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Synthetic Studies Towards Prismanes: Exploratory Efforts En Route to [7]-Prismane Homo- and Secologues

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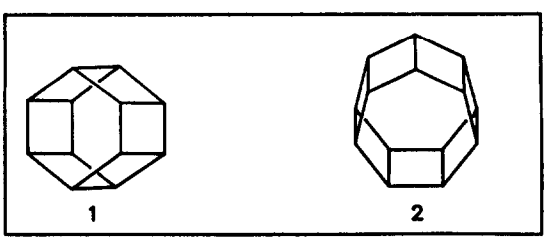
Abstract

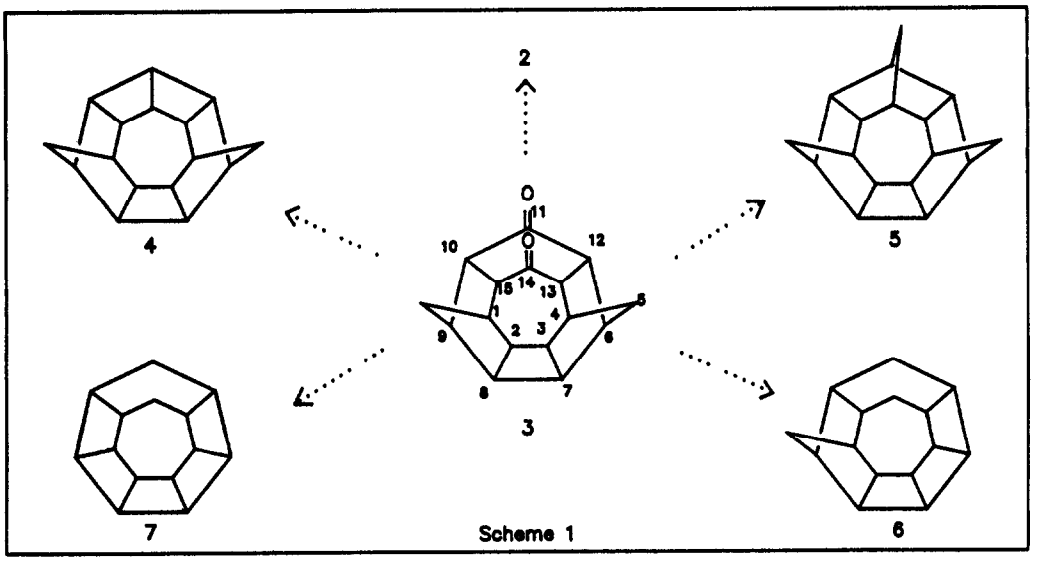
Novel heptacyclic triones 8 and 9 have been synthesised. A series of probing experiments on the heptacyclic ketones 3, 8 and 9, in quest for [7]-prismane homo- and secologues are described. Synthesis of novel polyhedranes 23-25 through thermal 2+2-cycloreversion of 3, 8 and 17, respectively, has been achieved. Our results point to the need for devising de novo strategy for the creation of higher prismanic frameworks.

Introduction

In the preceding two reports, we have outlined our synthetic quest for [6]-prismane 1.[1] While these travails have led to considerable progress towards 1, the ultimate target molecule remains unconquered. The next higher homologue of 1, the [7]-prismane 2 is a still more formidable proposition, with its $C_{14}H_{14}$ octacyclic framework of D_{7h} symmetry, constituted through the cis, syn, cis union of seven four membered rings. In any synthetic pursuit of 2, the problems posed by the considerably higher steric energy (215.3 Kcal/mol) [2a] compared to 1 (164.4 kcal/mol) and the large deviation in the tetrahedral C-C-C angle (128.6° for 2)[2b,c] from the normal range have to be overcome by some very deft manoeuvres. It is hardly any surprise, therefore, that practically no synthetic efforts, not even a strategy, targeted towards 2 has made its presence in the literature.[3] Herein, we describe some probing experiments, aimed at 'testing the waters' in pursuit of 2.



During the synthesis of 1,4-bishomo-[6]-prismane ("garudane"),[4] we developed a short (3 steps) and efficient approach to the heptacyclic dione 3 from the readily available norbornenobenzoquinone and cyclopentadiene. Interestingly, the dione 3 has present in it two face-to-face seven membered rings joined together through various bridges and, therefore, its framework is eminently suitable for further evolution towards [7]-prismane homo- and secologues. For example, either direct C-C bond or a one bond carbon bridge between carbon atoms bearing carbonyl groups could eventuate into 1,4-bishomo[7]-prismane 4 or 1,3,5-trishomo[7]-prismane 5 frameworks, respectively. Additionally, if one or both of the methano bridges in 3 could be functionalised to set up Favorskii ring contraction, homo-seco[7]-prismane 6, seco-[7]-prismane 7 or even 2 itself could be attained, Scheme 1. Emanating from these thoughts, our efforts initially focused on the synthesis of bridge functionalised derivatives of 3, e.g., 8 and 9 and on manoeuvres to establish a C-C bond between C_{11} and C_{14}, the site of the carbonyl groups in 3.

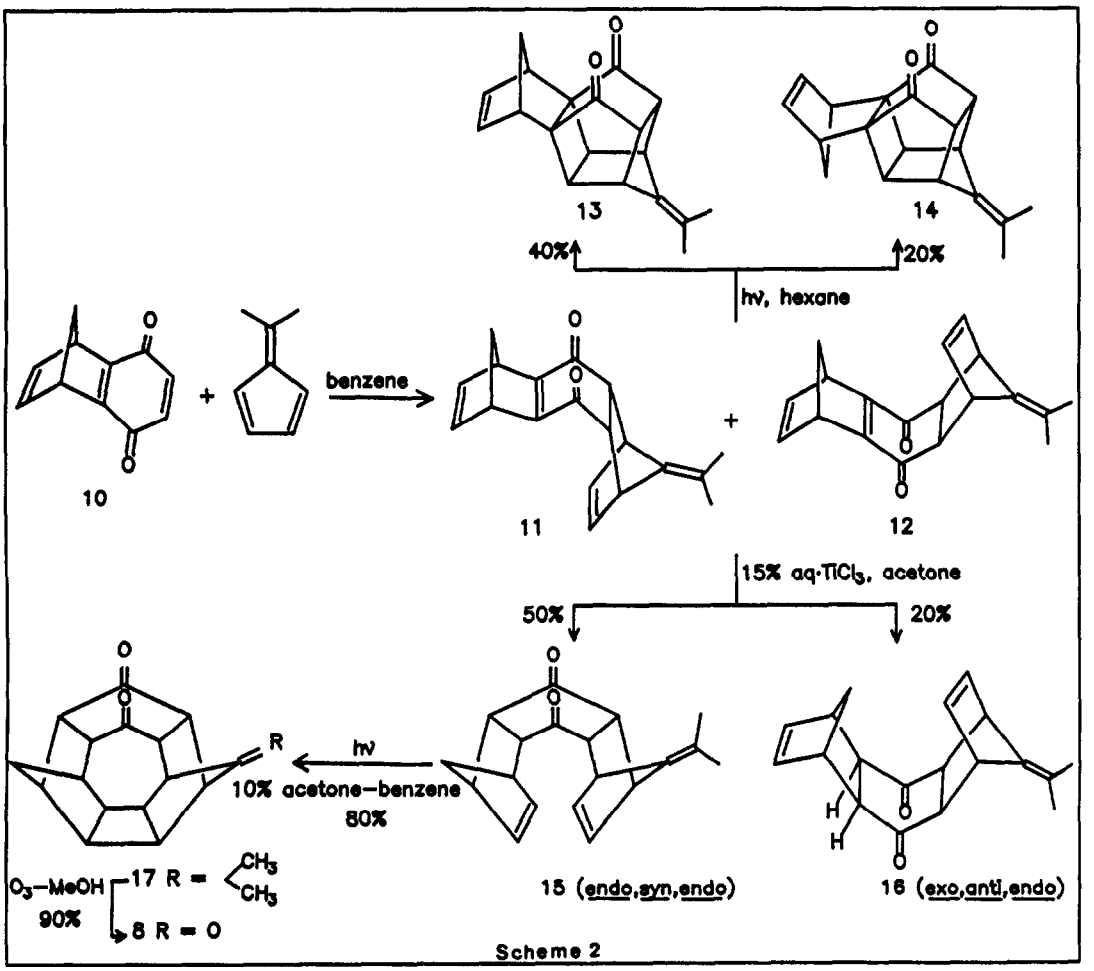


Scheme 1

Synthesis of heptacyclic triones 8 and 9

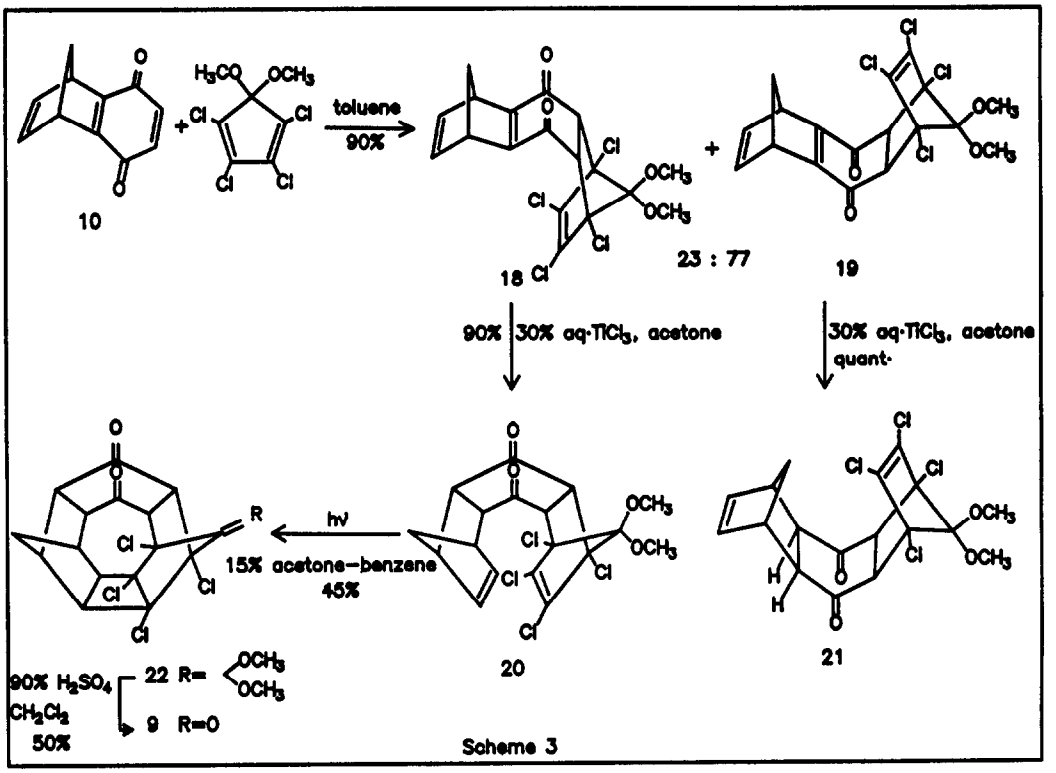
Keeping in view the steps through which dione 3 was synthesised, a convenient route to 8 was devised. Diels-Alder reaction between dimethylfulvene and norbornenobenzoquinone 10 furnished a mixture of endo,syn-11 and endo,anti-12 adducts in ~ 2 : 1 ratio. While the presence of 11 and 12 was quite apparent in the ^1H NMR spectrum of the crude reaction mixture, attempts to separate them led to substantial decomposition through retro-Diels-Alder reaction. However, the presence of 11 and 12 and their stereochemistry could be firmly established through the irradiation of this mixture to a readily separable mixture of heptacyclic diones 13 and 14, respectively. The ene-dione moiety in the mixture of adducts 11 and 12 was reduced with aq.$TiCl_3$[5] as described by us for related compounds[1b,4] to furnish 15 and 16 in good yield. The stereostructure of the minor pro-

duct 16 follows from the shielding of the 7-methylene group of the norbornene moiety by the spatially proximate double bond of the other norbornene moiety. The major product of the aq.$TiCl_3$ reduction had the required structure 15 and underwent smooth intramolecular 2+2-cycloaddition to furnish the heptacyclic dione 17. The masked carbonyl functionality in 17 was revealed through the oxidative disposal of the isopropylidene moiety in 17 to furnish the heptacyclic trione 8 in good yield, Scheme 2. The 9 line ^{13}C NMR spectrum of 8 was fully consonant with its structure.



Scheme 2

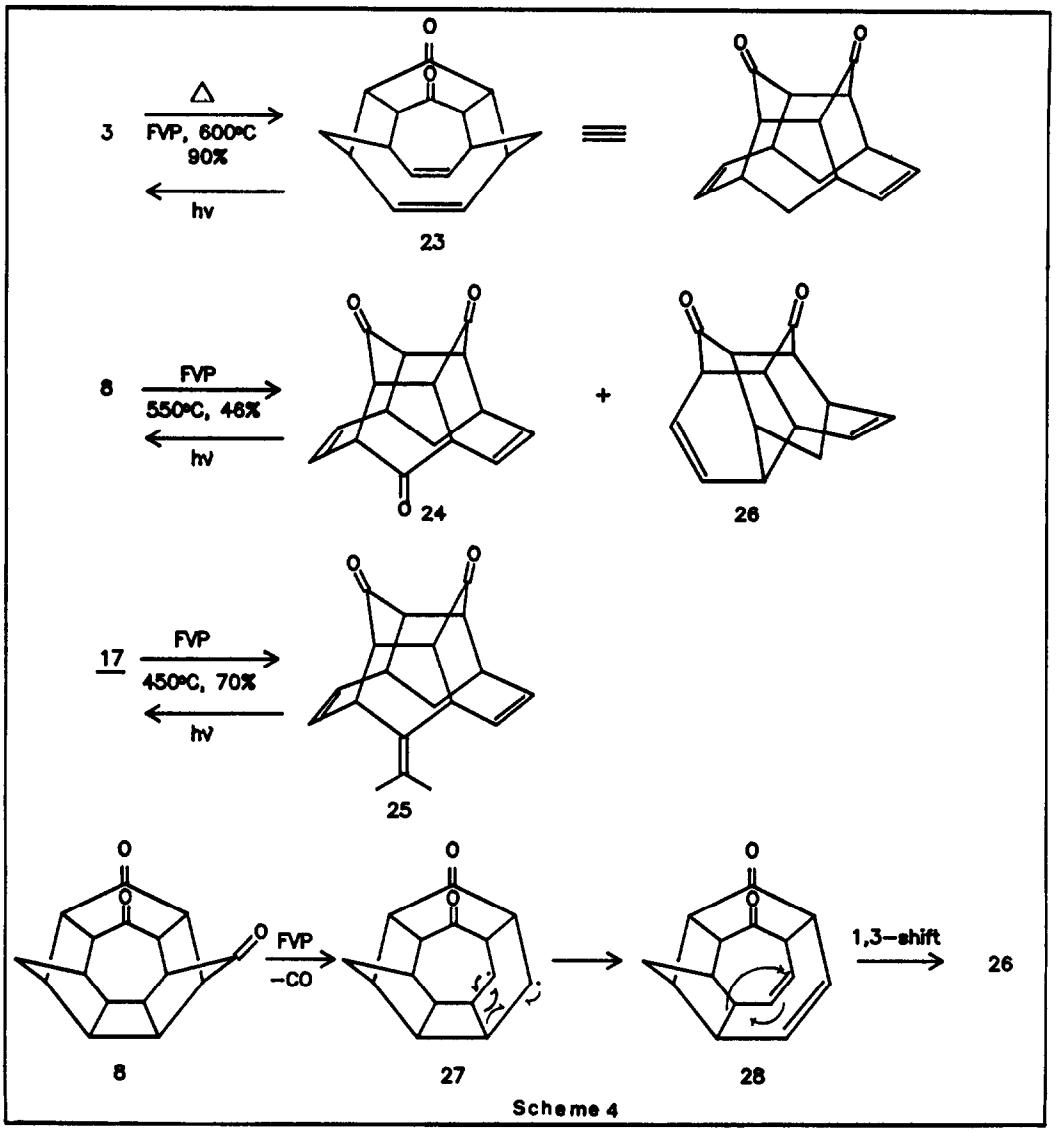
The tetrahalo-trione 9 was likewise assembled from 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and 10 as shown in Scheme 3. The diastereoselectivity in this cycloaddition was reversed and the desired endo,syn adduct 18 was obtained as the minor isomer.[6] Both, the adducts 18 and 19 underwent aq.$TiCl_3$ reduction with complete regio- and stereocontrol to furnish 20 and 21, respectively.[5] As expected, 20 on sensitised irradiation furnished the 2+2-cycloaddition product 22, in which the carbonyl group was unmasked to furnish the heptacyclic tetrachloro trione 9, Scheme 3.



Scheme 3

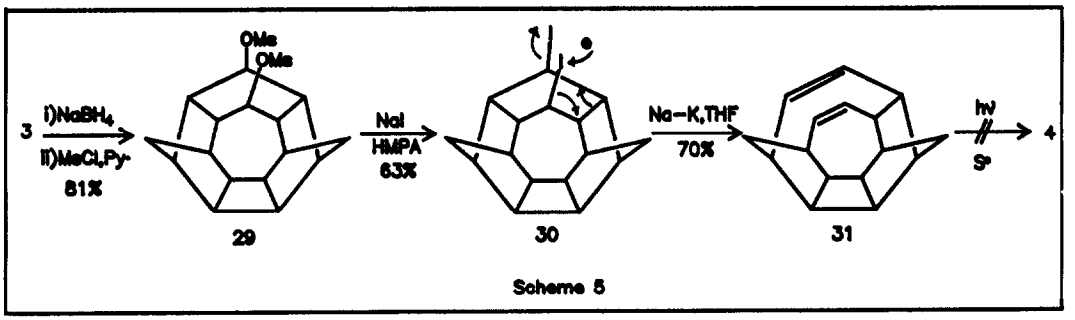
Reactions of heptacyclic ketones 3, 8 and 9

One of the first reactions to be attempted was the pinacolic coupling between the two transannular carbonyl groups in 3 and 8 to gain access to the system 4. Both 3 and 8 responded uneventfully to the various recipes (e.g., $TiCl_3$,[7] Mg-$TiCl_4$[8]) employed for this purpose. Attributing this failure to the unfavourable geometrical disposition of the carbonyl groups in the heptacyclic framework,[9] we sought to restructure 3, in a reversible manner, to secure better alignment of the carbonyl groups. For this purpose, 3 was subjected to thermal activation under flash pyrolysis conditions (600°/0.1torr)[10] to furnish the 2+2-cycloreversion product 23 in near quantitative yield. Pentacyclic dione 23 reversed back to 3 on irradiation in the presence of a sensitiser. The thermal 2+2-cycloreversion was found to be a general reaction of the heptacyclic system and ketones 8 and 17 furnished the interesting polyhedranes 24 and 25, respectively. In the case of 8, a decarbonylated and rearrangement product 26 was also obtained and its structure was established through X-ray crystal structure determination.[11] Formation of 26, probably proceeds through the intermediate diene 28, Scheme 4. While the novel pentacyclic diones 23-25 became readily accessible, they too showed complete resistance towards pinacolic coupling which was expected to establish the crucial C-C bond.



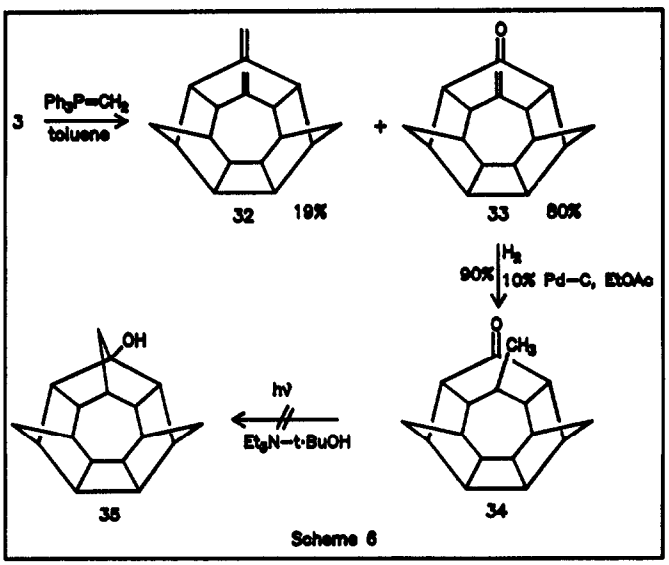
Scheme 4

Next, we attempted to install the C_{11}-C_{14} bond in 3 in an interesting but more circuitous way. $NaBH_4$ reduction of 3 furnished an endo,endo diol, which was converted to the dimesylate 29. Reaction of 29 with NaI in HMPA furnished the exo,exo-diiodide 30, which underwent smooth 1,4-fragmentation in the presence of Na-K alloy to furnish the diene 31 (Scheme 5), which was thought to be an excellent precursor of the 1,4-bishomo-[7]-prismane system 4. Irradiation of 31, under different conditions and sensitiser, proved totally unsuccessful and the 2+2-cycloaddition product 4 was not formed.[12]



Scheme 5

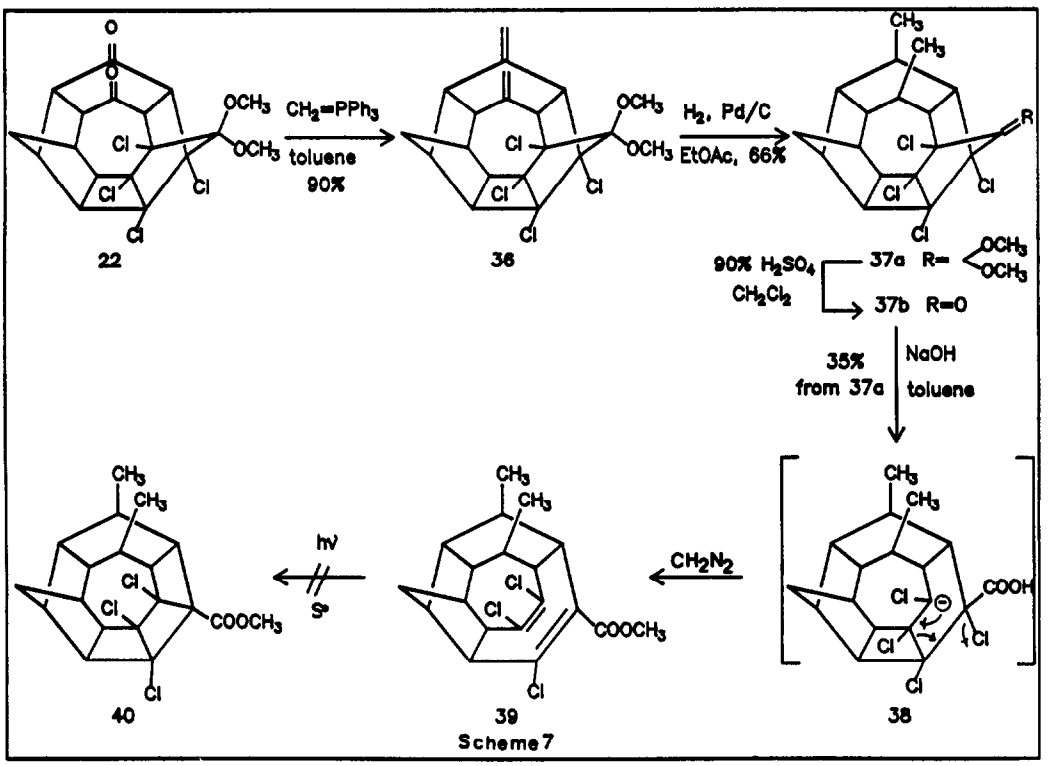
Concurrently, an attempt was also made to create the architecturally beautiful trishomo-[7]-prismane framework 5 *via* a homo-Norrish cyclisation that had proved so successful in dodecahedrane synthesis[13]. Thus, dione 3 was subjected to controlled Wittig olefination to furnish the diolefin 32 and keto-olefin 33 in 1 : 4 ratio. Catalytic hydrogenation of 33 furnished 34 with an *endo*-methyl group. Irradiation of 34 in benzene-t.BuOH in the presence of Et_3N, conditions employed earlier by Paquette, did not lead to the expected homo-Norrish product 35, Scheme 6. The failure in this case is perhaps due to the unfavourable stereo-electronic factors for the hydrogen abstraction.[14] The atomic separations in 34 were also found (MMX calculations) to be 3.31 and 3.37 Å for the O...H and C$_{\gamma}$...C distances, respectively, which are somewhat outside the normal range (~ 2.6 Å) for intramolecular hydrogen abstractions.



Scheme 6

At this stage, attention was turned to the tetrachloro-trione 9 and it was directly subjected to the Favorskii ring contraction. However, only intractable, aromatic proton containing products were detected. Realising that the two remote carbonyl groups were perhaps interfering with the reaction, we sought to render them ineffective. Consequently, 22,

the precursor of 9, was elaborated to the dimethyltetrachloroketone **37b** in three routine steps *via* the diolefin **36**. On subjecting **37b** to the Favorskii regiment, no ring contraction product was encountered but a novel diene ester **39**, formed through Haller-Bauer cleavage and cyclobutane ring cleavage in **38**, was obtained, after diazomethane esterification. Formation of **39** was initially not considered to be a totally disappointing outcome, as an intramolecular 2+2-cycloaddition in it could eventuate to the desired homo-seco-[7]-prismane system **40**. However, **39** also proved to be completely resistant to sensitised and direct intramolecular 2+2-cycloaddition, Scheme 7.[12]



In conclusion, we have successfully synthesised more functionalised derivatives **8** and **9** of **3** and also prepared some novel polyhedranes **23-25**, however, further progress towards [7]-prismane has presented considerable difficulties. Clearly, strain build-up and unfavourable stereoelectronic disposition of functionalities has thwarted the attempts towards establishment of additional C-C connectivities in **3**. Our experience therefore suggests exploration of alternate *de novo* strategies towards **2**.

Experimental

For a description of general procedures, see Ref.1a.

Reaction of 2,3-norbornenobenzoquinone (10) with dimethyl fulvene: To a solution of the quinone 10 (1g, 5.8 mmol) in benzene, excess dimethyl fulvene was added at 0°C and the reaction mixture stirred at ~ 25°C for 6h. Removal of solvent under vacuum gave a residual solid, which was washed with cold hexane to remove excess dimethyl fulvene. The crude material was a mixture of endo,syn-adduct 11 and endo,anti-adduct 12. As purification of this mixture was not possible due to the unstable nature of the adducts,it was directly used for the next step. IR: 2925, 1645, 1290, 710 cm^{-1}.

Irradiation of the endo,syn-adduct (11) and endo,anti-adduct (12) mixture: A solution of a mixture of enediones 11 and 12 (100 mg, 0.36 mmol) in hexane (125 mL) was purged with a slow stream of nitrogen and irradiated for 4h, using pyrex filter. The solvent was removed under vacuum and the residue charged on a silica gel (10 g) column. Elution with 3% ethyl acetate-hexane furnished the anti-heptacyclo[10.2.1.1 ^{5,8}.0^{2,11}.0^{4,9}.0^{2,6}.0^{7,11}]hexadec-13-ene-5-isopropylidene-3,10-dione 13 (40 mg, 40%) and was recrystallised from dichloromethane-hexane. mp.: 192-194°C; IR. 2965, 1745, 1720, 735 cm^{-1}; ^{1}H NMR: δ 6.36 (2H, dd, J_1=J_2=2Hz, -CH=CH-), 3.26 (2H, m), 2.93 (2H, dd, J_1=J_2=2Hz), 2.70 (2H, br s), 2.53 (2H, dd, J_1=J_2=2Hz), 1.72 (6H, s, isopropylidene methyl), 1.75-1.51 (1H, ½ ABq, masked under CH_3 singlet), 1.22 (1H, ½ ABq, J=9Hz, >C<H H); ^{13}C NMR: δ 213.8, 141.7, 136.7, 121.1, 62.5, 54.8, 50.8, 42.7, 41.3, 38.6, 21.1. Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.00; H, 6.56.

Further elution with the same eluent furnished the syn-heptacyclo-[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{2,6}.0^{7,11}]hexadec-13-ene-5-isopropylidene-3,10-dione 14 (20 mg, 20%) and was recrystallised from dichloromethane-hexane, m.p.: 201-202°C; IR: 2965, 1745, 1725, 720 cm^{-1}; ^{1}H NMR· δ 6.23 (2H, dd, J_1=J_2=1.5Hz, -CH=CH-), 3.25 (2H, m), 2.82 (2H, br s), 2.73 (2H, br s), 2.55 (2H, br s), 1.74 (6H, s), 1.88-1.64 (1H, ½ ABq, masked under CH_3 singlet), 1.55 (1H, ½ ABq, J=9Hz, >C<H H); ^{13}C NMR· δ 212.0, 141.4, 135.3, 121.5, 63.1, 53.6, 45.7, 43.0, 42.0, 38.9, 21.1. Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.78; H, 6.53.

Reduction of the enediones (11) and (12) with aq.$TiCl_3$: To a solution of the mixture of enediones 11 and 12 (600 mg, 2.16 mmol) in acetone (30 mL) 15% aq.$TiCl_3$ was added dropwise at 0°C until a pale purple colour persisted.[5] The reaction mixture was poured into brine solution (100 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic extract was washed with 10% $NaHCO_3$, water and dried. After removal of solvent, the residue was charged on a silica gel (40g) column. Elution with 10% ethyl acetate-hexane furnished the exo, anti, endo-adduct 1α,4α,4aα,10aα,-5β,8β,8aα,9aα-octahydro-1,4-methano-5,8-isopropylidenemethano-anthracene-9,10-dione 16 (120 mg, 20%) and was recrystallised from dichloromethane-hexane. m.p.: 208-210°C (decomp.); IR 3000, 1705, 725 cm^{-1}; ^{1}H NMR. δ 6.24 (2H, s with st., -CH=CH-), 6.14 (2H, s, -CH=CH-), 3.74 (2H, br s),

3.69 (2H, br s), 3.40 (2H, br s), 2.63 (2H, br s), 1.55 (6H, s), 1.26 and 0.57 (2H, ABq, J=9Hz, -CH$_2$-); ^{13}C NMR: δ 209.3, 144.4, 137.1(2C), 110.0, 54.8, 52.1, 47.1, 43.4, 43.0, 19.5. Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.38, H, 7.19.

Further elution with the same solvent gave endo,syn,endo-adduct, 1α,4α,4aβ,10aβ,5α,8α,8aβ,9aβ-octahydro-1,4-methano-5,8-isopropylideneme-thano-anthracene-9,10-dione 15 (300 mg, 50%) and was recrystallised from dichloromethane-hexane. m.p.: 212-215°C(decomp.); IR: 2975, 1700,730 cm^{-1}; ^{1}H NMR: δ 6.09 (2H, s with st., -CH=CH-), 5.95 (2H, s, -CH=CH-), 3.68 (2H, br s), 3.36 (4H, s), 3.25 (2H, br s), 1.52 (6H, s), 1.30 (2H, ABq, J_1=J_2=8Hz, -CH$_2$-); ^{13}C NMR: δ 209.4, 144.3, 137.4, 136.9, 109.8, 53.9, 53.7, 46.9, 43.8, 43.7, 19.5. Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.10; H, 7.13.

Irradiation of the endo,syn,endo-adduct (15): Heptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadeca-5-isopropylidene-11,14-dione (17): A solution of the endo,syn,endo-adduct 15 (400 mg, 1.43 mmol) in 10% acetone-benzene (125 mL) was purged with a slow stream of nitrogen and irradiated for 1h using vycor filter. The solvent was evaporated off and the residue charged on a silica gel (10g) column. Elution with 30% ethyl acetate-hexane furnished the heptacyclic dione 17 (320 mg, 80%) and was recrystallised from dichloromethane-hexane. m.p.:187-189°C; IR: 2935, 1705, 1695, 1280, 1225 cm^{-1}; ^{1}H NMR: δ 3.10 (4H, br s), 3.01 (2H, br s), 2.84 (4H, br s), 2.65 (2H, br s), 1.60 (6H, s), 1.88-1.36 (2H, ABq, masked under CH$_3$ singlet); ^{13}C NMR: δ 210.2, 140.4, 117.5, 55.2, 54.0, 46.4, 45.0, 43.4, 41.0, 37.5, 20.5. Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.04; H, 7.22.

Ozonolysis of heptacyclic dione (17): Heptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadeca-5,11,14-trione (8): To a solution of heptacyclic dione 17 (140 mg, 0.5 mmol) in methanol (25 mL), a slow stream of ozone was bubbled at -78°C until a blue colour persisted. Then, the reaction mixture was quenched with dimethyl sulphide at -78°C and stirred for 3h at ~25°C, methanol was removed under reduced pressure and the residue dissolved in ethyl acetate (50 mL). The organic layer was washed with water and dried. The crude product obtained after removal of solvent was charged on silica gel (10g) column. Elution with 50% ethyl acetate-hexane furnished the triketone 8 (115 mg, 90%) and was recrystallised from dichloromethane-hexane. m.p.: 227-229°C; IR: 2920, 1760, 1680 cm^{-1}; ^{1}H NMR: δ 3.42 (2H, s with st), 3.38-2.89 (6H, m), 2.77 (2H, br s), 2.38 (2H, dd, J_1=J_2=2Hz), 1.67 (2H, ABq, J=9Hz, -CH$_2$-); ^{13}C NMR: δ 206.0, 204.1, 55.6, 47.8, 46.1, 45.8, 44.4, 42.1, 31.1. Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.70; H, 5.60.

Preparation of adducts 18 and 19 : The adducts 18 and 19 were prepared according to the procedure reported by us[6] from the norbornenobenzoquinone 10 and dimethoxytetrachlorocyclopentadiene.

Reduction of the enedione (18) with aq.$TiCl_3$: 5α,6,7,8α-Tetrachloro-1α,4α,4aβ,10aβ,8aβ,9aβ-hexahydro-1,4-methano-5,8-dimethoxymethanoanthracene-9,10-dione (20): To a stirred solution of the syn-enedione 18 (300 mg, 0.68 mmol) in acetone (8 mL) 30% aq.$TiCl_3$ was added dropwise until a pale purple colour persisted.[5] The reaction mixture was poured into water (20 mL) and extracted with ether (3 x 20 mL). The combined ethereal extract was washed with 10% $NaHCO_3$, water and dried. Removal of solvent gave the crude reduced adduct which was filtered through a silica gel (10 g) column. Elution with 25% ethyl acetate-hexane furnished the pure endo,syn,endo- adduct **20** (270 mg, 90%) and was recrystallised from dichloromethane-hexane. mp.: 175°C; IR: 3050, 2925, 1710, 1600, 1195, 720 cm^{-1}; ^1H NMR: δ 6.01 (2H, dd, J_1=J_2=2Hz, -HC=CH-), 4.04 (2H, s,-ClC-CH-), 3.58 (3H, s, $-OCH_3$), 3.54 (2H, br s), 3.52 (3H, s, $-OCH_3$), 3.2 (2H, br s), 1.33 (2H, ABq, $-CH_2-$); ^{13}C NMR: δ 202.8, 136.5, 130.9, 113.9, 74.2, 59.0, 54.1, 53.1, 52.1, 46.5, 43.6. Anal. Calcd. for $C_{18}H_{16}Cl_4O_4$: C, 49.34; H, 3.68. Found: C, 49.60; H, 3.67.

Reduction of enedione 19 with aq.$TiCl_3$: 5β,6,7,8β-Tetrachloro-1α,4α,4aα,-10aα,8aα,9aα-hexahydro-1,4-methano-5,8-dimethoxymethanoanthracene-9,10-dione (21): To a stirred solution of anti-enedione 19 (200 mg, 0.458 mmol) in acetone (5 mL) 30% aq.$TiCl_3$ was added dropwise until a pale purple colour persisted.[5] The reaction mixture was poured into water (15 mL) and extracted with ether (3 x 20 mL). The combined ethereal extract was washed with 10% $NaHCO_3$, water and dried. Removal of solvent and filtration of the residue through a silica gel (10g) column furnished a single reduced product 21 (195 mg) in near quantitative yield which was recrystallised from dichloromethane-hexane. mp.: 164°C; IR: 3050, 2950, 1720, 1600, 700 cm^{-1}; ^1H NMR: δ 6.12 (2H, dd, J_1 = J_2 = 2Hz, -HC=CH-), 4.22 (2H, s, -ClC-CH-), 3.6 (3H, s, $-OCH_3$), 3.54 (3H, s, $-OCH_3$), 3.34 (2H, dd, J_1 = J_2 = 2Hz), 2.86 (2H, br s), 1.34 (1H, ½ ABq with st., J = 8Hz, $\succ C\langle^{H}_{H}$), 0.66 (1H, ½ ABq, J = 8Hz, $\succ C\langle^{H}_{H}$); ^{13}C NMR: δ 203.5, 136.9, 131.0, 113.2, 74.0, 60.5, 53.1, 52.7, 52.2, 46.8, 42.1. Anal. Calcd. for $C_{16}H_{16}Cl_4O_4$: C, 49.34; H, 3.68. Found: C, 49.25; H, 3.66.

3,4,6,7-Tetrachloro-5,5-dimethoxyheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$. $0^{6,12}$.-$0^{10,15}$]hexadeca-11,14-dione (22): A solution of the endo, syn, endo-adduct **20** (300 mg, 0.68 mmol) in 15%acetone-benzene (125 mL) was purged with a slow stream of nitrogen and irradiated for 3h, using vycor filter. The solvent was evaporated off and the residue charged on a silica gel (20 g) column. Elution with 40% ethyl acetate-hexane furnished the heptacyclic dione **22** (135 mg, 45%) and was recrystallised from dichloromethane-hexane. mp.: >250°C; IR: 2950, 1710, 1200, 790 cm^{-1}.^1H NMR: δ 3.8-3.68 (2H, m), 3.66 (3H, s, $-OCH_3$), 3.64 (3H, s, $-OCH_3$), 3.52 (2H, dd, J_1 = J_2 = 2Hz), 3.2 (2H, br s), 2.96 (2H, br s), 1.69 (2H, ABq with st., J_1 = J_2 = 10Hz, $-CH_2-$); ^{13}C NMR: δ 202.7, 107.0, 78.7, 74.8, 56.2, 55.9, 54.6, 52.2, 51.5, 45.6, 43.4; Anal. Calcd. for $C_{18}H_{16}Cl_4O_4$: C, 49.34; H, 3.68. Found: C, 49.29; H, 3.60.

Hydrolysis of 22: 3,4,6,7-Tetrachloroheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadeca-5,11,14-trione (9): The heptacyclic dione 22 (25 mg, 0.057 mmol) in dichloromethane (0.5 mL) was cooled to 0°C in an ice bath and 90% H_2SO_4 (1.5 mL, v/v) was added dropwise. The reaction mixture was stirred further for 5 h at ~ 25°C and poured over crushed ice. The aqueous layer was neutralised with $NaHCO_3$ and extracted with dichloromethane (3 x 10 mL). The combined organic extract was washed with water and dried. Removal of solvent and recrystallisation from dichloromethane gave the highly insoluble heptacyclic trione 9 (11 mg, 50%). mp. >250°C; IR: 2925, 1815, 1710 cm^{-1}; ^1H NMR: 3.78 (2H, m), 3.68 (2H, m), 3.44 (2H, br s), 3.12 (2H, m), 1.82 (2H, ABq, J_1=J_2=10Hz, -C<u>H</u>$_2$-).

Flash vacuum pyrolysis (FVP) of heptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadeca-11,14-dione (3): The heptacyclic dione 3 (240 mg, 1 mmol) was slowly sublimed (200°C/0.1 torr) through quartz tube equilibrated to 600°C(± 10°C). The condensate was carefully chromatographed over a neutral alumina (30g) column. Elution with 20% ethyl acetate-hexane furnished the olefinic dione 23 (168 mg, 90% based on starting material recovered) and was recrystallised from dichloromethane-hexane. m.p.: 251°C (decomp.); IR: 2925, 1695, 765 cm^{-1}; ^1H NMR: δ 5.35 (4H, d, J=2.5Hz, -C<u>H</u>=C<u>H</u>-), 3.44 (4H, m), 3.13 (4H, m), 2.08-1.56 (4H, m, -C<u>H</u>$_2$-); ^{13}C NMR: δ 208.3, 130.6, 56.9, 44.2, 35.7. Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.82; H, 6.74.

FVP of heptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadeca-5,11,14,-trione (8): The heptacyclic dione 8 (254 mg, 1 mmol) was slowly sublimed (200°C/0.2 torr) through quartz tube equilibrated to 550°C (± 10°C). The condensate was carefully chromatographed over a silica gel (15g) column. Elution with 30% ethyl acetate -hexane furnished the rearranged product 26 (63mg, 28%) and was recrystallised from dichloromethane-hexane. m.p.: 220°C; IR: 2940, 1710, 1130, 705 cm^{-1}; ^1H NMR: δ 6.62 (1H, t, J=8Hz), 6.23 (1H, t, J=8Hz), 6.07 (1H, t, J=8Hz), 5.92 (1H, t, J=8Hz), 3.56-2.68 (6H, series of m), 2.56 (2H, t, J=7Hz), 1.86 (2H, dd, J_1=J_2=2Hz, -C<u>H</u>$_2$-); ^{13}C NMR: δ 210.6, 203.7, 141.1, 139.8, 132.0, 123.0, 61.3, 56.5, 53.4, 53.1, 50.7, 41.2(2C), 39.3(2C). Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.74; H, 6.25.

Further elution with the same eluent gave the metathetic dione 24 (46 mg, 18%) and was recrystallised from dichloromethane-hexane. m.p. 235°C (decomp.); IR: 2940, 1735, 1700, 775 cm^{-1}; ^1H NMR: δ 5.59 (4H, dq, J_1=15Hz, J_2=4Hz, -C<u>H</u>=C<u>H</u>-), 3.74 (4H, dd with st, J_1=J_2=4Hz), 3.25 (4H, m), 2.28-1.72 (2H, m, -C<u>H</u>$_2$-); ^{13}C NMR: δ 210.1, 205.2, 134.0, 127.7, 57.8, 51.3, 50.3, 45.1, 34.2. Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.72; H, 5.51.

FVP of heptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadeca-5-isopropylidene-11,14-dione (17): The heptacyclic dione 17 (28 mg, 0.1 mmol) was slowly sublimed (190°C/0.2 torr) through quartz tube equilibrated to 450°C (± 10°C). The condensate was carefully chromatographed over a silica gel (5g) column. Elution with 30% ethyl acetate-hexane furnished olefinic dione 25 (20 mg, 70%) and was recrystallised from dichloromethane-hexane,

m.p.: 238-240°C; IR: 2930, 1695, 770 cm^{-1}; ^1H NMR: δ 5.36 (4H, t, J = 4Hz, -CH=CH-), 3.71 (2H, m), 3.55. (4H, m), 3.16 (2H, m), 1.80 (6H, s), 1.94-1.64 (2H, m, $-CH_2-$); ^{13}C NMR: δ 208.0, 132.3, 129.1, 128.3, 125.8, 57.1, 55.4, 45.4, 44.1, 36.4, 20.8. Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.25; H, 7.18.

Heptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadeca-11,14-dimesylate (29): A solution of compound 3 (200 mg, 0.83 mmol) in methanol (5 mL) was cooled in an ice-bath and sodium borohydride (25 mg, 0.65 mmol) was added and the reaction mixture stirred for 15 min. Methanol was removed at ~ 25°C under reduced pressure and the residue diluted with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL)) and the combined organic layer washed with water and dried. Removal of solvent gave a crude diol (200 mg) which was directly used for the next step. IR: 3350(br), 2925, 1030 cm^{-1}.

To the above obtained diol (200 mg) in pyridine (5 mL) cooled in an ice-bath was added dropwise methanesulphonyl chloride (500 mg, 4.3 mmol). The reaction mixture was stirred further for 4h at ~ 25°C and then poured into water (20 mL). The aqueous layer was extracted with ethyl acetate (3 x 20 mL) and the combined organic extract was successively washed with 10% HCl (5 x 15 mL), 10% $NaHCO_3$, water and dried. The residue obtained after removal of solvent was filtered through a silica gel (5 g) column. Elution with 30% ethyl acetate-hexane furnished the pure dimesylate 29 (268 mg, 81%) and was recrystallised from dichloromethane-hexane. mp.: 166°C (decomp.); IR: 2925, 1340, 1160, 1000, 970 cm^{-1}; ^1H NMR: δ 5.26 (2H, br s, $-HC-OSO_2CH_3$), 3.02 (4H, s), 2.72 (4H, br s), 2.66 (10H, br s), 1.32 (4H, ABq, $J_1 = J_2$ = 8Hz, $-CH_2-$); Anal. Calcd. for $C_{18}H_{24}S_2O_6$: C, 53.98; H, 6.04. Found: C, 53.97; H, 6.04.

11,14-Diiodoheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadecane (30): A mixture of the dimesylate 29 (150 mg, 0.37 mmol), excess sodium iodide (1.1 g) and HMPA (10 mL) was stirred at 100°C for 7h under a nitrogen atmosphere. The reaction mixture was cooled and poured into water (30 mL). The aqueous layer was extracted with ether (3 x 25 mL)) and the combined ethereal extract washed with water and dried. Removal of solvent gave a crude material which was charged on a silica gel (10 g) column. Elution with hexane furnished the pure diiodo compound 30 (110mg, 63%), which was recrystallised from hexane. mp.: 170-171°C; IR: 2925, 1110, 935, 700 cm^{-1}; ^1H NMR: δ 5.02 (2H, br s, -HC-I), 3.01 (4H, br s, cyclobutyl-CH), 2.7 (8H, br s), 1.26 (4H, ABq with st., $J_1 = J_2$ = 10Hz, $-CH_2-$); ^{13}C NMR: δ 51.8(d), 49.2(d), 41.5(t), 38.9(d), 37.1(d). Anal. Calcd. for $C_{16}H_{18}I_2$: C, 41.40; H, 3.91. Found: C, 41.51; H, 4.01.

Hexacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$]hexadeca-10,14-diene (31): Into a 25 mL three necked RB flask equipped with a dry N_2 inlet, condenser and mercury seal was placed sodium (75 mg, 0.003 g atom), potassium (35 mg, 0.0001 g atom) and toluene (5 mL). The mixture was refluxed with vigorous stirring until a fine dispersion of the Na-K alloy was formed. The flask was cooled and toluene syringed out carefully after which THF (10 mL) was introduced. Then the d iodo compound 30 (50 mg, 0.11 mmol) in THF (2 mL) was introduced and the contents of the flask stirred for 15 min at ~ 25°C.

The reaction mixture was diluted with ether (10 mL) and cautiously filtered through a celite pad under a nitrogen atmosphere into a flask containing t-butanol. The residue was washed with dry ether (2 x 10 mL)) and was immediately destroyed with t-butanol. The filtrate was washed with water and dried. The crude hydrocarbon obtained after removal of solvent was charged on a silica gel (5 g) column. Elution with pentane furnished the pure hexacyclic diene 31 (16 mg, 70%) and was recrystallised from methanol. mp.: 200-202°C; IR: 3000, 2500, 750 cm^{-1}; ^1H NMR: δ 5.84-5.7 (2H, m, -HC=CH-), 5.32-5.0 (2H, m, -HC=CH-), 2.86 (6H, m), 2.66 (2H, br s), 2.52 (2H, br s), 1.44 and 1.04 (4H, ABq, J = 8Hz, -CH2-); ^{13}C NMR: δ 136.4, 128.6, 46.3, 45.4, 44.2, 43.3 (2C), 40.7, 38.6; Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.22; H, 8.65.

11-Methyleneheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadecan-14-one (33): In a 25 mL two necked RB flask equipped with a dry nitrogen inlet was placed methyltriphenylphosphonium bromide (223 mg, 0.624 mmol). The solid was suspended in toluene (3 mL) and freshly sublimed t-amyl oxide (50 mg, 0.454 mmol) in toluene (1 mL) was introduced and the mixture stirred for 5 min at ~ 25°C. To the canary yellow ylide that formed immediately, the diketone 3 (100 mg, 0.416 mmol) in toluene (2 mL) was added. The reaction mixture was stirred further for 15 min and quenched with water (5 mL). The toluene layer was separated and the aqueous layer extracted with benzene (2 x 10 mL). The combined organic layer was washed with water and dried. Removal of solvent and tlc examination of the residue (5% ethyl acetate-hexane) indicated the presence of two products. The residue was charged on silica gel (15 g) column. Elution with hexane initially furnished the di-Wittig product 32 (15 mg, 19%) and was recrystallised from hexane. mp.: 105°C; IR: 3050, 2925, 890 cm^{-1}; ^1H NMR: δ 4.98 (4H, s, >=CH2), 2.98 (4H, br s), 2.64 (4H, br s), 2.4 (4H, br s), 1.4 (4H, ABq, J_1 = J_2 = 8Hz, -CH2-); ^{13}C NMR: δ 150.0, 112.0, 50.8, 48.5, 43.8, 39.3; Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 89.96; H,8.32.

Continued elution of the column with 2% ethyl acetate-hexane furnished the mono-Wittig product 33 (65 mg, 80% based on recovered starting material) and was recrystallised from hexane. mp.: 166°C; IR: 3050, 2950, 1680, 910, 760 cm^{-1}; ^1H NMR: δ 4.84 (2H, s, >=CH2), 3.1 (4H, ddd, J_1 = J_2 = 12Hz, J_3 = 2Hz), 2.72 (4H, s), 2.52 (4H, br s), 1.48 (4H, ABq, J_1 = J_2 = 10Hz); ^{13}C NMR: δ 214.7, 146.4, 113.1, 54.2, 50.8, 50.0, 46.5, 43.9, 39.6, 39.2; Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.50; H, 7.60.

Further elution of the column with 30% ethyl acetate-hexane gave the unreacted starting material (20 mg).

11-Methylheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadecan-14-one (34): A solution of compound 33 (50 mg, 0.21 mmol) in ethyl acetate (3 mL) was hydrogenated at atmospheric pressure over 10% Pd/C (2 mg) for a period of 2h. Pd/C was filtered off and the residue obtained after removal of solvent was filtered through a silica gel (3 g) column. Elution with 5% ethyl acetate-hexane furnished the methyl ketone 34 (45 mg, 90%) and was recrystallised from dichloromethane-hexane. mp.: 201°C;IR: 2925,1680 cm^{-1};

^{1}H NMR: δ 3.0-2.0 (13H, m), 1.4 (4H, ABq, $J_1 = J_2 = 10$Hz, -C<u>H</u>$_2$-), 1.12 (3H, d, J = 7Hz, -C<u>H</u>$_3$); Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.64; H, 8.30.

3,4,6,7-Tetrachloro-5,5-dimethoxy-11,14-dimethyleneheptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadecane (36): In a 50 mL two necked RB flask fitted with a dry nitrogen inlet was placed methyltriphenylphosphonium bromide (540 mg, 1.5 mmol). The solid was suspended in toluene (3 mL) and freshly sublimed t-amyl oxide (110 mg, 1.0 mmol) in toluene (2 mL) was introduced and the mixture stirred for 10 min. A canary yellow ylide formed almost immediately and to this the diketone 22 (110 mg, 0.25 mmol) in toluene (2 mL) was added. The reaction mixture was stirred further for 30 min and quenched with water (5 mL). The toluene layer was separated and the aqueous layer extracted with ethyl acetate (2 x 10 mL). The combined organic layer was washed with water and dried. Removal of solvent gave a crude material which was charged on a silica gel (10 g) column. Elution with 5% ethyl acetate-hexane furnished the pure dimethylene product 36 (100 mg, 90%) and was recrystallised from dichloromethane-hexane. mp.: 241-242°C; IR: 3050, 2925, 1180, 900 cm^{-1}; ^{1}H NMR: δ 5.16-5.0 (4H, m, >C=C<u>H</u>$_2$), 3.68 (3H, s, -OC<u>H</u>$_3$), 3.64 (5H, s), 3.30 (2H, br s), 3.02 (2H, br s), 2.66 (2H, br s), 1.68 and 1.21 (2H, ABq, J = 10Hz, -C<u>H</u>2-); ^{13}C NMR: δ 139.9, 119.2, 111.1, 79.2, 79.0, 56.1, 51.8, 51.4, 51.3, 48.9, 46.9, 43.0; Anal. Calcd. for $C_{20}H_{20}Cl_4O_2$: C, 55.32; H, 4.64. Found: C, 55.02; H, 4.55.

3,4,6,7-Tetrachloro-5,5-dimethoxy-11,14-dimethylheptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadecane (37a): A solution of the diolefin 36 (60 mg, 0.14 mmol) in ethyl acetate (5 mL) was hydrogenated at atmospheric pressure, over 10% Pd/C (3 mg) for a period of 6h. Pd/C was filtered off and the residue obtained after removal of solvent was charged on a silica gel (5 g) column. Elution with 5% ethyl acetate-hexane furnished the dimethyl compound 37a, as the major product (40 mg, 66%) and was recrystallised from dichloromethane-hexane. mp.: 232-233°C; IR: 2950, 1445, 1180 cm^{-1}; ^{1}H NMR: δ 3.65 (3H, s, -OC<u>H</u>$_3$), 3.6 (3H, s, -OC<u>H</u>$_3$), 3.28 (2H, m), 3.14 (2H, m), 2.76 (2H, m), 2.4-2.04 (4H, m), 1.32 (6H, d, J = 8Hz, -C<u>H</u>$_3$), 1.48-1.08 (2H, hidden under methyl doublet); ^{13}C NMR: δ 106.5, 79.6, 79.3, 56.2, 51.8, 51.2, 45.9, 43.7, 42.8, 30.0, 19.3; HRMS: M^+ Calcd. for $C_{20}H_{24}Cl_4O_2$: 436.0533 . Found: 436.0531.

Hydrolysis of dimethylacetal in 37a: To a solution of compound 37a (40 mg, 0.09 mmol) in dichloromethane 0.5 mL) cooled in an ice-bath, was added 90% H_2SO_4 (1 mL, v/v). The reaction mixture was stirred further for 5h at ~ 25°C and then quenched by pouring over crushed ice (5 g). The aqueous layer was extracted with dichloromethane (3 x 8 mL). The combined organic extract was washed with 10% $NaHCO_3$, water and dried. Removal of solvent gave the keto compound 37b(32 mg) which was directly used for the next step. IR: 1800 cm^{-1}.

11,14,15-Trichloro-2,8-dimethylpentacyclo[7.6.0.0^{3,7}.0^{4,13}.0^{6,12}]pentadeca-10,14-diene-10-carboxylic acid methyl ester (39): A suspension of powdered NaOH (150 mg, 3.75 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 crude heptacyclic ketone **37b** (32 mg, 0.81 mmol) in toluene (3 mL) was added and the contents of the flask refluxed for 3h. The reaction mixture was diluted with water (5 mL) and acidified with dil.HCl. The toluene layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with water and dried. Removal of solvent gave 20 mg of a crude material which was dissolved in methanol (2 mL) and esterified with ethereal solution of diazomethane at 0°C. Tlc examination of the material showed a single UV absorbing product. The solvent was evaporated and the residue charged on a silica gel (5 g) column. Elution with 5% ethyl acetate - hexane furnished the pure diene ester **39** (12 mg, 35% from **37a**) and was recrystallised from dichloromethane-hexane. mp.: 167-168°C; IR: 2950, 1715, 1250, 1240, 830 cm^{-1}; ^{1}H NMR: δ 3.76 (3H, s, -C(O)-OC<u>H</u>$_3$), 3.28-2.9 (4H, m), 2.7 (2H, br s), 2.2 (4H, br s), 1.44 (2H, s), 1.18 (3H, d, J=4Hz, -C<u>H</u>$_3$), 1.1 (3H, d, J=4Hz, -C<u>H</u>$_3$); ^{13}C NMR: δ 169.5, 136.1, 134.5 (2C), 129.5, 54.6, 52.1, 51.9, 49.8, 42.3, 41.6, 41.4, 40.6, 40.2, 40.1, 28.8 (2C), 17.6, 17.1; HRMS: M^{+} Calcd. for $C_{19}H_{21}Cl_3O_2$: 386.0609. Found: 386.0607.

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References

1. (a) Mehta, G.; Padma, S. Preceding paper in this issue . (b) Mehta, G.; Padma, S. Preceding paper in this issue .
2. (a) Reddy, V.P.; Jemmis, E.D. <u>Tetrahedron Lett.</u>, 1986, <u>27</u>, 3711. (b) Schultz, H.P. <u>J. Org. Chem.</u>, 1965, <u>30</u>, 1361. (c) Disch, R.L. Schulman, J.M. <u>J. Am. Chem. Soc.</u>, 1988, <u>110</u>, 2102.
3. (a) Mehta, G.; Padma, S. Synthesis of Prismanes. In <u>Chemistry of Three-Dimensional Polycyclic Molecules</u>; Osawa, E.; Yonemitsu, O. Eds., VCH, New York, in press. (b) Mehta, G. Quest for Higher Prismanes. In <u>Strain and Its Implications in Organic Chemistry</u>; De Meijere, A.; Blechert, S. Eds.; NATO ASI series, Kluwer Academic Publishers, Dordrecht, 1989; pp.269. (c) For a homo-[7]-prismane derivative, see, Mehta, G.; Padma, S.<u>J. Org. Chem.</u>, 1991, <u>56</u>, 1298.
4. Mehta, G.; Padma, S. <u>J. Am. Chem. Soc.</u>, 1987, <u>109</u>, 7230.
5. Blaszczak, L.C.; McMurry, J.E. <u>J. Org. Chem.</u>, 1974, <u>39</u>, 258.
6. Mehta, G., Padma, S.; Karra, S.R.; Gopidas, K.R.; Cyr, D.R.; Das, P.K.; George, M.V. <u>J. Org. Chem.</u>, 1989, <u>54</u>, 1342.
7. McMurry, J.E. <u>Acc. Chem. Res.</u>, 1974, <u>7</u>, 281.
8. Corey, E.J.; Danheiser, R.L.Chandrasekaran, S.<u>J. Org. Chem.</u>, 1976, <u>41</u>, 260.
9. Osawa, E.; Barbiric, D.A.; Lee, O.S.; Kitano, Y.; Padma, S.; Mehta, G. <u>J. Chem. Soc., Perkin Trans. II</u>, 1989, 1161.

10. Mehta, G.; Srikrishna, A.; Reddy, A.V.; Nair, M.S. Tetrahedron, 1981, 37, 4543.
11. We thank Dr. Vasantha Pattabhi, University of Madras, India and Dr. M. Nethaji, Indian Institute of Science, Bangalore, India, for the X-ray crystal structure determination.
12. Mehta, G.; Padma, S.; Jemmis, E.D.; Leela, G.; Osawa, E.; Barbiric, D.A. Tetrahedron Lett., 1988, 28, 1613.
13. Paquette, L.A.; Balogh, D.W. J. Am. Chem. Soc., 1982, 104, 774.
14. (a) Sauers, R.R.; Scimone, A.; Shams, H. J. Org. Chem., 1988, 53, 6084. (b) Wagner, P.J. Acc. Chem. Res. 1983, 16, 461.