Synthesis of Spheroidal C_{20}-Polyquinanes in a Route towards Dodecahedrane †

Goverdhan Mehta,* Mangalam S. Nair and K. Raja Reddy
School of Chemistry, University of Hyderabad, Hyderabad–500 134, India

An approach to the hydrocarbon dodecahedrane **1** has been formulated based on a retrosynthetic theme. The starting *exo,exo*-tetraquinane diester **9** was conveniently synthesized from the readily available C_{2v}-tetraquinane dione **5**. Bis-cyclopentannulation of compound **9** employing the dichloroketene addition–ring-expansion methodology of Greene furnished the hexaquinane diester **12**. The newly appended cyclopentanone rings in compound **12** were inverted *via* a three-step sequence involving dehydrogenation to bisenone **13**, acetalisation to give compound **17**, and catalytic hydrogenation to compound **18**. Attempts to epimerise the *exo,exo*-diester functionality within the spheroidal cavity in the all-*cis*-hexaquinane dione diester **18** for the pivotal 'molecular stitching' step have so far proved unsuccessful. Cyclopentannulation reactions on Hedaya–Paquette ester **23** employing Greene methodology and the Pauson–Khand reaction have been carried out. Several interesting cyclisations and transannular reactions in the resulting polyquinanes have been observed.

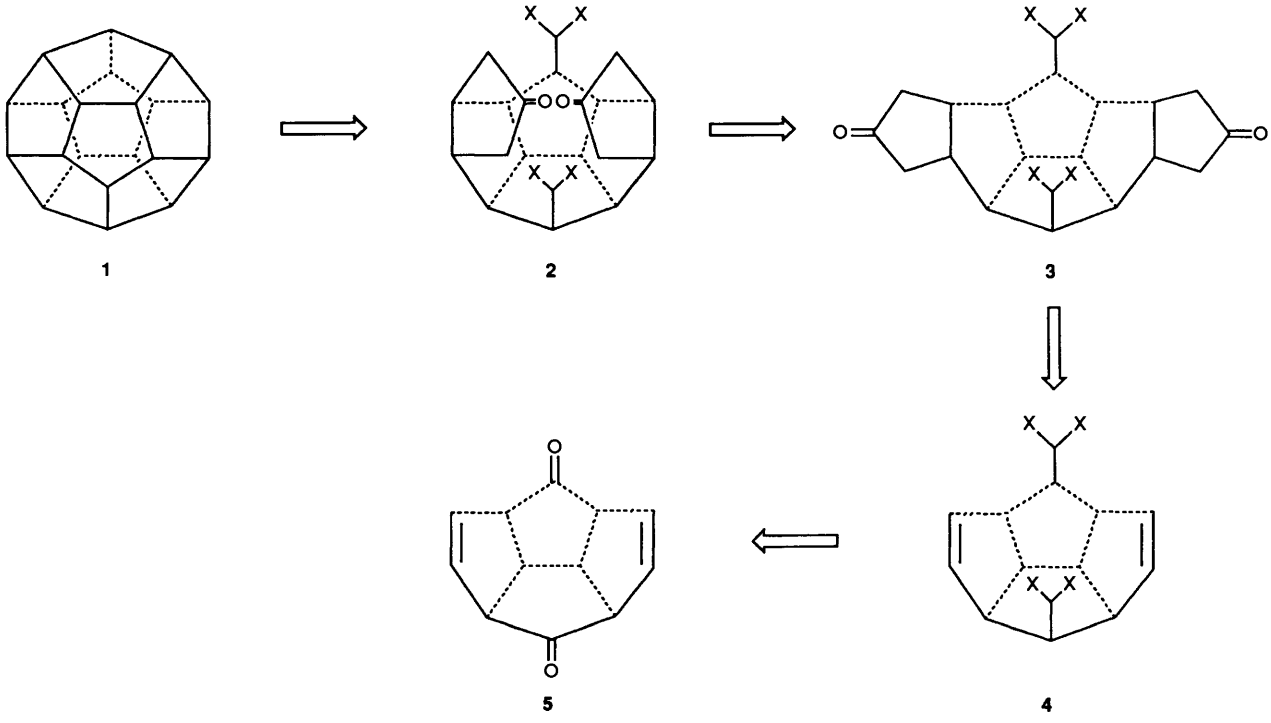
Despite the successful synthesis of the $C_{20}H_{20}$ hydrocarbon dodecahedrane **1** by Paquette[1] and Prinzbach,[2] the pursuit of this molecule by shorter, alternative routes holds considerable challenge.[3] Our own initiatives towards dodecahedrane **1** have been based on the retrosynthetic theme shown in Scheme 1.[4] Five strategic bond disconnections in dodecahedrane and placement of appropriate complementary functionality led to the spheroidal all-*cis*-C_{20} hexaquinane **2**. The pretarget **2** embodies the complete carbon content and stereochemical requirements for dodecahedrane **1**. It was planned to effect the 'molecular stitching' with an appropriate choice of *endo*-CX_2 functional groups protruding inside the spheroidal substrate **2** by a single-shot, four-fold molecular displacement. Further elaboration of the resulting secododecahedrane dione could be achieved through a reductive carbonyl coupling and deoxygenation sequence. The C_{20}-hexaquinane dione **2** could be further broken down to tetracycle **4** *via* dione **3** with retention of C_{2v}-symmetry by dismantling the two cyclopentanone rings. It was reasoned that substrate **4** could be bis-cyclopentannulated to the hexacycle **3** and ring inversion of this dione would then afford the pretarget **2**. The functionalised tetraquinane **4** could be further simplified to the known dione **5**.[5]

We have previously effected an efficient assembly of the C_{12}-C_{2v}-tetraquinane dione precursor **5** through a photothermal metathesis strategy employing 7-t-butoxynorbornadiene and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene.[4a] In order to introduce $-CX_2$ groups, dione **5** was elaborated to the stable C_{14}-diester **9** by a four-step strategy (Scheme 2). On subjecting dione **5** to modified Wittig olefination, a mixture of enol ethers **6** and **7** was obtained. Hydrolysis of the mixture (**6** and **7**) with 35% perchloric acid led to the exclusive formation of the thermodynamically more stable C_{14}-dialdehyde **8** (δ 9.64, 2 H, s) in 68% yield. Oxidation of compound **8** with pyridinium dichromate (PDC) in dimethylformamide (DMF) medium[6] furnished the corresponding dicarboxylic acid, which was directly esterified to give *exo,exo*-diester **9** (Scheme 2). The C_{2v}-diester **9** was found to be spectroscopically identical with the compound previously synthesized by Paquette[7] following a different route. In compound **9**, we now had access to a precursor that was equivalent to compound **4** (Scheme 1). The *exo*-functionalisation was considered advantageous as there would be minimal steric encumbrance with the developing hemisphere of higher polyquinanes such as compound **2**. However, a deprotonation and kinetic protonation sequence was expected to fulfil the steric requirements of projecting the ester moieties 'inside' the nest-like structure through epimerisation at a later stage.

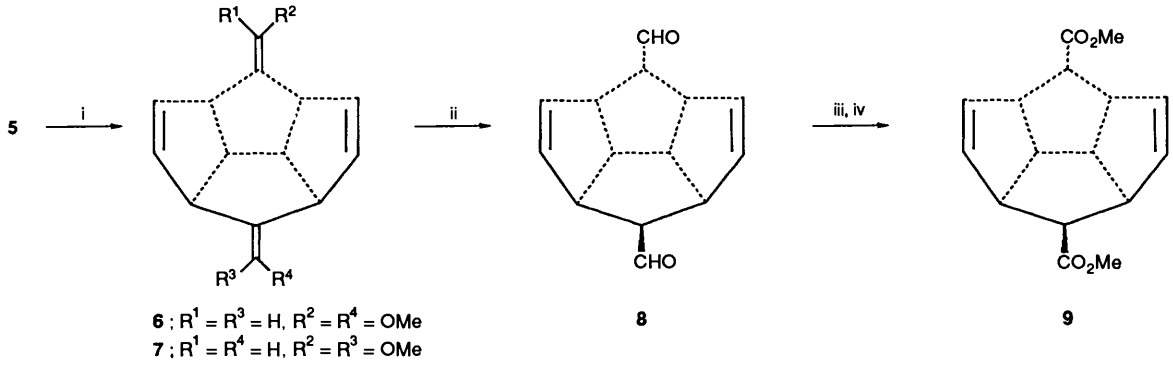
Attention was now turned towards building cyclopentanone rings on the basic structure of compound **9**. Among the available methods, the Greene methodology[8] of dichloroketene addition to olefins followed by regiospecific ring expansion and reductive dechlorination was found to be suitable as it would render possible the strategic placement of functional groups. When compound **9** was treated with large excess of dichloroketene (*in situ*),[9] a mixture of the dichloroketene adducts **10** and **11** was obtained in 74% yield (Scheme 3). Exposure of the mixture of compounds **10** and **11** to ethereal diazomethane and reductive dechlorination with Zn–NH_4Cl furnished the expected bis-cyclopentannulated C_{20}-hexaquinane dione **12** in 50% overall yield. The dione diester **12** exhibited an eight-line ^{13}C NMR spectrum, in conformity with its symmetry.

Although the desired cyclopentannulation was carried out as planned, the C_{20}-hexquinane **12** could be harnessed in the synthesis of dodecahedrane **1** only if the cyclopentane rings could be projected within the cavity of the polyquinane framework, *e.g.*, compound **2**. To implement the stereochemical inversion in compound **12**, dehydrogenation involving ring-junction hydrogens and stereoselective catalytic hydrogenation from the convex face was considered to be a suitable strategy. The hexaquinane dione **12** was deprotonated with an excess of lithium hexamethyldisilazide (LiHMDS) at -78 °C and quenched with trimethylsilyl chloride (TMSCl) and the resulting bis-TMS enol ether was directly subjected to dehydrogenation with palladium(II) acetate to give compound **13** in 72% yield.[10] The ^{13}C NMR spectrum revealed the C_{2v}-symmetry element in compound **13** and ruled out the regioisomeric bis-enone structure. The reasons for exclusive formation of compound **13** in a regioselective manner are not completely apparent but the outcome was satisfying as no chemical separation was required in this key step (Scheme 4). After the acquisition of compound **13**, the next task towards the ring-inversion objective was relocation of the double bonds. In the initial study, compound **13** was subjected to equilibration, under thermal ($\sim$300 °C in benzyl benzoate) or photochemical (imidazole–DMF) conditions and deprotonation and kinetic protonation [lithium diisopropylamide (LDA), LHDMS] to

† Taken from the Ph.D. thesis of K. R. Reddy, University of Hyderabad, 1989.



Scheme 1



Scheme 2 *Reagents, conditions and yields:* i, $Ph_3P^+CH_2OMe\ Cl^-$, $NaOC_5H_{11}$, THF, 0 °C, 30 min, 85%; ii, 35% $HClO_4$, Et_2O, 12 h, 68%; iii, PDC, DMF, 12 h; iv, CH_2N_2, Et_2O, 0 °C, 76%

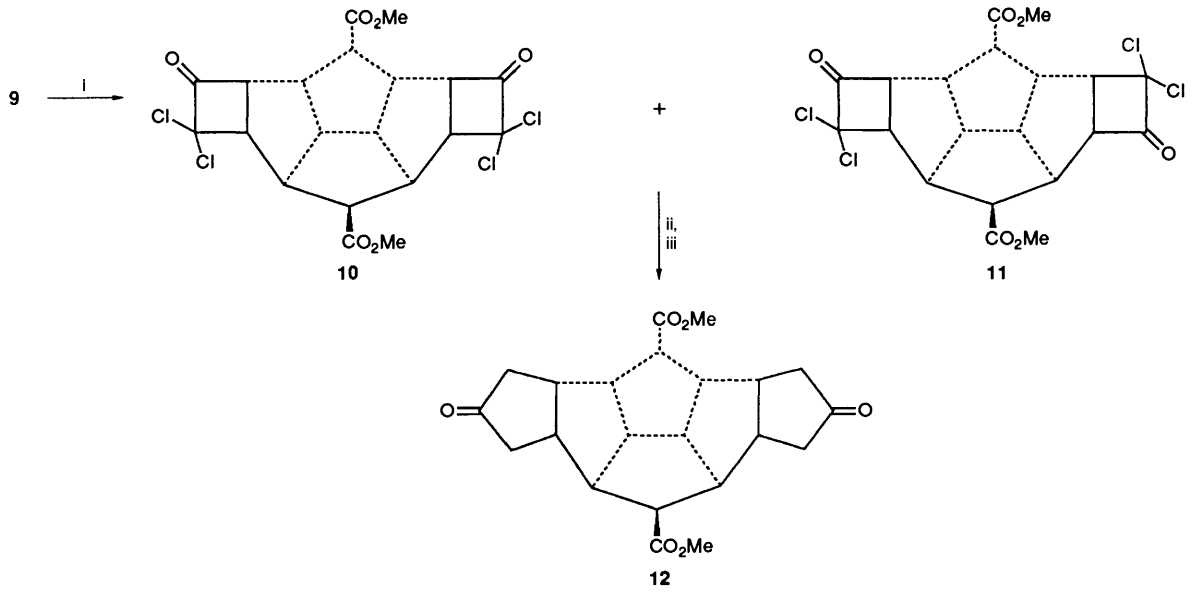
obtain the stereoisomer **14**, but without success. In the same vein, when compound **13** was exposed to the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), an unexpected but interesting transannular cyclisation occurred and compound **15** was isolated in 72% yield. Structure **15** is preferred for this product in the light of our earlier experience, wherein products from cross-transannular cyclisation were obtained with these tetraquinane systems.[11]

Attempts to overcome the difficulty encountered in the conversion of compound **13** into the β,γ-unsaturated isomer were now carried out through acetal formation in which concomitant double-bond isomerisation was expected.[12] When compound **13** was treated with ethylene glycol in the presence of toluene-*p*-sulphonic acid (PTSA) or pyridinium toluene-*p*-sulphonate (PPTS), a complex mixture of products resulted. After much experimentation, acetalisation of compound **13** could be effected through controlled reaction with ethylene glycol, in the presence of camphorsulphonic acid (CSA) to give bis-acetal **16**. Although isomerisation of the double bonds during acetalisation was successfully achieved, the reaction yield was less than satisfactory. To overcome this, 2,2-dimethylpropane-1,3-diol was used in the presence of CSA to furnish compound **17** in 80% yield (Scheme 5).

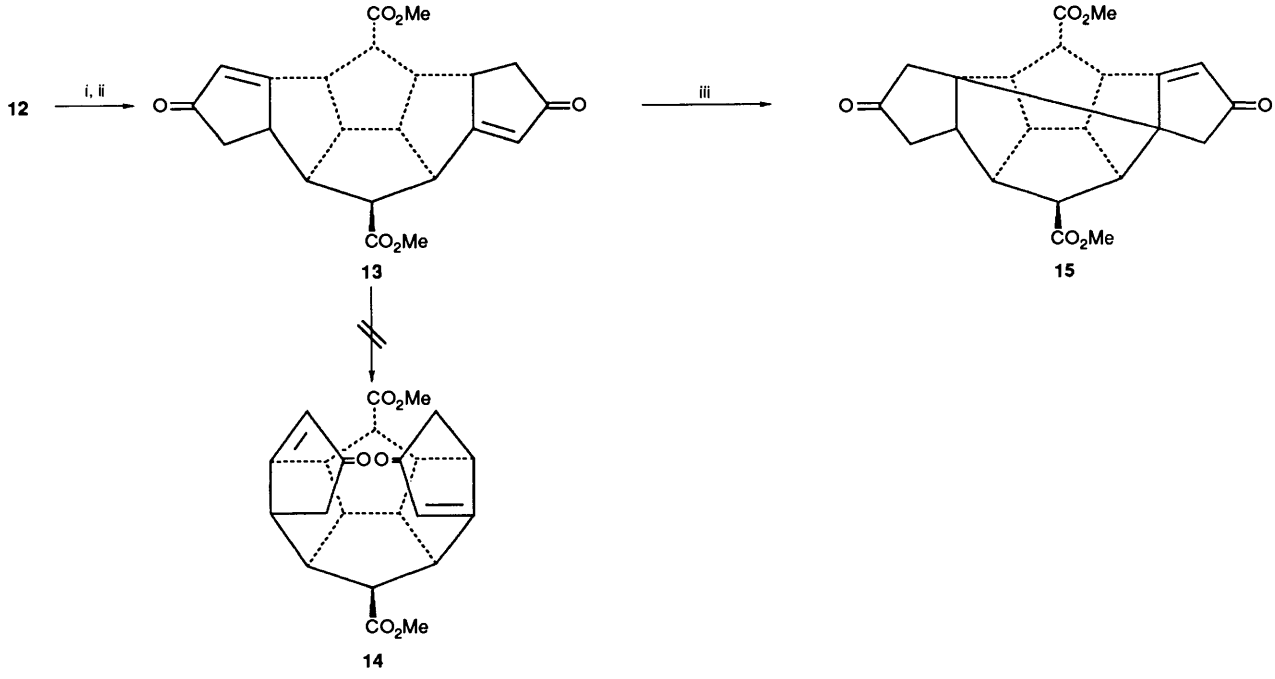
Bis-acetals **16** and **17** were now ready for stereoselective hydrogenation from the convex face to project the five-membered rings inward. This was achieved in a straightforward sequence of hydrolysis and hydrogenation from compound **16**. Hydrolysis of compound **16** by dil. HCl followed by hydrogenation of the crude product over 10% Pd–C resulted in the formation of hexaquinane dione **18** in 58% yield. However, when bis-acetal **17** was shaken in ethyl acetate under hydrogen over 10% Pd–C catalyst, compound **18** was directly obtained in 80% yield; perhaps some acid (acetic) impurity in the solvent was responsible for the hydrolysis during hydrogenation. The eight-line ^{13}C NMR spectrum of C_{20}-hexaquinane **18** not only showed the absence of sp^2-carbons but also revealed its higher order of symmetry. The structure of compound **18** was further secured through X-ray crystal-structure determination.*

With a reasonable supply of the pivotal pretarget diester **18**, we then attempted to carry out the 'molecular stitching' plan. In order to implement the intramolecular ring closure envisaged in Scheme 1, to give a secododecahedrane derivative, it was

* We thank Dr. T. N. Guru Row, National Chemical Laboratory, Pune for the crystal-structure determination.



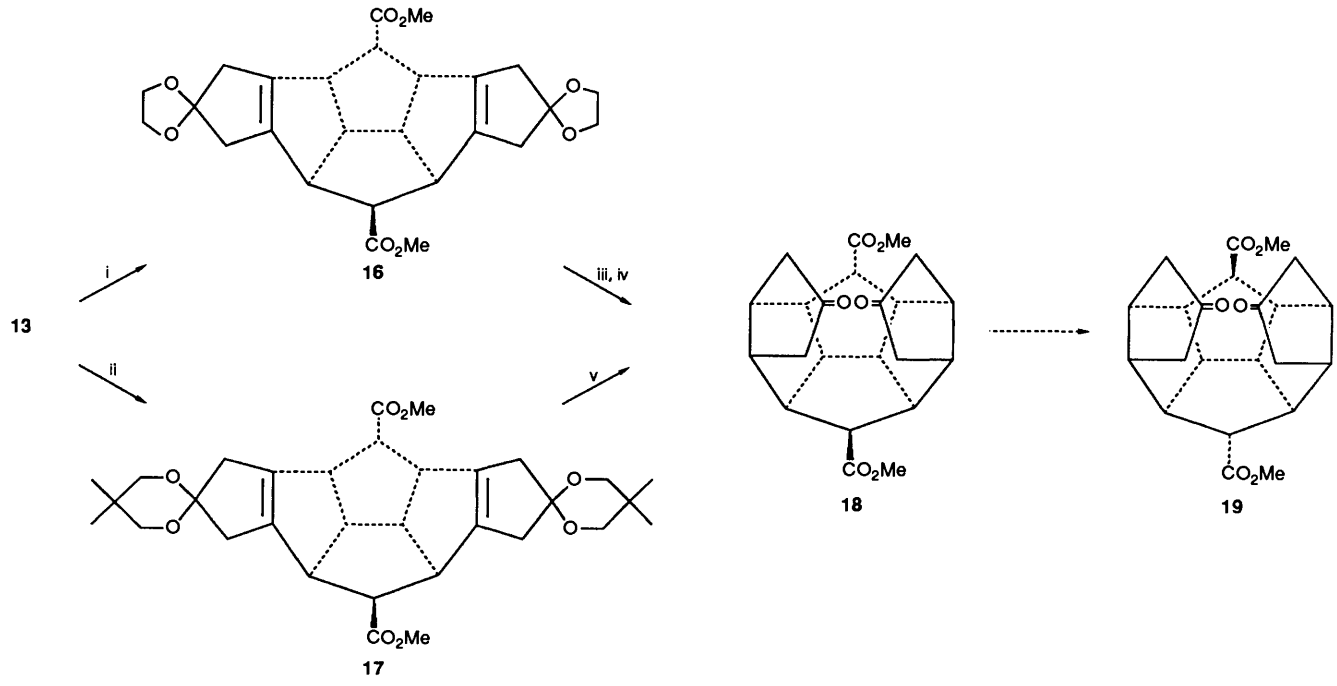
Scheme 3 *Reagents, conditions and yields:* i, Cl_3CCOCl, Zn(Cu), Et_2O, 16 h, 74%; ii, CH_2N_2, Et_2O–MeOH, 0 °C, 30 min; iii, Zn, NH_4Cl, MeOH, 30 min, 50% from **10** and **11**



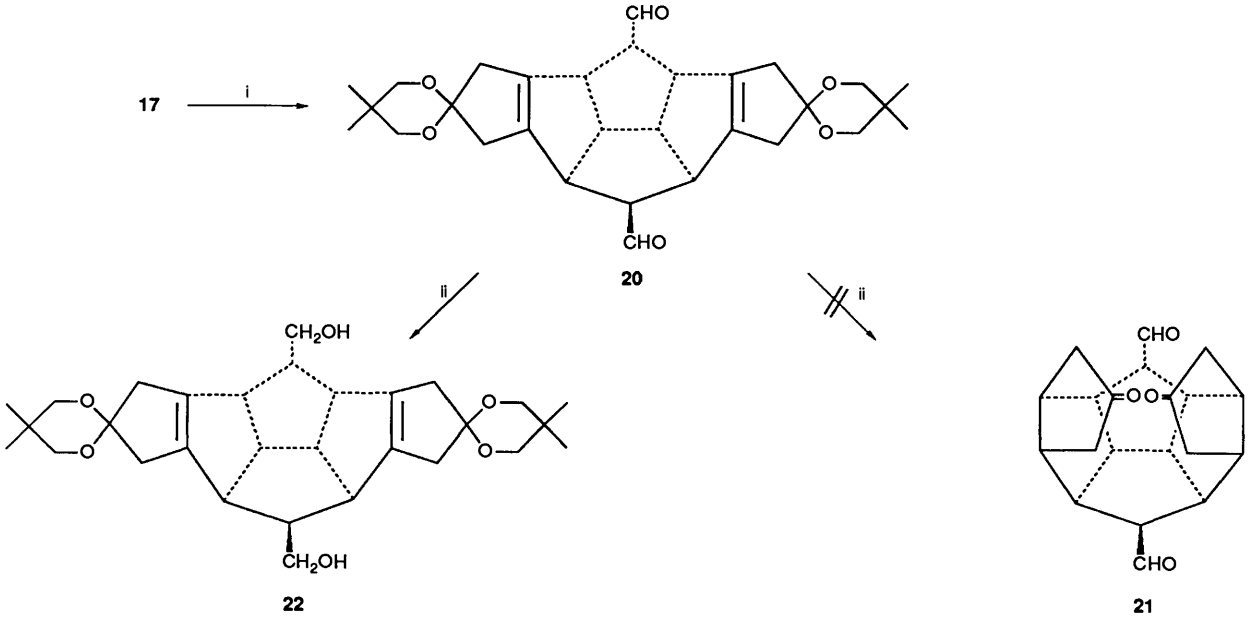
Scheme 4 *Reagents, conditions and yields:* i, HMDS, BuLi, THF, − 78 °C, TMSCl; ii, $Pd(OAc)_2$, MeCN, 72%; iii, DBU, toluene, heat, 20 min, 72%

imperative that the ester moieties in compound **18** be made to fall within the polyquinane cavity. To achieve this, we planned to employ a deprotonation–kinetic protonation method using non-nucleophilic bases. The resulting isomer **19** was to undergo a simultaneously expected cascade of anion-induced ring closures leading to a secododecahedrane diol dione. Thus, compound **18** was exposed to a variety of bases under kinetically controlled conditions and quenched with either a protic solvent or methyl iodide. In a majority of these reactions considerable loss of precious material occurred and no product from the reaction could be firmly characterised. The diester **18** was also exposed to $Bu^tO^-K^+$ and 3 mol dm^{-3} HCl under equilibrating conditions. However, despite many trials the desired epimerisation cyclisation could not be effected. At this stage we thought of modifying the diester group in compound **18** to a more electrophilic functionality in order to facilitate the epimerisation as well as the anionic ring-closure process. For this purpose, diketo dialdehyde **21** appeared to be an appropriate substrate. As an attempted, direct diisobutylaluminium hydride (DIBAL-H) reduction[13] of diester **18** was unsuccessful, the bis-acetal **17** was subjected to the reaction and the desired dialdehyde **20** was obtained in 70% yield. When the dial **20** was subjected to catalytic hydrogenation, only the diol **22** was isolated in 80% yield, through preferential aldehyde carbonyl group reduction (Scheme 6). The diol **22** could not be reduced further to invert the five-membered rings. Several other variations of this theme were attempted but the ester moieties could not be projected inside the polyquinane framework.

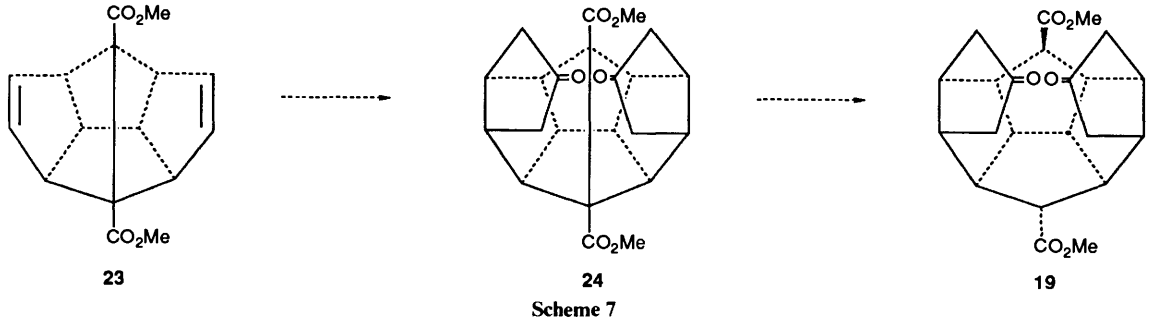
Cyclopentannulation of Hedaya–Paquette Ester: Attempts to elaborate a C_{20}-Hexaquinane to Dodecahedrane.—Our inability to induce the key transformation **18** ⟶ **19**, perhaps on



Scheme 5 *Reagents, conditions and yields:* i, Ethylene glycol, benzene, CSA, heat, 45 min, 55%; ii, 2,2-dimethylpropane-1,3-diol, CSA, heat, 15 h, 80%; iii, 20% HCl, THF, 8 h; iv, 10% Pd/C–H_2, EtOAc, 25 psi, 3 h, 58%; v, 10% Pd/C–H_2, EtOAc, 40 psi, 1 h, 80%

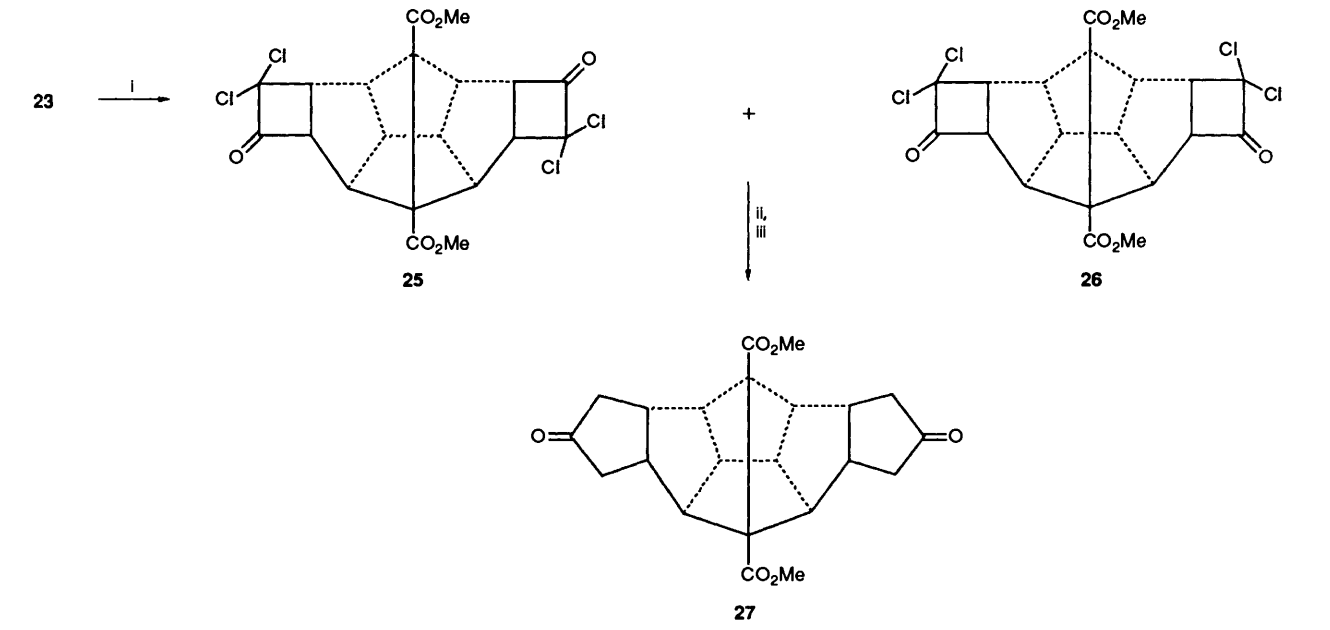


Scheme 6 *Conditions and yields:* i, DIBAL-H, CH_2Cl_2, −78 °C, 15 min, 70%; ii, 10% Pd/C–H_2, EtOAc, 25 psi, 20 min, 80%

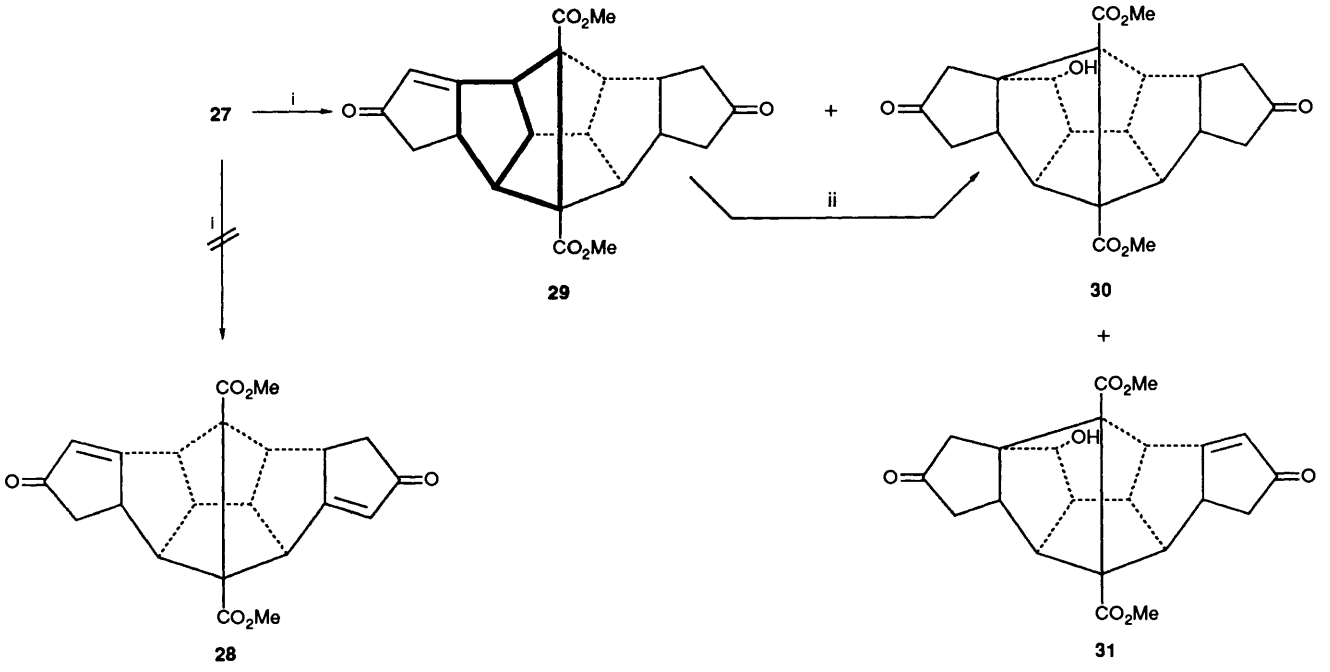


Scheme 7

account of steric overcrowding due to the cyclopentane rings already present within the polyquinane hemisphere, forced us to explore an alternative strategy to compound **19** (Scheme 7). A transannularly fused, bridged tetraquinane diester **23** (Hedaya–Paquette ester)[14] appeared to be an alternative building block to dodecahedrane **1**, within the ambit of our 'molecular



Scheme 8 *Reagents, conditions and yields:* i, Cl_3COCl, Zn(Cu), Et_2O, 16 h, 85%; ii, CH_2N_2, MeOH–Et_2O, 0 °C, 4 h; iii, Zn, NH_4Cl, MeOH, 42% from **25** and **26**

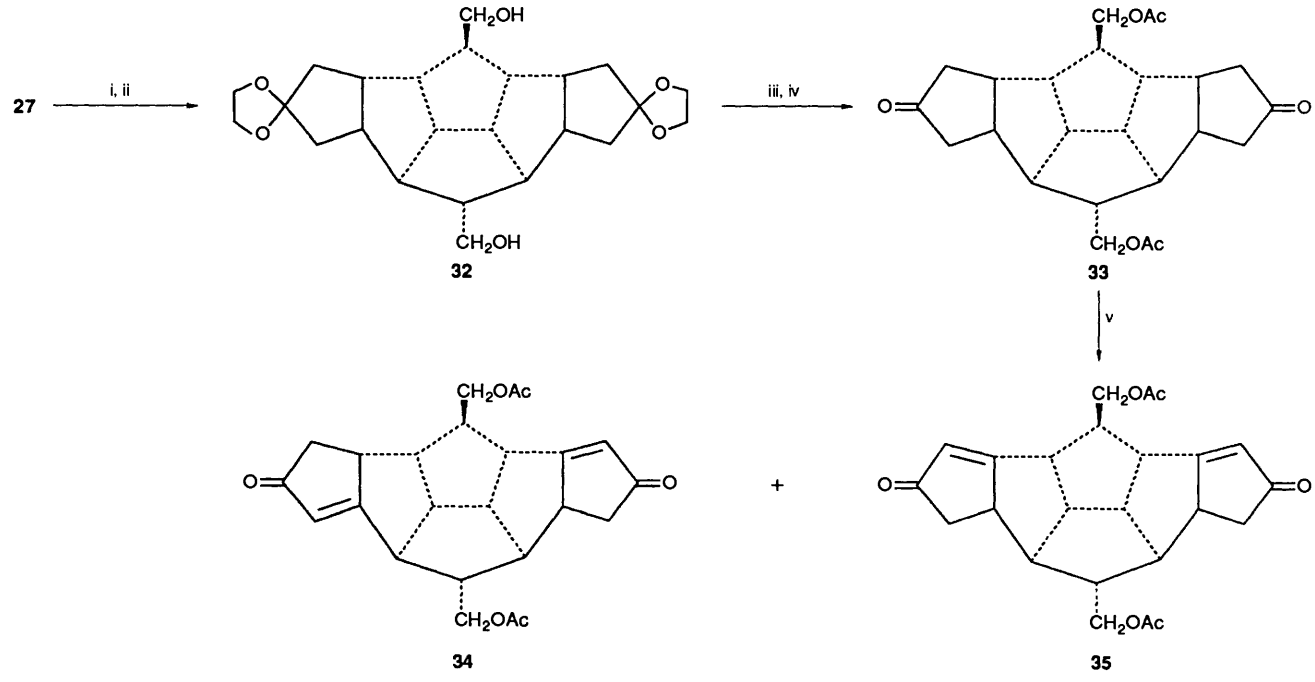


Scheme 9 *Reagents, conditions and yields:* i, $PdCl_2$, Bu^{t}OH, heat, 20 h, 35% (**29**), 25% (**30**), 12% (**31**); ii, PTSA, benzene

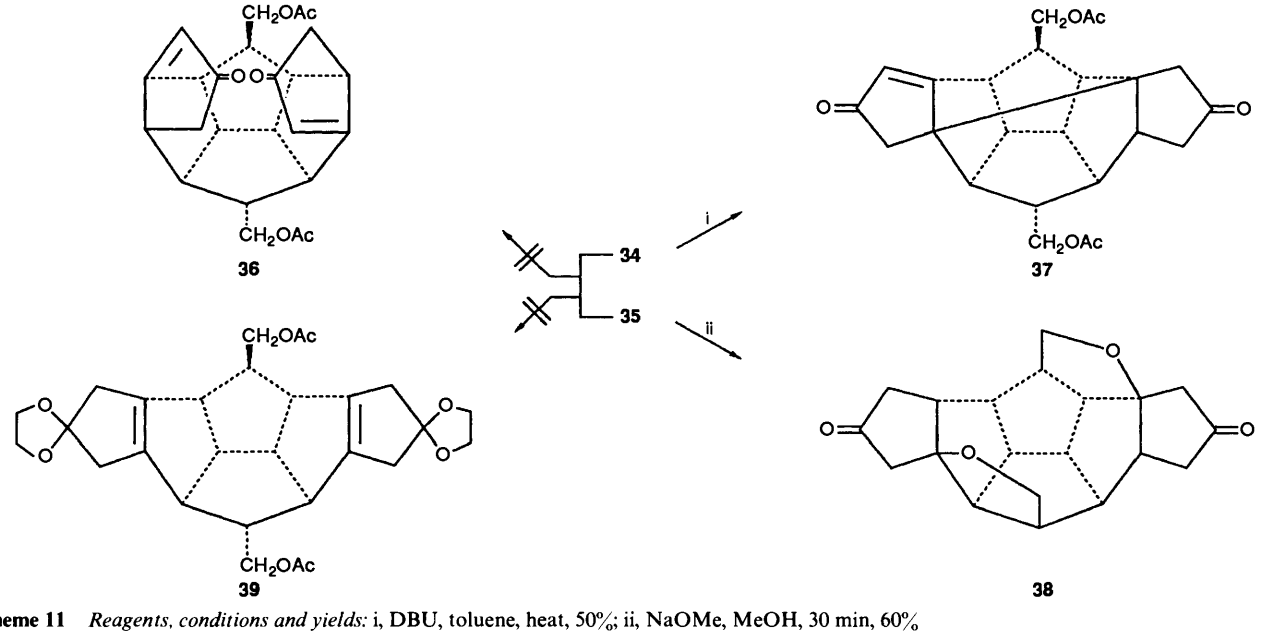
stitching' plan. Thus, bis-cyclopentannulation and inversion was expected to lead to the C_{20}-hexaquinane dione **24**. A planned stereoselective reductive C–C bond cleavage was to furnish the ultimate precursor **19** for the 'molecular stitching' plan.

In order to effect the bis-cyclopentannulation sequence, diester **23** was treated with an excess of dichloroketene (*in situ*) under high-dilution conditions to give the regioisomeric adduct mixture **25** + **26** in 85% yield (Scheme 8). This mixture was subjected to ring expansion and reductive dechlorination to give the bis-cyclopentannulated C_{20}-heptacyclic dione **27** in 40% yield after two steps.

The C_{20}-heptacyclic dione **27** has all the requisite functionality and the correct carbon skeleton for target molecule **24** but required the projection of the two newly appended cyclopentane rings within the spheroidal cavity. In an attempt to adopt the previously described inversion sequence, compound **27** was subjected to Mincionne's direct Pd^{2+} dehydrogenation methodology[15] in order to obtain the corresponding bis-enone **28**. However, no product corresponding to structure **28** was detected and instead a mixture of three products, *viz.* **29** (35%), **30** (25%) and **31** (12%), was obtained (Scheme 9). The major product was formulated as compound **29** on the basis of its ^1H NMR spectrum (δ_H 5.84, 1 H, d, J 3) and ^{13}C NMR spectrum (δ_C 218.4, 207.4, 187.9 and 123.8). The other two products (**30** and **31**) were hydroxy ketones and were formulated on the basis of complementary IR, ^1H NMR and HRMS data (see Experimental section). Formation of the novel heptacycles **30** and **31** indicated that the generation of enone **29** or bis-enone **28** triggers an extremely easy Wagner–Meerwein rearrangement within the bicyclo[2.2.1]heptane moiety present within them (heavy lines



Scheme 10 *Reagents, conditions and yields:* i, Ethylene glycol, benzene, PTSA, heat, 30 min, 82%; ii, Na–liq. NH_3, THF, Bu^{t}OH, 15 min, − 50 °C, 92%; iii, Ac_2O, pyridine, 7 h; iv, acetone, PTSA, 6 h, 50% from **32**; v, $PdCl_2$, Bu^{t}OH, heat, 72 h, 46% (**35**), 24% (**34**)

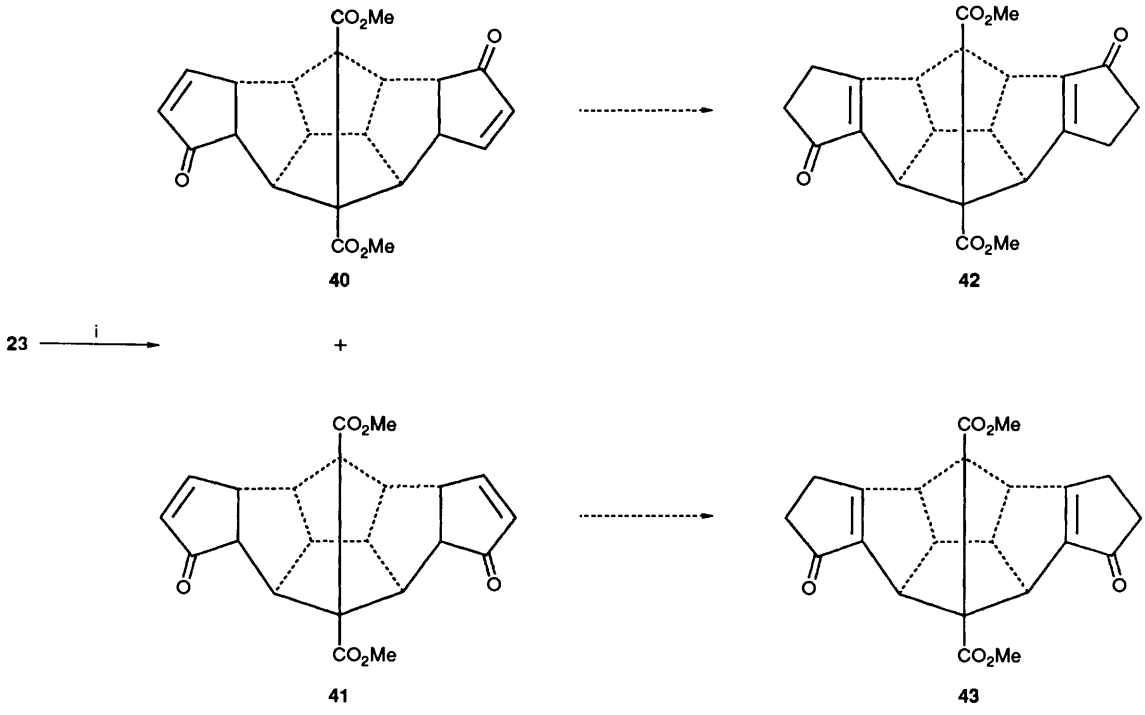


Scheme 11 *Reagents, conditions and yields:* i, DBU, toluene, heat, 50%; ii, NaOMe, MeOH, 30 min, 60%

in structure **29**) to furnish compounds **30** and **31**. Indeed, compound **29** on exposure to mild acidic conditions readily rearranged to compound **30**.

Since the presence of the trinorbornane moiety in compound **27** emerged as a complicating feature we decided, first of all, to remove it by central C–C bond cleavage.[7] For this purpose, the bis-ethylene acetal of dione **27** was prepared and subjected to reductive cleavage by Na–liq. NH_3. However, we unexpectedly obtained the *endo,endo*-diol **32** of axial symmetry, through simultaneous reduction of the C–C bond as well as of the ester moiety (Scheme 10). Acetylation and deprotection gave hexacyclic diacetate **33**. Now, direct Pd(II) dehydrogenation was successfully attempted and led to bis-enones **34** and **35** in 24 and 46% yield, respectively. Distinction between products **34** and **35** was readily made on the basis of their ^{13}C NMR spectra. While bis-enone **35** having axial symmetry, had a 12-line spectrum, the other isomer, compound **34**, having mirror-plane symmetry, showed a 15-line spectrum.

Attempts were now directed to relocate the enone double bonds in the enones **34** and **35** in order to obtain compound **36**. When C_s-bis-enone **34** was treated with DBU in refluxing toluene, a new crystalline product, compound **37**, was formed in 50% yield, which turned out to be a transannularly cyclised product (Scheme 11).[11] In another attempt at double-bond relocation, the C_{2v}-bis-enone **35** was exposed to methanolic sodium methoxide. A C_{20}-dioxaoctaquinane **38** arising from acetate hydrolysis followed by intramolecular Michael addition of -CH_2OH groups to enones was obtained. Structure **38** is based on mechanistic considerations and is fully commensurate with the spectral data obtained. Once again the interesting but unwanted transannular cyclisations became a major impediment to our ring-inversion protocol. Attempts to prepare bis-



Scheme 12 *Reagents, conditions and yields:* i, $CO_2(CO)_8$, C_2H_2, CO, benzene, 2 h, heat, 37% (**40**), 39% (**41**)

acetate **39** from **34** and **35** also failed, and a complex mixture of more polar products was observed.

Before abandoning our efforts toward the synthesis of dodecahedrane, we made one more attempt to achieve 'molecular stitching', *via* bis-cyclopentannulation of Paquette–Hedaya ester **23** by employing Pauson–Khand methodology.[16] Our expectation was that the resulting enones **40** and **41** will be immune to the problem of unwanted transannular cyclisation, due to the altered positions of the carbonyl groups. We planned to transpose the carbonyl groups to the required sites after implementing the ring-inversion protocol. When diester **23** was subjected to standard Pauson–Khand reaction conditions, a 1:1 mixture of regioisomeric bis-enones **40** and **41** was formed (Scheme 12). The two regioisomers were readily separated and fully characterised. The bis-enone **40**, of C_{2v}-symmetry, and the C_s-bis-enone **41**, were obtained in 37 and 39% yield, respectively. Various methods were attempted to isomerise the double bonds in compounds **40** and **41** to give required enones **42*** and **43**, respectively, using bases (DBU, LDA, $Bu^tO^-K^+$), acids (polyphorphonic acid, $MeSO_3H$, BF_3, H_2SO_4), heat and light but were found to be ineffective.

Conclusions.—We have successfully carried out bis-cyclopentannulation reactions on tetraquinanes **9** and **23** to furnish several interesting hexaquinanes. The C_{20}-hexaquinane diester **12** has been further elaborated to the all-cis-**18**, the penultimate target in our approach to dodecahedrane. However, the pivotal step, involving four-fold, base-catalysed cyclisation, has so far eluded us. Nonetheless, some interesting polyquinanes have been synthesized and some interesting reactions encountered.

Experimental

All m.p.s are uncorrected and were determined on a Buchi SMP-20 apparatus. ^1H NMR and ^{13}C spectra were recorded in $CDCl_3$ at 100 MHz and 25 MHz, respectively, unless mentioned otherwise, on a JEOL FX-100 spectrometer. *J*-Values are in Hz. Column chromatography was performed using Acme's silica gel (100–200 mesh). All solvents were freshly distilled and dried under appropriate conditions. All solvent extracts were washed with brine and dried over anhydrous sodium sulphate. High-resolution mass spectroscopy (HRMS) was carried out on a JEOL JMS DX-303 spectrometer. Light petroleum refers to the fraction boiling in the range 60–70 °C.

exo,exo-*Tetracyclo*[7.2.1.0.^{4,11}.0.^{6,10}]*dodeca*-2,7-*diene*-5,12-*dicarbaldehyde* **8**.—In a flame-dried, 50 cm^3, three-necked RB flask equipped with dry N_2 inlet, septum and a reflux condenser with mercury seal was placed methoxymethyl(triphenyl)-phosphonium chloride (740 mg, 2.16 mmol. The solid was suspended in dry diethyl ether (10 cm^3) and freshly sublimed sodium t-amyloxide (178 mg, 1.62 mmol) in diethyl ether (5 cm^3) was added. The resulting dark red reaction mixture was stirred for 30 min at room temperature. A solution of the tetraquinanedione **5**[5] (100 mg, 0.54 mmol) in dry diethyl ether (5 cm^3) was added and the reactants were stirred further for 1 h. The reaction mixture was then quenched with water and extracted with diethyl ether (20 cm^3 × 3). The extract was washed and dried. The solvent was removed and the residue was charged over a silica gel (10 g) column. The isomeric mixture of bis-enol ethers **6** and **7** (110 mg, 85%) was eluted with 5% ethyl acetate–light petroleum, ν_{max}(KBr)/cm^{-1} 3050, 2950, 1680 and 1110; δ_H 5.96 (2 H, s, C=C*H*OMe), 5.5–5.1 (4 H, m, HC=CH), 3.60 (6 H, s, C=CHO*Me*), 4.1–3.8 (2 H, m) and 3.5–3.2 (4 H, m); δ_C 139.2, 134.8, 134.7, 133.0, 132.9, 131.8, 128.7, 59.5, 54.3, 53.9, 52.9, 52.3, 52.2, 52.0 and 51.5.

The enol ether mixture obtained above was dissolved in diethyl ether (10 cm^3) and 4–5 drops of 35% perchloric acid were added at ice temperature. The reaction mixture was then stirred for 18 h, diluted with diethyl ether and slowly quenched with 5% aq. sodium hydrogencarbonate. The ethereal layer was washed and dried. The residue obtained after removal of the solvent was charged on a silica gel (10 g) column. Elution with 5% ethyl acetate–light petroleum furnished the *dialdehyde* **8** (65

* This bis-enone is the Paquette intermediate in dodecahedrane synthesis[1] and is obtained in eight steps from the pentacyclic ester **23**. Our isomerisation of diester **41** would have made compound **43** available in only two steps.

mg, 68%), which was crystallised from light petroleum, m.p. 112–113 °C; ν_{max}(KBr)/cm^{-1} 3050, 2950, 2720, 1700 and 720; δ_H 9.64 (2 H, d, *J* 2, CCHO), 5.42 (4 H, s, CH=CH), 3.76–3.0 (6 H, series of m) and 2.88 (2 H, s, CHC=O) (Found: C, 78.5; H, 6.5. $C_{14}H_{14}O_2$ requires C, 78.46; H, 6.58%).

Dimethyl exo,exo-*Tetracyclo*[7.2.1.0^{4,11}.0^{6,10}]*dodeca*-2,7-*diene*-5,12-*dicarboxylate* **9**.—To a solution of the tetraquinane dialdehyde **8** (50 mg, 0.23 mmol) in dry DMF (5 cm^3) was added PDC (345 mg, 0.92 mmol). The reactants were vigorously stirred for 13 h at room temperature. The reaction mixture was quenched with water and extracted with diethyl ether (15 cm^3 × 3). The extract was washed with water and dried. The concentrated extract was treated with excess of ethereal diazomethane and after 10 min the excess of diazomethane was quenched (acetic acid). The reaction mixture was diluted with more diethyl ether, washed successively with water and aq. $NaHCO_3$ and dried. The concentrate was charged over a silica gel (10 g) column. Elution with 20% ethyl acetate–light petroleum afforded diester **9**[7] (30 mg, 76%), which was crystallised from light petroleum, m.p. 76–78 °C; ν_{max}(KBr)/cm^{-1} 3050, 2925, 1730, 1160 and 740; δ_H 5.38 (4 H, s, CH=CH), 3.69 (6 H, s, CO_2Me), 3.7–3.2 (6 H, m) and 2.92 (2 H, s, C*H*CO_2Me); δ_C 176.4, 135.2, 56.1, 54.6, 52.7 and 51.9.

Dichloroketene Addition to Dimethyl exo,exo-*Tetracyclo*[7.2.1.0^{4,11}.0^{6,10}]*dodeca*-2,7-*diene*-5,12-*dicarboxylate* **9**.—To a vigorously stirred mixture of the *exo,exo*-diester **9** (100 mg, 0.36 mmol) and Zn–Cu couple (235 mg, 3.6 mmol) in dry diethyl ether (350 cm^3) was added a solution of trichloroacetyl chloride (635 mg, 3.6 mmol) in dry diethyl ether (150 cm^3) dropwise during 2 h. The reaction mixture was stirred further for 12 h at room temperature and was then filtered through a Celite pad to remove unchanged Zn and zinc chloride. The filtrate was washed successively with water and aq. $NaHCO_3$ and dried. Removal of solvent furnished a dark viscous material (500 mg), which was charged on a silica gel (20 g) column. Elution with 20% ethyl acetate–light petroleum yielded a 1:1 regioisomeric adduct mixture of compounds **10** and **11** (135 mg, 74%), ν_{max}(KBr)/cm^{-1} 1810, 1730, 1180 and 760.

Dimethyl 2β,6β,10β,14β-exo,exo-4,12,*Dioxohexacyclo*[13.2.1.0^{2,6}.0^{7,17}.0^{9,16}.0^{10,14}]*octadecane*-8,18-*dicarboxylate* **12**.—To an ice-cooled solution of compounds **10** and **11** (135 mg, 0.27 mmol) in diethyl ether (10 cm^3) was added an excess of ethereal diazomethane followed by a few drops of methanol. The reaction was maintained at 0–5 °C for 30 min, with occasional swirling. Excess of diazomethane was destroyed (acetic acid) and the reaction mixture was diluted with more diethyl ether, washed successively with water and aq. $NaHCO_3$ and dried. Removal of solvent furnished crude ring-expanded products which were directly used for dechlorination without purification.

To a solution of the above product in methanol (10 cm^3) cooled in an ice-bath was added excess of ammonium chloride (100 mg) followed by zinc (130 mg, 2 mmol) and the resulting suspension was stirred for 30 min. Excess of zinc was removed by filtration through a Celite pad. After removal of methanol under reduced pressure, the residue was diluted with water and extracted with methylene dichloride (25 cm^3). The extract was washed and dried. The crude product obtained after removal of solvent was charged over a silica gel (10 g) column. Elution with 70% ethyl acetate–light petroleum furnished the *hexaquinane diester* **12** (52 mg, 50%) and this was crystallised from methylene dichloride–light petroleum, m.p. 177–178 °C; ν_{max}(KBr)/cm^{-1} 2950, 1730 and 1220; δ_H(400 MHz) 3.70 (6 H, s, CO_2Me), 3.40–3.30 (2 H, m), 3.0–2.9 (4 H, m), 2.78–2.68 (4 H, m), 2.55–2.40 (6 H, m), 2.13 (2 H, d, *J* 7.84) and 2.07 (2 H, d, *J* 3.92); δ_C 218.9, 174.9, 58.2, 55.3, 52.3, 48.1 and 44.3 (Found: C, 68.25; H, 6.7. $C_{22}H_{26}O_2$ requires C, 68.37; H, 6.78%).

Dimethyl 6β,14β-4,12-*Dioxohexacyclo*[13.2.1.0^{2,6}.0^{7,17}.0^{9,16}.0^{10,14}]*octadeca*-2,10-*diene*-8,18-*dicarboxylate* **13**.—In a flame-dried, 50 cm^3, three-necked RB flask fitted with a dry N_2 inlet, septem and a mercury seal was placed butyllithium (0.3 cm^3; 0.3 mmol in hexane) and the reaction vessel was cooled to −78 °C. Hexamethyldisilazane (HMDS) (0.1 cm^3, 0.46 mmol) was carefully injected and the resulting slurry was stirred for 30 min. A solution of the hexaquinanedione **12** (50 mg, 0.13 mmol) in dry tetrahydrofuran (THF) (3 cm^3) was then slowly added. The reaction mixture was stirred for 30 min and quenched with TMSCl (0.1 cm^3, 0.78 mmol) and further stirred for 1 h. The reaction mixture was diluted with brine and extracted with diethyl ether (15 cm^3 × 3). The extract was washed and dried.

A solution of the above crude product in acetonitrile (5 cm^3) was cooled in an ice-bath and palladium(II) acetate (60 mg, 0.2 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and filtered through an alumina pad. The filtrate was concentrated and chromatographed over a silica gel (10 g) column. Elution with 70% ethyl acetate–light petroleum gave *title compound* **13** (36 mg, 72%), which was crystallised from methylene dichloride–light petroleum, m.p. 205–207 °C; ν_{max}(KBr)/cm^{-1} 2950, 1730, 1710 and 1620; δ_H 5.96 (2 H, d, *J* 3, C=CHC=O), 3.68 (6 H, s, CO_2Me) and 3.4–1.8 (14 H, series of m); δ_C 208.9, 186.9, 173.2, 125.5, 58.1, 54.0, 51.6, 50.7, 48.5, 47.4 and 46.5 (Found: C, 69.1; H, 5.8. $C_{22}H_{22}O_6$ requires C, 69.09; H, 5.79%).

Dimethyl 14β-4,12,*Dioxoheptacyclo*[13.2.1.0^{2,6}.0^{2,10}.0^{7,17}.0^{9,16}.0^{10,14}]*octadec*-5-*ene*-8,18-*dicarboxylate* **15**.—To a solution of bis-enone **13** (25 mg, 0.06 mmol) in dry toluene (10 cm^3) was added DBU (2 drops) and the resulting mixture was stirred at reflux for 20 min, quenched with water and diluted with ethyl acetate (15 cm^3). The organic layer was separated, washed with water and dried. The solvent was removed and the residue was charged over a silica gel (15 g) column and eluted with 70% ethyl acetate–light petroleum to furnish the *title compound* **15** (18 mg, 72%), which was crystallised from methylene dichloride–light petroleum, m.p. 143–144 °C; ν_{max}(KBr)/cm^{-1} 2950, 1730 and 1710; δ_H 6.01 (1 H, d, *J* 2, C=CHC=O), 3.72 (3 H, s, CO_2Me), 3.68 (3 H, s, CO_2Me) and 3.6–1.1 (15 H, series of m); δ_C 213.9, 208.7, 190.3, 173.4 (2 C), 126.3, 62.9, 61.8, 59.3, 54.4 (2 C), 54.1, 52.7, 52.6, 52.3, 52.0, 51.8, 51.6, 46.7, 46.2, 45.7 and 44.5 (Found: C, 69.2; H, 5.8. $C_{22}H_{22}O_6$ requires C, 69.09; H, 5.79%).

Dimethyl exo,exo-4,12-*Bis*(*ethylenedioxy*)*hexacyclo*[13.2.1.0^{2,6}.0^{7,17}.0^{9,16}.0^{10,14}]*octadeca*-2(6),10(14)-*diene*-8,18-*dicarboxylate* **16**.—A mixture of bis-enone **13** (25 mg, 0.06 mmol), ethylene glycol (2–3 drops) and a catalytic amount of CSA in dry benzene (20 cm^3) was refluxed using a Dean–Stark apparatus for 45 min. The reaction mixture was diluted with diethyl ether (20 cm^3), washed successively with water and sodium hydrogencarbonate and dried. The residue obtained after removal of solvent was charged over a silica gel (10 g) column. Elution with 50% ethyl acetate–light petroleum furnished bis-acetal **16** (17 mg, 55%) which, on crystallisation from light petroleum separated as crystals, m.p. 149–150 °C; ν_{max}(KBr)/cm^{-1} 2950, 1730, 1620 and 1300; δ_H 3.9 (8 H, s, OCH_2CH_2O), 3.66 (6 H, s, CO_2Me), 3.9–3.1 (4 H, m), 2.86 (2 H, s, C*H*CO_2Me) and 2.4–2.1 (10 H, m); δ_C 176.5, 143.5, 120.8, 64.5, 64.2, 58.5, 52.8, 51.9, 47.2 and 40.4 (Found: C, 66.25; H, 6.45. $C_{26}H_{30}O_8$ requires C, 66.35; H, 6.43%).

Dimethyl exo,exo-4,12-*Bis*-(2,2-*dimethyltrimethylenedioxy*)-*hexacyclo*[13.2.1.0^{2,6}.0^{7,17}.0^{9,16}.0^{10,14}]*octadeca*-2(6),10(14)-

diene-8,18-*dicarboxylate* **17**.—To a solution of *exo,exo*-bis-enone **13** (25 mg, 0.06 mmol) in dry benzene (20 cm^3) was added 2,2-dimethylpropane-1,3-diol (20 mg, 0.2 mmol) along with a catalytic amount of CSA. The reaction mixture was refluxed using a Dean–Stark apparatus for 1.5 h. Work-up as described in the previous experiment gave a crude product, which was charged on a silica gel (10 g) column. Elution with 30% ethyl acetate–light petroleum furnished *bis-acetal* **17** (28 mg, 80%), which was crystallised from light petroleum, m.p. 184–185 °C; ν_{max}(KBr)/cm^{-1} 2950, 1730 and 1100; δ_H(400 MHz) 3.90–3.80 (2 H, m), 3.67 (6 H, s, CO_2Me), 3.44 (8 H, d, *J* 12, OCH_2), 3.32–3.25 (4 H, m), 2.87 (2 H, s, $CHCO_2Me$), 2.42 (8 H, br s) and 0.95 (12 H, s, CMe); δ_C 176.3, 143.0, 112.9, 71.7, 58.9 and 52.6 (Found: C, 69.4; H, 7.3. $C_{32}H_{42}O_8$ requires C, 69.27; H, 7.63%).

Dimethyl 2α,6α,10α,14α-exo,exo-4,12-*Dioxohexacyclo*-[13.2.1.$0^{2,6}$.$0^{7,17}$.$0^{9,16}$.$0^{10,14}$]*octadeca*-8,18-*dicarboxylate* **18**.—To a solution of the acetal **16** (15 mg, 0.03 mmol) in THF (10 cm^3) was added 20% HCl (2 cm^3). The reaction mixture was stirred at room temperature for 8 h and THF was then removed. The residue was diluted with water and extracted with methylene dichloride (15 cm^3 × 3). Drying and removal of solvent gave the crude enone mixture, which was directly hydrogenated over pre-activated 10% Pd/C (5 mg) in ethyl acetate (10 cm^3) for 3 h at 25 psi hydrogen pressure. The catalyst was removed by filtration and the crude product was chromatographed over an alumina (5 g) column. Elution with 50% ethyl acetate–light petroleum afforded the *hexacyclic dione* **18** (7 mg, 58%), which was crystallised from methylene dichloride–light petroleum, m.p. 233 °C; ν_{max}(KBr)/cm^{-1} 2950, 1740 and 1200; δ_H(400 MHz) 3.68 (6 H, s, CO_2Me), 3.30–3.20 (2 H, m), 3.14–3.0 (8 H, m) and 2.45–2.24 (10 H, m); δ_C 219.6, 175.7, 57.1, 55.4, 52.1, 49.2, 42.9 and 40.4 (HRMS: Found: M^+, 386.1721. $C_{22}H_{26}O_2$ requires *M*, 386.1729).

Alternative Preparation of Compound **18**.—Diacetal **17** (25 mg, 0.045 mmol) was hydrogenated over 10% Pd/C catalyst (5 mg) in ethyl acetate (10 cm^3) for 1 h at 40 psi. The catalyst was filtered off and the solvent was removed. The residue, on crystallisation, afforded the hexaquinanedione **18** (14 mg, 80%).

exo,exo-4,12-*Bis*-(2,2-*dimethyltrimethylenedioxy*)*hexacyclo*-[13.2.1.$0^{2,6}$.$0^{7,17}$.$0^{9,16}$.$0^{10,14}$]*octadeca*-2(6),10(14)-*diene*-8,18-*dicarbaldehyde* **20**.—To a flame-dried, 25 cm^3, three-necked RB flask equipped with a septum, dry N_2 inlet and mercury seal was added a solution of the diacetal **17** (15 mg, 0.02 mmol) in dry methylene dichloride (10 cm^3). After the reaction vessel had been cooled to −70 °C, DIBAL-H (0.1 mmol, 0.1 cm^3 of 1 mol dm^{-3} solution in hexane) was added and the reactants were stirred for 15 min. The reaction mixture was quenched with methanol and diluted with methylene dichloride. The organic layer was washed and dried. The solvent was removed and the residue was charged on a silica gel (10 g) column. Elution with 70% ethyl acetate–light petroleum furnished the *dial* **20** (9 mg, 70%), which was crystallised from light petroleum, m.p. 230–231 °C; ν_{max}(KBr)/cm^{-1} 2960, 2720, 1720 and 1110; δ_H 9.66 (2 H, s, CHO), 3.46 (8 H, br s, CH_2OC), 2.85 (2 H, s, $CHCHO$), 2.44 (14 H, br s) and 0.94 (12 H, s, CMe_2); δ_C 208.7, 118.0, 71.7, 57.3, 54.0, 48.9, 39.1, 29.9 and 22.5 (HRMS: Found: M^+, 494.2659. $C_{30}H_{38}O_6$ requires *M*, 494.2669).

exo,exo-8,18-Bis(*hydroxymethyl*)*hexacyclo*[13.2.1.$0^{2,6}$.$0^{7,17}$.$0^{9,16}$.$0^{10,14}$]*octadeca*-2(6),10(14)-*diene*-4,12-*dione Bis*(2,2-*dimethyltrimethylene*) *Acetal* **22**.—A solution of diacetal **20** (5 mg, 0.011 mmol) was hydrogenated over 10% Pd/C (5 mg) in ethyl acetate (5 cm^3) at 25 psi for 20 min. The catalyst was filtered off and the filtrate was concentrated. The residue was chromatographed over a silica gel (5 g) column. Elution with ethyl acetate furnished *compound* **22** (4 mg, 80%), which was crystallised from methylene dichloride–light petroleum, m.p. 205–206 °C; ν_{max}(KBr)/cm^{-1} 3400, 2950 and 1100; δ_H 3.64–3.28 (14 H, m, OCH_2 and CH_2OH), 3.64–2.72 (6 H, m), 2.42 (8 H, d, *J* 2), 2.16 (2 H, t, *J* 6, $CHCH_2OH$) and 0.96 (12 H, s, CMe_2); (HRMS: Found: M^+, 498.2995. $C_{30}H_{42}O_6$ requires *M*, 498.2982).

Dichloroketene Addition to Dimethyl Pentacyclo[6.4.0.0^{2,6}.0^{5,12}.0^{7,11}]*dodeca*-3,9-*diene*-1,12-*dicarboxylate* **23**.—To a vigorously stirred mixture of the diester **23** (1.36 g, 5 mmol) and Zn–Cu couple (12 g, 0.18 g-atom) in dry diethyl ether (400 cm^3) was added a solution of trichloroacetyl chloride (12 g, 66 mmol) in dry diethyl ether (400 cm^3) dropwise during 4 h. The reaction mixture was stirred at room temperature for 12 h, filtered through a Celite pad and worked up as described in an earlier experiment. Removal of the solvent furnished a dark viscous material, which was charged on a silica gel (40 g) column. Elution with 5% ethyl acetate–light petroleum yielded a regioisomeric mixture of the bisdichloroketene adducts **25** and **26** (2.1 g, 85%); ν_{max}(KBr)/cm^{-1} 1810, 1740, 1300 and 1110; δ_H 4.4–4.0 (4 H, m), 3.8 (3 H, s, CO_2Me), 3.76 (6 H, s, CO_2Me), 3.72 (3 H, s, CO_2Me), 3.6–3.3 (4 H, m) and 3.1–2.6 (12 H, m).

Dimethyl 3β,7β,12β,16β-5,14-*Dioxoheptacyclo*[9.7.0.0^{2,9}.0^{3,7}.0^{8,18}.0^{10,17}.0^{12,16}]*octadecane*-1,18-*dicarboxylate* **27**.—To a solution of the bisdichloroketene adducts **25** and **26** (2.0 g) in diethyl ether (400 cm^3), cooled to 0 °C, was added an excess of cold ethereal diazomethane followed by methanol (5 cm^3). The reaction mixture was kept at 0 °C for 4 h with occasional swirling. Excess of diazomethane was destroyed and the ethereal solution was washed successively with water and aq. $NaHCO_3$ and dried. Removal of solvent furnished crude material (2.3 g), consisting of an isomeric mixture of ring-expanded products, ν_{max}(KBr)/cm^{-1} 1770, 1740 and 1300.

To a solution of the above crude material (2.1 g) in methanol (40 cm^3) were added zinc powder (0.65 g, 0.01 g-atom) and ammonium chloride (0.54 g, 0.01 mmol). The resulting suspension was stirred for 45 min and filtered through a Celite pad. Methanol was removed under reduced pressure and the crude product was extracted with methylene dichloride. Purification on a silica gel column furnished *diester* **27** (650 mg, 42%), which was crystallised from methylene dichloride–light petroleum, m.p. 200 °C; ν_{max}(KBr)/cm^{-1} 1730, 1610 and 1100; δ_H 3.66 (6 H, s, CO_2Me) and 3.18–1.60 (18 H, m); δ_C 219.2 (s), 171.1 (s), 63.9 (d), 59.6 (s), 51.6 (q), 43.4 (t), 42.9 (d) and 35.1 (d) (Found: C, 68.95; H, 6.5. $C_{22}H_{24}O_6$ requires C, 68.74; H, 6.29%).

$PdCl_2$-*Mediated Dehydrogenation of Compound* **27**.—A solution of diketone **27** (120 mg, 0.32 mmol) and $PdCl_2$ (200 mg, 1.1 mmol) in t-butyl alcohol (25 cm^3) was refluxed for 20 h. Unchanged $PdCl_2$ as well as the Pd metal formed during the reaction was filtered off. The filtrate was concentrated and products (120 mg) were separated by preparative TLC to furnish the unchanged diketone **27** (50 mg, 40%) and compounds **29**, **30** and **31**. *Monoenone* **29** (25 mg, 35% based on starting material consumed) was crystallised from methylene dichloride–light petroleum, m.p. 190 °C; ν_{max}(KBr)/cm^{-1} 730, 1690 and 1620; δ_H 5.84 (1 H, d, *J* 3, C=CHC=O), 3.76 (3 H, s, CO_2Me), 3.68 (3 H, s, CO_2Me) and 3.5–1.7 (15 H, m); δ_C 218.4, 187.9, 170.7, 170.6, 123.8, 64.1, 63.3, 61.2, 60.0, 56.9, 52.0, 51.0, 50.7, 44.6, 44.4, 43.7, 43.1, 40.3, 35.4 and 34.9 (HRMS: Found: M^+, 382.1431. $C_{22}H_{22}O_6$ requires *M*, 382.1416).

Hydroxy dione **30** (18 mg, 25% based on starting material consumed) was crystallised from methylene dichloride–light petroleum, m.p. 215 °C; ν_{max}(KBr)/cm^{-1} 3525, 1740 and 1620; δ_H 4.24 (1 H, s, CHO), 3.8 (3 H, s, CO_2Me), 3.78 (3 H, s, CO_2Me)

and 3.2–1.7 (17 H, m) (HRMS: Found: M^+, 400.1520. $C_{22}H_{24}O_7$ requires *M*, 400.1536).

Hydroxy enone **31** (9 mg, 12% based on starting material consumed) was crystallised from methylene dichloride–light petroleum, m.p. 238 °C; ν_{max}(KBr)/cm^{-1} 3525, 1740, 1710 and 1620; δ_H 5.84 (1 H, d, C=CH), 3.78 (3 H, s, CO_2Me), 3.70 (3 H, s, CO_2Me) and 3.5–1.4 (15 H, m).

2β,6β,10β,14β,-8,18-*Bis*(*hydroxymethyl*)*hexacyclo*-[13.2.1.0^{2,6}.0^{7,17}.0^{9,16}.0^{10,14}]*octadecane*-4,12-*dione Diethylene Acetal* **32**.—A solution of hexacyclic dione **27** (1 g, 2.6 mmol), ethanediol (0.7 cm^3, 13 mmol) and a catalytic amount of PTSA in dry benzene (50 cm^3) was refluxed using a Dean–Stark apparatus for 30 min. The reaction mixture was diluted with ethyl acetate (75 cm^3) and the organic layer was washed successively with aq. $NaHCO_3$ and water and dried. Removal of solvent, and crystallisation of the residue from methylene dichloride–light petroleum, furnished the *diacetal* (1 g, 82%), m.p. 226 °C; ν_{max}(KBr)/cm^{-1} 2950, 1740 and 1100; δ_H 3.88 (8 H, s, O–CH_2CH_2O), 3.64 (6 H, s, CO_2Me), 3.8–3.4 (8 H, m), 3.4–3.2 (2 H, m), 2.1–1.7 (4 H, m) and 1.48–1.1 (4 H, m); δ_C 171.6, 117.0, 64.9, 64.0, 62.5, 59.3, 51.4, 42.5, 40.0 and 36.7 (Found: C, 66.2; H, 6.9. $C_{22}H_{32}O_8$ requires C, 66.09; H, 6.81%).

A solution of the bis-acetal (500 mg, 1.06 mmol) in THF (10 cm^3) was added dropwise to a stirred solution of distilled liquid ammonia (30 cm^3) containing THF (10 cm^3) and sodium (230 mg, 10 mmol). At the end of 15 min, Bu^{t}OH (2 cm^3) was introduced and the ammonia was allowed to evaporate off. The remaining organic solution was extracted with diethyl ether (200 cm^3), and the extract was washed successively with water and brine. After evaporation of solvent, the crude product was charged on a silica gel (25 g) column and eluted with ethyl acetate to obtain *compound* **32** (407 mg, 92%), which was crystallised from methylene dichloride–light petroleum, m.p. 195–196 °C; ν_{max}(KBr)/cm^{-1} 3250, 1100 and 1020; δ_H 3.85 (8 H, s, OCH_2CH_2O) and 3.8–1.4 (26 H, series of m); δ_C 118.9, 64.7, 63.9, 62.6, 59.0, 53.8, 51.6, 44.26 and 44.24 (Found: C, 69.0; H, 8.2. $C_{24}H_{34}O_6$ requires C, 68.88; H, 8.18%).

2β,6β,10β,14β-8,18-*Bis*-(*acetoxymethyl*)*hexacyclo*-[13.2.1.0^{2,6}.0^{7,17}.0^{9,16}.0^{10,14}]*octadecane*-4,12-*dione* **33**.—To a solution of diol **32** (400 mg, 0.95 mmol) in pyridine (5 cm^3) was added acetic anhydride (1 cm^3, 10 mmol) and the mixture was stirred for 7 h at room temperature. The reaction mixture was poured into water (20 cm^3) and extracted with ethyl acetate (30 cm^3 × 3). The extract was washed successively with 20% HCl and water prior to being dried and evaporated. The crude residual diacetate was dissolved in acetone (20 cm^3) and a catalytic amount of PTSA was added. The reaction mixture was then stirred at reflux for 6 h and most of the acetone was removed under reduced pressure. The resulting residue was extracted with ethyl acetate (30 cm^3 × 3) and the extract was washed successively with $NaHCO_3$ and water and dried. Evaporation of solvent and purification of the crude product over a silica gel (25 g) column with 80% ethyl acetate–light petroleum as eluent gave *diacetate* **33** (200 mg, 50%), which was crystallised from methylene dichloride–light petroleum, m.p. 190–192 °C; ν_{max}(KBr)/cm^{-1} 1740, 1250 and 1030; δ_H 4.20 (4 H, d, *J* 8, CH_2OCO), 3.4–1.4 (20 H, m) and 1.96 (6 H, s, OAc); δ_C 217.9, 170.5, 63.1, 58.0, 53.3, 46.8, 45.6, 42.8 and 20.7 (Found: C, 69.4; H, 7.3. $C_{24}H_{30}O_6$ requires C, 69.54; H, 7.29%).

$PdCl_2$-*Mediated Dehydrogenation of Compound* **33**.—To a solution of dione **33** (100 mg, 0.24 mmol) in dry t-butyl alcohol (20 cm^3) was added an excess of palladium(II) chloride (177 mg, 1 mmol) and the mixture was heated to reflux for 72 h, then filtered through a neutral alumina pad and the filtrate was concentrated. The residue obtained was charged on a silica gel (15 g) column and eluted with ethyl acetate to furnish *bis-enone* **35** (46 mg, 46%), which was crystallised from methylene dichloride–light petroleum, m.p. 173–175 °C; ν_{max}(KBr)/cm^{-1} 1740, 1720 and 1240; δ_H 5.9 (2 H, d, *J* 2, C=CHC=O), 4.1–3.9 (4 H, dd, J_1 3, J_2 8, CH_2OAc), 3.8–1.7 (14 H, m) and 1.96 (6 H, s, OAc); δ_C 208.3, 188.5, 170.7, 129.1, 63.4, 59.3, 51.9, 48.3, 47.4, 46.3, 45.4 and 20.8 (HRMS: Found: M^+, 410.1741. $C_{24}H_{26}O_6$ requires *M*, 410.1729).

Further elution of the column with the same solvent afforded the bis-enone **34** (24 mg, 24%); ν_{max}(KBr)/cm^{-1} 1740, 1730 and 1140; δ_H 5.84 (2 H, d, *J* 2, C=CHC=O), 4.24 (2 H, d, *J* 8, CH_2OAc), 3.8 (2 H, d, *J* 8), 3.88–1.88 (14 H, m), 1.96 (3 H, s, OAc) and 1.90 (3 H, s, OAc); δ_C 208.4, 187.9, 170.5, 170.2, 127.9, 63.3, 62.5, 60.7, 53.0, 49.4, 48.0, 46.9, 44.8, 43.9 and 20.8.

14β-8,18-*Bis*(*acetoxymethyl*)*heptacyclo*[13.2.1.0^{2,6}.0^{2,10}.-0^{7,17}.0^{9,16}.0^{10,14}]*octadec*-5-*ene*-4,12-*dione* **37**.—To a solution of bis-enone **34** (35 mg, 0.085 mmol) in dry toluene (10 cm^3) was added DBU (0.05 cm^3, 0.33 mmol) and the mixture was heated under reflux for 1 h. The reaction mixture was diluted with ethyl acetate (10 cm^3), washed successively with 5% HCl and water and dried. Evaporation of solvent gave a crude product, which was charged on a silica gel (10 g) column. Elution of the column with ethyl acetate furnished the *title compound* **37** (18 mg, 50%), which was recrystallised from methylene dichloride–light petroleum to give needles, m.p. 169–171 °C; ν_{max}(KBr)/cm^{-1} 1740, 1720 and 1640; δ_H(400 MHz) 5.96 (1 H, d, *J* 1.1, C=CHC=O), 4.25–4.17 (4 H, m, CH_2OAc), 4.02–3.97 (1 H, dd, J_1 8, J_2 11), 3.25–3.24 (1 H, t, *J* 5.2), 2.96–2.94 (2 H, m), 2.62–2.17 (10 H, m), 2.07 (3 H, s, OAc), 2.05 (3 H, s, OAc), 1.90–1.82 (1 H, dd, J_1 10.8, J_2 19.0); δ_C 214.7, 208.9, 190.2, 170.7, 127.4, 63.6, 62.7, 61.7, 61.6, 54.1, 53.9, 53.7, 52.0, 50.0, 49.9, 48.3, 48.0, 47.0, 46.1, 45.2 and 21.0 (HRMS: Found: M^+, 410.1720. $C_{24}H_{26}O_6$ requires *M*, 410.1729).

5β,17β,12,21-*Dioxaoctacyclo*[17.2.1.0^{1,5}.0^{6,10}.0^{7,22}.0^{8,18}.-0^{9,13}.0^{13,17}]*docosane*-3,15-*dione* **38**.—To an ice-cold, magnetically stirred solution of bis-enone **35** (15 mg, 0.036 mmol) in dry methanol (5 cm^3) was added sodium methoxide (10 mg, 0.18 mmol). The cooling bath was removed and the reaction mixture was stirred at room temperature for 30 min. Methanol was removed under reduced pressure and the residue was diluted with water (15 cm^3). The aq. layer was acidified with 20% HCl and extracted with methylene dichloride (15 cm^3 × 3); usual work-up furnished crude material, which was charged on a silica gel (5 g) column. Elution with 80% ethyl acetate–light petroleum gave *dioxaoctacyclic bis-ether* **38** (7 mg, 60%), which was crystallised from methylene dichloride–light petroleum, m.p. 184–185 °C; ν_{max}(KBr)/cm^{-1} 1740, 1180 and 1060; δ_H(400 MHz) 4.15–4.12 (2 H, dd, J_1 2.4, J_2 9.6, CH_2O), 3.98–3.94 (2 H, dd, J_1 6.6, J_2 9.6, OCH_2), 3.47–3.42 (2 H, m), 3.30–3.24 (2 H, m), 3.20–3.12 (2 H, m), 3.12–3.05 (2 H, m), 2.82–2.75 (2 H, dd, J_1 10.2, J_2 18.5), 2.64 (4 H, s), 2.62–2.55 (2 H, m) and 2.08–2.02 (2 H, dd, J_1 5.0, J_2 18.8); (HRMS: Found: M^+, 326.1509. $C_{20}H_{22}O_4$ requires *M*, 326.1512).

Pauson–Khand Annulation of Compound **23**.—In a 100 cm^3, three-necked, RB flask fitted with a reflux condenser was placed a solution of dicobalt octacarbonyl (685 mg, 2 mmol) in dry benzene (60 cm^3). Acetylene gas was bubbled for 1 h through the above, stirred solution while the reaction mixture was kept at room temperature to form the acetylene complex. A solution of diester **23** (270 mg, 1 mmol) in dry benzene (10 cm^3) was then added slowly. The reaction mixture was heated to reflux with simultaneous gentle bubbling of carbon monoxide and acetylene gases for 1 h. The reaction mixture was cooled and then filtered through a Florisil pad. The filtrate was evaporated and the residue was charged over a silica gel (40 g) column. Elution with

60% ethyl acetate–light petroleum gave *compound* **40** (53 mg, 37%), which was crystallised from methylene dichloride–light petroleum, m.p. 238–240 °C; ν_{max}(KBr)/cm^{-1} 2950, 1720, 1680 and 1100; δ_H 7.68–7.52 (2 H, dd, J_1 6, J_2 3, *H*C=CHC=O), 6.4–6.2 (2 H, dd, J_1 4, J_2 2, CH=C*H*C=O), 3.72 (6 H, s, CO_2Me), 3.6–3.4 (2 H, m), 2.86 (2 H, d, *J* 5), 2.64 (4 H, d, *J* 8) and 2.2–1.7 (2 H, m); δ_C 211.1, 170.7, 165.9, 136.7, 60.3, 59.5, 57.3, 52.0, 46.9, 42.9 and 41.3; (Found: C, 69.4; H, 5.3. $C_{22}H_{20}O_6$ requires C, 69.45; H, 5.30%).

Further elution of the column with the same solvent system gave the *regioisomer* **41** (55 mg, 39%), which was crystallised from methylene dichloride–light petroleum, m.p. 263–264 °C; ν_{max}(KBr)/cm^{-1} 2950, 1720, 1680 and 1120; δ_H 7.60–7.44 (2 H, dd, J_1 6, J_2 3, C*H*=CHC=O), 6.36–6.20 (2 H, dd, J_1 4, J_2 2, CH=C*H*(C=O), 3.68 (6 H, s, CO_2Me), 3.56–3.36 (2 H, m), 2.92 (2 H, d, *J* 6), 2.64 (4 H, d, *J* 12) and 2.2–1.6 (2 H, m); δ_C 210.9, 171.0, 170.5, 165.3, 136.9, 60.9, 59.9, 58.4, 58.3, 52.0, 46.9, 43.7 and 41.3 (Found: C, 69.35; H, 5.4. $C_{22}H_{20}O_6$ requires C, 69.45; H, 5.30%).

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