The mechanism of directed remote asymmetric reduction of carbonyl groups *via* homochiral boronate esters

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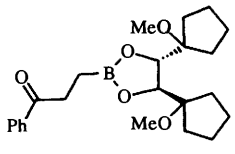
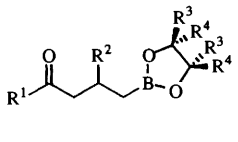
In order to determine whether the remote asymmetric induction in the reduction of compounds such as **1** and **2** using borane is really controlled by intramolecular chelates of type **3**, rather than dioxaborolane oxygen-borane chelates of type **12**, a study was undertaken to examine related reductions involving the corresponding homochiral acetal **30** and comparative reductions of the dioxaborolane **14** and the acetal **23b**. While this study showed that reductions of the dioxaborolane **14** and the acetal **23b** with borane and L-Selectride were virtually identical, this result did not necessarily indicate that dioxaborolane oxygens or acetal oxygens were directing borane reduction. However, that the more likely explanation for the remote asymmetric induction observed for **1** and **2** being mediated by complex **3** was confirmed by the fact that the acetal **30** gave no asymmetric induction with borane. A crystal structure of the phenylboronate ester **10** has been carried out.

Introduction

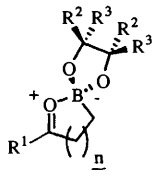
The control of remote asymmetric centres has recently become a matter of some interest for the synthesis of stereochemically unusual products.[1] To this end, boronate esters such as **1**[2] and **2**[3] have been particularly useful for controlling the 1,6- and 1,7-asymmetric reduction of ketone functions. A possible explanation of the mode by which the remote boronate ester asymmetric centres are able to influence the reduction of the ketones **1** and **2** has been proposed by Molander,[3] and involves an intramolecularly activated carbonyl complex of type **3** (n = 1 or 2), which is then reduced in an intermolecular manner by borane.



1



2



3

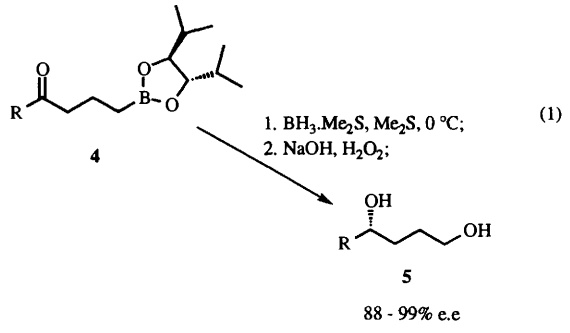
a n = 1
b n = 1

Our interest in the application of β-boronate carbonyl derivatives[4] for the synthesis of compounds containing multiple chiral centres, led us to examine related systems, with and without the boron atom, in order to probe the reactions further. In this paper, we document these studies to determine whether reductions of **1** and **2** in the presence of borane are indeed mediated by transient intramolecularly activated complexes of type **3**.

Molander[3b] demonstrated that the boronate esters **4** could direct [eqn. (1)] borane reduction at a remote carbonyl centre with high levels of asymmetric induction. This prompted us to report our own preliminary work on the borane reduction of the boronate ester **1** [eqn. (2)].[2] We have found that borane-mediate reduction also resulted in high asymmetric induction, whereas L-Selectride gave no induction (Table 1).

Table 1

Entry	Reduction conditions	% Yield of **6**	$[\alpha]_D$; % ee of **6**	Confign. of **6**
1	BH_3·Me_2S–THF, −45 °C	81	−29; 55	*S*
2	BH_3·THF–CH_2Cl_2, −45 °C	87	−48; 89	*S*
3	L-Selectride®–THF, −78 °C	76	+2; ~0	—

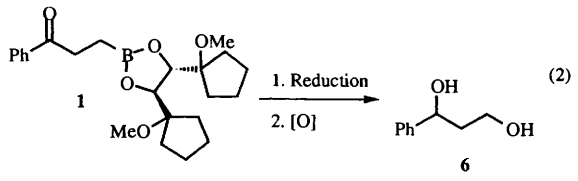


4 (1)

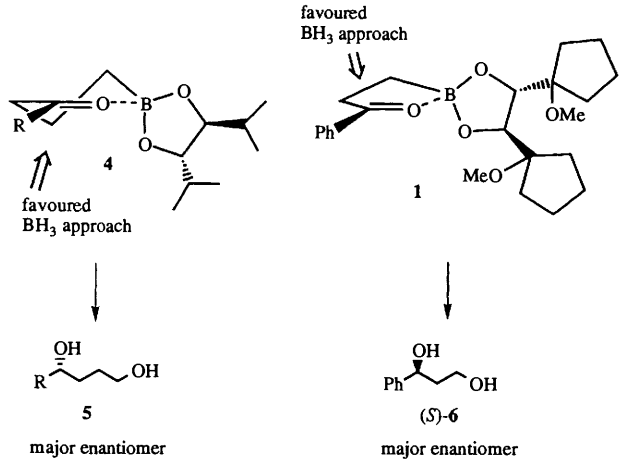
5

88 - 99% e.e

The asymmetric induction observed in the reduction of compounds **4** and **1** may be rationalised[3b] by assuming that the carbonyl group could be activated towards reduction *via* chelation to the boronate ester group involving a complex of type **3**. Thus, as the proportion of reduction occurring *via* the chelated carbonyl group (*i.e.* **3**) pathway increases over direct carbonyl reduction, the asymmetric induction in the reduction products **5** and **6** increases. The fact that L-Selectride-mediated reduction of **1** gave no asymmetric induction (Table 1, entry 3) seems entirely consistent with this mechanism, since the reduction was complete after 3 h at −78 °C, a temperature at which borane had displayed little reactivity. The absence of any induction observed with this reagent suggests that L-Selectride does not require boronate activation by chelation to reduce the carbonyl group, indeed many boron hydride reagents are



known [5] to reduce ketones at this temperature. Hence reduction of the 'unactivated', non-chelated form of the boronate ester **1** in which the chiral auxiliary is remote from the reacting carbonyl centre would be expected to give poor levels of induction, as was found to be the case. The sense of asymmetric induction for the reductions of **1** and **4** may both be predicted using Molander's model [3b] (Scheme 1), assuming intramolecular boron-carbonyl



Scheme 1

chelation and the reducing reagent approaching *via* the least hindered face of the coordinated carbonyl group.

However, there is no direct physical evidence to indicate that the carbonyl lone pair of a ketone can be chelated by the boron of a boronate ester, although Matteson has prepared [6] an amide **7**, in which chelation was evidenced by X-ray crystallography. This contrasts with amide functionalised boronate esters **8** prepared in our laboratories,[7] which have failed to show any evidence for chelation in solution by ^{11}B NMR spectroscopy, even at low temperatures, and for which the IR carbonyl stretching absorption is as expected for unchelated carbonyl groups.[11] Also, our attempts to find crystalline analogues of β-boronate derivatives showing chelation have been unsuccessful to date; the only X-ray structure we have been able to determine is that of the same ligand as **1**, but a phenylboronate ester **10** (Fig. 1). Selected bond distances and angles for **10** are listed in Table 5. This structure clearly reinforces the planarity of the boron atom [as also indicated by ^{11}B NMR (δ 30)] and is, therefore, able to behave as a Lewis-acid; this rules out any steric blocking of the boron atom by the methoxy substituents or chelation of the methoxy groups to boron.

There are, however, a number of reactions which have been implied to proceed *via* chelated intermediates, for example the stereochemical outcome of allylboration and reduction using Corey's oxazaborolidine [8] can be predicted by assuming initial chelation (*via* **9**) of the least hindered lone pair of a carbonyl group to the boron. Of more significance are the stereocontrolled hydride reductions of β-hydroxy ketones controlled by a postulated [9] intramolecular carbonyl chelation to a borinate ester group, which is directly comparable to Molander's earlier [3a] examination of γ-keto boronate reductions. However, studies by Hoffmann [10] to detect such 'ate' complexes between aldehydes and boronate esters have been uniformly unsuccessful,

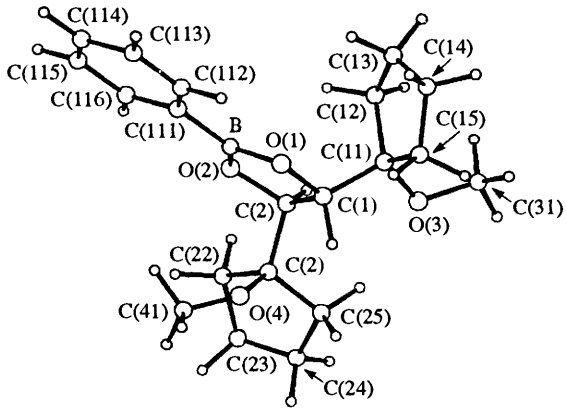
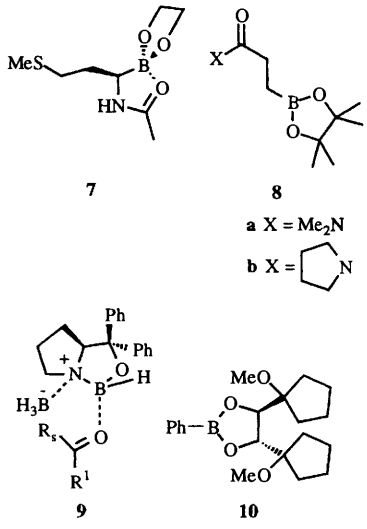


Fig. 1 The crystal structure the phenylboronate ester **10**

even with sterically undemanding boronate esters and a 20-fold excess of propionaldehyde at −90 °C, no signal in the ^{11}B NMR spectrum indicative of a tetrahedral boron,[12] *i.e.* its' 'ate' complex, being detected.



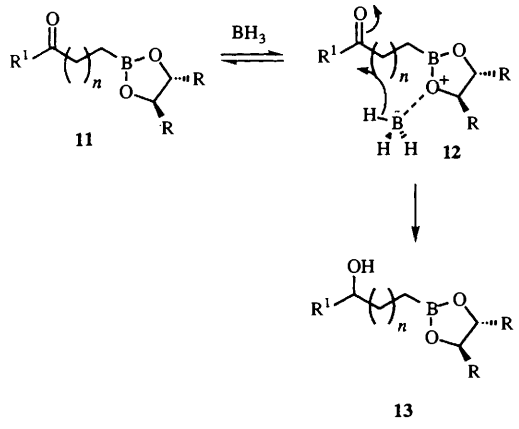
Thus, although chelation activated species have been proposed to be minor equilibrium forms of the unchelated ketones and that such intermediates can effectively rationalise the stereocontrol observed in a variety of reactions, including allylboration and reduction processes, there remains to be reported compelling evidence for their existence. The absence of spectroscopic or other physical evidence for the detection of such chelation activated species (*i.e.* **3**) raises some doubt as to their existence, even as transitory intermediates. The question remains as to what other reaction mechanisms are available to explain the observed reduction reactions of compounds **1** and **4**.

An alternative explanation could involve coordination of borane to the ring oxygens of the dioxaborolane ring of **1** and **4**, or to the methoxy group of the boronate ester **1**. This mode of borane chelation could result in intramolecular delivery of borane (Scheme 2) preferentially to one face of the carbonyl group and thus effecting asymmetric induction in the product.

Precedents for such boron chelation are not unknown, for example, reduction of acetals by diborane have been postulated [13] to proceed by initial complexation of borane to an acetal oxygen. Examples of hydroborations or reductions intramolecularly directed by an ether oxygen are rare, but benzylic ethers have been reported [14] to direct borane addition to a vinyl group intramolecularly. Furthermore, an ester

directed hydroboration has been proposed by House[15] to account for the stereoselectivity observed with diethylborane hydroboration of a precursor to epiallogibberellic acid.

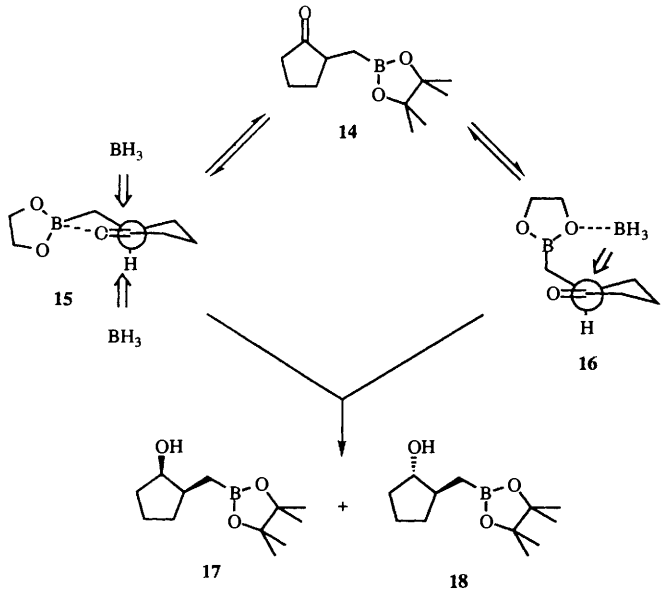
We decided, therefore, to test the validity of a mechanism for the reduction of **1** which involved the dioxaborolane oxygen directed delivery of borane to the carbonyl group, *i.e.* as shown in Scheme 2.



Scheme 2

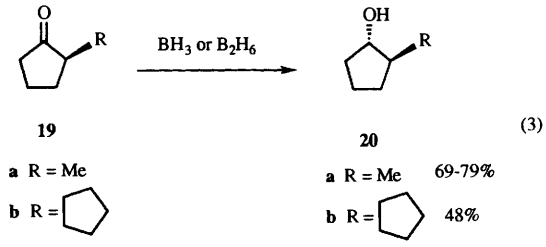
Results and discussion

We initially examined the borane reduction of the cyclic boronate ester **14**. Models[16] of compound **14** in which the carbonyl group is intramolecularly coordinated to the boronate ester group (*i.e.* **15**) show little difference in shielding between either face of the carbonyl group (Scheme 3). But upon



Scheme 3

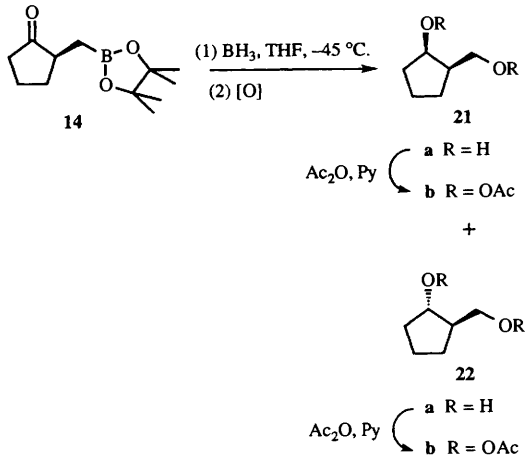
coordination of borane to the dioxaborolane oxygens (*i.e.* **16**) in which the boronate group is not complexed to the carbonyl group, it becomes apparent that delivery of borane from the same side of the cyclopentanone ring as the methyl boronate ester group is a sterically more favourable process than delivery to the opposite face. The only 2-substituted cyclopentanone reductions reported to date have been the reaction of 2-methylcyclopentanone **19** with borane, which was found[17] to furnish the *trans*-alcohol **20** in 69–75% [eqn. (3)]. A similar report[18] was also made of the diborane reduction of 2-cyclo-



(3)

pentylcyclopentanone which provided the corresponding *trans*-alcohol in 48% yield, although no experimental conditions were reported. On this basis, we expected that the ketoboronate **14** should give 48–75% of *trans*-alcohol **18** if the steric demand of the methyl–boronate substituent was approximately similar to the methyl or cyclopentyl groups.

The boronate ester[7] was thus subjected to borane reduction in tetrahydrofuran at −45 °C (Scheme 4), but upon oxidation of



Scheme 4

the crude reduction products **21a** and **22a** with alkaline, aqueous hydrogen peroxide a number of problems became evident. First, the diols **21a** and **22a** were partially water soluble, and only moderate yields of product were obtained after multiple extractions. Second, identification and integration of the crude reaction products was not feasible owing to the similarity of the products. The water solubility problem was simply overcome by utilising *m*-chloroperbenzoic acid as the oxidant, which afforded a mixture of *cis*- and *trans*-diols **21a** and **22a**, in addition to pinacol.

The products **21a** and **22a** could be separated by column chromatography, furnishing compounds identical with those reported in the literature.[19] Acetylation (Scheme 4) of the diols **21a** and **22a** gave the corresponding diacetates **21b** and **22b** in good yield and their relative stereochemistry could be unambiguously assigned by reference to the stereochemically pure starting diols **21a** and **22a**. The acetate methyl signals and α-acetoxy methine hydrogen signals were separated in the 300 MHz ^{1}H NMR spectrum. Having prepared the pure acetates **21b** and **22b**, the crude reaction mixtures, from the reduction (followed by oxidation) of **14**, could be directly acetylated to assess the ratio of the diols **21a** to **22a**, and hence the ratio of **17** to **18**. The ratios of the products obtained from the reduction of the ketone **14**, using borane and L-Selectride, are shown in Table 2.

From the results shown in Table 2, it can be seen that the predominant mode of reduction of **14** with borane is from the same side of the carbonyl as the methylboronate group, which could be accounted for by the prior chelation of the dioxa-

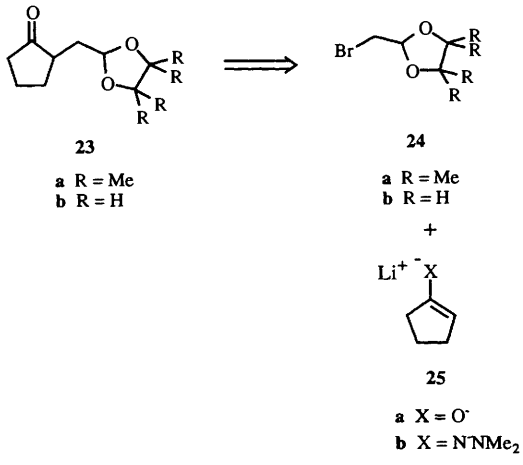
Table 2

Entry	Reduction conditions	Ratio **21**:**22**	Total % yield
1	BH_3–THF, 0 °C	33:67	91
2	BH_3–THF, −45 °C	7:93	72
3		9:91	98[b]
4	BH_3–CH_2Cl_2, 0 °C	43:57	82
5	BH_3–CH_2Cl_2, −45 °C	21:79	73
6	L-Selectride®–THF, −78 °C	96:4[a]	76[b]

[a] Ratio by mass after chromatography. [b] Mass of alcohols **19** + **20** after chromatography.

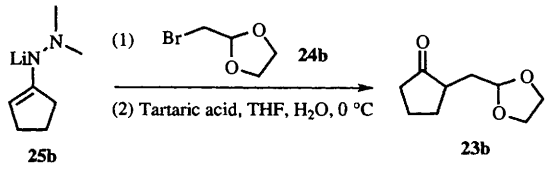
borolane oxygens to borane (*i.e.* **16**, Scheme 3). L-Selectride gives reduction from the opposite face of the carbonyl group to the methylboronate function. This may be interpreted in terms of addition to the marginally less hindered face of the carbonyl group.

If this possibly simplistic mechanistic explanation was correct, then the corresponding acetal should be able to direct reduction to the carbonyl group in a similar manner. We therefore proposed to prepare ketone **23a** as shown in Scheme 5,



Scheme 5

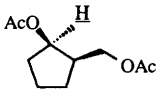
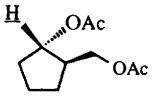
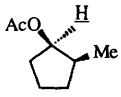
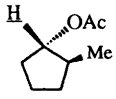
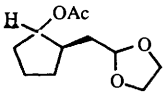
by reaction of the bromo acetal **24a** with cyclopentanone enolate **25a** or the hydrazone derivative **25b**.[20] However, since the bromo acetal **24a** proved too unreactive[21] with either **25a** or **25b**, the bromo acetal **24b** was used instead. In this case, reaction of the hydrazone anion **25b** reacted with the bromo acetal **24b** to afford the derivative **23b** in 25% yield from the hydrazone, after hydrolysis [eqn. (4)].[22]

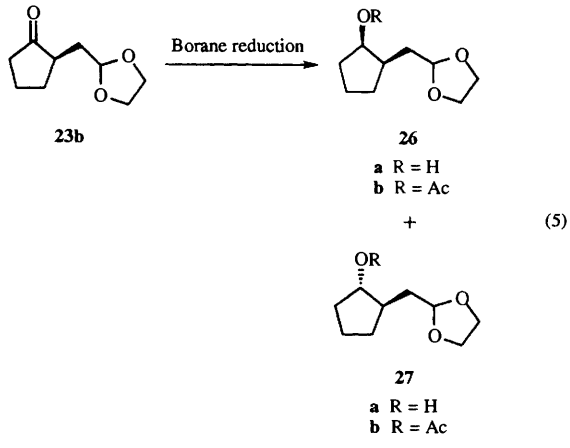


The keto acetal **23b** having been prepared, determination of the *cis*:*trans* ratios (*i.e.* **26a**:**27a**) obtained on reduction was required for comparison with the keto boronate ester **14** [eqn. (5)].

Although reduction of the keto acetal **23b** at 0 °C in tetrahydrofuran was found to furnish the *cis*- and *trans*-hydroxy acetal stereoisomers **26a** and **27a**, these could not be satisfactorily differentiated by ^{1}H NMR spectroscopy. However, their separation by chromatography furnished two hydroxy

Table 3

Entry	Acetate	δ(^{1}H) *H*	Coupling pattern/coupling constants
1	 *cis*-**21**	5.23	doublet triplet, *J* 1.9 and 4.9 Hz
2	 *trans*-**22**	4.93	multiplet
3	 *cis*-**28**	5.12	not quoted
4	 *trans*-**29**	4.52	not quoted
5	 relative stereoisomers **D**	5.19	broad triplet, *J* 4.8 Hz
6	**C**	4.80	multiplet

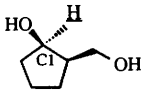
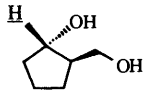
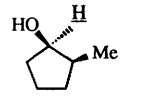
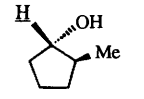
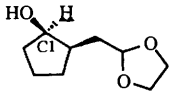
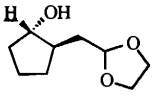


(5)

acetals **A** and **B** in a 63:35 ratio, respectively, with a total yield of 84%. The minor hydroxy acetal stereoisomer **B**, was found to exhibit a signal at δ 4.19 for [C*H*(OH)]. The major stereoisomeric hydroxy acetal **A** was found to give similar ^{1}H and ^{13}C NMR spectra, the major difference by ^{1}H NMR spectroscopy being a [C*H*(OH)] signal at δ 3.79.

Acetylation of the major stereoisomer **A** yielded an acetate derivative **C** in 73% after chromatography. Conversion of this isomer **A** into the acetate gave a new signal at δ 4.80 in the ^{1}H NMR spectrum for 1-H. Acetylation of the minor stereoisomer **B** by the same procedure used for **A**, furnished an acetate derivative **D** in 82% yield which exhibited a signal at δ 5.19 for 1-H in its ^{1}H NMR spectrum. Comparison of the chemical shift and coupling patterns of the [C*H*(OAc)] signal in each of these acetates **C** and **D** was made with the *cis*-**21b** and *trans*-**22b** diacetates prepared earlier, and those of the *cis*- and *trans*-acetates **28** and **29a**, respectively[23] (Table 3). It was hoped that

Table 4

Entry	Cyclopentanol	$\delta_H H$	$(\delta_{H\text{-}cis} - \delta_{H\text{-}trans})$	$\delta_{C\text{-}1}$	$(\delta_{C\text{-}trans} - \delta_{C\text{-}cis})$
1	 *cis*-**21a**	4.41		77.4	
2	 *trans*-**22a**	4.02	0.39	77.7	3.3
3	 *cis*-**29b**	3.96		—	
4	 *trans*-**20a**	3.60	0.36	—	
5	 *cis*-**26a**	4.19		73.6	
6	 *trans*-**27a**	3.79	0.40	79.2	4.6

a trend in the chemical shift and coupling patterns could be established, thus allowing assignment of *cis* and *trans* stereochemistry to the acetates **C** and **D** and the hydroxy acetals **A** and **B** for which they were derived.

Thus, the acetal stereoisomer **D** corresponding to a signal at δ 5.19 (entry 5) was assigned as having the same relative stereochemistry as those isomers exhibiting signals at δ 5.23 and 5.12 (entries 1 and 3), that is the *cis*-isomer, *i.e.* **26b**. Since the broadness of the triplet in this case was suggestive of a small unresolved splitting of ≤ 1 Hz, the coupling constants was also in agreement with the assignment. Hence, the *trans*-acetal must be assigned as having the δ 4.80 signal, that is stereoisomer **C** (*i.e.* **27b**); this chemical shift is in general agreement with that found for the *trans*-diacetate **22b** of δ 4.93. Since each acetate stereoisomer **C** and **D** was prepared separately from a single relative stereoisomer of the hydroxy acetal, that is **A** or **B**, the relative stereochemistry of these isomers could also be assigned, *i.e.* stereoisomer **A** was **26a** and stereoisomer **B** was **27a**.

Having made the assignments, we checked whether the ^{1}H and ^{13}C NMR data for **26a** and **27a** agreed with chemical shift values (or trends) found for the *cis*- and *trans*-stereoisomers of 2-methylcyclopentanol **29b** and **20a** and 2-hydroxymethylcyclopentanol **21a** and **22a** (Table 4).

Although the ^{1}H NMR chemical shift values (Table 4) for the cyclopentanols are not very predictive, it is noted that 1-H has a higher chemical shift in both *cis*-**21a** (entry 1) and *cis*-**29b** (entry 3). Since this trend is in agreement with the *cis*-hydroxy acetal **26a** (entry 5), assigned on the basis of its acetate derivative **26b**, it is thus additional evidence that the original assignment of stereochemistry for this compounds was correct. Although it is also interesting to note that the difference in chemical shift between the *cis*- and *trans*-isomers ($\delta_{H\text{-}cis} - \delta_{H\text{-}trans}$) is very similar, there are too few examples to assess if this is a general pattern for 2-substituted cyclopentanols.

Table 5 Selected bond distances (Å) and angles (°) for (10)

(*a*) Bond distances (Å)			
O(1)–B	1.37(2)	O(1)–C(1)	1.46(2)
O(2)–B	1.40(2)	O(2)–C(2)	1.45(2)
O(3)–C(11)	1.45(2)	O(3)–C(31)	1.41(2)
O(4)–C(21)	1.42(2)	O(4)–C(41)	1.27(2)
B–C(111)	1.53(2)	C(1)–C(2)	1.50(2)
C(1)–C(11)	1.52(2)	C(2)–C(21)	1.55(2)
C(11)–C(12)	1.57(2)	C(11)–C(15)	1.55(2)
C(12)–C(13)	1.49(3)	C(13)–C(14)	1.37(3)
C(14)–C(15)	1.51(3)	C(21)–C(22)	1.58(2)
C(21)–C(25)	1.51(2)	C(22)–C(23)	1.53(2)
C(23)–C(24)	1.46(3)	C(24)–C(25)	1.53(3)
(*b*) Bond angles (°)			
C(1)–O(1)–B	109(1)	C(2)–O(2)–B	107(1)
C(31)–O(3)–C(11)	118(1)	C(41)–O(4)–C(21)	132(2)
O(2)–B–O(1)	112(1)	C(111)–B–O(1)	124(2)
C(111)–B–O(2)	124(1)	C(2)–C(1)–O(1)	104(1)
C(11)–C(1)–O(1)	110(1)	C(11)–C(1)–C(2)	116(1)
C(1)–C(2)–O(2)	106(1)	C(21)–C(2)–O(2)	109(1)
C(21)–C(2)–C(1)	113(1)	C(1)–C(11)–O(3)	101(1)
C(15)–C(11)–O(3)	114(1)	C(12)–C(11)–C(1)	112(1)
C(15)–C(11)–O(3)	111(1)	C(15)–C(11)–C(1)	113(1)
C(15)–C(11)–C(12)	105(1)	C(13)–C(12)–C(11)	106(1)
C(14)–C(13)–C(12)	110(2)	C(15)–C(14)–C(13)	111(2)
C(14)–C(15)–C(11)	105(1)	C(2)–C(21)–O(4)	108(1)
C(22)–C(21)–O(4)	113(1)	C(22)–C(21)–C(2)	111(1)
C(25)–C(21)–O(4)	107(1)	C(25)–C(21)–C(2)	114(1)
C(25)–C(21)–C(22)	104(1)	C(23)–C(22)–C(21)	106(1)
C(24)–C(23)–C(22)	106(1)	C(25)–C(24)–C(23)	111(1)
C(24)–C(25)–C(21)	106(1)	C(112)–C(111)–B	121(1)
C(116)–C(111)–B	119(1)		

Finally, in a study of the ^{13}C NMR spectra of a number of cyclopentanols, Jurs[24] has found that for several 2-substituted cyclopentanols ($\delta_{C\text{-}1\text{-}trans} - \delta_{C\text{-}1\text{-}cis}$) is of the order (positive) of 3–4 ppm. Thus, it was interesting to see if this trend is followed in the case of *cis*-**21a** and *trans*-**22a** and the hydroxy acetals **26a** and **27a** (Table 4); 2-methylcyclopentanol is not considered since it was one of the compounds studied by Jurs.

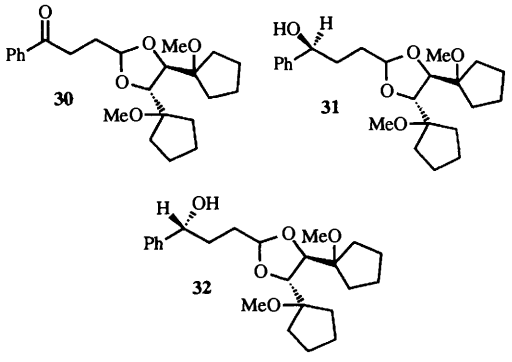
The positive values for $\delta_{C\text{-}1\text{-}trans} - \delta_{C\text{-}1\text{-}cis}$ are of the same order as those observed by Jurs, and are thus another indicator that the stereochemistry assigned to the hydroxy acetal isomers was the correct one. To summarise, the trends in ^{1}H and ^{13}C NMR data for *cis*- and *trans*-2-methylcyclopentanol **29b** and **20a**, and *cis*- and *trans*-2-hydroxymethylcyclopentanol **21a** and **22a**, all serve to confirm that the original assignment of *cis*- and *trans*-stereochemistry to the hydroxy acetals **26a** and **27a** was correct.

Whilst preparing the acetates *cis*-**27b** and *trans*-**27b**, it was considered that reduction of the keto acetal **23b** with L-Selectride (Table 5, entry 3) might also help in assigning the stereochemistry since this sterically demanding hydride reagent has been found[25] to give very high *cis*:*trans* ratios with other α-substituted cyclic ketones. The borane reductions (entries 1 and 2) of this same keto acetal **23b** were studied in conjunction with those of L-Selectride, and the isomer ratios in each case determined by mass recovery after chromatographic separation.

As expected, L-Selectride afforded predominantly one stereoisomeric hydroxy acetal *cis*-**26a** or *trans*-**27a**, assumed to be the *cis*-**27a** by analogy to other literature reductions by this reagent, but later found to correspond to *cis*-**26a** assigned by the δ_H and δ_C NMR comparison techniques.

When these results are compared with those found for reduction of the keto boronate **14** under the same conditions, it is observed that the *cis*:*trans* ratios are very similar. Hence these results appeared to support the hypothesis that a remote acetal

oxygen could direct borane to a reactive site by pre-chelation, as proposed (Scheme 3) earlier. However, there was still uncertainty about whether these results were mainly due to dioxaborolane oxygen-borane chelation or merely an enhancement of the normal stereoelectronic influences of an α-substituted cyclopentanone ring undergoing reduction. In order to finally probe this matter further, we decided to examine the reduction of the acyclic acetal **30**, *i.e.*, the direct acetal analogue of the boronate **1**. The expectation was (assuming acetal-directed reduction) that borane reduction of **30** would lead to: (1) asymmetric induction in the resulting alcohol (*i.e.* **31**:**32**), and (2) the same sense of induction at the resulting alcohol, depending on which diol acetal was utilised. We therefore prepared compound **30** as illustrated in Scheme 6.



Hydroboration followed by oxidation of the homoallylic alcohol **33**[26] gave the diol **34**, which was then oxidised under Swern conditions and transformed into the corresponding dimethyl acetal **35**. After several unsuccessful attempts to exchange the dimethyl acetal of **35** for the diol **37** (obtained in three steps from the ester **36**) under acidic conditions (*e.g.* cat. TsOH or BF_3/toluene, heat), we found that the diol **37** and the acetal **35** when simply heated together in the absence of a solvent, *in vacuo* underwent a clean reaction to give the required acetal **30**. Reduction of the ketone function of this with borane and L-Selectride at −45, and −78 °C respectively, *i.e.* under conditions identical with those used for the reduction of boronate **1** was then studied. The reactions were quenched and the crude reaction mixtures were examined by ^1H NMR (300 MHz) to show that a 1 : 1 mixture of the diastereoisomers **31** and **32** had been formed with both borane and L-Selectride.

These results clearly show that in the case of the acetal **30**, neither the dioxolane ring oxygen atoms, nor the methoxy groups are capable of directing asymmetric induction of the ketone function by a borane-oxygen chelation mechanism, *i.e.* involving an intermediate of type **12**. This being the case, the fact that the cyclopentanone derivatives **14** and **23b** behave similarly in the reductions must largely be due to the stereoelectronic similarity between the dioxaborolane and the dioxolane rings and not due to the intervention of intermediates of type **15** or **16**. Therefore, it is concluded that the asymmetric induction observed for the reduction of the ketones **1** and **4** with borane reagents, does indeed result from an intermolecularly activated complex (*i.e.* **3**) formed from the carbonyl and boron groups (Scheme 1), and that this is followed by intermoledular borane-mediated reduction.

Conclusion

By examining the reductions of non-boron containing derivatives of **1** and **2**, we have shown that the boron atom in both these structures is essential for controlling the asymmetric reduction of the carbonyl groups using borane. This result supports the hypothesis of Molander and co-workers,[3] that such reductions are mediated by intramolecularly activated carbonyl complexes of type **3**.

Experimental

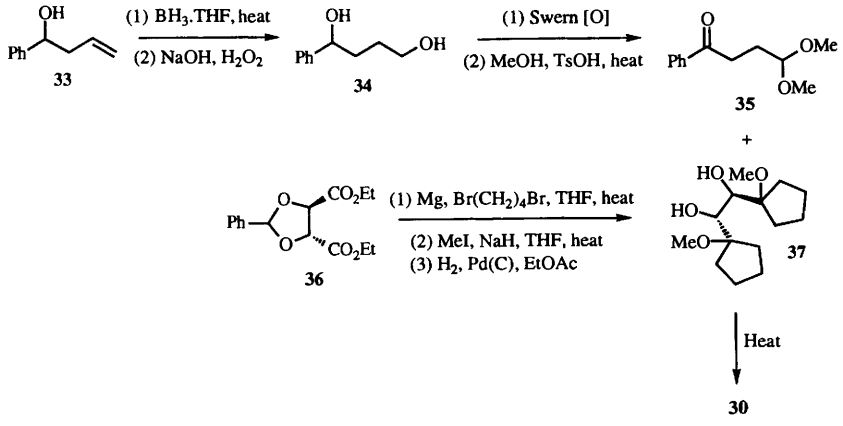
Butyllithium was purchased as a solution in hexanes from Aldrich or Janssen Chimica. Diisopropylamine was purchased from Aldrich or Janssen Chimica and stored under argon, over KOH pellets. Dry tetrahydrofuran was freshly distilled from benzophenone and sodium, under argon, immediately prior to use. Dichloromethane was distilled over calcium hydride. Light petroleum refers to the fraction boiling in the range 40–60 °C. Pivaldehyde was purchased as 99.8% + purity reagent and used directly as purchased and stored under argon. Benzaldehyde was distilled from calcium hydride and stored under argon.

TLC was performed on Merck plastic or aluminium sheets coated with silica gel 60 F_{254} (Art. 5735); the chromatograms were initially examined under UV light and then developed either with iodine vapour or an ethanolic anisaldehyde (1.0%) solution containing sulfuric acid (9%) or phosphomolybdic acid in ethanol (20%) used as a spray and visualised by heating with a heat gun. Column chromatography was achieved under medium pressure, using Merck Kieselgel H (Type 60).

All anhydrous, low-temperature reactions were carried out in glassware which was dried prior to use by storage in a glass oven maintained at 140 °C and cooled under a stream of argon. Evaporations were carried out using a Buchi rotary evaporator or Buchi cold-finger rotary evaporator. Kugelruhr distillations were carried out using a Buchi GKR-51 Kugelruhr apparatus. Mps were determined using an Electrothermal melting point apparatus and were uncorrected. ^1H NMR spectra were recorded at 200 or 300 MHz on a Bruker AC200 or AC300 NMR spectrometer. ^{13}C NMR spectra were recorded at 75.6 MHz on a Bruker AC300. Both ^1H and ^{13}C spectra were recorded using $CDCl_3$ and $CHCl_3$ as internal standards respectively. ^{11}B NMR spectra were recorded at either 25.7 MHz Bruker WP80 NMR spectrometer or at 64.2 MHz on a Bruker AC200 NMR spectrometer and resonances are quoted upfield of $BF_3{\cdot}Et_2O$ as external standard. *J* Values given in Hz. IR spectra were recorded on a Perkin-Elmer 783 equipped with a PE600 data station and UV spectra were recorded on a Perkin-Elmer 115 spectrometer. Electron impact (EI) (70 eV) and chemical ionisation (CI) spectra were recorded with a Kratos MS25. Fast-atom bombardment (FAB) spectra were recorded on a Kratos MS50, using a *m*-nitrobenzyl alcohol matrix and accurate mass determinations were carried out on a Kratos Concept IS spectrometer. Microanalyses were performed using a Carlo-Erba 1106 elemental analyser. $[\alpha]_D$ Values are recorded in units of 10^{-1} deg cm^2 g^{-1}.

4,5-Bis(1-methylcyclohexyl)-2-phenyl-1,3,2-dioxaborolane 10

To a stirred solution of phenylboronic acid (0.20 g, 1.65 mmol) in chloroform (10 cm^3), was added (1*S*,2*S*)-1,2-bis(1-methoxycyclopentyl)ethane-1,2-diol[2] (0.380 g, 1.49 mmol) followed by 1 mol dm^{-3} hydrochloric acid (10 cm^3) at room temperature. After 12 h, the organic layer was separated and washed with water (2 × 30 cm^3) and the aqueous layer was re-extracted with chloroform (2 × 50 cm^3). The combined organic layer and extracts were dried and evaporated to give a crude solid (0.589 g), purification of which by silica gel chromatography (ethyl acetate–hexane, 3:7 as eluent) afforded the title compound **10** a white solid (0.509 g, 90%). The white solid was slowly recrystallised (2 d) from hexane to afford a single crystal for X-ray analysis; mp 57–60 °C; $[\alpha]_D$ = +28 (*c* = 0.25 $CHCl_3$); ν_{max}/cm^{-1} *inter alia* 2970 (CH); λ_{max}(EtOH)/nm 270 (ε/dm^3



Scheme 6

mol^{-1} cm^{-1}) 576 and 254 (7338); δ_H($CDCl_3$, 300 MHz) 1.59–1.82 (16 H, m, cyclopentyl H), 3.26 (6 H, s, OMe), 4.52 (2 H, s, CH), 7.36–7.48 (3 H, m, ArH) and 7.81–7.84 (2 H, m, ArH); δ_C($CDCl_3$) 31.7, 31.0, 25.0, 24.6 and 14.2 (cyclopentyl CH_2), 50.6 (OMe), 81.4 (CB), 88.0 (*C*OMe), 128.2 (ArC-4), 130.0 (ArC-3,5) and 135.1 (ArC-2,6); *m/z* (FAB) *inter alia* 99 (M − $C_6H_{11}O^+$, base peak) (Found: C, 69.7; H, 8.7; B, 3.0. $C_{20}H_{29}BO_4$ requires C, 69.8; H, 8.4; B, 3.1%).

Reduction of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-ylmethyl)cyclopentanone 14 with borane

To a stirred solution of compound **14** (0.112 g, 0.50 mmol) in tetrahydrofuran (4.0 cm^3) at −45 °C under argon, was introduced borane (1.0 mol dm^{-3} solution in tetrahydrofuran; 0.54 cm^3, 0.54 mmol) dropwise. After 12 h, the reaction was quenched by addition of several drops of water to the mixture which was then subjected to rotary evaporation to remove solvent and residual water. To the residual oil were added dichloromethane (4.0 cm^3), *m*-chloroperbenzoic acid (0.185 g; 5.4–6.4 mmol) a 50–60% mixture with 3-chlorobenzoic acid and sodium hydrogen carbonate 0.055 g, 0.65 mmol). After being stirred for 14 h, the resulting slurry was filtered under pressure through a plug of magnesium sulfate and washed through with additional dichloromethane. After evaporation of the filtrate, the product was purified by silica gel chromatography (9:1, hexane–ethyl acetate eluent), to furnish the *trans*-1,3-diol **22a** (0.053 g, 0.46 mmol, 91%) and the *cis*-1,3-diol **21a** (0.006 g, 0.05 mol, 9%) as colourless oils. *trans*-1,3-Diol **22a**; ν_{max}(film)/cm^{-1} as reported;[27] δ_H(^{1}H, $CDCl_3$) as reported except 3.56 (1 H, dd, *J* 8.9, 10.2, C*H*HOH), 3.74 (1 H, dd, *J* 5.3, 10.2, CH*H*OH); δ_C($CDCl_3$) 21.6, 26.1, 34.3 (CH_2 cyclopentyl), 49.4 (*C*HCH$_2$-OH), 66.0 (CH_2OH) and 76.5 [CH(OH)]; *m/z* (FAB) 447 (4M − OH)$^+$, 233 (2M + H)$^+$ and 99 (M − OH)$^+$ (Found: C, 62.3; H, 10.4. Calc. for $C_6H_{12}O_2$: C, 62.0; H, 10.4%). *cis*-1,3-Diol **21a**; ν_{max}(film)/cm^{-1} as reported;[27] ^{1}H NMR as reported; δ_C($CDCl_3$) 21.8, 25.3, 34.5 (CH_2 cyclopentyl), 46.3 (*C*HCH$_2$-OH), 62.1 (CH_2OH) and 74.4 [CH(OH)]; *m/z* (CI) 134 (M + NH_4)$^+$ base peak, 117 (M + H)$^+$, 99 (M − OH)$^+$, 81 (M − H_3O_2)$^+$ [Found (HRMS): *m/z* 134.1175. $C_6H_{16}NO_2$ requires (M + NH_4)$^+$ 134.1181].

Acetylation of *cis*-2-hydroxymethylcyclopentanol 21a

To the *cis*-diol **21a** (0.179 g, 1.54 mmol) in a glass vial were introduced acetic anhydride (5.0 cm^3, 53 mmol) and pyridine (1.0 cm^3, 12 mmol). After being stirred at room temperature for 2 d, the reaction mixture was slowly introduced to rapidly stirred, saturated aqueous sodium hydrogen carbonate, and further sodium hydrogen carbonate introduced until no more effervescence was observed. This solution was extracted with ethyl acetate, and the extract washed with dilute hydrochloric acid and saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), filtered and evaporated to furnish the diacetate **21b** (0.395 g, 1.52 mmol, 98%) as a pale yellow oil; ν_{max}(film)/cm^{-1} *inter alia* 1740 (CO); δ_H($CDCl_3$) 1.40–1.97 (6 H, m, CH_2/CH cyclopentyl), 2.01 (3 H, s, CH_3CO_2), 2.02 (3 H, s, CH_3CO_2), 2.21–2.32 (1 H, m, CH_2/CH cyclopentyl), 4.06 (1 H, dd, *J* 6.5, 10.8, C*H*HOAc), 4.12 (1 H, dd, *J* 8.1, 10.8, CH*H*OAc) and 5.23 (1 H, dt, *J* 1.9, 4.9; CHOAc); δ_C($CDCl_3$) 20.7 and 20.8 (2 × CH_3CO_2), 22.1, 26.6 and 32.4 (CH_2 cyclopentyl), 42.9 (*C*HCH$_2$OAc), 63.3 (CH_2OAc), 76.0 (CHOAc), 170.2 and 170.7 (2 × CO); *m/z* (FAB) 141 (M − OAc)$^+$ base peak [Found (HRMS): *m/z* 141.0932. $C_8H_{13}O_2$ requires (M − OAc)$^+$, 141.0919].

Acetylation of *trans*-2-hydroxymethylcyclopentanol 20a

To the *trans*-diol **20a** (0.053 g, 0.46 mmol) was added acetic anhydride (0.50 cm^3, 5.3 mmol) and pyridine (0.074 cm^3, 0.92 mmol). After 20 h, the acetic anhydride was removed by evaporation, to furnish a pale yellow oil. This was partitioned between chloroform and dilute hydrochloric acid, and the organic phase separated, dried ($MgSO_4$) and evaporated to give the crude diacetate. Purification of this by silica gel chromatography (dichloromethane eluent) afford the *trans*-diacetate **22b** (0.037 g, 0.19 mmol, 41%) as a colourless oil; ν_{max}(film)/cm^{-1} *inter alia* 1740 (CO); δ_H($CDCl_3$) 1.24–1.38, 1.61–1.73 and 1.86–2.02 (6 H, m, CH_2 cyclopentyl), 2.02 (3 H, s, CH_3CO_2), 2.05 (3 H, s, CH_3CO_2), 2.22–2.33 (1 H, m, C*H*CH$_2$OAc), 4.02 (2 H, d, *J* 6.5, CH_2OAc) and 4.93 (1 H, m, CHOAc); δ_C($CDCl_3$) 21.0 and 21.3 (CH_3CO_2), 23.0, 27.4, 32.2 (CH_2 cyclopentyl), 44.6 (*C*HCH$_2$OAc), 65.6 (CH_2OAc), 78.1 (CHOAc), 170.8 and 171.2 (C:O); *m/z* (CI) 218 (M + NH)$^+$ base peak, 201 (M + H)$^+$, 141 (M − OAc)$^+$ [Found (HRMS): *m/z* 201.1122. $C_{10}H_{17}O_4$ requires (M + H)$^+$ 201.1127].

Borane–tetrahydrofuran reduction of the ketone 14 at 0 °C

To a stirred solution of compound **14** (0.050 g, 0.22 mmol) in tetrahydrofuran (3.0 cm^3) at 0 °C under argon, was introduced borane (1.0 mol dm^{-3} solution in tetrahydrofuran; 0.27 cm^3, 0.27 mmol). After 12 h, the reaction was quenched by addition of 2–3 drops of water to the mixture from which solvent was then removed by evaporation. The residual oil was diluted with dichloromethane (3.0 cm^3) and *m*-chloroperbenzoic acid (0.090 g, 0.26–0.31 mmol a 50–60% mixture with *meta*-chorobenzoic acid) and sodium hydrogen carbonate (0.027 g, 3.2 mmol) introduced. Filtration of the resulting slurry through a plug of magnesium sulfate and sodium hydrogen carbonate after 24 h gave, after evaporation, a colourless oil. This was dissolved in dichloromethane (1.0 cm^3), and acetic anhydride (0.30 cm^3, 3.2

mmol) and pyridine (0.09 cm^3, 1.1 mmol) were introduced. After 2 d the mixture was worked up by the procedure described above, and the crude acetates examined by ^1H NMR spectroscopy. Purification by silica gel chromatography (96:4, hexane–dichloromethane eluent), furnished the *cis*- and *trans*-diacetates **21b** and **22b** (0.041 g, 0.20 mmol, 91%) as an inseparable mixture. Integration of the δ 5.23 and 4.93 signals of the crude acetylation products gave a **21b**:**22b** ratio of 33:67, respectively.

Borane–tetrahydrofuran reduction of the ketone 14 at −45 °C

Reduction and acetylation employed the same procedure and quantities of reagents described above, except that reduction was quenched after 9 h at −45 °C. Purification by silica gel chromatography furnished the *cis*- and *trans*-diacetates **21b** and **22b** (0.032 g, 0.16 mmol, 72%) respectively, as an inseparable mixture. Integration of the ^1H NMR spectrum of the crude acetylation products gave a 7:93 ratio of *cis*- and *trans*-diacetates **21b** and **22b**.

Borane–tetrahydrofuran reduction of the ketone 14 at 0 °C in dichloromethane

Reduction and acetylation employed the same procedure and quantities of reagents as described above, except that reduction employed dichloromethane (3.0 cm^3) as the solvent, and was quenched after 12 h at 0 °C. Purification by silica gel chromatography furnished the *cis*-and *trans*-diacetates **21b** and **22b** (0.035 g, 0.18 mmol, 82%), respectively, as an inseparable mixture. Integration of the ^1H NMR spectrum of the crude acetylation products gave a 43:57 ratio of *cis*- and *trans*-diacetates **21b** and **22b**.

Borane–tetrahydrofuran reduction of the ketone 14 at −45 °C in dichloromethane

Reduction and acetylation employed the same procedure and quantities of reagents described above, except that reduction employed dichloromethane (3.0 cm^3) as the solvent, and was quenched after 9 h at −45 °C. Purification by silica gel chromatography furnished the *cis*- and *trans*-diacetates **21b** and **22b** (0.031 g, 0.16 mmol, 73%), respectively, as an inseparable mixture. Integration of the ^1H NMR spectrum of the crude acetylation products gave a 21:79 ratio of *cis*- and *trans*-diacetates **21b** and **22b**.

L-Selectride reduction of the ketone 14 at −78 °C in tetrahydrofuran

To a stirred solution of the ketone **14** (1.00 g, 4.46 mmol) in tetrahydrofuran (20.0 cm^3) at −78 °C under argon, was introduced L-Selectride (1.0 mol dm^{-3} solution in tetrahydrofuran; 8.90 cm^3, 8.9 mmol). After 7 h, the reaction was quenched by addition of a minimum volume of water to the reaction mixture until no more effervescence was observed. Sodium hydroxide (4.0 mol dm^{-3} solution; 50 cm^3, 20 mmol) and hydrogen peroxide (30 wt. %; 4.0 cm^3, 44 mmol) were added to the mixture the temperature being kept < 10 °C. After 1 h, the tetrahydrofuran and water were removed by evaporation, and the resulting aqueous slurry was extracted with tetrahydrofuran. Evaporation of the extract yielded a colourless oil which was dissolved in ethyl acetate, and the solution dried ($MgSO_4$) and evaporated. Purification of the residue by silica gel chromatography, furnished the *cis*-diol **21a** (0.378 g, 3.25 mmol, 73%) and *trans*-diol **22a** (0.015 g, 0.13 mmol, 3%). These yields correspond to a *cis*:*trans* ratio in the reduction process of 96:4.

2-(Bromomethyl-4,4,5,5-tetramethyl-1,3-dioxolane 24a

To a stirred mixture of pinacol (6.00 g, 0.051 mol) and bromoacetaldehyde diethyl acetate (5.00 g, 51 mmol) was added toluene-*p*-sulfonic acid monohydrate (0.20 g, 1.0 mmol). This mixture was heated to 110 °C for 2 h with collection of the ethanol distillate *via* a Vigreux column under a water aspirator vacuum, after which it was purified by Kugelrohr distillation at 90 °C under water aspirator vacuum to give the acetal **24a** (9.98 g, 0.045 mol, 88%) as a colourless oil; ν_{max}(film)/cm^{-1} *inter alia* 590 (C − Br); $\delta_H(CDCl_3)$ 1.22 and 1.23 [12 H, total, 2 × s, 2 × $(CH_3)_2CO$], 3.31 (2 H, d, *J* 5.0, CH_2Br), 5.21 (1 H, t, *J* 5.0, CHO_2); $\delta_C(CDCl_3)$ 21.9 and 23.5 [$(CH_3)_2CO$], 33.7 (CH_2Br), 82.8 [$(CH_3)_2CO$] and 99.1 (CHO_2); *m*/*z* (FAB) 223 ($M - H^{81}Br)^+$, 221 ($M - H^{79}Br)^+$ and 101 $(C_6H_{13}O)^+$ (Found: C, 42.9; H, 6.8; Br, 36.2. Calc. for $C_8H_{15}BrO_2$: C, 43.1; H, 6.8; Br, 35.8%).

Cyclopentanone *N*,*N*-dimethylhydrazone

N,*N*-Dimethylhydrazine (30.0 cm^3, 0.395 mol) was introduced to stirred cyclopentanone (25.00 g, 0.297 mol) (exothermic), and the mixture refluxed for 4 h. After cooling, the reaction mixture was diluted with diethyl ether, washed with water, dried ($MgSO_4$) and evaporated to afford a pale yellow oil which was dried over calcium hydride for 2 days. Distillation through a Vigreux column under a water aspirator vacuum, furnished the title compound (31.34 g, 0.248 mol, 84%) as a colourless oil; IR and ^1H NMR spectra as reported;[28] $\delta_C(CDCl_3)$ 23.5 and 24.2 ($CH_2CH_2CCH_2C$=N), 28.6 and 32.8 [$CH_2(C$=N$)CH_2$], 46.3 [$N(CH_3)_2$] and 174.9 (CN); *m*/*z* (FAB) 125 $(M - H)^+$ (Found: C, 66.6; H, 11.5; N, 22.0. Calc. for $C_7H_{14}N_2$: C, 66.6; H, 11.2; N, 22.2%).

2-(Bromomethyl)-1,3-dioxolane 24b

This compound was prepared by a procedure similar to that described for **24a**, employing ethylene glycol (2.83 g, 45 mmol), bromoacetaldehyde diethyl acetal (10.00 g, 51 mmol) and toluene-*p*-sulfonic acid monohydrate (0.20 g, 1.0 mmol). Distillation (67 °C, water aspirator vacuum) furnished the 1,3-dioxolane **24b** (6.51 g, 0.039 mol, 87%) as a colourless oil; IR and $^1H/^{13}C$ NMR spectra were identical with those of a commercially available sample (Found: C, 28.8; H, 4.2; Br, 48.1. Calc. for $C_4H_7BrO_2$: C, 28.8; H, 4.2; Br, 47.9%).

2-(1,3-Dioxolan-2-ylmethyl)cyclopentanone 23b

To a vigorously stirred solution of cyclopentanone *N*,*N*-dimethylhydrazone (4.00 g, 31.7 mmol) in tetrahydrofuran (40.0 cm^3) at 0 °C under argon, was introduced butyllithium (2.5 mol dm^{-3} solution in hexanes; 12.69 cm^3, 31.7 mmol). After 30 min, formation of a colourless precipitate was observed, and 1,3-dioxolane **24b** (5.03 g, 31.7 mmol) was added to the mixture. After 18 h at ~10 °C the mixture was treated with saturated aqueous ammonium chloride to quench the reaction and then partitioned between ethyl acetate and saturated aqueous ammonium chloride. The organic layer was separated, dried ($MgSO_4$) and evaporated to give the crude alkylated hydrazone from which unchanged starting materials were removed by Kugelrohr distillation (≤100 °C, 20 mmHg). The distillation residue was dissolved in tetrahydrofuran (40 cm^3) and water (12 cm^3), and tartaric acid (4.00 g, 26.7 mmol) introduced to the solution. After the mixture had been stirred for 90 min tetrahydrofuran was removed by evaporation and the aqueous was residue extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated, after which Kugelrohr distillation (145 °C, 1 mmHg) furnished the keto acetal **23b** (1.335 g, 7.9 mmol, 25%) as a pale orange oil; ν_{max}(film)/cm^{-1} *inter alia* 1738 (CO); $\delta_H(CDCl_3)$ 1.51–1.85 (6 H, m, $CH_2CH_2CHCH_2$), 1.98–2.37 [3 H, m, $CH_2C(O)CH$], 3.80–3.98 (4 H, m, OCH_2-CH_2O), 4.98 (1 H, t, *J* 4.7, CHO_2); $\delta_C(CDCl_3)$ 20.7, 30.2, 35.5, 37.4 (4 × CH_2), 45.2 (*C*HCO), 64.6 and 64.7 (OCH_2CH_2O), 103.1 (CHO_2) and 220.0 (CO); *m*/*z* (FAB) 171 $(M + H)^+$, 169 $(M - H)^+$ and 73 $(C_3H_5O_2)^+$ [Found (HRMS): *m*/*z*, 171.1020. Calc. for $C_9H_{15}O_3$: $(M + H)^+$, 171.1021] (Found: C, 63.2; H, 8.6. Calc. for $C_9H_{14}O_3$: C, 63.5; H, 8.3%).

2-(1,3-Dioxolan-2-ylmethyl)cyclopentanol 26a and 27a

To a stirred solution of the keto acetal **23b** (0.302 g, 1.78 mmol) in tetrahydrofuran (12.0 cm^3) at 0 °C under argon, was introduced borane (1.0 mol dm^{-3} solution in tetrahydrofuran; 2.10 cm^3, 2.1 mmol). After 10 h, the reaction was quenched by addition of water (1.5 cm^3) to the mixture which was then allowed to warm to room temperature. After concentration of the mixture by evaporation of the solvent, the residue was redissolved in ethyl acetate and the solution dried ($MgSO_4$), and evaporated to furnish a pale yellow oil. Purification of this by silica gel chromatography (hexane–ethyl acetate, 9:1) yielded the two hydroxy acetals *cis*-**26a** (0.089 g, 0.52 mmol, 29%) and *trans*-**27a** (0.167 g, 0.97 mmol, 54%) as colourless oils. Compounds *cis*-**26a** (stereoisomer **B**): ν_{max}(film)/cm^{-1} *inter alia* 3456 (OH); δ_H($CDCl_3$) 1.38–1.96 [9 H, m, CH_2 cyclopentyl, C*H*CH(OH) and CH_2CHO_2], 2.48 [1 H, d, *J* 2.3, CH(O*H*)], 3.82–4.05 (4 H, m, OCH_2CH_2O), 4.19 [1 H, m, C*H*(OH)], 4.91 (1 H, m, CHO_2) (addition of D_2O caused the peak at δ 2.48 to disappear); δ_C($CDCl_3$) 22.3, 30.1, 32.9, 34.1 (CH_2 cyclopentyl and CH_2CHO_2), 41.4 [*C*HCH(OH)], 64.6 and 65.1 (OCH_2-CH_2O), 73.6 [CH(OH)] and 104.2 (CHO_2); *m/z* (CI) 173 $(M + H)^+$, 171 $(M - H)^+$, 154 $(M - H_2O)^+$ and 111 $(M - C_2H_5O_2)^+$ [Found (HRMS): *m/z* 173.1171 and 171.1022. Calc. for $C_9H_{17}O_3$ and $C_9H_{15}O_3$: $(M + H)^+$, 173.1178 and $(M - H)^+$, 171.1.021]. Compound *trans*-**27a** (steroisomer **A**): ν_{max}(film)/cm^{-1} *inter alia* 3390 (OH); δ_H-($CDCl_3$) 1.19–1.96 and 1.50–2.04 [9 H, m, CH_2 cyclopentyl, C*H*CH(OH) and CH_2CHO_2], 3.31 [1 H d, *J* 2.0, CH(O*H*)], 3.79 [1 H, dq, *J* 7.1, 1.9, C*H*(OH)], 3.84–4.05 (4 H, m, OCH_2CH_2O), 4.93 (1 H, dd, *J* 2.8, 6.5, CHO_2) (addition of D_2O caused the peak at δ 3.31 to disappear and that at δ 3.79 to collapse to a *J* 7.1 q); δ_C($CDCl_3$) 21.3, 31.3, 33.8, 38.0 (CH_2 cyclopentyl and CH_2CHO_2), 44.1 [*C*HCH(OH)], 65.0 (OCH_2CH_2O), 79.2 [CH(OH)] and 104.3 (CHO_2); *m/z* (FAB) 173 $(M + H)^+$ and 154 $(M - H_2O)^+$.

1-Acetoxy-2-(1,3-dioxolan-2-ylmethyl)cyclopentane 27b

Acetylation of the *trans*-hydroxy acetal **27a** employed the procedure described above for the preparation of the *cis*-diacetate **21b**. Chromatographically pure *trans*-alcohol **27a** (0.100 g, 0.58 mmol), furnished the *trans*-acetate **27b** (stereoisomer **C**) (0.091 g, 0.42 mmol, 73%) as a colourless oil after chromatography; ν_{max}(film)/cm^{-1} *inter alia* 1732 (CO); δ_H($CDCl_3$) 1.27–2.17 (9 H, m, CH_2 and CH cyclopentyl, and CH_2CHO_2), 2.02 (3 H, s, CH_3CO_2), 3.78–3.99 (4 H, m, OCH_2CH_2O), 4.80 (1 H, m, CHOAc), 4.88 (1 H, t, *J* 5.0, CHO_2); δ_C($CDCl_3$) 21.3 (CH_3CO_2), 22.4, 30.2, 31.3, 37.4 (CH_2 cyclopentyl and CH_3CHO_2), 41.1 (*C*HCHOAc), 64.7 and 64.8 (OCH_2CH_2O), 81.0 (*C*HOAc), 103.6 (CHO_2) and 170.9 (CO); *m/z* (CI) 232 $(M + NH_4)^+$, 215 $(M + H)^+$, 155 $(M - OAc)^+$ and 73 $(C_3H_5O_2)^+$ base peak [Found (HRMS): *m/z*, 215.1283. $C_{11}H_{19}O_4$ requires $(M + H)^+$ 215, 1283].

1-Acetoxy-2-(1,3-dioxolan-2-ylmethyl)cyclopentane 26b

Acetylation of the *cis*-hydroxy acetal **26a** employed the procedure described above for the preparation of the *cis*-diacetate **21b**. Chromatographically pure *cis*-hydroxy acetal **26a** (0.115 g, 0.67 mmol), furnished the *cis*-acetate **26b** (stereoisomer **D**) (0.118 g, 0.55 mmol, 82%) as a colourless oil after chromatography; ν_{max}(film)/cm^{-1} *inter alia* 1738 (CO); δ_H($CDCl_3$) 1.39–2.04 (9 H, m, CH_2 and CH cyclopentyl, and CH_2CHO_2), 2.02 (3 H, s, CH_3CO_2), 3.80–3.99 (4 H, m, OCH_2CH_2O), 4.86 (1 H, t, *J* 5.0, CHO_2), 5.19 (1 H, br t, *J* 4.8, CHOAc); δ_C($CDCl_3$) 21.4 (CH_3CO_2), 22.1, 30.0, 32.6, 33.5 (CH_2 cyclopentyl and CH_2CHO_2), 41.5 (*C*HCHOAc), 64.9 and 65.0 (OCH_2CH_2O), 104.0 (CHO_2) and 171.0 (CO); *m/z* (FAB) 215 $(M + H)^+$, 213 $(M - H)^+$, 155 $(M - OAc)^+$, 153 $(M - C_2H_5O_2)^+$ and 111 $(M - C_4H_7O_3)^+$ base peak [Found (HRMS): *m/z* 215.1287. $C_{11}H_{19}O_4$ requires $(M + H)^+$, 215.1283].

Borane–tetrahydrofuran reduction of the keto acetal 23b at −45 °C in tetrahydrofuran

To a stirred solution of the keto acetal **23b** (0.100 g, 0.59 mmol) in tetrahydrofuran (4.0 cm^3) at −45 °C under argon, was introduced borane (1.0 mol dm^{-3} solution in tetrahydrofuran; 0.70 cm^3, 0.70 mmol). After 10 h, the reaction was quenched by the addition of water (0.5 cm^3) to the mixture which was then allowed to warm to room temp. Solvent was evaporated from the mixture and the residue dissolved in ethyl acetate (20 cm^3), the solution dried ($MgSO_4$), and the solvent re-evaporated. Purification of the residue by silica gel chromatography (9:1, hexane–ethyl acetate) yielded the *trans*-hydroxy acetal **27a** (0.073, 0.42 mmol, 72%) and the *cis*-hydroxy acetal **26a** (0.009 g, 0.05 mmol, 9%), corresponding to a *cis*:*trans* ratio of 11:89. The identity of both isomers were established by comparison of the ^1H NMR spectra with those prepared above.

L-Selectride reduction of the keto acetal 23b at −78 °C in tetrahydrofuran

To a stirred solution of the keto acetal **23b** (0.100 g, 0.59 mmol) in tetrahydrofuran (5.0 cm^3) at −78 °C under argon, was introduced L-Selectride (1.0 mol dm^{-3} solution in tetrahydrofuran; 0.70 cm^3, 0.70 mmol). After 4 h, the reaction was quenched by addition of water (0.5 cm^3) to the mixture which was then allowed to warm to 0 °C. With the temperature maintained at 0 °C, aqueous sodium hydroxide (1.0 mol dm^{-3} solution; 3.0 cm^3, 3.0 mol) and hydrogen peroxide (30 wt % solution; 1.5 cm^3, 0.013 mol) were introduced slowly to the mixture with vigorous stirring. After 1 h, tetrahydrofuran and water were removed from the mixture by evaporation, and butan-2-ol azeotroped with water to afford an aqueous slurry. Following addition of water to this slurry the latter was extracted with ethyl acetate and the extract dried ($MgSO_4$) and subjected to rotary evaporation to furnish a pale yellow oil. Purification of this by silica gel chromatography gave the *cis*-hydroxy acetal **26a** (0.067 g, 0.39 mmol, 66%) and the *trans*-hydroxy acetal **27a** (0.003 g, 0.02 mmol, 3%) as colourless oils, corresponding to a *cis*:*trans* ratio of 96.4.

(4*R*,5*R*)-(−)-Dimethyl 2,3-*O*-benzylidene-L-tartrate 36

The procedure of Kocienski,[29] followed on a 0.561 mol scale, furnished the ester **36** (130.63 g, 0.491 mol, 88%) after recrystallisation from dichloromethane–hexane. The ^1H NMR spectrum was identical with that reported, $[\alpha]_D^{20}$ −47 (*c* 1.04, methanol) {lit. $[\alpha]_D^{21}$ −47.2 at same concentration in methanol[29]}.

(4*R*,5*R*)-4,5-Bis(1-hydroxycyclopentyl)-2-phenyl-1,3-dioxolane

Into a stirred flask containing dry tetrahydrofuran (800 cm^3) under argon, were introduced magnesium turnings (17.84 g, 0.734 mol), 1,4-dibromobutane (38.75 cm^3, 0.324 mol) and several crystals of iodine. Once Grignard formation had been initiated (exothermic), the temperature was initially maintained at 25 °C by cooling in an ice-bath and then, after 15 min, allowed to rise to room temperature; after this the solution was refluxed for 2 h. After the mixture had been cooled to 0 °C, a solution of the ester **36** [30.00 g, 0.168 mol in tetrahydrofuran (100 cm^3)], was slowly introduced to the rapidly stirred solution, care being taken not to allow the temperature to rise above 25 °C. The solution was stirred at room temperature for a further 10 h and then directly filtered through a pad of Celite. After solvent removal by rotary evaporation, the resultant foam was dissolved in chloroform and the solution washed with saturated aqueous ammonium chloride, dried ($MgSO_4$) and

subjected to rotary evaporation to furnish a colourless solid. Recrystallisation of this from refluxing cyclohexane yielded the title compound (26.83 g, 0.084 mol, 50%) as a fine crystalline solid, mp 118 °C; ν_{max}(KBr disc)/cm^{-1} *inter alia* 3340 and 3240 (OH); δ_H($CDCl_3$) 1.59–1.86 (16 H, m, CH_2, cyclopentyl), 2.05 (2 H, br s, OH, disappears on D_2O shake), 4.20 and 4.25 [2 H, AB, q, $J_{A,B}$ 5.8, $\delta\nu$ = 12.1 Hz, C(OH)C*H*O], 6.06 (1 H, s, CHPh), 7.38 (3 H, m, *m*-, *p*-H) and 7.49 (2 H, m, *o*-H); δ_C($CDCl_3$) 23.3, 23.4, 23.7 and 23.8 [*C*H_2*C*H_2*C*H_2*C*(OH)], 36.0, 36.1, 37.1, 37.4 [*C*H_2C(OH)*C*H_2], 82.1 [C(OH), not present in DEPT spectrum], 82.7 and 83.2 [C(OH)*C*HO], 104.0 (Ph*C*H), 126.5, 128.3, 129.3 and 137.7 (ArC); *m*/*z* (FAB) 317 (M − H)$^+$, 195 (M − $C_7H_7O_2$)$^+$ base peak (Found: C, 71.5; H, 8.5. Calc. for $C_{19}H_{26}O_4$: C, 71.7; H, 8.2%); $[\alpha]_D^{23}$ −4 (*c* 3.0, $CHCl_3$).

(4*R*,5*R*)-4,5-Bis(1-methoxycyclopentyl)-2-phenyl-1,3-dioxolane 37

To a stirred solution of the above dioxolane (29.06 g, 84 mmol) in dry toluene (85 cm^3) under argon, was added toluene-washed sodium hydride (60% dispersion in oil; 1.44 g, 36.0 mmol) and iodomethane (10.4 g, 73.0 mmol), and the mixture was heated under reflux for 24 h. It was then cooled, diluted with chloroform and carefully quenched with water (dropwise), separated, dried ($MgSO_4$) and evaporated to give the title compound **37** (28.24 g, 96%) as a pale yellow oil. This material was of sufficient purity for further use; ν_{max}(film)/cm^{-1} *inter alia* 1095 (CO); δ_H($CDCl_3$) 1.58–2.01 (16 H, m, CH_2, cyclopentyl), 3.26 (3 H, s, OMe), 3.31 (3 H, s, OMe), 4.17 [1 H, d, *J* 4.3, C(OMe)C*H*O], 4.43 [1 H, d, *J* 4.3, C(OMe)C*H*O], 6.08 (1 H, s, PhCH), 7.36 (3 H, m, *m*-, *p*-H), 7.49 (2 H, m, *o*-H); δ_C($CDCl_3$) 24.5, 24.6, 24.7, 24.8 [*C*H_2*C*H_2*C*H_2*C*(OMe)], 31.3, 31.4, 32.3, 32.4 [*C*H_2C(OMe)*C*H_2], 50.3 and 50.4 (OCH_3), 80.0 and 83.1 [C(OMe)CHO], 87.7 and 89.2 [*C*(OMe) not present in DEPT], 104.2 (PhCH), 126.6, 128.3, 129.0 and 138.2 (ArC); *m*/*z* (FAB) 345 (M − H)$^+$ and 283 (M − $C_2H_7O_2^+$ (Found: C, 72.5; H, 8.9. Calc. for $C_{21}H_{30}O_4$: C, 72.8; H, 8.7%); $[\alpha]_D^{20}$ −22 (*c* 1.0, chloroform).

(1*R*,2*R*)-Bis(1-methoxycyclopentyl)ethane-1,2-diol 37

To a solution of the dioxolane **37** (0.300 g, 0.87 mmol) in methanol (5.90 cm^3) was introduced 10% palladium-on-carbon (0.020 g), and the mixture degassed *via* a water aspirator connected to a hydrogenation apparatus. After introduction of hydrogen, the solution was rapidly stirred for 48 h under a slight positive pressure of this gas. Removal of methanol by rotary evaporation from the mixture followed by dilution of the residue with ethyl acetate and filtration through a plug of magnesium sulfate, furnished the title compound **37** (0.219 g, 0.85 mmol, 98%) as a colourless solid after rotary evaporation and drying under high vacuum. The ^{1}H NMR spectrum was identical with that of the corresponding (1*S*,2*S*) compound (Found: C, 64.9; H, 10.4. Calc. for $C_{14}H_{26}O_4$: C, 65.1; H, 10.1%); $[\alpha]_D^{20}$ −24 (*c* 1.0, $CHCl_3$).

Preparation of 1-phenylbutane-1,4-diol 34

To a stirred solution of 1-phenylbut-3-en-1-ol (5.0 g, 0.0338 mol) in dry tetrahydrofuran (150 cm^3), at 0 °C under argon, was added borane–tetrahydrofuran (1.0 mol dm^{-3} solution in tetrahydrofuran; 50 cm^3). After 1 h the reaction mixture was warmed to room temperature and then refluxed overnight. The reaction mixture was quenched with hydrogen peroxide (4.0 cm^3, 37.2 mmol), and sodium hydroxide (2.0 mol dm^{-3} solution; 30 cm^3) over 0.5 h to give a clear solution. Evaporation of this followed by extraction of the residue with ethyl acetate (4 × 50 cm^3), drying ($MgSO_4$) of the extract and then re-evaporation gave a crude oil (7.80 g). Purification of this by silica gel chromatography (hexane–ethyl acetate, 8:2 as eluent) gave the title compound (4.75 g, 85%) as a colourless oil; ν_{max}(film)/cm^{-1} *inter alia* 3400 (OH, br); λ_{max}(EtOH)/nm 207 (ε/dm^3 mol^{-1} cm^{-1} 8922); δ_H($CDCl_3$, 300 MHz), 1.62–1.71 (2 H, m, $CH_2C\mathit{H}_2CH_2$), 1.81–1.88 (2 H, m, CH_2OH), 3.62–3.68 (2 H, m, CH_2CH), 4.68–4.72 (1 H, t, *J* 12.5, OCH*H*) and 7.33–7.34 (5 H, m, ArH); δ_C($CDCl_3$) 29.4 (*C*H_2*C*H_2OH), 36.2 [CH(OH)*C*H_2], 62.5 (*C*H_2OH), 74.1 (*C*HOH), 125.7 (4-ArC), 127.3 (3-, 5-ArC), 128.3 (2-, 6-ArC) and 144.6 (1-ArC); *m*/*z* (EI) *inter alia* 166 (M$^+$), 149 (M − OH$^+$) and 131 (M − $2H_2O^+$, base peak) [Found (NRMS): *m*/*z*, 166.1000. $C_{10}H_{14}O_2$ requires *m*/*z*, 166.0994].

Preparation of 4-oxo-4-phenylbutanal

After oxalyl chloride (2.20 cm^3, 25.3 mmol) and dimethyl sulfoxide (3.41 cm^3, 48.2 mol) had been added dropwise to dry dichloromethane (40 cm^3) in a three-neck round-bottom flask at −60 °C over 15 min, 1-phenylbutane-1,4-diol **34** (1.0 g, 6.0 mol) in dry dichloromethane (5.0 cm^3) was added to the mixture, using a cannula, over 10 min at −60 °C. After the mixture had been stirred for 15 min, triethylamine (20 cm^3) was added dropwise to it, the temperature being kept below −50 °C. After continued stirring for 20 min, the mixture was allowed to warm to room temperature when it was quenched with water. The aqueous layer was extracted with dichloromethane (2 × 50 cm^3) and the combined extracts were washed with brine (2 × 50 cm^3), dried and concentrated. The product obtained was diluted with dichloromethane (50 cm^3) and the solution washed with 1.0 mol dm^{-3} hydrochloric acid until no longer basic, washed with water (25 cm^3) and sat. brine (25 cm^3), and then dried and concentrated to give a crude oil (1.8 g). The product was distilled (Kugelrohr, 125 °C, 0.05 mmHg) to give the title compound (0.775 g, 80%) as a pale brown oil; ν_{max}/cm^{-1} *inter alia* 1690 (CO); λ_{max}(EtOH)/nm 259 (ε/dm^3 mol^{-1} cm^{-1} 5528) and 221 (13 618); δ_H($CDCl_3$; 300 MHz) 2.91–2.95 (2 H, t, *J* 12.6, CH_2COH), 3.30–3.34 (2 H, t, *J* 12.6, $COCH_2$), 7.44–7.60 (3 H, m, ArH), 7.96–7.99 (2 H, m, ArH) and 9.90 (1 H, s, COH); δ_C($CDCl_3$) 31.1 (*C*H_2CHO), 37.7 (PhCO*C*H_2), 128.1 (ArC), 128.4 (ArC), 133.4 (ArC), 136.5 (ArC), 197.9 (COH) and 200.6 (*C*COC); *m*/*z* (FAB) *inter alia* 163 (M + H$^+$) and 147 (M − O$^+$) [Found (HRMS): *m*/*z*, 163.0758. $C_{10}H_{11}O_2$ requires *m*/*z* 163.0759].

Preparation of 4,4-dimethoxy-1-phenylbutanone 35

Toluene-*p*-sulfonic acid monohydrate (0.02 g) was added to a stirred mixture of 4-oxo-4-phenylbutanal (0.20 g, 1.23 mmol) in methanol (10 cm^3) at room temperature. After the mixture had been refluxed overnight it was washed with saturated aqueous sodium hydrogen carbonate (2 × 30 cm^3) and dried ($MgSO_4$) to give the title compound as a pale brown oil (0.197 g, 87%); ν_{max}(neat)/cm^{-1} *inter alia* 1690 (CO); λ_{max}(EtOH)/nm 234 (ε/dm^3 mol^{-1} cm^{-1} 9920); δ_H($CDCl_3$; 300 MHz) 2.04–2.07 (2 H, m, CH_2CH), 3.05 (2 H, t, *J* 14.6, CH_2CO), 3.34 (6 H, s, 2 × OMe), 4.47 [1 H, t, *J* 11.0, C*H*$(OMe)_2$], 7.45–7.95 (3 H, m, ArH) and 7.98–7.99 (2 H, m, Ar*H*); *m*/*z* (FAB) *inter alia* 207 (M − H$^+$) and 177 (M − OCH_3^+, base peak) [Found (HRMS): *m*/*z*, 207.1021. $C_{12}H_{15}O_3$ requires *m*/*z* 207.1021].

Preparation of 3-[4,5-bis(1-methoxycyclopentyl)dioxan-2-yl)]-1-phenylpropan-1-one 30

A mixture of 4,4-dimethoxy-1-phenylpropan-1-one **35** (20 mg, 0.096 mmol) and the (1*R*,2*R*)-diol **37** (22 mg, 0.11 mmol) was heated on a Kugelrohr at 95 °C *in vacuo* (0.05 mmHg) for 4 h to give a crude syrup (0.045 g). Purification of this by silica gel chromatography (hexane–ethyl acetate, 4:6 as the eluent) gave the title compound **3** (26 mg, 68%) as a pale brown syrup; ν_{max}/cm^{-1} *inter alia* 1700 (CO); λ_{max}(EtOH)/nm 224

(ε/dm^3 mol^{-1} cm^{-1} 9928); δ_H($CDCl_3$, 300 MHz) 1.59–1.82 (16 H, m, cyclopentyl H), 2.02–2.13 (2 H, m, CH_2CH), 3.12 (2 H, t, J 7.6, $COCH_2$), 3.23 (6 H, s, 2 × OMe), 4.01 (1 H, d, J 4.1, CH), 4.23 (1 H, d, J 4.1, CH), 5.28 (1 H, t, J 9.4, CH_2CHO_2), 7.45–7.55 (3 H, m, ArH) and 7.95–7.98 (2 H, m, ArH); δ_C($CDCl_3$) 24.5, 24.8, 31.1, 32.0, 32.9 and 33.1 (cyclopentyl C's), 50.2 (2 × OMe), 79.7 (OCHC), 82.3 (MeOCCH), 87.6 (OCHC), 88.9 (MeOCCH), 102.5 ($OCHO_2$), 104.0 ($COCH_2$), 127.9 (4-ArC), 128.3 (3-, 5-ArC), 132.9 (2-, 6-ArC), 136.6 (1-ArC) and 199.3 (CO); m/z (FAB) *inter alia* 403 ($M + H^+$) and 325 ($M - C_6H_5^+$) [Found (HRMS): m/z 403.2483 $C_{24}H_{35}O_5$ requires m/z 403.2484]; $[\alpha]_D^{25}$ −29 (c 0.75, $CHCl_3$).

Reduction of the ketone 30 with borane

To a solution of the ketone **30** (16 mg, 0.04 mmol) in dry dichloromethane under argon at −45 °C, was added borane (1.0 mol dm^{-3} solution in tetrahydrofuran; 0.2 cm^3). The reaction mixture was stirred at −45 °C for 13 h and then quenched at −45 °C with saturated aqueous ammonium chloride (10 cm^3). The mixture was extracted with dichloromethane (3 × 25 cm^3) and the combined extracts were dried ($MgSO_4$) and evaporated to give the alcohols **31** and **32** (15 mg, 94%) as a colourless oil; ν_{max}/cm^{-1} *inter alia* 3400 br (OH); δ_H($CDCl_3$, 300 MHz) 1.38–1.77 (16 H, m, cyclopentyl H), 1.81–1.89 (4 H, m, 2 × CH_2), 3.23 (6 H, s, 2 × OMe), 4.01 (1 H, d, J 4.0, OCH), 4.23 (1 H, d, J 4.0, OCH), 5.19 (1 H, t, J 2.3, CH_2CH), 5.45 (1 H, s, OH) and 7.30–7.34 (5 H, m, ArH) (addition of D_2O caused the signal at δ to disappear); m/z (FAB) *inter alia* 403 ($M - H^+$), 99 ($M - C_6H_{11}O^+$, base peaks) [Found (HRMS): m/z, 403.2742. $C_{24}H_{35}O_5$ requires m/z, 403.2484].

Reduction of the ketone 30 with L-Selectride

To a solution of the ketone **30** (40 mg, 0.1 mmol, 1 mmol dm^{-3} in THF) in dry dichloromethane (10 cm^3) under argon at −45 °C, was added L-Selectride (1.0 mol dm^{-3} in tetrahydrofuran; 0.042 cm^3, 0.1 mmol) and stirred at −45 °C for 5 h. The reaction was quenched at −45 °C with saturated aqueous ammonium chloride (15 cm^3) and extracted with dichloromethane (2 × 30 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated to give the alcohols **31** and **32** (41 mg, 100%) which were identical in all respects with the sample prepared in the previous experiment.

Preparation of (4*S*,5*S*)-4,5-bis(1-methoxycyclopentyl)-2-phenyl-1,3,2-dioxaborolane 10

To a solution of phenylboronic acid (2 mg, 1.65 mmol) in chloroform (10 cm^3), was added (1*S*,2*S*)-1,2-bis(1-methoxycyclopentyl)ethane-1,2-diol[2] (380 mg, 1.49 mmol) followed by 1 mol dm^{-3} hydrochloric acid (10 cm^3) and was stirred at room temperature for 12 h. The organic layer was separated and washed with water (2 × 30 cm^3) and the aqueous layer was extracted with chloroform (2 × 50 cm^3); the combined organic layers and extracts were dried ($MgSO_4$) and evaporated to give a crude solid **10** (589 mg). Purification of this by silica gel chromatography (ethyl acetate–hexane, 3:7 as eluent) gave a white solid (509 mg, 90%); ν_{max}/cm^{-1} *inter alia* 2970 (CH); λ_{max}(EtOH)/nm 270 (ε/dm^3 mol^{-1} cm^{-1} 576) and 254 (7338); δ_H($CDCl_3$, 300 MHz) 1.59–1.82 (16 H, m, cyclopentyl H's), 3.26 (6 H, s, 2 × OMe), 4.52 (2 H, s, CH), 7.36–7.48 (3 H, m, ArH) and 7.81–7.84 (2 H, m, ArH); δ_C($CDCl_3$) 14.2, 24.6, 25.0, 31.0 and 31.7 (cyclopentyl H's), 50.6 (OCH_3), 81.4 (CB), 88.0 (MeOC), 128.2 (4-ArC), 130.0 (3-, 5-ArC), 135.1 (2-, 6-ArC); m/z (FAB) *inter alia* 99 ($M - C_6H_{11}O^+$, base peak) (Found: C, 69.7; H, 8.7; B, 3.0. $C_{20}H_{29}BO_4$ requires C, 69.8; H, 8.40; B, 3.14%); $[\alpha]_D^{25}$ +28 (c 0.25, $CHCl_3$).

Crystal data for compound 10. $C_{20}H_{29}BO_4$, M = 344.26, orthorhombic, space group $P2_12_12_1$, a = 13.950(3), b = 21.563(5), c = 6.552(1) Å, $\alpha = \beta = \gamma$ = 90.0, U = 1970.87 Å^3, Z = 4, D_c = 1.16 g cm^{-3}, F(000) = 744. A colourless crystal of size 0.16 × 0.35 × 0.40 nm, μ(Mo-Kα) = 0.45 cm^{-1} was used in the data collection. Temperature of data collection: room temperature (25 °C). Final shift/esd < 0.05. Final max./min. residual electron density 0.69 and 0.85 e Å^3.

Data collection. Data were collected on a Phillips PW 1100 diffractometer in the range θ-range 3–20°, with a scan width of 0.80°, using the technique described previously.[30] Equivalent reflections were merged to give 592 data with $I/\sigma(I) > 3.0$. Absorption corrections were applied to the data after initial refinement with isotropic thermal parameters for all atoms.[31]

Structure solution and refinement.[32] The structure was solved by direct methods. The hydrogen atoms attached to C(1) and C(2) were located in a difference Fourier synthesis calculation using data with sin θ < 0.35. These were included in the structure factor calculations with thermal factors of 0.08 Å^2 but their parameters were not refined. The remaining hydrogen atoms were included in geometrically idealised positions and were constrained to 'ride' on the relevant carbon atoms with common group isotropic thermal parameters of 0.08 Å^2. The four oxygen atoms and the boron atom were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which converged at R 0.0746 and R_w 0.0772 with weights of $w = 1/\sigma^2F_o$ assigned to the individual reflections.

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