# Simple synthetic entries into the tricyclo[5.3.1.1$^{3,9}$]dodecane and 8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane ring systems

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**The bis(enolate) of diester 1 undergoes a double intramolecular alkylation reaction with 3-chloro-2-chloromethylprop-1-ene 2 to form the tricyclic product 3 in 75% yield. This conversion represents the first high-yielding route to derivatives of tricyclo[5.3.1.1$^{3,9}$]dodecane, an alicyclic ring system of considerable theoretical and structural interest. Diol derivatives 5, 7, 10, 16 and 17 are prepared to investigate further the crystal engineering requirements for obtaining new helical tubuland hosts. The X-ray structures of 5, 10 and 7 reveal one-, two- and three-dimensional hydrogen bonded lattice structures, respectively, despite their remarkable molecular similarity. Solid 5 comprises chains assembled through intermolecular · · · H–O · · · H–O · · · H–O · · · and novel intramolecular alkene · · · H–O hydrogen bonds; while diol 10 forms double layers of diols constructed from recurved spiral chains (four molecules per repeat unit) of intermolecular · · · H–O · · · H–O · · · H–O · · · hydrogen bonds. When crystallised from diethyl ether, the hydroxy groups of 7 are linked · · · H–O · · · H–O · · · H–O · · · around threefold screw axes to give a further example of the helical tubuland lattice. This is a microporous solid with empty tubes of cross-sectional area 17.8 Å$^2$ parallel to *z*. Appropriately functionalised tricyclo[5.3.1.1$^{3,9}$]dodecanes undergo efficient intramolecular cyclisation providing compounds 18, 20, 22 and 24 which are the first reported derivatives of 8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane.**

## Introduction

During the course of our continuing studies into the helical tubuland family of diol inclusion hosts[1] we required a convenient preparation of 2,5,8-trisubstituted tricyclo[5.3.1.1$^{3,9}$]-dodecane derivatives in order to investigate compounds such as **5**, **7**, **10**, **16** and **17**. The closely related molecular structures of these diols fit the formal molecular rules required for potential helical tubuland lattice formation[2,3] and therefore were important target molecules. Relatively little work had been reported previously on syntheses of this alicyclic skeleton, and none which could supply the necessary functionality at these three positions. This paper provides a simple solution to this problem and also describes the first derivatives of the previously unknown 8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane system.

## Results and discussion

### Synthetic entry to 2,5,8-trisubstituted tricyclo[5.3.1.1$^{3,9}$]-dodecanes

Few synthetic data on tricyclo[5.3.1.1$^{3,9}$]dodecane (1,1-bis-homoadamantane) derivatives have been published despite this ring system being of considerable interest from a theoretical viewpoint. Parker *et al.*[4] have predicted enhanced reactivity due to relief of angle strain at positions C3 and C7 in reactions leading to bridgehead carbocation or radical formation. Similarly the formation of bridgehead alkene derivatives is expected to be particularly favourable. Even the possible formation of bridgehead inside-pyramidalised hydrogen structures has been mooted.[5]

The 1,1-bishomoadamantane skeleton is therefore quite different in its behaviour to simpler homologues such as adamantane. These properties, which are reflected in the difficulty of its synthesis, arise because part of its skeleton comprises a bicyclo-[3.3.3]undecane (manxane) sub-structure where flattening of the bridgehead sites creates significant strain.[4] Hence preparative methods involving formation of the required eight-membered rings by closure methods are rarely effective, although syntheses of double bridgehead 1,5-diaza- and 1,5-diphospha-manxanes have been most successful.[6,7]

The following approaches to the 1,1-bishomoadamantane skeleton have been reported. Adamantanone may be ring expanded easily into homoadamantan-4-one, and this in turn subjected to Tiffeneau–Demjanov ring expansion which produced tricyclo[5.3.1.1$^{3,9}$]dodecan-4-one (15% yield). From this material Sasaki and co-workers were able to prepare several other 4-substituted derivatives and also the parent hydrocarbon, but attempts to obtain the ring system through ring expansion of 3-tosyloxymethylhomoadamantane were unsuccessful.[8]

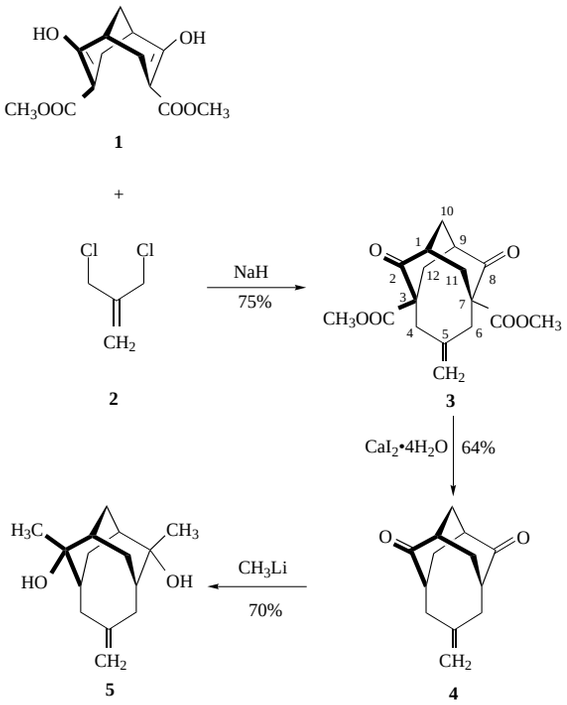
In an alternative approach, Ag$^{I}$-assisted hydrolysis of the dichlorocarbene adduct of homoadamant-4-ene gave a mixture of products including 5-chlorotricyclo[5.3.1.1$^{3,9}$]dodec-5-en-4-ol (30%).[9]

Ward and Murray[10] used the route to tricyclo[5.3.1.1$^{3,9}$]-dodecan-4-one outlined above to prepare several bridgehead enolate derivatives, and ultimately the bridgehead alkene itself, in accord with the above ideas of favoured sp$^2$ carbon hybridisation at this site.

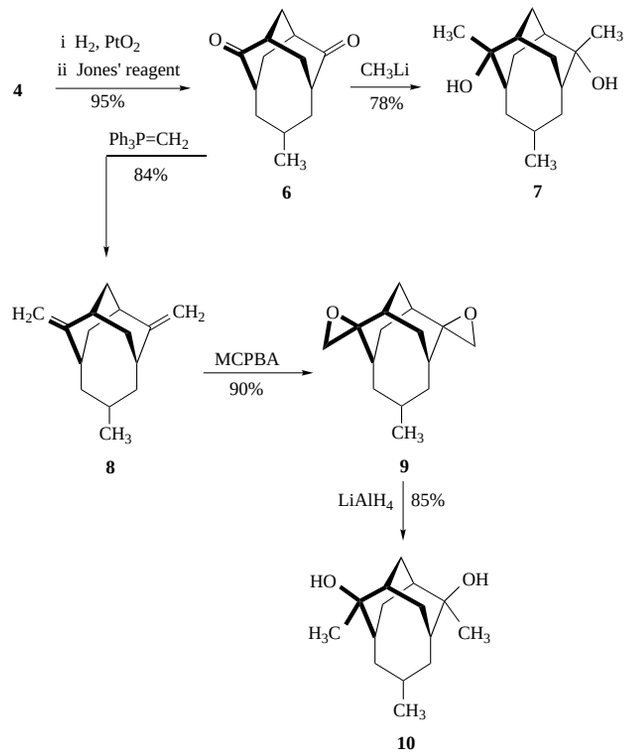
The final approach is our own, whereby the bicyclic diester **1**[11] was treated with sodium hydride in 1,2-dimethoxyethane and then refluxed with 1,3-dibromopropane affording 3,7-bis(methoxycarbonyl)tricyclo[5.3.1.1$^{3,9}$]dodecane-2,8-dione in 26% yield.[12] Unfortunately this reaction is capricious, isolation of pure product is difficult, and the low yield obtained discourages further synthetic steps. Nonetheless we have used this approach to obtain helical tubuland diols containing this tricyclic skeleton and have studied their inclusion properties.[1,13]

It was therefore a welcome surprise that the corresponding double intramolecular alkylation of **1** using 3-chloro-2-chloromethylprop-1-ene **2**[14] (Scheme 1) afforded the required 5-substituted diester **3** cleanly and in excellent yield (75%). Both Schulze *et al.*[6] and Bell *et al.*[15] have found the diiodo analogue of **2** to be an effective eight-membered ring-forming reagent in heteroatom cyclisations, and the discovery of this efficient reaction now allows detailed investigation of the rare 1,1-bishomoadamantane ring system.

Product **3** was fully characterised using conventional methods and several X-ray structures have been determined of compounds synthesised from it. Hence there is no doubt about the authenticity of this structural assignment, even though its proton-decoupled $^{13}$C NMR spectrum in $(CD_3)_2SO$ contained



**Scheme 1**



**Scheme 2**

some unusual features. At 355 K the ten signals required for structure **3** appeared as sharp singlets at the expected $\delta$ values. However, at 300 K only six sharp singlets were observed. A further two broad peaks were present at $\delta$ 58.8 (C) and 45.4 ($CH_2$), and two very broad and extremely weak peaks at $\delta$ 211.1 (C=O) and 38.6 ($CH_2$). These signals correspond to C3/C7, C4/C6, C2/C8 and C11/C12, respectively. Clearly **3** is undergoing slow conformational motion at room temperature. This process will be examined in future work, but similar effects were observed for other derivatives of this ring system. In fact, the appearance of broad $^{13}$C NMR signals in room temperature spectra could be used here as a crude diagnostic indicator that new products actually did have this molecular skeleton.

### Syntheses of the 5-substituted tricyclo[5.3.1.1$^{3,9}$]dodecanediols 5, 7 and 10

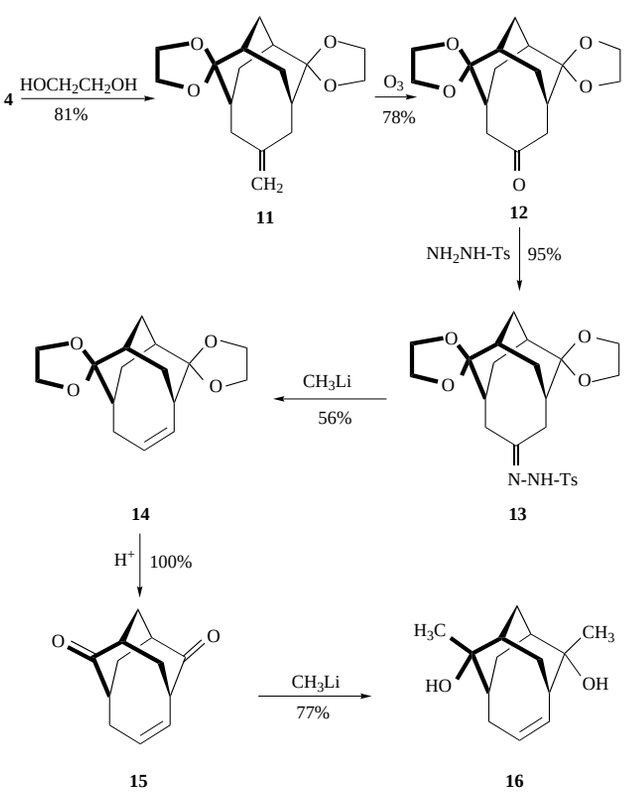
Removal of the methoxycarbonyl groups of **3** using simple acidic hydrolysis methods failed to yield the expected diketone **4** for reasons examined later. An alternative reaction, heating with calcium iodide tetrahydrate in dimethyl sulfoxide following the method of Chang and co-workers,[16,17] overcame this problem. Under carefully monitored conditions of temperature and reaction time, a 64% conversion was obtained. Preferential attack of methyllithium on the more exposed *exo*-faces of **4**, afforded the target 2,8-dimethyl-5-methylenetricyclo[5.3.1.1$^{3,9}$]-dodecane-2-*syn*,8-*syn*-diol **5** (Scheme 1). (In accord with our previous papers we designate hydroxy groups as *syn*- or *anti*- with respect to the larger of the bridges across the molecular twofold or pseudo-twofold axis.)

Also as described later, attempts to prepare diol **7** by direct catalytic reduction of **5** were not successful and therefore the dione **4** was reacted instead. Reduction of the alkene group proceeded slowly using $H_2$–$PtO_2$ (50 °C, 45 psi) and took 3 days for completion. At this stage a 4:1 mixture of ketol and diol products was present from concomitant reduction of the carbonyl functionality. Jones' oxidation gave the dione **6** in overall 95% yield, and further reaction using methyllithium produced 2,5,8-trimethyltricyclo[5.3.1.1$^{3,9}$]dodecane-2-*syn*,8-*syn*-diol **7** (Scheme 2).

Diol **10** is the double epimer of **7** and its preparation employed the methodology used previously in such circumstances.[1] Wittig reaction on dione **6** using the Dehmlow method[18] produced an excellent yield of the corresponding diene. Epoxidation of the more exposed *exo*-faces of **8** provided **9** which underwent reductive ring opening using $LiAlH_4$ to provide 2,5,8-trimethyltricyclo[5.3.1.1$^{3,9}$]dodecane-2-*anti*,8-*anti*-diol **10**.

### Syntheses of the tricyclo[5.3.1.1$^{3,9}$]dodec-4-ene diols 16 and 17

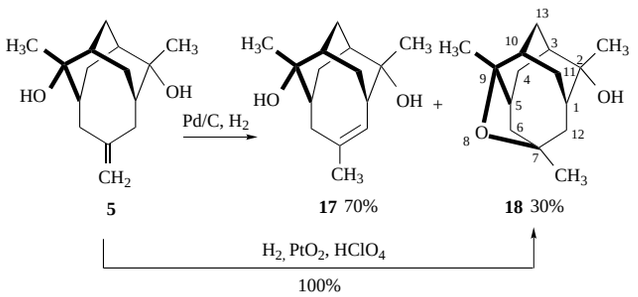
The preparation of diol **16** (Scheme 3) commenced from dione **4** by protection of the carbonyl groups through reaction with ethylene glycol to give diketal **11**. This reaction was catalysed by just one crystal of toluene-*p*-sulfonic acid since greater amounts



**Scheme 3**

caused a significant degree of isomerisation of the alkene to the *endo*-isomer. Ozonolysis gave ketone **12** which was readily converted into its tosylhydrazone derivative **13**. This reacted with methyllithium in a Shapiro reaction to yield the alkene **14**. Finally compound **14** was deprotected in quantitative yield, and then the resulting dione **15** alkylated using methyllithium to afford 2,8-dimethyltricyclo[5.3.1.1$^{3,9}$]dodec-4-ene-2-*syn*,8-*syn*-diol **16**. This diol was obtained as a colourless oil after column chromatography, and as an amorphous semi-solid from pentane or hexane.

Attempts to convert diol **5** to **7** through catalytic reduction using $H_2$ and Pd/C were completely unsuccessful. An initial experiment conducted at ambient temperature and pressure in ethyl acetate solution gave 70% of the isomerised diol **17** and 30% of another compound (Scheme 4). These products were




**Scheme 4**

separated by column chromatography. 2,5,8-Trimethyltricyclo-[5.3.1.1$^{3,9}$]dodec-4-ene-2-*syn*,8-*syn*-diol **17** was obtained as an oil and proved to be resistant to hydrogenation. A further experiment on **5** (50 °C, 45 psi $H_2$, 3 days) still gave **17** as the major product, and diol **7** eventually had to be prepared by the different method above.

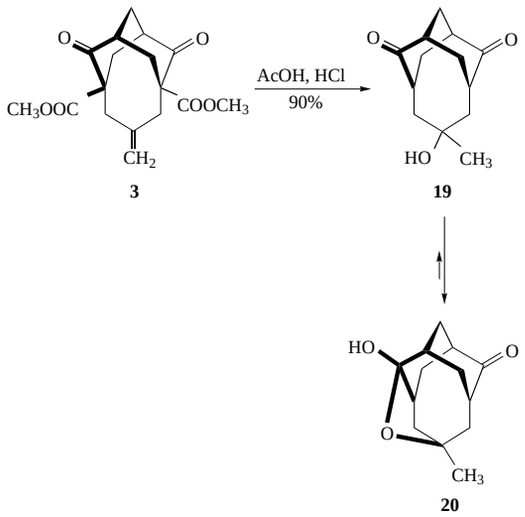
### Syntheses of the 8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane derivatives 18, 20, 22 and 24

As noted above, attempted reduction of diol **5** gave the isomerised diol **17** plus a 30% yield of a new and unexpected product. This compound was obtained quantitatively if the hydrogenation reaction was attempted in ethyl acetate solution using $H_2$ and $PtO_2$ with addition of two drops of 70% perchloric acid. Its $^{13}$C NMR data revealed loss of both the $C_2$ symmetry and the alkene functionality present in the starting material. Microanalytical and mass spectral data showed that this product was isomeric and hence an additional ring must have been produced. Taking into account the other data available (see Experimental section) the cyclic ether structure 2,7,9-trimethyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane-2-*endo*-ol **18** had been produced (Scheme 4). Models of diol **5** (and its crystal structure) show that the alkene group is in proximity to one of the two hydroxy groups, so formation of **18** presumably involves an acid-catalysed intramolecular addition process.

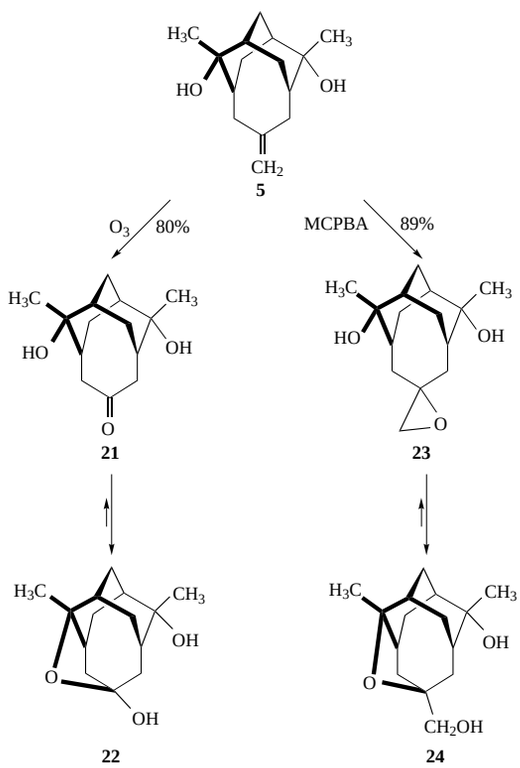
Other derivatives of this previously unreported ring system also could be obtained simply and in high yield. As related earlier, acidic hydrolysis of diester **3** did not yield the expected product **4**. Instead, the hemiketal 9-hydroxy-7-methyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane-2-one **20** was produced in 90% yield (Scheme 5). Presumably loss of the ester groups was accompanied by hydration of the alkene group to produce the ketol **19** which then cyclised, although no evidence for this equilibrium was visible from the $^{13}$C NMR spectrum of **20** in $CDCl_3$.

Similarly the hemiketal 2,9-dimethyl-8-oxatetracyclo-[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane-2-*endo*,7-diol **22** was isolated in 80% yield (Scheme 6) from ozonolysis of diol **5** and no sign of an equilibrium with the open ketol structure **21** was apparent from solution NMR data.

A fourth example of this class of compounds was obtained when diol **5** was reacted with *m*-chloroperbenzoic acid. The product was not the anticipated epoxide **23**, but rather was




**Scheme 5**




**Scheme 6**

7-hydroxymethyl-2,9-dimethyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]-tridecane-2-*endo*-ol **24** which was formed in 89% yield. This material is the formal result of an acid-catalysed epoxide ring-opening where one hydroxy group of **23** has acted as an intramolecular nucleophile.

The $^{13}$C NMR spectra of all four 8-oxatetracyclo-[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane compounds showed sharp signals and were free of the line broadening effects observed earlier for the tricyclo[5.3.1.1$^{3,9}$]dodecane derivatives. This difference was a useful pointer to those reactions which had undergone intramolecular cyclisation to this new tetracyclic skeleton.

### Crystal structures of the diols 5, 7 and 10

The X-ray structures of the three crystalline diols were determined, and numerical details relating to these are presented in Table 1. Details of the solution and refinement of the structures are described in the Experimental section. Of these three candidate compounds only **7** exhibited any inclusion host properties.

**Discussion of crystal structure of 5.** The molecular structure

**Table 1** Numerical details of the solution and refinement of structures of diols **5**, **7** and **10**

| | Compound | | |
|---|---|---|---|
| | **5** | **7** | **10** |
| Formula | $C_{15}H_{24}O_2$ | $C_{15}H_{26}0_2$ | $C_{15}H_{26}O_2$ |
| $M$ | 236.4 | 238.4 | 238.4 |
| Crystal description | {100} {010} (1−1−2) (11−2) (−102) | {100} (00−1) (011) (1−11) (0−11) (−101) (−111) | {010} {021} (−100) (11 0−8) |
| Space group | $P2_1/c$ | $P3_121$ | $P2_1/c$ |
| $a$/Å | 7.707(2) | 13.708(1) | 7.416(3) |
| $b$/Å | 14.790(3) | 13.708(1) | 23.175(6) |
| $c$/Å | 12.615(3) | 7.0046(8) | 9.416(4) |
| $\beta$/° | 115.11(1) | (90) | 123.28(1) |
| $V$/Å$^3$ | 1302.1(6) | 1139.9(2) | 1353.0(9) |
| $T$/°C | 21(1) | 21(1) | 21(1) |
| $Z$ | 4 | 3 | 4 |
| $D_c$/g cm$^{-3}$ | 1.21 | 1.04 | 1.17 |
| Radiation, $\lambda$/Å | Cu-K$\alpha$, 1.5418 | Cu-K$\alpha$, 1.5418 | Cu-K$\alpha$, 1.5418 |
| $\mu$/cm$^{-1}$ | 5.73 | 4.91 | 5.51 |
| Crystal dimensions/mm | 0.19 × 0.16 × 0.45 | 0.35 × 0.35 × 0.36 | 0.27 × 0.07 × 0.15 |
| Scan mode | $\theta$–2$\theta$ | $\theta$–2$\theta$ | $\theta$–2$\theta$ |
| $2\theta_{max}$/° | 140 | 140 | 120 |
| $\omega$ scan angle | 0.50 + 0.15 tan $\theta$ | 0.60 + 0.15 tan $\theta$ | 0.60 + 0.15 tan $\theta$ |
| No. of intensity measurements | 2700 | 1613 | 2209 |
| Criterion for observed reflection | $I/\sigma(I) > 3$ | $I/\sigma(I) > 3$ | $I/\sigma(I) > 3$ |
| No. of independent obsd. reflections | 1997 | 1383 | 1209 |
| No. of reflections ($m$) and variables ($n$) in final refinement | 1997, 161 | 1383, 90 | 1209, 160 |
| $R = \Sigma^m\|\Delta F\|/\Sigma^m\|F_o\|$ | 0.051 | 0.037 | 0.077 |
| $R_w = [\Sigma^m w\|\Delta F\|^2/\Sigma^m w\|F_o\|^2]^{\frac{1}{2}}$ | 0.087 | 0.058 | 0.103 |
| $s = [\Sigma^m w\|\Delta F\|^2/(m - n)]^{\frac{1}{2}}$ | 3.35 | 2.50 | 3.05 |
| Crystal decay | 1 to 0.93 | 1 to 0.96 | 1 to 0.96 |
| Max., min. transmission coefficients | 0.92, 0.83 | 0.87, 0.85 | 0.98, 0.90 |
| Largest peak in final diff. map/e Å$^{-3}$ | 0.26 | 0.25 | 0.27 |
| Extinction coefficient | 5.34 × 10$^{-4}$ | — | — |
| $R$ for (no. of) multiple measurements | 0.042 (178) | 0.012 (358) | 0.036 (168) |

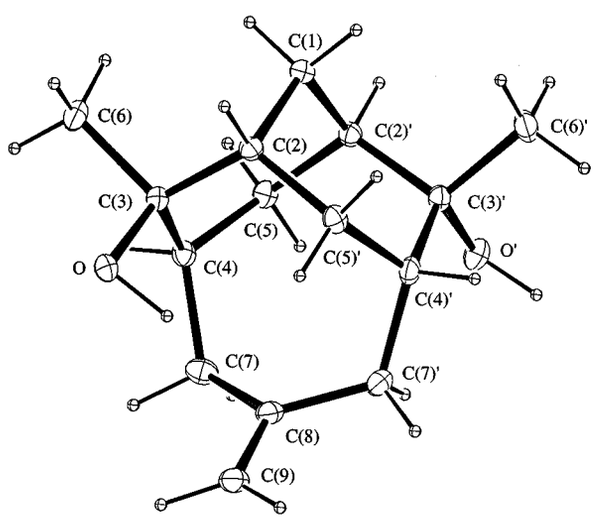



**Fig. 1** Molecular structure and conformation of diol **5** from its X-ray determination, showing the crystallographic numbering system used. Diol **7** uses the same basic system but has average $C_2$ symmetry in the solid state.

and conformational arrangement of diol **5** is shown in Fig. 1. Each molecule takes part in only two intermolecular H−O···H−O hydrogen bonds, one at each of the two hydroxy groups, such that the diols link together in chains along direction $2a+c$ with the hydrogen bonds following the sequence –donor–acceptor–donor–acceptor– *etc.* Molecules in each chain have the enantiomeric sequence –A–B–A–B–A– *etc.* (where A and B represent the two enantiomers of **5**) and these also have alternating orientations along the chain (Fig. 2). There are no particularly close contacts (C···C <3.6 Å or H···H <2.2 Å) between individual diol chains.

The hydroxy hydrogen atom which does not take part in the above hydrogen bonding is directed towards the double bond

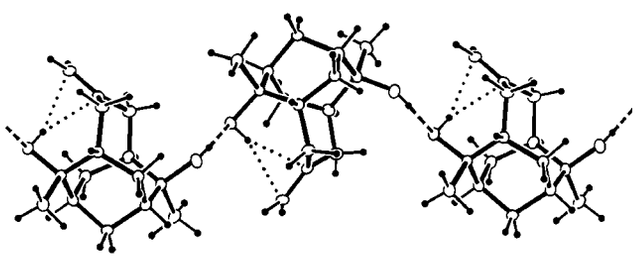


**Fig. 2** The molecular chain arrangement present in solid diol **5** showing the intermolecular H−O···H−O (dashed lines) and intramolecular alkene···H−O (dotted lines) hydrogen bonds present. Enantiomers of **5** alternate along the chains which interact with each other by means of dispersion forces.

of the methylene group generating an intramolecular alkene π···H−O hydrogen bond. These hydrogen bonds are also oriented on alternating sides of the chain and consequently all the diol propano bridges point in the same direction along the chain. The C=C···H−O distances are 2.14 Å to C(8) and 2.30 Å to C(9).

Typically each hydroxy group of our alicyclic diols participates in two hydrogen bonds (one donor and one acceptor).[1] In this instance, however, one of the groups is less completely hydrogen bonded since it only participates as a donor. Examination of the structure (Fig. 2) reveals that this arrangement is a compromise. The planarity forced on the molecular bridge atoms C(7), C(8), C(9) and C(7)′ by the alkene functionality means that it is sterically impossible to place three diol hydroxy groups close enough to generate the threefold hydrogen bonded spine motif (see Fig. 3) required for the helical tubuland structure.[1] Hence diol **5** cannot form this lattice despite otherwise satisfying the required structural features.[2,3]

Alkene π···H−O hydrogen bonding is a rare solid state interaction as revealed by recent examinations of the Cambridge Structural Database (CSD) carried out by Desiraju[19]

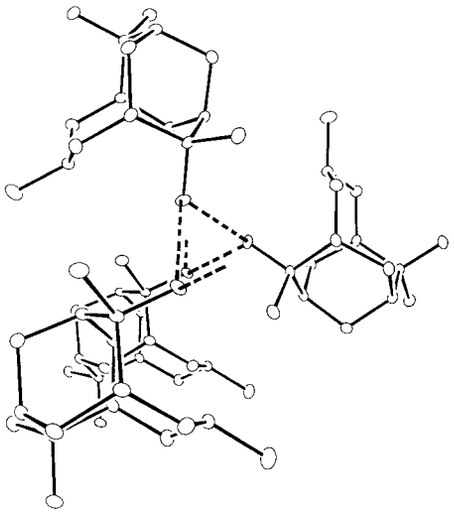


**Fig. 3** The trigonal hydrogen bonded spine structure present in the helical tubuland lattice of diol **7** with the hydrogen bonds shown as dashed lines. Hydrogen atoms have been omitted for clarity.

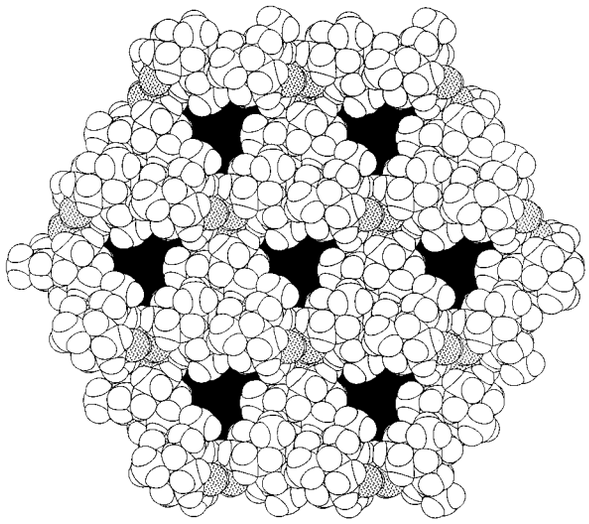


**Fig. 4** Projection view in the *ab* plane of the helical tubuland lattice of diol **7** using space filling representation. Oxygen atoms involved in the hydrogen bonded spines are stippled, and the cross-sectional areas (each 17.8 Å$^2$) of the parallel canals are coloured black. The methyl groups projecting into the canals are disordered to create average symmetry in the resulting crystal but, for convenience, these are all arbitrarily oriented up in this drawing.

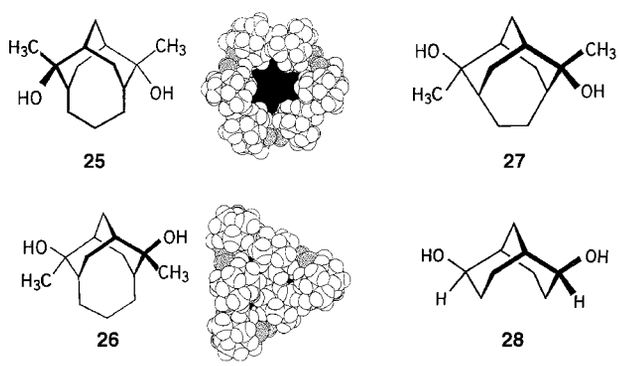



**Fig. 5** Left: Structures of the helical tubuland diols **25** and **26** showing a projection view of one canal only. The canal unobstructed cross-sectional areas are shaded black and oxygen atoms are stippled. Right: Molecular structures of diols **27** and **28** which involve recurved spirals of hydrogen bonds in the solid state.

and Rzepa[20] and their co-workers. The latter more comprehensive search (CSD March 1993 version: 109 992 crystal structures) produced only four hits for C=C · · · H ⩽ 2.5 Å involving *both* carbon atoms; or eleven hits where only *one* carbon was required to be within 2.4 Å of the hydrogen atom. Two of these were intermolecular examples, seven were purely intramolecular, but only two cases (refcodes CUSCIC and POITDL)[21] involved an intramolecular C=C · · · H–O interaction plus an additional intermolecular O · · · H–O hydrogen bond. A similar search using the CSD October 1996 version (160 091 structures) revealed additional recent cases of this phenomenon. There are six further examples of H–O interactions with C=C but of these only one (PILCES) also takes part in additional intermolecular hydrogen bonding.[21] Of these three refcodes only in this latter case did the second oxygen belong to a hydroxy group as here for diol **5**.

Since diols forming the helical tubuland lattice normally produce good crystals, it is tempting to speculate that the failure to obtain crystalline **16** or **17** could be due to the presence of weak alkene π · · · H–O interactions in these substances also.

**Discussion of crystal structure of 7.** When crystallised from diethyl ether, diol **7** yields a conglomerate (*i.e.* each crystal is comprised of chirally pure material) in space group $P3_121$. Molecules of **7** take part in four hydrogen bonds, with each hydroxy group acting as both a donor and as an acceptor. The hydroxy groups of **7** are linked · · · H–O · · · H–O · · · H–O · · · around threefold screw axes (Fig. 3) to give a further example of the helical tubuland system.[1] As shown in the projection view in the *ab* plane (Fig. 4) its lattice contains parallel tubes in the *z* direction which have a propeller-shaped cross-section.

Inclusion of diethyl ether was not indicated by microanalytical data but nonetheless was considered in the refinement. However, when the largest peaks in the final difference Fourier were introduced as possible positions for a guest molecule, the residual increased. It is therefore unlikely that inclusion had occurred in this particular instance and hence the material described here is a genuine microporous solid.

The unobstructed cross-sectional area of each empty tube projected in the *ab* plane is 17.8 Å$^2$. Once again, the analogy with looking along an indented pipe is worth emphasising here. Although this area is considerably reduced because of the protruding methyl groups over its parent normethyl diol **25** (Fig. 5; *ca.* 35 Å$^2$),[22] the value of 17.8 Å$^2$ represents a minimum value since greater areas are available at various heights along *z*. So although **7** behaves here as an apohost, this diol would be expected to show versatile inclusion properties and this is indeed the case. Preliminary work has revealed formation of cocrystalline materials with substances such as benzene and hydroquinone, and these inclusion compounds are currently under detailed investigation.

**Discussion of crystal structure of 10.** The molecular structure and conformation of diol **10** in the solid state is shown in Fig. 6. Each molecule of **10** takes part in four hydrogen bonds, with each hydroxy group acting as both a donor and as an acceptor. The resulting structure contains spiral chains of hydrogen bonds, with a repeat unit of four molecules parallel to the *c* axis as illustrated in Fig. 7. These chains have the enantiomeric sequence –A–A′–B–B′–A–A′– *etc.*, where A and B represent the two enantiomeric forms of **10**, and A′ and B′ indicate translation along *a*. Identical spiral chains are subtended by both diol hydroxy groups in such a way that the diol molecules form double layers each of which bears the C(9) methyl groups on its exterior surface (Fig. 8). Only hydrocarbon dispersion forces operate between these layers.

Viewed in the *ab* plane (Fig. 8) the hydrogen bonded chains are seen to have a figure-of-eight projection which we have described previously as a recurved spiral. We have observed this hydroxy hydrogen bonding motif in the crystal structures of diols **27**[23] (four diol molecules representing the spiral repeat unit) and **28**[24] (eight molecules per repeat unit). For these diols the same enantiomeric sequence was observed along a helical chain as found in the structure of **10**. However, for both **27** and **28** the propagation of the hydrogen bonding led to a three-

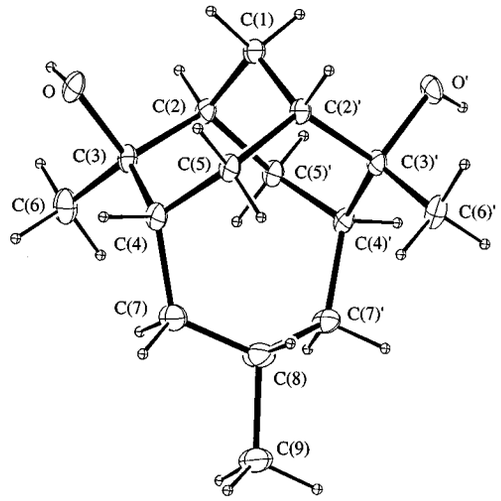



**Fig. 6** Molecular structure and conformation of diol **10** from its X-ray determination, showing the crystallographic numbering system used

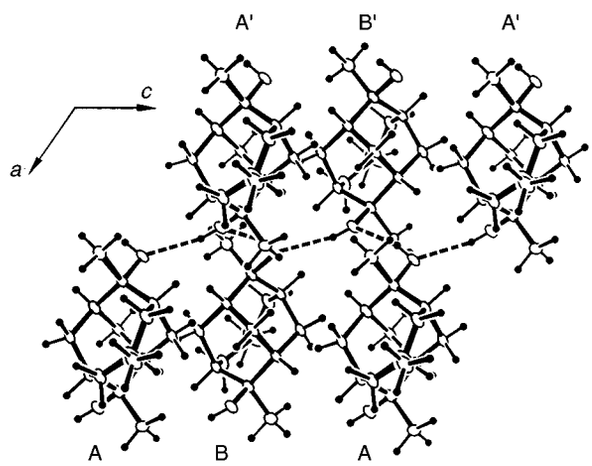



**Fig. 7** Part of a spiral chain of diol **10** molecules illustrating the repeat nature of this hydrogen bonded structure. Four molecules labelled A,A′,B,B′ constitute the hydrogen bonding repeat unit in the *c* direction, where A and B represent the two enantiomers and A′ and B′ indicate translation along *a*.

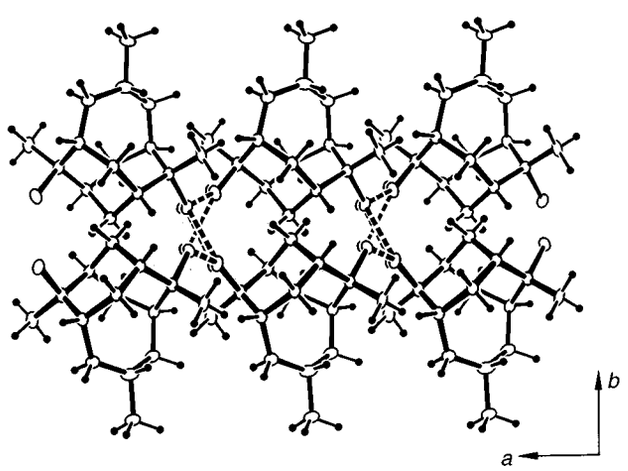



**Fig. 8** The hydrogen bonding arrangement of **10** viewed down the *c* axis showing formation of the double layer of diol molecules. Neighbouring layers interact through hydrocarbon interactions only. In this perspective view the recurved spiral topology of the hydroxy hydrogen bonding sequences can be seen clearly.

dimensional network rather than a two-dimensional layer structure as here.

Although possessing the formal structural requirements,[2,3] diol **10** did not adopt the helical tubuland lattice. This is unsurprising since it is a methylated derivative of the helical tubuland diol **26** whose molecular structure already almost entirely occupies its own tubes (Fig. 5).[23]

**Crystal engineering conclusions.** These results support our earlier suggestion[25] that probably the greatest single factor influencing hydrogen bonding in a crystalline alicyclic diol is the steric environment. For **5** the surroundings of the hydroxy group itself are unable to permit these molecules to assemble into the trigonal spine motif, and a one-dimensional chain results instead through utilisation of the weaker alkene hydrogen bond. Formation of a helical tubuland lattice is impossible for diol **10** because the potential canals would be overcrowded due to the C(9) methyl groups, and the alternative two-dimensional layer structure is produced. However, steric factors for **7** are ideal for formation of the three-dimensional helical tubuland lattice. The methyl groups protruding into the canals of this structure increase the tube chirality and hence modify the molecular recognition properties of the host. These features suggest intriguing possibilities for enhanced guest discrimination properties in future helical tubulate structures.

## Experimental

$^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra were recorded with a Bruker AC300F instrument and are reported as chemical shifts ($\delta$) relative to $SiMe_4$. The substitution of carbon atoms was determined by the DEPT procedure and coupling constants ($J$) are measured in Hz. Melting points were determined with a Kofler instrument and are uncorrected. Mass spectra (electron impact) were recorded on a VG Quattro triple quadrupole instrument (Dr J. J. Brophy). IR spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. Elemental analyses were carried out at the University of New South Wales (Dr H. P. Pham). Petrol refers to light petroleum (bp 60–80 °C).

### 3,7-Bis(methoxycarbonyl)-5-methylenetricyclo[5.3.1.1$^{3,9}$]-dodecane-2,8-dione 3

Diester **1**[11] (5.63 g, 21.0 mmol) was dissolved in tetrahydrofuran (THF) (120 cm$^3$; freshly distilled from $LiAlH_4$), stirred under argon, and then sodium hydride (2.30 g; 50% suspension in oil) was added in portions. After reaction was complete, 3-chloro-2-chloromethylprop-1-ene **2**[14] (3.94 g, 31.5 mmol) was added and the mixture stirred and refluxed (20 h). Filtration of the warm suspension removed NaCl which was washed with chloroform. Solvent was evaporated under reduced pressure from the combined filtrates to give a viscous brown oil which was chromatographed on silica gel eluting with petrol and increasing proportions of diethyl ether. The product **3** was obtained as a white solid using 2:3 petrol–diethyl ether (5.15 g, 75%), mp 138–140 °C (from acetone). (Alternatively, if a small amount of acetone was added to the brown oil, then most of the product crystallised as an off-white solid.) (Found: C, 63.9; H, 6.5. $C_{17}H_{20}O_6$ requires C, 63.7; H, 6.3%); $\nu_{max}$(paraffin mull)/cm$^{-1}$ 2740m, 2680m, 1745s, 1705s, 1225m, 1080m, 1030m, 1000m, 980m, 940m; $\delta_H$[$(CD_3)_2SO$] 4.89 (2H, s), 3.65 (6H, s), 3.03 (2H, br s), 2.86 (2H, m), 2.57–2.53 (2H, m), 2.29–2.24 (4H, m), 2.10 (2H, d, $J$ 8.4); $\delta_C$[$(CD_3)_2SO$] (355 K) 210.3 (C), 172.8 (C), 140.5 (C), 123.3 ($CH_2$), 58.9 (C), 52.8 ($CH_3$), 45.4 ($CH_2$), 42.5 (CH), 38.6 ($CH_2$), 30.0 ($CH_2$); *m/z* ($M^+$ and >15%) 320 ($M^+$, 5%), 289 (28), 288 (72), 261 (23), 260 (39), 256 (18), 232 (19), 229 (39), 228 (40), 204 (15), 201 (30), 200 (31), 193 (17), 173 (31), 172 (20), 161 (20), 154 (17), 153 (29), 145 (38), 138 (15), 129 (17), 121 (16), 105 (15), 91 (26), 79 (22), 77 (27), 67 (17), 65 (29), 59 (100), 55 (92), 53 (45), 51 (20), 45 (33), 42 (32), 41 (52).

### 5-Methylenetricyclo[5.3.1.1$^{3,9}$]dodecane-2,8-dione 4

Diester **3** (5.00 g, 15.6 mmol) and calcium iodide tetrahydrate (5.68 g, 15.6 mmol) were dissolved in dimethyl sulfoxide (30 cm$^3$) in a flask set up for distillation. This mixture was stirred magnetically, heated (7 h; oil bath at 185–190 °C) and volatile

material distilled over. The mustard yellow reaction residue was cooled to room temperature (rt), dissolved in water (50 $cm^3$) and extracted using chloroform. The combined extracts were washed with HCl (1 mol $dm^{-3}$; ×3), saturated aqueous $NaHCO_3$ (30 $cm^3$), water (30 $cm^3$) and then dried ($Na_2SO_4$). Evaporation of solvent from the filtrate gave a brown oil which was chromatographed on silica gel eluting with petrol and increasing proportions of diethyl ether. The product **4** was obtained as a white solid using 2:3 petrol–diethyl ether (2.04 g, 64%), mp 152–154 °C (from acetone) (Found: C, 76.1; H, 8.15. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3070w, 1700s, 1630w, 1230m, 1120m, 1080w, 1040m, 1000m, 960m, 905m, 795w, 780w; $\delta_H(CDCl_3)$ 4.83 (2H, s), 2.96–2.91 (2H, m), 2.89–2.76 (2H, m), 2.68 (2H, br s), 2.27–2.04 (8H, m); $\delta_C(CDCl_3)$ 216.4 (C), 142.2 (C), 120.8 ($CH_2$), 44.5 (CH), 43.5 ($CH_2$), 43.3 (CH), 34.5 ($CH_2$), 32.3 ($CH_2$); *m/z* (>20%) 204 ($M^+$, 100%), 147 (24), 133 (32), 121 (25), 117 (27), 110 (22), 109 (56), 108 (57), 107 (47), 105 (36), 96 (87), 95 (82), 94 (36), 93 (39), 92 (25), 91 (85), 81 (34), 80 (27), 79 (95), 77 (65), 67 (37), 65 (25), 55 (72), 53 (34).

### 2,8-Dimethyl-5-methylenetricyclo[5.3.1.1$^{3,9}$]dodecane-2-*syn*,8-*syn*-diol 5

Diketone **4** (1.40 g, 6.85 mmol) was dissolved in THF (120 $cm^3$; freshly distilled from $LiAlH_4$) under dry $N_2$ in a flask fitted with a condenser/drying tube and a septum. Methyllithium solution in diethyl ether (1.4 mol $dm^{-3}$; 14.7 $cm^3$) was added dropwise to the solution at 0 °C using a syringe. The mixture was stirred at this temperature (1 h) then at rt (24 h). Damp diethyl ether was added cautiously, followed by water (30 $cm^3$). After 10 min the organic layer was separated, the aqueous layer extracted using diethyl ether and the combined extracts dried ($Na_2SO_4$). Evaporation of solvent from the filtrate gave a milky oil which was purified by elution through silica gel eluting with petrol and increasing proportions of diethyl ether. The product **5** was obtained as a white solid using 1:1 petrol–diethyl ether (1.13 g, 70%), mp 133–134 °C (from diethyl ether) (Found: C, 76.5; H, 10.6. $C_{15}H_{24}O_2$ requires C, 76.2; H, 10.2%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3500s, 3420s, 3060w, 1620m, 1250m, 1130s, 1095m, 1070m, 1035m, 1005m, 980w, 940s, 890s, 780w; $\delta_H(CDCl_3)$ 4.96 (2H, s), 3.00–2.95 (2H, m), 2.44 (2H, br s), 2.17–2.08 (4H, m), 2.01–1.79 (6H, m), 1.59–1.52 (2H, m), 1.46 (6H, s); $\delta_C(CDCl_3)$ 152.7 (C), 116.6 ($CH_2$), 74.1 (C), 39.4 ($CH_2$), 39.2 (CH), 39.0 (CH), 32.9 ($CH_3$), 31.0 ($CH_2$), 28.1 ($CH_2$); *m/z* ($M^+$ and >10%) 236 ($M^+$, 0.2%), 200 (18), 185 (12), 145 (13), 143 (12), 131 (12), 121 (19), 120 (13), 119 (20), 117 (11), 109 (12), 108 (17), 107 (27), 106 (25), 105 (32), 95 (27), 94 (18), 93 (39), 92 (11), 91 (32), 81 (16), 79 (27), 77 (19), 71 (23), 67 (15), 55 (18), 53 (12), 43 (100).

### 5-Methyltricyclo[5.3.1.1$^{3,9}$]dodecane-2,8-dione 6

Diketone **4** (1.00 g, 4.90 mmol) was dissolved in ethyl acetate (30 $cm^3$) and $PtO_2$ (20 mg) added. The resulting mixture was shaken under a $H_2$ atmosphere (45 psi; 50 °C; 2 d) on a hydrogenation apparatus. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure to give a milky oil. This was dissolved in acetone (10 $cm^3$) and reacted with excess Jones' reagent (1.94 mol $dm^{-3}$; 3 $cm^3$) in acetone, initially at 0 °C and then at rt for 3 h. Water (20 $cm^3$) was added, followed by extraction with chloroform. The combined extracts were washed with saturated aqueous $NaHCO_3$, then water, and dried ($Na_2SO_4$). Evaporation of solvent from the filtrate gave a yellow oil which was purified by elution through silica gel, eluting with petrol and increasing proportions of diethyl ether. The product **6** was obtained as a white solid using 1:1 petrol–diethyl ether (0.95 g, 95%), mp 102–103 °C (from petrol–diethyl ether) (Found: C, 75.6; H, 8.7. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 1690s, 1250m, 1235m, 1190m, 1105m, 1080m, 1050m, 1020w, 1000m, 960w, 780w, 760w; $\delta_H(CDCl_3)$ 2.92–2.86 (1H, m), 2.74–2.59 (3H, m), 2.27–2.06 (5H, m), 2.00–1.90 (2H, m), 1.80–1.70 (1H, m), 1.60–1.42 (2H, m), 0.94–0.86 (1H, m), 0.78 (3H, d, *J* 6.0); $\delta_C(CDCl_3)$ 219.6 (C), 216.5 (C), 44.2 (CH), 44.0 (CH), 43.3 ($CH_2$), 43.0 (CH), 42.8 (CH), 42.2 ($CH_2$), 40.1 ($CH_2$), 32.4 ($CH_2$), 29.9 ($CH_2$), 27.3 (CH or $CH_3$), 24.4 ($CH_3$ or CH); *m/z* (>10%) 206 ($M^+$, 54%), 178 (12), 163 (12), 150 (11), 149 (11), 145 (10), 137 (17), 136 (14), 135 (15), 131 (10), 124 (30), 123 (14), 122 (20), 121 (16), 111 (31), 110 (17), 109 (36), 108 (27), 107 (30), 105 (16), 97 (13), 96 (53), 95 (75), 94 (40), 93 (38), 92 (12), 91 (39), 83 (16), 82 (28), 81 (52), 80 (18), 79 (68), 77 (39), 69 (17), 68 (30), 67 (81), 65 (22), 55 (100), 53 (36), 51 (11), 43 (11).

### 2,5,8-Trimethyltricyclo[5.3.1.1$^{3,9}$]dodecane-2-*syn*,8-*syn*-diol 7

Diketone **6** (0.95 g, 4.61 mmol) was dissolved in THF (50 $cm^3$; freshly distilled from $LiAlH_4$) and reacted with methyllithium in diethyl ether solution (1.4 mol $dm^{-3}$; 10 $cm^3$) using an identical procedure and work up to that used to obtain **5**. Evaporation of solvent from the dried organic extracts gave a milky oil which was purified by elution through silica gel eluting with petrol and increasing proportions of diethyl ether. The product **7** was obtained as a white solid using 1:1 petrol–diethyl ether (0.75 g, 68%), mp 117–120 °C (from diethyl ether) (Found: C, 75.3; H, 11.2. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3400s, 1220w, 1180w, 1120m, 1080s, 1020m, 950m, 920s, 860m; $\delta_H(CDCl_3)$ 2.30 (1H, br m), 2.14–1.93 (4H, m), 1.88–1.72 (2H, m), 1.68–1.55 (5H, m), 1.50–1.43 (2H, m), 1.41–1.30 (2H, m), 1.39 (3H, s), 1.37 (3H, s), 0.93 (1H, t), 0.83 (3H, d, *J* 6.2); $\delta_C(CDCl_3)$ 75.5 (C), 72.5 (C), 43.5 ($CH_2$), 39.3 (two CH), 39.0 (CH), 38.4 (CH), 34.3 ($CH_3$), 33.5 ($CH_3$), 33.4 ($CH_2$), 31.1 ($CH_2$), 31.0 ($CH_2$), 27.5 (CH), 25.6 ($CH_3$), 25.4 ($CH_2$); *m/z* (significant peaks and >20%) 238 ($M^+$, not observed), 223 [$(M - 15)^+$, 11%], 220 [$(M - 18)^+$, 8], 202 (20), 177 (23), 149 (21), 147 (23), 146 (20), 145 (21), 135 (35), 125 (41), 121 (47), 119 (24), 109 (36), 108 (21), 107 (57), 105 (36), 95 (95), 94 (24), 93 (78), 92 (22), 91 (35), 81 (69), 79 (36), 77 (24), 71 (61), 69 (28), 67 (31), 55 (49), 43 (100).

### 5′-Methyldispiro[oxirane-2,2′-tricyclo[5.3.1.1$^{3,9}$]dodecane-8′,2″-oxirane] 9

Diketone **6** (0.45 g, 2.18 mmol), methyltriphenylphosphonium bromide (1.95 g, 5.45 mmol) and potassium *tert*-butoxide (0.61 g, 5.54 mmol) were reacted in dry benzene (20 $cm^3$) at 80 °C following the standard Wittig reaction and work up conditions devised by Dehmlow and Barahona-Naranjo.[18] Triphenylphosphine oxide was filtered, the solvent distilled off, the concentrated residue eluted through silica gel using petrol and the solvent removed by distillation to give the diene **8** as a colourless oil (0.38 g, 84%), $\nu_{max}$(liquid film)/$cm^{-1}$ 3050m, 2900s, 1620m, 1440m, 875s.

A solution of *m*-chloroperbenzoic acid (MCPBA; 0.77 g of 80% purity, 3.7 mmol) in dichloromethane (10 $cm^3$) was added dropwise to a vigorously stirred mixture of diene **8** (0.37 g, 1.8 mmol) and aqueous sodium hydrogen carbonate (0.5 mol $dm^{-3}$; 5.3 $cm^3$). Stirring was continued for 4 h at rt, then aqueous $Na_2S$ was added to destroy remaining peracid. The organic layer was separated, the aqueous layer was extracted using dichloromethane and the combined extracts washed with water then dried ($Na_2SO_4$). Evaporation of solvent from the filtrate gave a sticky colourless oil (0.45 g) which was purified by elution through silica gel using petrol and increasing proportions of diethyl ether to give the bis(epoxide) **9** as an oil (0.39 g, 90%) pure by $^{13}C$ NMR spectroscopy, $\nu_{max}$(liquid film)/$cm^{-1}$ 3020w, 1270w, 1240m, 1210w, 1120w, 1090w, 1080w, 1020w, 945s, 930s, 890m, 855s, 795s, 725s; $\delta_H(CDCl_3)$ 2.70–2.50 (4H, m), 2.30–2.15 (1H, m), 2.05–1.59 (10H, m), 1.55–1.42 (1H, m), 1.42–1.10 (2H, m), 0.91 (1H, t, *J* 12.3), 0.79 (3H, d, *J* 6.1); $\delta_C(CDCl_3)$ 65.5, 61.4, 52.5, 52.1, 44.0, 40.7, 35.2, 34.9 (two peaks), 34.8, 34.7, 30.4, 27.6, 27.2, 25.3.

### 2,5,8-Trimethyltricyclo[5.3.1.1$^{3,9}$]dodecane-2-*anti*,8-*anti*-diol 10

The bis(epoxide) **9** (0.45 g, 1.91 mmol) was dissolved in THF (25 $cm^3$; freshly distilled from $LiAlH_4$), $LiAlH_4$ (0.10 g) was

added and the mixture was stirred at rt overnight. Wet diethyl ether was added cautiously, followed by careful addition of cold water. Organic solvents were evaporated under reduced pressure, the aqueous solution extracted thoroughly using ethyl acetate and the combined extracts dried ($Na_2SO_4$). Evaporation of solvent from the filtrate gave a white solid which was recrystallised from ethyl acetate to yield **10** (0.38 g, 85%), mp 203–204 °C (Found: C, 75.8; H, 10.7. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%); $\nu_{max}$(paraffin mull)/cm$^{-1}$ 3320s, 1250m, 1215w, 1085s, 1040m, 1020m, 965w, 890m, 865m, 790w, 750w; $\delta_H$($CDCl_3$) 2.40–2.21 (1H, m), 2.19–1.74 (11H, m), 1.71–1.57 (2H, m), 1.55–1.27 (2H, m), 1.39 (3H, s), 1.25 (3H, s), 1.02–0.85 (1H, m), 0.81 (3H, d, *J* 6.15); $\delta_C$($CDCl_3$) 75.6 (two peaks), 42.6, 40.3, 39.5, 39.1, 38.6, 36.7, 31.8, 28.5, 27.6, 27.4, 25.3, 25.0, 24.5; *m/z* ($M^+$ and >10%) 238 ($M^+$, 0.15%), 220 (13), 205 (26), 177 (27), 151 (16), 149 (17), 145 (11), 137 (11), 136 (13), 135 (44), 123 (16), 121 (37), 119 (17), 111 (17), 110 (11), 109 (33), 108 (11), 107 (36), 106 (11), 105 (27), 97 (10), 95 (34), 93 (36), 91 (27), 81 (25), 79 (20), 77 (17), 71 (36), 69 (16), 67 (20), 55 (27), 53 (16), 45 (13), 43 (100).

### 5′-Methylenedispiro[dioxolane-2,2′-tricyclo[5.3.1.1$^{3,9}$]dodecane-8′,2″-dioxolane] 11

The unsaturated diketone **4** (1.40 g, 6.8 mmol), ethylene glycol (1.30 g, 20.4 mmol), one crystal of toluene-*p*-sulfonic acid and benzene (50 cm$^3$) were placed in a flask fitted with a Dean and Stark trap and the mixture was heated overnight. After cooling, solvent was evaporated and the residue filtered under suction through a short silica gel column, washing with 20% diethyl ether in petrol. The solvent was removed under reduced pressure to give the product **11** as an oil (1.61 g, 81%), $\nu_{max}$(paraffin mull)/cm$^{-1}$ 3050m, 1630m, 1255m, 1220m, 1100s, 1010s, 980m, 930s, 910s, 880s, 850m, 820w, 790w, 750m; $\delta_H$($CDCl_3$) 4.75 (2H, s), 4.02–4.76 (8H, m), 2.67 (2H, dd, *J* 13.40 and 3.95), 2.22–1.16 (12H, m); $\delta_C$($CDCl_3$) 147.0, 116.2, 112.4, 64.8, 63.5, 39.3, 37.2, 35.3, 29.5, 27.3.

### Dispiro[dioxolane-2,2′-tricyclo[5.3.1.1$^{3,9}$]dodecane-8′,2″-dioxolan]-5′-one 12

A solution of the unsaturated diketal **11** (0.14 g, 0.48 mmol) in dichloromethane (15 cm$^3$) was cooled to −78 °C. A stream of ozonised oxygen was passed through the solution until TLC of an aliquot showed the reaction was complete (1 h). While still at −78 °C dimethyl sulfide (2 cm$^3$) was added, the solution was stirred at 0 °C (0.5 h) and then at room temperature (1 h). Solvent was removed under reduced pressure, water added, and the residue extracted with diethyl ether. The diethyl ether solution was washed with water, dried ($Na_2SO_4$) and solvent evaporated from the filtrate to give a mixture of solid products which were eluted through a silica column using petrol and increasing amounts of diethyl ether. The pure product **12** was obtained as a white solid using 1:1 petrol–diethyl ether (0.11 g, 78%), mp 145–148 °C (from diethyl ether) (Found C, 65.1; H, 7.6. $C_{16}H_{22}O_5$ requires C, 65.3; H, 7.5%); $\nu_{max}$(paraffin mull)/cm$^{-1}$ 1680m, 1290m, 1210m, 1130m, 1100s, 1060s, 1010m, 960m, 940m, 920m, 880w, 840w, 790w; $\delta_H$($CDCl_3$) 4.02–3.68 (8H, m), 3.00–2.81 (2H, m), 2.41–1.59 (12H, m); $\delta_C$($CDCl_3$) 212.1 (C), 111.1 (C), 64.8 ($CH_2$), 63.8 ($CH_2$), 46.7 ($CH_2$), 36.4 (CH), 34.8 (CH), 28.8 ($CH_2$), 27.7 ($CH_2$); *m/z* (>10%) 294 ($M^+$, 28%), 251 (20), 249 (10), 223 (14), 221 (15), 205 (12), 195 (10), 139 (25), 138 (21), 126 (35), 125 (45), 113 (39), 112 (32), 100 (20), 99 (100), 96 (13), 91 (17), 86 (13), 82 (14), 79 (16), 77 (18), 73 (16), 69 (14), 68 (12), 67 (14), 55 (70), 54 (11), 53 (12), 45 (13), 43 (11), 41 (22).

### Dispiro[dioxolane-2,2′-tricyclo[5.3.1.1$^{3,9}$]dodecane-8′,2″-dioxolane]-5′-one tosylhydrazone 13

Ketone **12** (0.10 g, 0.34 mmol) and tosylhydrazine (0.065 g, 0.34 mmol) were dissolved in a minimum of warm ethanol and concentrated hydrochloric acid (1 drop) was added. The mixture was allowed to stir overnight at rt, during which time a white solid precipitated. After cooling with ice, the solid was filtered, washed with a little cold ethanol and then dried in air. $^{13}$C NMR spectroscopy indicated that the sample of **13** was almost pure (0.15 g, 95%), mp 179–180 °C (Found: C, 60.0; H, 6.5; N, 6.15. $C_{23}H_{30}O_6N_2S$ requires C, 59.7; H, 6.5; N, 6.1%); $\nu_{max}$(paraffin mull)/cm$^{-1}$ 3200m, 1595w, 1210w, 1160s, 1130w, 1100s, 1060m, 1030m, 970w, 940m, 920m, 900w, 850w, 830w, 800w; $\delta_H$($CDCl_3$) 7.26 (1H, br s), 7.07 (2H, d, $H_{AB}$), 6.48 (2H, d, $H_{AB}$), 3.10–2.90 (8H, m), 2.87–2.63 (1H, m), 2.20–2.05 (1H, m), 2.05–1.88 (1H, m), 1.62 (3H, s), 1.72–1.12 (11H, m); $\delta_C$($CDCl_3$) 162.2, 143.6, 135.6, 129.0, 128.3, 112.1, 111.0, 64.8, 64.7, 63.9, 63.7, 38.4, 36.7, 36.3, 35.0, 34.5, 33.7, 31.5, 29.3, 23.6, 21.6; *m/z* (>20%) 463 [$(M + 1)^+$, 43%], 307 (78), 280 (21), 279 (87), 278 (20), 235 (42), 217 (87), 191 (23), 173 (14), 155 (32), 145 (57), 139 (44), 137 (22), 125 (25), 120 (24), 113 (97), 107 (30), 105 (31), 103 (23), 99 (100), 94 (42), 92 (48), 91 (100), 82 (27), 78 (42), 76 (34), 73 (47), 67 (28), 65 (35), 55 (67), 46 (22).

### Dispiro[dioxolane-2,2′-tricyclo[5.3.1.1$^{3,9}$]dodec-4-ene-8′,2″-dioxolane] 14

A suspension of the tosylhydrazone **13** (0.82 g, 1.8 mmol) in benzene (40 cm$^3$) was cooled in an ice bath and ethereal methyllithium (1.4 mol dm$^{-3}$; 3.8 cm$^3$, 5.4 mmol) was added over 5 min. The mixture was stirred for 4 h at rt during which time the original white suspension became a colourless solution, then an orange solution and finally an orange suspension. After this time, the reaction was quenched by addition of saturated aqueous $NH_4Cl$ (20 cm$^3$). The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with water (×3), dried ($Na_2SO_4$) and the filtrate evaporated to give a sticky oil which was purified by column chromatography on silica gel eluting with light petroleum and increasing amounts of diethyl ether. The product **14** was obtained using 1:4 diethyl ether–petrol (0.28 g, 56%), mp 122–124 °C (Found: C, 68.85; H, 8.1. $C_{16}H_{22}O_4$ requires C, 69.0; H, 8.0%); $\nu_{max}$(paraffin mull)/cm$^{-1}$ 1670w, 1260m, 1210s, 1100s, 1040s, 1020s, 985s, 920s, 880m, 870m, 790m, 740s, 690m; $\delta_H$($CDCl_3$) 5.75–5.57 (1H, m), 5.51–5.20 (1H, m), 4.01–3.81 (8H, m), 2.73–2.60 (2H, m), 2.37–1.60 (10H, m); $\delta_C$($CDCl_3$) 128.9, 127.9, 112.4, 112.2, 65.0, 64.6, 63.9, 63.5, 38.5, 36.6, 34.2, 33.8, 33.5, 29.3, 29.0, 27.8; *m/z* (>10%) 278 ($M^+$, 15%), 233 (33), 217 (12), 216 (18), 209 (11), 149 (12), 139 (19), 137 (13), 125 (20), 113 (21), 112 (36), 106 (13), 99 (100), 95 (13), 91 (24), 79 (13), 77 (11), 55 (16).

### Tricyclo[5.3.1.1$^{3,9}$]dodec-4-ene-2,8-dione 15

Tricyclic diketal **14** (0.12 g, 0.43 mmol) was added to a stirred solution of acetone (10 cm$^3$) and hydrochloric acid (2 mol dm$^{-3}$; 5 cm$^3$), then stirred overnight at rt. Acetone was removed by evaporation and the residue extracted with chloroform. The combined extracts were washed successively with water and saturated aqueous $NaHCO_3$, dried ($Na_2SO_4$) and the solvent evaporated from the filtrate to give a yellowish solid. This was purified by column chromatography on silica gel eluting with light petroleum and increasing amounts of diethyl ether. The white solid product **15** was obtained using 1:1 diethyl ether–petrol (0.082 g, 100%), mp 150–155 °C, $\nu_{max}$(paraffin mull)/cm$^{-1}$ 3010w, 1705s, 1685m, 1260w, 1230w, 1150w, 1120w, 1100w, 1085w, 1070w, 1030w, 1000m, 950w, 900w, 820w; $\delta_H$($CDCl_3$) 5.95–5.75 (1H, m), 5.44–5.30 (1H, m), 3.41–3.24 (1H, m), 3.01–1.84 (11H, m); $\delta_C$($CDCl_3$) 217.5 (C), 214.1 (C), 128.9 (CH), 127.5 (CH), 45.1 (CH), 41.8 (CH), 41.5 (two CH), 37.5 ($CH_2$), 35.5 ($CH_2$), 32.9 ($CH_2$), 31.4 ($CH_2$); *m/z* (>20%) 190 ($M^+$, 35%), 172 (28), 144 (20), 133 (37), 129 (40), 117 (22), 116 (21), 108 (39), 107 (40), 105 (28), 96 (47), 95 (61), 94 (44), 93 (27), 92 (25), 91 (100), 80 (22), 79 (61), 78 (30), 77 (53), 67 (29), 66 (28), 65 (27), 55 (41), 54 (29), 53 (27), 52 (53), 51 (57), 50 (53), 41 (26).

### 2,8-Dimethyltricyclo[5.3.1.1$^{3,9}$]dodec-4-ene-2-*syn*,8-*syn*-diol 16

Unsaturated diketone **15** (0.15 g, 0.79 mmol) was dissolved in THF (20 cm$^3$; freshly distilled from $LiAlH_4$) in a flask fitted

with a septum and a condenser plus drying tube and stirred under a dry $N_2$ atmosphere. Methyllithium solution in diethyl ether (1.4 mol $dm^{-3}$; 2.1 $cm^3$, 2.94 mmol) was added dropwise into the flask at 0 °C using a syringe. The reaction mixture was stirred at room temperature (24 h). Damp diethyl ether was added to the reaction mixture, followed by water (5 $cm^3$) and stirring continued for a further 10 min. The two layers were separated, the aqueous layer extracted with diethyl ether, and the combined organic layers dried ($Na_2SO_4$). Evaporation of solvent from the filtrate gave the crude product which was purified by column chromatography on silica gel eluting with light petroleum and increasing amounts of diethyl ether. The product **16** was eluted as a colourless oil using 1:1 diethyl ether–petrol (0.135 g, 77%); $\nu_{max}$(liquid film)/$cm^{-1}$ 3460s, 1675w, 1280m, 1255m, 1220w, 1130s, 1075m, 1015m, 1000s, 970w, 940s, 910m, 895m, 850w, 780m, 740m, 710m; $\delta_H(CDCl_3)$ 5.85–5.74 (1H, m), 5.68–5.57 (1H, m), 2.76–2.58 (2H, m), 2.36–2.53 (12H, m), 1.38 (3H, s), 1.36 (3H, s); $\delta_C(CDCl_3)$ 132.8, 128.2, 73.6, 72.0, 41.0, 38.2, 38.1, 37.7, 33.9, 32.8, 31.3, 30.8, 29.4, 29.1.

### 2,5,8-Trimethyltricyclo[5.3.1.1$^{3,9}$]dodec-4-ene-2-*syn*,8-*syn*-diol 17

Unsaturated diol **5** (0.30 g, 1.27 mmol) was dissolved in ethyl acetate (10 $cm^3$) and palladium catalyst on charcoal (5 mg) was added. The reaction flask was evacuated, filled with hydrogen and stirred at room temperature (24 h). The reaction mixture was filtered through Celite and solvent removed under reduced pressure to give a sticky colourless oil. $^{13}$C NMR spectroscopy indicated a mixture of two products was present. This was carefully separated by column chromatography on silica gel eluting with petrol and increasing amounts of diethyl ether. The cyclic ether **18** eluted first (eluent: 15% diethyl ether in petrol) as a solid and was followed by the diol **17** (eluent: 25% diethyl ether in petrol) as an oil (0.21 g, 70%), $\nu_{max}$(liquid film)/$cm^{-1}$ 3400s, 1660w, 1285s, 1245s, 1210m, 1120s, 1080s, 1020s, 980s, 950m, 920s, 900m, 880s, 840w, 820m, 785w; $\delta_H(CDCl_3)$ 5.51 (1H, d, *J* 11.5), 2.70–1.50 (14H, m), 1.80 (3H, br s), 1.38 (3H, s), 1.37 (3H, s); $\delta_C(CDCl_3)$ 139.5 (C), 123.6 (CH), 73.5 (C), 71.9 (C), 41.5 (CH), 38.9 (CH), 38.4 ($CH_2$), 38.2 (CH), 37.8 (CH), 32.6 ($CH_3$), 31.4 ($CH_2$), 30.8 ($CH_3$), 29.7 ($CH_2$), 29.3 ($CH_2$), 28.6 ($CH_3$); *m/z* ($M^+$ and >10%) 236 ($M^+$, 8%), 107 (16), 105 (12), 95 (17), 93 (18), 91 (17), 81 (13), 79 (15), 77 (14), 71 (24), 69 (10), 67 (18), 55 (26), 53 (13), 43 (100), 41 (32).

### 2,7,9-Trimethyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecan-2-*endo*-ol 18

During the preparation of diol **17** described above, the cyclic ether **18** eluted first (0.09 g, 30%), mp 128–129 °C (from diethyl ether) (Found: C, 76.6; H, 10.5. $C_{15}H_{24}O_2$ requires C, 76.2; H, 10.3%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3420m, 1245m, 1200s, 1170w, 1110s, 1060s, 1030m, 990w, 950s, 920m, 890m, 820m, 800w, 780w, 710m; $\delta_H(CDCl_3)$ 2.42–1.33 (15H, m), 1.38 (3H, s), 1.29 (3H, s), 1.21 (3H, s); $\delta_C(CDCl_3)$ 83.2 (C), 82.5 (C), 72.9 (C), 49.1 ($CH_2$), 42.7 (CH), 41.6 ($CH_2$), 41.4 (CH), 40.1 (CH), 38.3 (CH), 34.1 ($CH_3$), 33.8 ($CH_2$), 33.1 ($CH_2$), 32.8 ($CH_3$), 32.0 ($CH_2$), 30.6 ($CH_3$); *m/z* (>10%) 236 ($M^+$, 20%), 175 (12), 149 (13), 119 (12), 109 (15), 107 (24), 106 (17), 105 (25), 97 (17), 96 (12), 95 (18), 94 (11), 93 (34), 91 (36), 85 (11), 81 (21), 79 (28), 77 (24), 71 (19), 69 (17), 67 (22), 65 (10), 57 (11), 55 (27), 53 (15), 43 (100), 41 (28). A quantitative yield of **18** was obtained when hydrogenation of **5** using $H_2$ and $PtO_2$ was attempted in ethyl acetate solution with addition of two drops of 70% perchloric acid.

### 9-Hydroxy-7-methyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecan-2-one 20

Diester **3** (1.00 g, 3.12 mmol) was heated under reflux with acetic acid (8.7 $cm^3$) and hydrochloric acid (5 mol $dm^{-3}$; 5.8 $cm^3$) with stirring for 16 h. The reaction mixture was evaporated to dryness under reduced pressure to give a brown waxy solid. A small amount of water was added and then organic material extracted with chloroform. The combined extracts were washed with saturated aqueous sodium carbonate, dried ($Na_2SO_4$) and solvent evaporated from the filtrate to leave a solid product. This crude solid was recrystallised from diethyl ether to give clean hemiketal **20** (0.62 g, 90%), mp 132–134 °C (Found: C, 70.1; H, 8.2. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3410s, 1690s, 1250m, 1230m, 1170m, 1140w, 1120s, 1100s, 1080s, 1070s, 1015s, 990s, 980m, 960m, 940s, 915s, 885w, 855m, 840m, 785w, 750s, 695w, 680w, 660m; $\delta_H(CDCl_3)$ 3.69 (1H, s), 2.77–1.68 (14H, m), 1.24 (3H, s); $\delta_C(CDCl_3)$ 220.5 (C), 106.4 (C), 82.4 (C), 48.4 ($CH_2$), 46.0 ($CH_2$), 45.5 (CH), 44.8 (CH), 43.5 (CH), 42.4 (CH), 38.7 ($CH_2$), 33.4 ($CH_2$), 33.2 ($CH_2$), 29.7 ($CH_3$); *m/z* (>20%) 222 ($M^+$, 25%), 204 (25), 194 (24), 179 (23), 176 (24), 161 (26), 138 (25), 135 (22), 133 (23), 121 (23), 110 (24), 109 (55), 108 (36), 107 (47), 105 (30), 97 (31), 96 (57), 95 (100), 94 (43), 93 (51), 91 (74), 83 (23), 82 (29), 81 (71), 80 (25), 79 (84), 77 (69), 69 (34), 68 (26), 67 (57), 65 (29), 55 (95), 53 (36), 43 (45), 41 (30).

### 2,9-Dimethyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]tridecane-2-*endo*,7-diol 22

A solution of the unsaturated diol **5** (0.10 g, 0.34 mmol) in dichloromethane (15 $cm^{-3}$) was cooled to −78 °C. A stream of ozonised oxygen was passed through the solution for 30 min. While still at −78 °C, dimethyl sulfide (1 $cm^3$) was added, the solution was then stirred at 0 °C (0.5 h), and at rt (1 h). Solvent was evaporated under reduced pressure, water was added, then the residue extracted with diethyl ether. The extract was then washed with water, dried ($Na_2SO_4$) and solvent evaporated from the filtrate to give a solid product which was purified by column chromatography on silica gel using light petroleum and increasing amounts of diethyl ether. The pure product **22** was eluted with 1:1 diethyl ether–petrol (0.08 g, 80%), mp 144–145 °C (from 1:1 diethyl ether–petrol) (Found: C, 70.9; H, 9.5. $C_{14}H_{22}O_3$ requires C, 70.6; H, 9.3%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3440–3120m (br), 1150m, 1120m, 1070m, 1020m, 1000w, 980m, 960m, 935m, 910m, 850w, 820w; $\delta_H(CDCl_3)$ 2.51–1.48 (15H, m), 1.43 (3H, s), 1.37 (3H, s), 1.29–1.19 (1H, m); $\delta_C(CDCl_3)$ 106.9, 80.7, 72.6, 48.1, 41.1 (two peaks), 39.8, 39.1, 38.0, 34.1, 33.5, 32.8, 32.7, 31.6; *m/z* (significant peaks, plus >10%) 238 ($M^+$, 2%), 223 (7), 220 (6), 205 (7), 179 (10), 177 (12), 161 (15), 160 (17), 159 (13), 150 (15), 149 (13), 145 (15), 137 (12), 136 (12), 135 (25), 133 (24), 123 (18), 122 (63), 121 (25), 120 (22), 119 (36), 118 (10), 114 (12), 111 (17), 110 (13), 109 (30), 108 (17), 107 (75), 106 (68), 105 (60), 97 (11), 95 (28), 94 (18), 93 (51), 92 (16), 91 (44), 85 (15), 83 (11), 81 (29), 79 (34), 77 (26), 71 (36), 70 (10), 69 (21), 67 (23), 65 (10), 55 (32), 53 (15), 43 (100), 41 (36).

### 7-Hydroxymethyl-2,9-dimethyl-8-oxatetracyclo[5.4.1.1$^{3,10}$.0$^{5,9}$]-tridecane-2-*endo*-ol 24

A solution of *m*-chloroperbenzoic acid (MCPBA; 0.16 g, 80–85% purity, *ca.* 0.76 mmol) in dichloromethane (5 $cm^3$) was added dropwise to a vigorously stirred mixture of the unsaturated diol **5** (0.18 g, 0.75 mmol) and aqueous sodium hydrogen carbonate (0.5 mol $dm^{-3}$; 1.1 $cm^3$). The reaction mixture was stirred at rt for 4 h, then saturated aqueous sodium sulfide (1.5 $cm^3$) was added to destroy the remaining peracid. The organic layer was separated, and the aqueous layer extracted with dichloromethane. The combined extracts were washed with water and dried ($Na_2SO_4$). After evaporation of solvent from the filtrate, a white sticky oil was obtained which crystallised on addition of diethyl ether giving **24** (0.15 g, 89%), mp 135–138 °C (Found: C, 71.1; H, 9.3. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%); $\nu_{max}$(paraffin mull)/$cm^{-1}$ 3380s, 1260m, 1215w, 1145m, 1130m, 1085s, 1075s, 1060s, 1020m, 1000w, 960m, 940m, 920m, 900m, 840m, 815w, 775w; $\delta_H(CDCl_3)$ 3.45–3.38 (1H, m), 3.34–3.25 (1H, m), 2.50–2.37 (1H, m), 2.31–2.12 (5H, m), 2.00–1.67 (6H, m), 1.65–1.42 (4H, m), 1.40 (3H, s), 1.29 (3H, s); $\delta_C(CDCl_3)$ 85.6, 83.1, 72.7, 68.3, 42.3, 42.2, 41.2, 40.0, 38.4, 36.4, 34.3, 33.9, 33.0, 32.3, 32.1; *m/z* (significant peaks, plus

>10%) (252, $M^+$, not observed), 237 [$(M - 15)^+$, 4%], 234 [$(M - 18)^+$, 13], 161 (14), 147 (18), 146 (13), 135 (11), 133 (20), 132 (12), 121 (16), 120 (10), 119 (26), 111 (10), 109 (18), 107 (33), 106 (18), 105 (37), 97 (15), 95 (28), 94 (10), 93 (32), 91 (34), 83 (18), 81 (26), 79 (30), 77 (24), 71 (26), 69 (45), 67 (26), 57 (23), 55 (45), 53 (17), 44 (18), 43 (100), 41 (46).

**Determination of the crystal structures of 5, 7 and 10**

Crystals of diols **5** and **7** were grown from diethyl ether solution and diol **10** from ethyl acetate. There was no indication of guest inclusion by IR and $^1$H NMR spectroscopy or by microanalysis in any case. Data for all three structures were recorded using an Enraf-Nonius CAD4 X-ray diffractrometer in $\theta$–$2\theta$ scan mode using nickel filtered copper radiation ($\lambda$ 1.5418 Å). Data collection and processing procedures have been described.[26] Corrections were made for absorption[27] and for any crystal decomposition.

For **5** and **10**, the structures were determined by direct phasing (MULTAN[28]) and Fourier methods. The positions of the hydroxy hydrogen atoms were determined from difference Fourier maps. All other hydrogen atoms were included in calculated positions. The positions of the hydroxy hydrogen atoms were refined and all hydrogen atoms were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full matrix least squares.[29] The final residuals were 0.051 and 0.077, and the largest peaks in the final difference maps were 0.26 and 0.27 e Å$^{-3}$, for **5** and **10** respectively.

For **7**, the initial positional parameters for the diol were taken from a previously determined structure of the non-methylated diol **25**[22] since the two structures were clearly isomorphous. A difference Fourier synthesis revealed the additional methyl carbon position. The structure was refined anisotropically.[30] The hydroxy hydrogen position was taken from a difference Fourier and its position was refined. Methyl and methylene hydrogen atoms were included in calculated positions with isotropic temperature factors set equal to those of the atoms to which they were bonded. However, it was clear from a difference map that the hydrogen atoms of the C(6) methyl group were disordered. Two different sets of hydrogen atom positions were included with equal occupancy. The final residual was 0.037. The *R* factor for the other enantiomer was the same. The largest peak in the final difference map was 0.25 e Å$^{-3}$.

Reflection weights used for all three structure refinements were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{\frac{1}{2}}$. The weighted residual was defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[31] ORTEP-II[32] running on a Macintosh IIcx was used for the structural diagrams, and a DEC Alpha AXP workstation was used for calculations.

In previous analyses of diols **25**[13,22] and **26**[23] we have observed that the central atom C(8) of the propano bridge was disordered as required by space group symmetry. This uncertainty in the position of C(8), which is indicated by the higher standard deviation associated with it, is reflected by an inequality and/or a shortening of the C(7)–C(8) and C(7)′–C(8) bond distances together with an increase in the bridge angles from the tetrahedral value. There is again evidence for this phenomenon in **7** (where space group symmetry requires disorder) and in **10**. In these structures the bridge angle values are larger, and the bridge bond length values shorter, than expected.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/128.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