyclo[6.5.0.0^{3,7}.0^{4,12}.0^{5,10}.0^{9,13}]tridecan-2-one (32): To a suspension of pyridinium chlorochromate (850 mg, 3.94 mmol) and molecular sieves (4 A°, 1g) in dichloromethane (10 mL) was added a solution of diol 30 (500 mg, 1.23 mmol) at 0°C. The reaction mixture was stirred further for 2h at ~ 25°C, diluted with ether and filtered through a short column of florisil. Removal of solvent and crystallisation from acetone-hexane furnished the aldol product 32 (400 mg, 80%). mp.: 233-244°C; IR: 3400, 1740, 1205, 1020 cm^{-1}; ^1H NMR: δ 3.66 (3H, s, -OCH_3), 3.60 (3H, -OCH_3), 3.56 (1H, m), 3.30-3.06 (3H, m), 2.56 (1H, dt, J_1 = 8Hz, J_2 = 2Hz), 2.34 (1H, s, -OH), 2.12- 2.0 (2H, m). Anal. Calcd. for $C_{15}H_{14}Cl_4O_4$: C, 45.01; H, 3.52. Found: C, 45.18; H, 3.45.

9,10,12,13-Tetrachloro-11,11-dimethoxypentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-tridecane-2,7-dimesylate (33): To a solution of diol 30 (4 g, 0.01 mol) in dry pyridine (20 mL) was added methanesulphonyl chloride (8 g, 0.07 mol) at 0°C. The reaction mixture was stirred further for 5h at ~ 25°C and then poured into ice-cold water (60 mL). The aqueous layer was extracted with ethyl acetate (3 x 40 mL) and the combined organic extract washed successively with 10% HCl (5 x 25 mL), 10% $NaHCO_3$, water and dried. Removal of solvent under vacuum and crystallisation from dichloromethane furnished the pentacyclic dimesylate 33 (4.7 g, 85%). mp.: 165°C; IR: 2950, 1320, 1170, 900 cm^{-1}; ^1H NMR: δ 5.06 (2H, t with st., -HC-OSO_2CH_3), 3.68 (3H, s, -OCH_3), 3.66 (3H, s, -OCH_3), 3.51 (2H, s, cyclobutyl-CH), 3.06 (8H, s, -OSO_2CH_3 and -CH_2-CH-), 2.44-2.2 (4H, m, -CH_2-). Anal. Calcd. for $C_{17}H_{22}Cl_4O_8S_2$: C, 36.44; H, 3.96. Found: C, 36.47; H, 4.01.

9,10,12,13-Tetrachloro-11,11-dimethoxypentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-trideca-2,6-diene (12): In a 100 mL two necked RB flask fitted with a nitrogen inlet was placed a mixture of dimesylate 33 (500 mg, 0.9 mmol), NaI (4 g) and HMPA (50 mL) and the contents heated at 125-130°C for 72h. The reaction mixture was cooled to ~ 25°C and poured into ice-cold water (150 mL). The aqueous layer was extracted with ether (3 x 100 mL) and the combined ethereal extract washed with water and dried. Removal of solvent

furnished a residue which was charged on a silica gel (10 g) column. Elution with 10% ethyl acetate - hexane furnished the pentacyclic diene 12 (240 mg, 73%) which was recrystallised from dichloromethane-hexane. The reaction was done in lots of 500 mg as the above mentioned ratio of reagents was crucial in obtaining optimum yield of the product. mp.: 236°C; IR:3025,2925,1460,1200,730 cm^{-1}; ^1H NMR(400 MHz):δ6.15-6.05 (2H,m,-HC=CH-), 5.92 - 5.82 (2H, m, -HC=CH-), 3.71 (3H, s, $-OCH_3$), 3.67 (3H, s, $-OCH_3$), 3.63-3.58 (2H, m, allylic cyclobutyl-CH), 3.43-3.38 (2H, m, -CH=CH-CH-); ^{13}C NMR: δ 128.1, 127.4, 104.1, 74.1, 72.5, 51.9, 51.1, 50.2, 47.8. Anal. Calcd. for $C_{15}H_{14}Cl_4O_2$: C, 48.94; H, 3.83. Found: C, 49.24; H, 3.72.

9,10,12,13-Tetrachloropentacyclo[6.5.0.$0^{4,12}$.$0^{5,10}$.$0^{9,13}$]trideca-2,6-dien-11-one (34): To a solution of the dimethoxyacetal diene 12 (600 mg, 1.62 mmol) in dichloromethane (1 mL) cooled to 0°C in an ice-bath was added dropwise 90% H_2SO_4 (v/v 6 mL). The reaction mixture was stirred further for 12h at ~ 25°C and then poured over 15g of crushed ice. The aqueous layer was neutralised with sodium bicarbonate and extracted with dichloromethane (3 x 30 mL). The combined organic extract was washed with water and dried. Removal of solvent gave 500 mg of the crude compound which was crystallised from dichloromethane-hexane to furnish the pure keto-diene 34 (450 mg, 85%). mp.: 213°C (shrinks), 218-219°C (melts); IR: 3050, 1805, 725 cm^{-1}; ^1H NMR: δ 6.34-5.80 (4H, m, -HC=CH-), 3.88-3.72 (2H, m, allylic cyclobutyl -CH), 3.44-3.24 (2H, m, -CH=CH-CH-); ^{13}C NMR: δ 201.2, 128.9, 126.9, 71.7, 68.1, 50.6, 46.1. Anal. Calcd. for $C_{13}H_8Cl_4O$: C, 48.49; H, 2.50. Found: C, 48.77; H, 2.35.

1,2,3,12-Tetrachlorotetracyclo[6.4.0.$0^{2,7}$.$0^{4,11}$]dodeca-5,9-diene-3- carboxylic acid methyl ester (15) and 2,3,12-trichloropentacyclo[6.4.0.$0^{2,7}$.-$0^{3,12}$.$0^{4,11}$]dodeca-5,9-diene-1-carboxylic acid methyl ester (13): A suspension of powdered NaOH (1.6 g, 40 mmol) in toluene (10 mL) was refluxed for 30 min and traces of water in NaOH was azeotropically removed using a Dean-Stark apparatus. The RB flask was cooled to ~ 25°C and the keto-diene 34 (400 mg, 1.24 mmol) in toluene (5 mL) was added and the reaction mixture refluxed for 10 min.[7a] It was then cooled, diluted with water (5 mL) and acidified to ~ pH 4 with dil.HCl. The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 x 25 mL). The combined organic layer was washed with water and dried. Removal of solvent gave a crude material which was dissolved in methanol (5 mL) and esterified with ethereal solution of diazomethane at 0°C. A tlc examination (15% ethyl acetate-hexane) of the mixture indicated the presence of two products. The solvent was evaporated off and residue charged on a silica gel (30 g) column. Elution with 10% ethyl acetate - hexane gave the Haller-Bauer product 15 (220 mg, 46%) which was recrystallised from dichloromethane-hexane. mp.: 138°C; IR: 3050, 1740, 1260, 1230, 740, 690 cm^{-1}; ^1H NMR: δ 6.36-6.08 (2H, m, -HC=CH-), 5.74-5.44 (2H, m,-HC=CH-), 4.34 (1H, d, J = 4Hz,-ClCH-), 3.9 (3H, s, -C(O)-OCH_3), 3.88-3.04 (4H, series of m); ^{13}C NMR: δ 168.1, 132.4, 131.5, 126.9, 126.6, 73.6, 72.4, 69.9, 58.8, 54.0, 53.2, 48.9, 44.8, 42.1. Anal. Calcd. for $C_{14}H_{12}Cl_4O_2$: C, 47.49; H, 3.42. Found: C, 47.53; H, 3.33. Continued elution of the column gave the Favorskii product 13 (182 mg, 46%) which was recrystallised from

dichloromethane-hexane. mp.: 135°C; IR: 3050, 1730, 1280, 1220,720 cm^{-1}; ^1H NMR: δ 6.36-6.0 (4H, m, -HC=CH-), 3.79 (3H, s, -C(O)-OCH_3), 3.74-3.36 (4H, m); ^{13}C NMR: δ 167.4, 128.4, 128.2, 127.5. 127.4, 71.9, 67.4, 65.7, 59.3, 52.2, 50.8, 49.9, 49.6, 41.4. Anal. Calcd. for $C_{14}H_{11}Cl_3O_2$: C, 52.94; H, 3.49. Found: C, 52.64; H, 3.42.

Hydrogenation of 13: A solution of compound 13 (5 mg,0.016 mmol) in dry ethyl acetate (3 mL) was hydrogenated at atmospheric pressure over 10%Pd/C (1 mg) for a period of 4h. Pd/C was filtered off and solvent removed to furnish the saturated ester 35 (5 mg, 100%) which was recrystallised from dichloromethane-hexane. mp.: 161°C (Lit.[7a] 161.5-162°C).

Tetracyclo[6.4.0.0^{2,7}.0^{4,11}]dodeca-5,9-diene-3-carboxylic acid methyl ester (44): To a solution of compound 15 (20 mg, 0.056 mmol) in methanol (5 mL) was added aq.KOH (10 mg in 1 mL of water) and the reaction mixture refluxed for 10h. Methanol was removed under vacuum and the residue was diluted with water (5 mL). The aqueous layer was acidified with dil.HCl and extracted thoroughly with ethyl acetate (4 x 5 mL). The combined organic extract was washed and dried. Removal of solvent gave 19 mg of the crude acid which was directly used in the next step.

In a 50 mL three necked RB flask fitted with KOH guard tube and septum, freshly distilled ammonia (15 mL) was placed and sodium (20 mg, 0.86 mmol) was added. The crude acid (19 mg) in THF (1.5 mL) was injected dropwise and the reaction mixture stirred for 15 min. The reaction was quenched by slow addition of NH_4Cl and ammonia was allowed to evaporate. The residue was diluted with water (5 mL). The aqueous layer was acidified with dil.HCl and extracted with ethyl acetate (3 x 10 mL). The combined organic extract was washed with water and dried. Removal of solvent gave the crude dechlorinated acid which was dissolved in methanol (5 mL) and esterified with ethereal solution of diazomethane at 0°C. Methanol was evaporated off and the residue chromatographed over a silica gel (5 g) column. Elution with 5% ethyl acetate - hexane furnished the pure dechlorinated ester 44 (5 mg, 41%) and was recrystallised from hexane. mp.: 85°C; IR: 3050, 2950, 1725, 1430, 1190, 810, 720 cm^{-1}; ^1H NMR: δ 6.4 (1H, dd, $J_1 = J_2 = 8Hz$), 6.2 (1H, dd, $J_1 = J_2 = 8Hz$), 5.42 (2H, dd, $J_1 = J_2 = 8Hz$), 3.53 (3H, s, -C(O)-OCH_3), 3.45 (2H, m, allylic cyclobutyl-CH), 2.8 (3H, m), 1.78 (1H, dd, $J_1=J_2 = 3Hz$, cyclobutyl-CH), 1.65 (1H, dd, $J_1 = J_2 = 3Hz$, cyclobutyl -CH), 1.02 (1H, dd, $J_1 = 4Hz$, $J_2 = 2Hz$, $>C<^{H}_{H}$), 0.9 (1H, dd, $J_1 = 4Hz$, $J_1 = 2Hz$, $>C<^{H}_{H}$).Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.71; H, 7.61.

2,3,6,7-Tetrachloropentacyclo[6.6.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-9,13- dien-4-one (45): To a solution of keto diene 34 (70 mg, 0.217 mmol) in ether (5 mL) maintained at 5-7°C was added a cold ethereal solution (10 mL) of diazomethane (prepared from 200 mg of nitrosomethyl urea) followed by methanol (1 mL). The reaction mixture was kept at 5-7°C for 7h with occasional swirling. Excess diazomethane was destroyed with a few drops of acetic acid and the ethereal solution washed with 10% $NaHCO_3$, water and dried. The solvent was evaporated off and residue charged on a silica gel (10 g) column. Elution with 10% ethyl acetate-hexane furnished the ring expanded product 45 (22 mg, 55% based on recovered starting material) and

was recrystallised from dichloromethane - hexane. mp.: 242-244°C (shrinks), 250°C (decomp); IR: 2925, 1740, 960, 740 cm^{-1}; ^1H NMR: δ 6.44-6.12 (2H, m, -HC=CH-), 5.86-5.56 (2H, m, -HC=CH-), 3.92-3.72(2H, m, allylic cyclobutyl -CH), 3.46 (1H, ½ ABq, J = 20Hz >CH), 3.28-3.16 (2H, m, -HC=CH-CH-), 3.02 (1H, ½ ABq,J = 20Hz, >CH). ^{13}C NMR: δ 196.0, 131.8, 130.6, 127.4, 126.6, 77.6, 75.3, 73.1, 66.1, 49.5 (2C), 48.8, 47.0, 44.7. Anal. Calcd. for $C_{14}H_{10}Cl_4O$: C, 49.99 ; H, 2.999. Found: C, 49.54 ; H, 3.02. Further elution of the column gave the unreacted starting material 34 (32 mg).

2,3,6,7-Tetrachloro-4-acetoxypentacyclo[6.6.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-9,13-diene (16): A solution of compound 45 (20 mg, 0.060 mmol) in methanol (2 mL) was cooled in an ice-bath and sodium borohydride (3 mg, 0.079 mmol) was added and the reaction mixture stirred for 30 min. Methanol was removed under reduced pressure and the residue diluted with water (5 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic extract was washed with water and dried. Removal of solvent gave the hydroxy diene (20 mg) which was directly used for the next step. A mixture of the above obtained hydroxy diene (20 mg), acetic anhydride (5 drops) and pyridine (2 mL) was stirred for 4h at ~ 25°C. The reaction mixture was poured into ice-cold (10 mL) water and extracted with ethyl acetate (3 x 10 mL). The combined organic extract was washed successively with 10% HCl (5 x 5 mL), water and dried. Removal of solvent and crystallisation from dichloromethane - hexane furnished the pentacyclic acetate 16 (18 mg, 80%). mp.: >250°C. IR: 1740, 1220, 1060, 960, 740 cm^{-1}; ^1H NMR: δ 6.22 (2H, dd, J_1 = 8Hz, J_2 = 6Hz, -HC=CH-), 5.79 (2H, dd, J_1 = J_2 = 7Hz, -HC=CH-), 5.26 (1H, dd, J_1 = 9Hz, J_2 = 6Hz, -HC-O-C(O)-CH_3), 3.79 (2H, dd, J_1 = J_2 = 5Hz, allylic cyclobutyl -CH), 3.09 (2H, dd, J_1 =J_2 = 5Hz, -HC=CH-CH-), 2.76 (1H, ½ ABq, J = 8Hz, >CH), 2.68 (1H, ½ ABq, J = 4Hz, >CH), 2.14 (3H, s,-O-C(O)—CH_3). Anal. Calcd. for $C_{16}H_{14}Cl_4O_2$: C, 50.56; H, 3.71. Found: C, 50.41; H, 3.65.

9,10,12,13-Tetrachloro-11,11-dimethoxypentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-tridecan-2-ene-7-mesylate (47): A mixture of dimesylate 33 (500 mg, 0.9 mol), NaI (2 g) and HMPA (40 mL) was heated at 100°C for 30h under N_2 atmosphere. The reaction mixture was cooled to ~ 25°C and poured into ice-cold water (150 mL). The aqueous layer was extracted with ether (5 x 125 mL) and the combined ethereal extract was washed and dried. The residue obtained after removal of solvent was charged on a silica gel (25 g) column. Elution with 10% ethyl acetate - hexane furnished first the diene 12 (85 mg, 35% based on starting material recovery) and was recrystallised from dichloromethane- hexane. mp.: 236°C. Continued elution with 20% ethyl acetate - hexane furnished the monomesyl olefin 47 (186 mg, 55% based on starting material recovery) which was recrystallised from dichloromethane-hexane. mp.: 167°C; IR: 2950, 1335, 1200, 1170, 940, 880 cm^{-1}; ^1H NMR : δ 6.24 - 6.04 (2H, m, -HC=CH-), 4.9-4.68 (1H, t, J = 6Hz, -HC-OSO_2CH_3), 3.68(3H, s -OCH_3), 3.64(3H, s, -OCH_3), 3.64-3.04 (4H, m), 3.02 (3H, s, -OSO_2CH_3), 2.12 (2H, dd, J_1 = J_2 = 5Hz, -CH_2-). Anal. Calcd. for $C_{16}H_{18}Cl_4O_5S$: C, 41.40; H, 3.90. Found: C, 41.43; H, 3.79. Further

elution of the column with 50% ethyl acetate - hexane gave the unreacted dimesylate 33 (95 mg).

1,2,7,9-Tetrachloro-8,8-dimethoxytetracyclo[7.4.0.0^{2,7}.0^{6,10}]trideca-3,12-diene (14): Into a 50 mL three necked RB flask equipped with a nitrogen inlet, bubbler, condenser and mercury seal was introduced THF (20 mL) and the flask was cooled to -78°C. In another 25 mL three necked RB flask equipped with nitrogen inlet and an outlet connected to the bubbler mentioned above, was placed $NaBH_4$ (1g, 0.026 mol) and diglyme (5 mL). $BF_3.Et_2O$ (2 mL, 0.016 mol) was added dropwise with a syringe and the diborane generated was bubbled into the flask containing THF. Then, the monomesylate 47 (500 mg, 1.08 mmol) in THF (5 mL) was added to the diborane solution and stirred for 2h at of ~ 25°C. The flask was cooled in an ice-bath and 25% NaOH solution (4 mL) was added dropwise and the contents of the flask refluxed for 1.5h.[22] After cooling, the reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with dil.HCl, 10% $NaHCO_3$, water and dried. Removal of solvent gave 400 mg of crude material which was filtered through a silica gel (10 g) column using 10% ethyl acetate-hexane as the eluent. The pure diene 14 obtained (295 mg, 74%) was recrystallised from hexane. mp.: 164-165°C; IR: 2950, 1445, 1240, 980 cm^{-1}; ^{1}H NMR: δ 5.8-5.56 (2H, ddd, J_1 10Hz, J_2 = J_3 = 4Hz, -HC=C<u>H</u>-), 5.52-5.28 (2H, ddd, J_1 = 10Hz, J_2 = J_3 = 2Hz, -C<u>H</u>=CH-), 3.74 (3H, s, -OC<u>H</u>$_3$), 3.68 (3H, s, -OC<u>H</u>$_3$), 3.0 (2H, m, -<u>H</u>C-CH$_2$-), 2.34 (2H ,½ ABq with st., J = 20 Hz, >C<$^{H}_{H}$), 2.0 (2H, ½ ABq with st., J = 20 Hz, >C<$^{H}_{H}$). ^{13}C NMR: δ 130.8, 120.0, 104.5, 72.5 (2C), 52.0, 50.8, 40.4, 20.7. Anal. Calcd. for $C_{15}H_{16}Cl_4O_2$: C, 48.68; H, 4.36. Found: C, 48.92; H, 4.37.

9,10,12,13-Tetrachloro-11,11-dimethoxyhexacyclo[6.5.0.0^{2,7}.0^{4,12}. 0.^{5,10}.-0^{9,13}]tridecane (49): A solution of the diene 14 (350 mg, 0.95 mmol) in acetone (125 mL) was purged with a slow stream of nitrogen and irradiated for 14h, using pyrex filter. The solvent was removed and the residue chromatographed over a silica gel (12 g) column. Elution with 4% ethyl acetate-hexane furnished the photolysed product 49 (152 mg, 60% based on starting material recovery) which was recrystallised from dichloromethane-hexane. mp.: 236-237°C; IR: 2950, 1450, 1430, 1200 cm^{-1}; ^{1}H NMR: δ 3.66 (3H, s, -OC<u>H</u>$_3$), 3.62 (3H, s, -OC<u>H</u>$_3$), 2.96 (4H, m, cyclobutyl-C<u>H</u>), 2.8-2.6 (2H, m, -ClC-C<u>H</u>-), 1.62 (4H, br s, -C<u>H</u>$_2$-). ^{13}C NMR: δ 106.5, 75.6, 73.0, 51.7, 51.0, 43.4, 39.6, 28.1, 16.3. Anal. Calcd. for $C_{15}H_{16}Cl_4O_2$: C, 48.68; H, 4.36. Found: C, 48.60; H, 4.34. On further elution the starting material 14 (80 mg) was recovered.

9,10,12,13-Tetrachlorohexacyclo[6.5.0.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tridecan-11-one (50): The hexacyclic compound 49 (150 mg, 0.40mmol) in dichloromethane (1 mL) was cooled to 0°C in an ice-bath and 90% H_2SO_4 (v/v) (4 mL) was added dropwise over a period of 15 min. The reaction mixture was stirred further for 10h at ~ 25°C and then poured over 10 g of crushed ice. The aqueous layer was neutralised with $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The combined organic extract was washed and dried. Removal of solvent and crystallisation from dichloromethane-hexane

furnished the pure hexacyclic ketone 50 (110 mg, 85%). mp.: 250-251°C; IR: 2925, 1810, 770, 600 cm^{-1}; ^1H NMR:δ 3.24-2.6 (6H, m), 1.76 (4H,br s,-C$\underline{H}_2$-). Anal. Calcd. for $C_{13}H_{10}Cl_4O$: C, 48.18; H, 3.11. Found: C, 48.13; H, 3.06.

6,7,9,10-Tetrachloro-8,8-dimethoxytetracyclo[7.4.0.0.^{2,7}0^{4,12}]tri-deca-5,10-diene (52): The tetracyclic diene 14 (25 mg, 0.067 mmol) in dichloromethane (0.5 mL) was cooled to 0°C in an ice bath and 90% H_2SO_4 (v/v) (2 mL) was added to it dropwise over a period of 5 min. the reaction mixture was stirred further for 5 h at ~ 25°C and then poured over 8g of crushed ice. The aqueous layer was neutralised with $NaHCO_3$ and extracted with dichloromethane (3 x 10 mL). The combined organic extract was washed and dried. Removal of solvent and recrystallisation from dichloromethane-hexane furnished 52 in near quantitative yield (20 mg). mp.: 250-251°C (decomp.); IR: 3050, 1760, 1620, 730 cm^{-1}; ^1H NMR: δ 6.0-5.84 (2H, m, -$\underline{H}$C=C$\underline{H}$-), 3.36-3.16 (4H, m), 1.85 (4H, ABq with st, J=10Hz, -C$\underline{H}_2$-). On storage and in DMSO, 52 readily forms a hydrate 53. ^1H NMR (DMSO-d_6):δ6.24-6.1 (2H, m), 3.34 (4H, s), 1.88 (4H, ABq, J=10 Hz); ^{13}C NMR(DMSO-d_6): δ 143.1, 133.6, 108.8, 68.7, 32.4, 22.6, 19.7; Anal. Calcd. for $C_{13}H_{10}Cl_4O$: C, 48.19; H, 3.11. Found: C, 48.15; H, 3.16.

Irradiation of 52: A solution of 52 (7 mg, 0.021 mmol) in acetone (10 mL) was purged with a slow stream of nitrogen and irradiated for 4h using pyrex filter. The solvent was evaporated and the residue filtered through a short silica gel column. Elution with 30% ethyl acetate-hexane furnished the hexacyclic ketone 50 (6.5 mg, 90%). mp.: 250°C; The IR spectrum was identical with the compound 50 obtained in the above experiment.

2,3,12-trichlorohexacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{4,11}.0^{5,10}]dodecane-1-carboxylic acid methyl ester (54) and 3,14,11,12-Tetrachloropentacyclo[6.4.0.0^{2,7}.-0^{3,12}.0^{5,10}]dodecane-4-carboxylic acid methyl ester (55): A suspension of powdered NaOH (520 mg, 13 mmol) in toluene (5 mL) was refluxed for 30 min and traces of water in NaOH were azeotropically removed using a Dean-Stark apparatus. The RB flask was cooled to ~ 25°C and the hexacyclic ketone 50 (130 mg, 0.4 mmol) in toluene (3 mL) was added and the reaction mixture refluxed for 10 min. The flask was then cooled, diluted with water (5 mL) and acidified to ~ pH 4 with dil.HCl. The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed and dried. Removal of solvent gave a crude material which was dissolved in methanol (3 mL) and esterified with ethereal solution of diazomethane at 0°C. The solvent was evaporated off and residue charged on a silica gel (20 g) column. Elution with 5% ethyl acetate - hexane gave the Haller-Bauer product 55 (85 mg, 60%) which was recrystallised from dichloromethane-hexane. mp.: 167°C; IR: 2950, 1740, 1250, 750 cm^{-1}; ^1H NMR: δ 4.38 (1H,d, J = 4Hz,ClC$\underline{H}$-), 3.88(3H, s,-C(O)-OC$\underline{H}_3$), 3.6-1.5 (10H, series of m). ^{13}C NMR: δ 169.8, 75.6, 74.3, 71.8, 61.8, 53.8, 45.5, 41.5, 38.8, 36.1, 29.4, 28.7, 21.1, 18.4. Anal. Calcd. for $C_{14}H_{14}Cl_4O_2$: C, 47.22; H, 3.96. Found: C, 47.27; H, 3.83. Further elution of the column furnished the required Favorskii product 54 (32 mg, 25%) which was recrystallised from dichloromethane- hexane. mp.: 159°C; IR: 2950, 1740, 1220, 1115, 720 cm^{-1}. ^1H NMR: δ 3.76 (3H, s, -C(O)-OC$\underline{H}_3$),

3.32-2.8 (6H, m), 2.8-2.6 (4H, m, -C<u>H</u>$_2$-); ^{13}C NMR: δ 168.5, 74.8, 68.6, 66.9, 59.1, 51.9, 44.4, 43.4, 40.0, 31.1, 28.6, 28.2, 17.5, 16.8; HRMS: $M^+/2$ Calcd. for $C_{14}H_{13}Cl_3O_2$: 171.0303 and 146.9769. Found: 171.0186 and 146.9773. The molecular ion peak was not seen in the mass spectrum.

1-Bromo-2,3,12-trichlorohexacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{4,11}.0^{5,10}]dodecane (57): To a solution of the hexacyclic ester 54 (25 mg, 0.078 mmol) in methanol (2 mL) was added KOH (10 mg) in water (0.5 mL) and the reaction mixture refluxed for 3h. Methanol was removed under vacuum and the residue diluted with water (5 mL) and acidified with dil. HCl. The aqueous layer was extracted with ethyl acetate (3 x 10 mL) and the combined organic extract washed and dried. Removal of solvent gave the crude acid 56 (24 mg) which was used directly for the next step.

A mixture of the above crude acid 56 (24 mg) in dibromomethane (2 mL) and red mercuric oxide (35 mg, 0.16 mmol) was refluxed for 1h. Then, 2 drops of bromine was added and it was refluxed further for 2h.[25b] The reaction mixture was diluted with dichloromethane (15 mL) and washed with water and dried. The residue obtained after removal of solvent was charged on a neutral alumina (3 g) column. Elution with 2% ethyl acetate - hexane furnished the bromo compound 57 (22 mg, 82% from 54) which was recrystallised from dichloromethane-hexane. mp.: 180°C (darkens), 197°C (melts); IR: 2950, 1250, 720 cm^{-1}; ^{1}H NMR: δ 3.44-3.10 (4H, m, cyclobutyl-C<u>H</u>), 3.08-2.84 (2H, m, -<u>H</u>C-CH$_2$-), 1.68 (4H, m, -C<u>H</u>$_2$-). HRMS: $M^+/2$ Calcd. for $C_{12}H_{10}Cl_3Br$: 192.9243 and 146.9769. Found: 192.9170 and 146.9785. The molecular ion peak was not seen in the mass spectrum.

Hexacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{4,11}.0^{5,10}]dodecane(secohexaprismane) (5): In a 25 mL three necked RB flask equipped with a nitrogen inlet, condenser and septum was placed compound 57 (22 mg, 0.064 mmol), THF (4 mL) and t-BuOH (0.06 mL). Lithium metal (14 mg, 0.002 g atom) was added to it as small pieces and the reaction mixture refluxed with vigorous stirring for 3h.[26] The unreacted lithium was filtered off and THF removed under reduced pressure. The residue was diluted with water (5 mL) and extracted with pentane (3 x 5 mL). The organic extract was washed with water and dried. Removal of solvent gave the crude hydrocarbon and it was charged on a silica gel (1 g) column. Elution of the column with pentane furnished secohexaprismane 5 (3.2 mg, 32%) and was sublimed (~ 80°C) to give a waxy solid.mp.:>250°C(sealed tube);IR.2950 cm^{-1};^{1}H NMR(300 MHz):δ3.12-3.06 (2H, m), 2.90-2.79 (8H, m), 1.78 (2H, d with st., J= 14Hz, >C<$^{\underline{H}}_{H}$), 1.30 (2H, d, J = 14Hz, >C<$^{\underline{H}}_{H}$). ^{13}C NMR: δ 35.0, 33.8, 29.2, 20.5. HRMS: $M^+/2$ Calcd. for $C_6H_7^+$: 79.0548. Found: 79.0559. The molecular ion peak was not seen in the mass spectrum.

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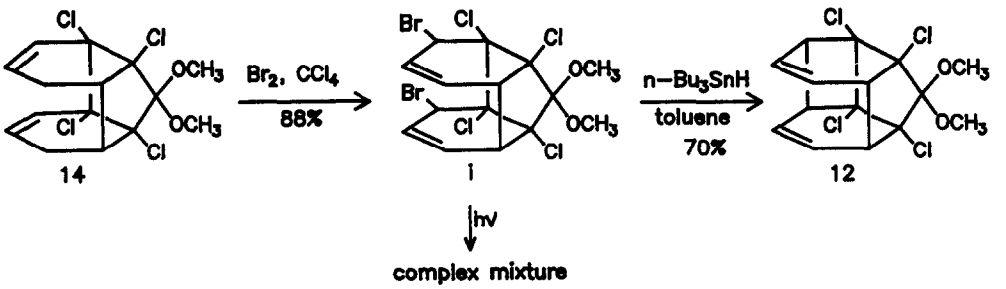

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