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CHIROPTICAL PROPERTIES OF TETRAHYDROPYRAN-3,4-DIOLS AND 2-HYDROXYMETHYLTETRAHYDROPYRAN-3-OLS DERIVED FROM L-ARABINOSE, D-GALACTOSE, D-GLUCOSE, AND D-XYLOSE, AND ENANTIOSELECTIVITY IN REDUCTION WITH THEIR COMPLEXES*

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ABSTRACT

(3*R*,4*R*)- (**1a**) and (3*S*,4*R*)-tetrahydropyran-3,4-diol (**2a**), and (2*R*,3*S*)- (**3a**) and (2*R*,3*R*)-2-hydroxymethyltetrahydropyran-3-ol (**4a**), derived from D-xylose, L-arabinose, D-glucose, and D-galactose, respectively, are structurally the simplest chiral carbohydrate-type precursors for bidentate ligands. The c.d. spectra of bidentate complexes between these diols and $[Mo_2(OAc)_4]$, as well as of the benzoates (**1b–4b**) and tosylates (**1c–4c**), and the copper(I) complexes (**1d–4d**) of the diphenylphosphinites (**1e–4e**) are discussed. The enantioselective reduction of acetophenone to *S*(*R*)-1-phenylethanol with the complexes (**10** and **11**, respectively) of the *trans* compounds **1a** and **3a** with lithium aluminium hydride has been studied. Low enantiomeric excess (≤15%) was obtained, which was enhanced when an achiral modifier (ethanol, 2-propanol) was added to the complexes **10** and **11** prepared *in situ*. Enantioselective catalytic hydrogenation of *Z*-α-acetamidocinnamic acid was performed with the Rh(I)-norbornadiene complexes **2f** and **4f**, derived from the *cis* compounds **2a** and **4a**; substantially lower enantiomeric excess (<30%) of *S*(*R*)-*N*-acetylphenylalanine was achieved than with the analogous complexes **1f** and **3f** (~90%). The results of the enantioselective reductions are discussed in the light of the conformational properties of **1a–4a** and their congeners deduced from the c.d. spectra.

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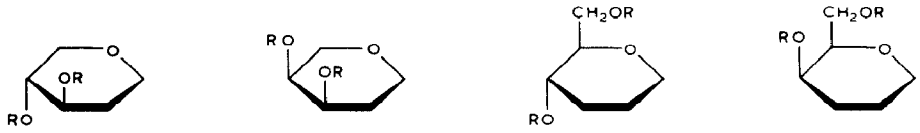
INTRODUCTION

The chiral diols, (2*R*,3*S*)-2-hydroxymethyltetrahydropyran-3-ol (**3a**) and (3*R*,4*R*)-tetrahydropyran-3,4-diol (**1a**), available in a few steps from D-glucose[2,3] and D-xylose[4,5], respectively, are of particular interest in the study of their chiroptical and conformational properties, and as chiral auxiliaries in enantioselective catalytic and non-catalytic transformations. We have used **1a** and **3a** as the immediate precursors of the chiral diphenylphosphinites **1e** and **3e**, the Rh(I) complexes of which (**1f** and **3f**, respectively) effected medium to high (~90%) enantioselectivity in hydrogenation of the prochiral model compound, *Z*-α-acetamidocinnamic acid[5]. We now describe the chiroptical properties of the diols **1a–4a** and of their congeners **1b–f**–**4b–f**, the enantioselective reduction of acetophenone with the complexes of **1a** and **3a** with lithium aluminium hydride (LAH), and the enantioselective catalytic hydrogenation of *Z*-α-acetamidocinnamic acid with the Rh(I) complexes **2f** and **4f**.



1 a – f 2 a – f 3 a – f 4 a – g

a R = H
b R = Bz
c R = Ts
d R = [(PPh2)CuCl], dimer
e R = PPh2
f R = [(PPh2)Rh(I)NBD] ClO4, dimer
g R = Ac

RESULTS AND DISCUSSION

Chiroptical and conformational properties. — (*a*) *Diols.* Since alcohols do not absorb at accessible wavelengths, their "cottonogenic derivatives" have been investigated, *e.g.*, nitrites, nitrates, xanthates, benzoates, *etc.*[6,7]. In the case of the 1,2- and 1,3-diols, their dibenzoates and transition metal complexes, which can accept diols as bidentate ligands, have found general application.

(*b*) *Dibenzoates.* In the *trans*-vicinal diol **1a**, the substituents are equatorial and there is a negative torsional angle BzO–C–C–OBz in **1b**. Therefore, the resulting exciton couplet[8] should be negative, and the strong negative Cotton effect at 238 nm is the first branch of this c.d. couplet (Fig. 1). The second, positive branch is much less pronounced, a situation mostly found for such dibenzoates[7–10].

In the vicinal *cis*-dibenzoate **2b**, the substituents are equatorial and axial. If only steric interactions are considered, then the two chair conformations should have similar energies and the two c.d. couplets expected should nearly compensate. However, the anomeric effect favours the 3*a*,4*e* conformer, which has a positive torsional angle around the C-3–C-4 bond, and therefore a positive c.d. is expected and found.

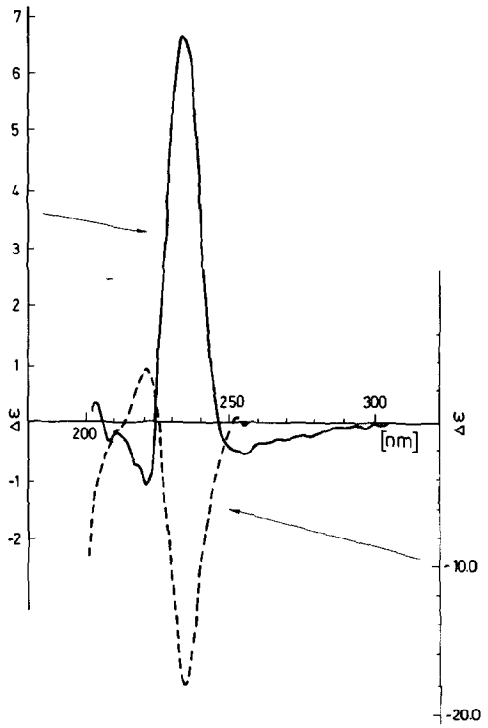
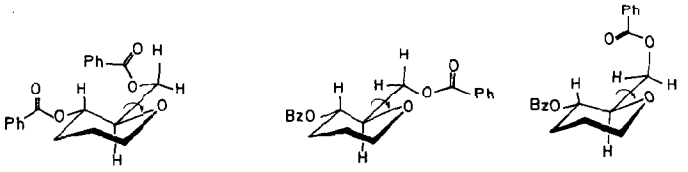


Fig. 1. C.d. spectra of **1b** (-----) and **2b**(——).

2b (3a,4e) 2b (3e,4a)



3b - A 3b - B 3b - C

Since the exciton interaction is observable over relatively large distances between the two chromophores, it is not surprising that the dibenzoates **3b** and **4b** show c.d. couplets (positive for **3b**, negative for **4b**) (Fig. 2). The magnitudes of these couplets are ~33% of that of the dibenzoate **1b**. These signs and ratios of magnitudes accord with those found for analogous sugar 4,6-dibenzoates[11,12] and they can be rationalised easily by conformational analysis. The three most preferred rotamers around the C-5–C-6 bonds (*A*–*C*, as exemplified for **3b**) will have the *pro-R* H-6, *pro-S* H-6, or 6-*O*-benzoyl bond, respectively, approximately antiperiplanar to H-5. For steric reasons, *B* is impossible for **3b** as is rotamer *C* for **4b**. For a 2,3,4,6-tetra-*O*-benzoyl-D-*manno* derivative, rotamer *C* is preferred in the crystal, and this arrangement leads to a positive couplet regardless of whether the C=O bond of BzO-6 is synperiplanar to the *pro-R* H-6 or *pro-S* H-6. Benzoyloxy groups attached to the tetrahydropyran ring assume the conformation with the O=C bond synperiplanar to the hydrogen geminal to the OBz for both equatorial and axial groups[12–13]. For the rotamer *A*, which is also stabilised by the general anomeric effect, a positive couplet is predicted also if the conformation of BzO-6 is analogous to that found for AcO-6 in a 1,3,4,6-tetra-*O*-acetyl-D-galactopyranose derivative[12].

Assuming a similar conformation for rotamer *A* of **4b** leads to an arrangement where the two transition moments are almost coplanar and the resulting couplet must be small. For rotamer *B*, a negative couplet is predicted (and found) if the conformation discussed for **3b** is used[14].

Each of the dibenzoates **1b**–**4b** had pronounced fine structure within the α-

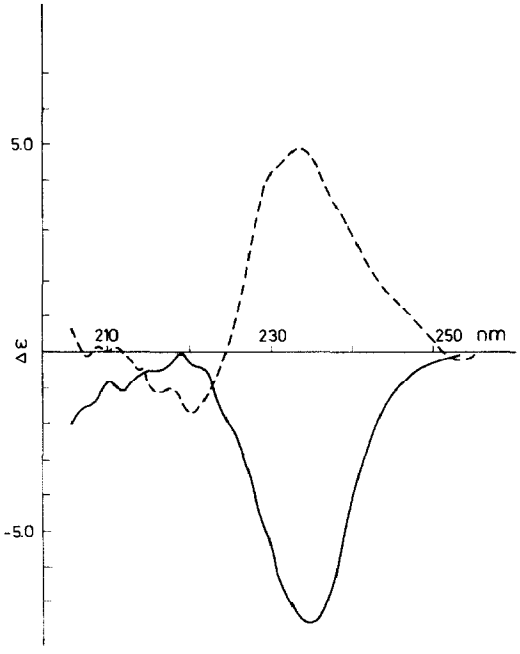


Fig. 2. C.d. spectra of **3b** (-----) and **4b** (——).

band of the benzoate chromophore (Figs. 1 and 2). The sign of these fine-structure bands is always opposite to that of the c.d. band at 235 nm (first wing of the c.d. couplet).

(*c*) *Complexes of* **1a–4a** *with* $Mo_2(OAc)_4$ (in situ). The sign of the Cotton effect at 300–310 nm of such complexes with diols which can be formed with a torsional angle HO–C–C–OH of ~60° is equal to the sign of that angle[10]. In accord with this rule, the complex of **1a** shows a negative c.d. at this wavelength (Fig. 3). The Cotton effect at 380 nm also has a negative sign, as is usually found[10].

In addition to two analogous negative Cotton effects, **2a** gives an intermediate stronger positive Cotton effect, a situation encountered only for such vicinal diols in the tetrahydropyranoside series where no axial substituent is present next to the diol unit[1]. The negative c.d. at ~300 nm shows that, for **2a**, the torsion angle in the complex is negative, *i.e.*, HO-3 is equatorial and HO-4 is axial. Both diols **3a** and **4a** complex with $[Mo_2(OAc)_4]$, and that with HO-3 equatorial shows a weak negative c.d. at 550 nm, a stronger negative c.d. at 415 nm, and a weak positive c.d. at 340 nm. In contrast, the complex of **4a** has a weak positive Cotton effect at ~485 nm, a negative one at 418, and the biggest effect at ~330 nm. These effects may be compared with those of D-glucose (for **3a**) or D-galactose (for **4a**)

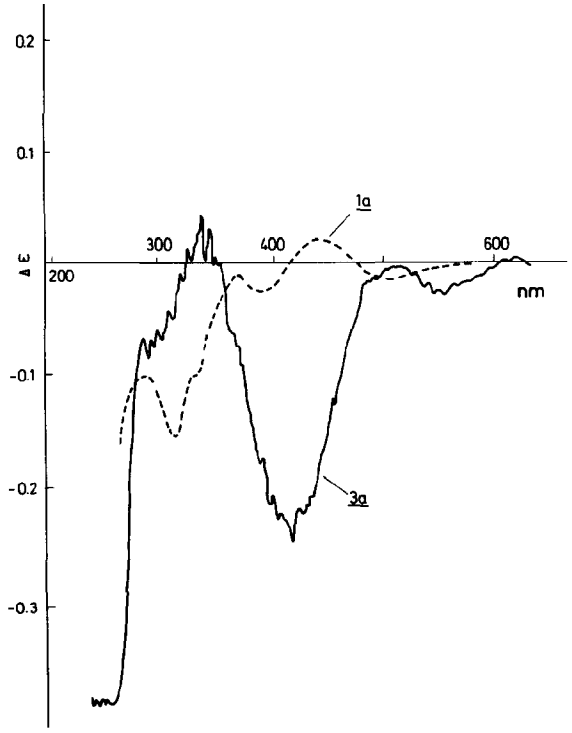


Fig. 3. C.d. spectra of *in situ* $[Mo_2(OAc)_4]$ complexes of **1a** (-----) and **3a** (——).

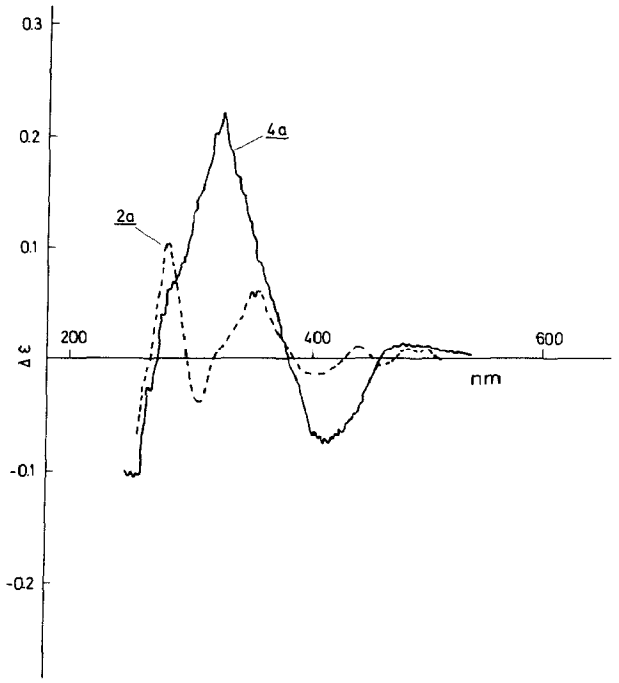


Fig. 4. C.d. spectra of *in situ* $[Mo_2(OAc)_4]$ complexes of **2a** (-----) and **4a** (——).

derivatives with HO-4,6 unsubstituted. For the former, the c.d. is indeed similar with the strongest negative Cotton effect at ~420 nm and the smaller negative one at ~520 nm. A third positive Cotton effect appears at still shorter wavelength, which is much better developed for **3a**[1]. The c.d. of the complex of an analogous D-galactose derivative corresponding to **4a** was only weak and positive at ~400 nm. The reason for the smaller c.d. may be the presence of 1,2,3-substituents in this model compound, which come closer to the metal cluster because of the axial OH. This feature may inhibit complex formation, or these substituents may contribute more to the c.d. but in a compensating mode.

(*d*) *Tosylates.* Tosylates of primary and secondary aliphatic alcohols show[15] u.v. absorption at 255–275 nm, wherein four distinct maxima at 271–272, 265–267, 260–261, and 255–257 nm can be distinguished, together with a fifth one at ~225 nm. These maxima appear in the u.v. spectra of the ditosylates **2c** and **4c** in the range 255–275 nm and the band at ~230 nm is much stronger. The tosyl group is not used usually in cottonogenic derivatives. In contrast to the dibenzoates, c.d. couplets were not seen (or expected) for the tosylates **1c**–**4c**, but a Cotton effect of medium magnitude at ~230 nm and a weak α-band Cotton effect with the usual fine structure was observed (except for **2c**) (Table I). The O–O-line c.d. is found at 272–273 nm, *i.e.*, at the same wavelength where the first distinct u.v. maximum

TABLE I

C.D. DATA FOR **1a–4a** (IN THE PRESENCE OF $[Mo_2(OAc)_4]$) AND **1b–d** TO **1d–4d**

Compound	λ *[nm]* $(\Delta\varepsilon)^a$
1a	284.0(+0.01), 302.0(−0.03), 313.0(−0.03), 375.0(−0.01), 407.0(−0.01)
2a	277.0(+0.10), 312.0(−0.04), 352.0(+0.06), 405.0(−0.01), 431.0(+0.01)
3a	258.0(−0.40), 298.0(−0.07), 330.0(+0.04), 413.0(−0.25), 555.0(−0.03)
4a	329.0(+0.21), 350.0(+0.12), 415.0(−0.08), 485(+0.03)
1b	220.8(+3.42), 235.5(−18.09), 257.3(+0.149), 263.9(+0.07), 266.0(+0.06), 274.0(+0.06), 282.3(+0.08)
2b	220.4(−1.68), 233.6(+5.26), 235.8(+5.64), 272.9(−0.03), 280.0(−0.04)
3b	208.4(−0.33), 221.5(−1.11), 234.8(+6.60), 254.3(−0.39), 270.6(0.15), 280.1(−0.10)
4b	234.7(−7.60), 265.4(+0.07), 274.4(+0.17), 280.4(+0.17)
1c	229.3(+6.21), 247.9(+0.14), 256.2(+0.21), 265.7(0.28), 273.2(+0.24)
2c	225.0(+2.56), 228.7(+2.96), 233.0(+2.12), 247.5(+0.31), 256.5(−0.09)
3c	214.7(−1.53), 219.5(−1.74), 222.9(−2.04), 265.2(−0.14), 272.2(−0.13)
4c	206.7(+0.58), 217.3(+0.80), 226.0(+1.78), 230.0(+1.91), 249.1(+0.09), 265.8(+0.11), 273.6(+0.12)
1d	249.4(7.40), 253.0(+7.29), 281.6(−14.62), 312.0(+11.95)
2d	250.0(−1.64), 255.8(−1.78), 299.0(+0.75), 305.0(+0.73), 344.0(+0.20)
3d	232.4(+12.81), 248.5(−3.10), 268.2(+5.49), 271.8(+5.40), 282.9(+4.25), 325.0(0.37)
4d	245.4(+1.19), 266.2(−5.08), 273.2(−4.74), 315.2(+0.30), 328.2(+0.09)

[a]Solvent: CH_3CN.

appears. The sign of both Cotton effects is the same and the ratio of $\Delta\varepsilon$ values within the α- and 230-bands is <1:10. The c.d. curve of **2c** showed a poor signal-to-noise ratio due to the presence of a mixture of 3*a*,4*e* and 3*e*,4*a* conformations.

(*e*) *Cu(I) Complexes of diphenylphosphinites.* In order to obtain crystalline and stable derivatives of diphenylphosphinites, their Cu(I) complexes were prepared. Their structure is not known and all attempts to obtain good crystals for X-ray studies have failed[5]. However, it is reasonable to assume that the structure is similar to that of the analogous bisdiphosphine complexes[16], *i.e.*, they are dimeric with a square-planar $(CuCl)_2$ centre. The two Cu–P bonds are in the plane perpendicular to this unit, and 7-membered rings are formed with **1d** and **2d**, and 8-membered rings with **3d** and **4d** as bidentate ligands. Since 7-membered rings formed by **1d** can only exist as 3,4-diequatorial conformers, this bidentate ligand must be present in the δ-conformation[17,18] with nearly C_2-symmetry. The c.d. of this complex shows, in addition to some minor features, three Cotton effects of approximately equal magnitude, at 312 (positive), 282 (negative), and 251 nm (positive) (Fig. 5).

The c.d. of the complex obtained from **2d** is much smaller and has its main Cotton effects at ~294 (positive) and 260 nm (negative). The smaller magnitude can be understood because **2d** can complex in two different conformations (δ for the 3*e*,4*a* and λ for the 3*a*,4*e* conformer) which will lead to partial compensation of the Cotton effects. The preponderant conformer cannot be determined from the c.d. spectrum, since there are only two bands between 240 and 330 nm. The 8-

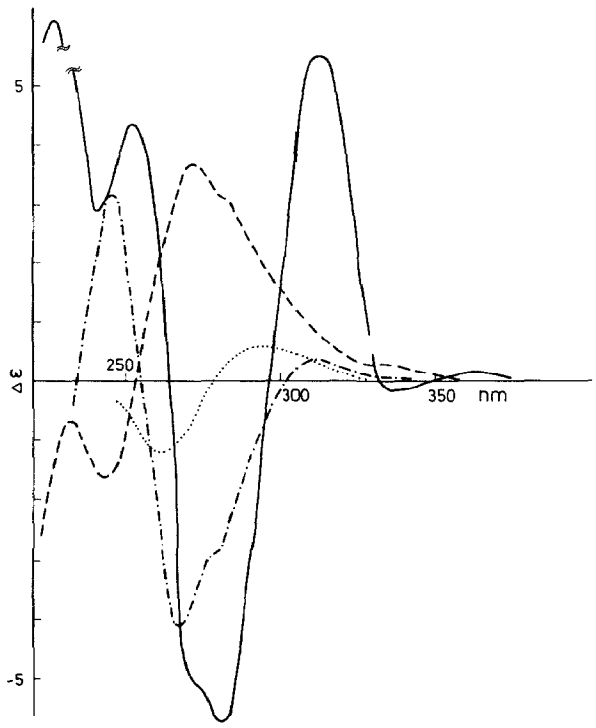


Fig. 5. C.d. spectra of Cu(I) complexes **1d** (——), **2d** (·····), **3d** (----), and **4d** (····).

membered rings of the complexes formed with **3d** and **4d** are much more flexible, and several possible geometries can be deduced with the help of molecular models. The second and third of the above-mentioned Cotton effects are somewhat smaller than those of the complex **1d**, the first one (positive) is small for **4d**, and is observable only as a shoulder (of the same sign as the second Cotton effect) for **3d**. The sign pattern of **3d** is thus +, +, −, and +, −, + for **4d**, and, therefore, within the larger two c.d. bands, they are enantiomorphous. This finding is expected since the 8-membered rings in the complex should be of enantiomeric shape for **3d** and **4d**.

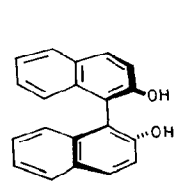
The c.d. data of the Cu(I) complexes cannot be compared directly with the enantioselectivity of the catalytically active Rh(I) complexes (see below), since the structure of the latter is unknown. Furthermore, for flexible bidentate ligands, the geometry of the transition state in which one more substrate molecule is bound may be different from that of the ligands in the Cu(I) complexes. A higher enantioselectivity is expected for the less-flexible Rh(I) complex analogues of **1d**, and, indeed, this amounts to 90%, as compared to 12% obtained the Rh(I) complex analogues of **2d**. As already noted[5], the opposite enantioselectivity obtained with Rh(I) complexes of **1d** and **3d** is reflected in the enantiomorphous behaviour of the respective c.d. curves of **1d** and **3d**. Such a correlation between c.d. and the sense

of the enantioselectivity can be expected only when the enantiomeric excess is high, and it fails for the Rh(I) complexes analogous to **2d** and **4d**.

Enantioselective reduction with complexes of **1a** *and* **3a** *with LAH.* — Acetophenone was reduced with LAH chirally modified with **3a** or **1a**. No comparative study of the enantioselectivity with simple, structurally related chiral 1,2- and 1,3-diols has been reported, although alcohols and diols[19–23], amines and diamines[20,24,25], and aminoalcohols[26,27] have been explored as chiral modifiers of LAH.

The enantioselectivity was fair to low. The highest enantiomeric excess has been cited[28,29] hitherto for the binaphthols (**5**). The outstandingly high enantiomeric excess (90%) was ascribed to a relatively rigid, 6-membered, cyclic transition state and to the homotopic nature of the hydrides within a modifying ligand that possesses a C_2 axis of symmetry[27].

However, low enantioselectivity was observed without the addition of the second modifier, usually a lower alcohol. The low enantioselectivity (<15%) achieved by Baggett and Stribblehill[30] with another pair of C_2-symmetric diols (**6** and **7**) derived from mannitol ultimately questions the C_2-symmetry of chiral diols as the decisive property required for reaching a high enantiomeric excess. Recent results indicate that, although two hydrogens in the species **8** are homotopic, high enantioselectivity is assured only in the complex **9**, where additional chelating possibility exists[27], *i.e.*, where an achiral modifier is added.



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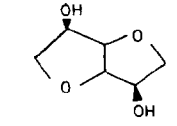

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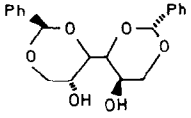

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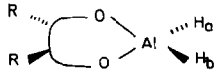

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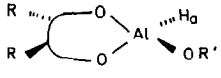

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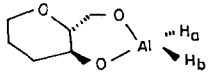

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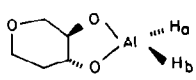

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In view of these results, the enantioselectivity of reduction with LAH complexes of **1a** and **2a** has been studied in the absence and presence of a second achiral modifier. The complexes **10** and **11** were prepared *in situ* following the method of Noyori *et al.*[27,28]. The second modifier (third alkoxy subunit in the LAH complexes **10** and **11**) was either ethanol or 2-propanol. The formation of the complexes **10** and **11**, as well as their interaction with achiral alcohols, was monitored on the basis of the volume of hydrogen evolved (see Experimental). The results are summarised in Tables II and III.

Using diol **1a** as a LAH modifier in the absence of achiral alcohol, a low enantiomeric excess (5–7%) of (*S*)-1-phenylethanol was obtained regardless of the reaction temperature. Introduction of ethanol as the second modifier did not improve the optical yields considerably (3.5–11%). A reversal of the sense of the asymmetric induction also occurred. The optical yield appeared to increase on lowering the reaction temperature to −35°. At −65°, reversal of the stereoselectivity was observed again (Table I). Reversal of sign associated with removal of one of the hydride atoms has been reported severally[21,22,31], whereas the reversal due to temperature change was observed only by Lund and Shaw[22].

Johnson and Klein[32] reported 2-propanol to be generally the most efficient second modifier in LAH reductions. Reduction of acetophenone using this alcohol as a second modifier proceeded with low optical yield (1.5–13.7%), without reversal of the sense of enantioselectivity. The optimal optical yield was obtained at −5° and decreased at lower temperatures (Table II).

Enantioselectivity in the reduction of acetophenone with diol **3a** as the chiral LAH modifier was also low, but more consistent results were obtained. The enantiomeric excess increased on lowering the reaction temperature (Table III).

Thus, it is assumed that, because of the *trans*-diequatorial orientation of the

TABLE II

ENANTIOSELECTIVE REDUCTION OF ACETOPHENONE BY CHIRALLY MODIFIED LAH WITH (3*R*,4*R*)-TETRAHYDROPYRAN-3,4-DIOL (**9**)

Entry	*Achiral modifier*	*Temperature (degrees)*	*Yield (%)*	*1-Phenylethanol*		*Configuration*
				$[\alpha]_D$ *(degrees)*	*E.e. (%)*[a]	
1	None	−5	59.2	−1.51	2.9	*S*
2	Ethanol	−5	70.3	−2.27	4.3	*S*
3	Ethanol	−30–−35	71.3	−6.30	12.0	*S*
4	Ethanol	−60–−65	64.3	−8.25	15.7	*S*
5	2-Propanol	−5	62.2	−1.66	3.2	*S*
6	2-Propanol	−25–−30	61.2	−1.87	3.6	*S*
7	2-Propanol	−35–−40	64.3	−4.70	8.9	*S*

[a]Enantiomeric excess.

TABLE III

ENANTIOSELECTIVE REDUCTION OF ACETOPHENONE BY CHIRALLY MODIFIED LAH WITH 2*R*,3*S*-2-HYDROXYMETHYLTETRAHYDROPYRAN-3-OL (**8**)

Entry	*Achiral modifier*	*Temperature (degrees)*	*Yield (%)*	*1-Phenylethanol*		*Configuration*
				$[\alpha]_D$ *(degrees)*	*E.e. (%)*[a]	
1	None	−5	80.7	−2.75	5.2	*S*
2		−65–−70	67.8	−3.90	7.4	*S*
3		−75–−80	72.3	−2.55	4.8	*S*
4	Ethanol	−5	60.2	+1.73	3.5	*R*
		−5	63.2	+2.35	4.8	*R*
5		−30–−35	40.2	+5.80	11.0	*R*
6		−65		−1.88	3.6	*S*
		−65	68.3	−0.56	1.1	*S*
7	2-Propanol	r.t.	19.1	−1.74	3.3	*S*
8		−5	59.2	−7.19	13.7	*S*
9		−25–−30	33.1	−4.64	8.8	*S*
		−25–−30	15.1	−4.13	7.9	*S*
10		−35–−40	56.2	−0.79	1.5	*S*

[a]Calculated on the basis of the reported[21] value for the optically pure compound *S*-1-phenylethanol, $[\alpha]_D$ −52.5° (*c* 2.27, dichloromethane).

TABLE IV

ENANTIOSELECTIVE HYDROGENATION[a] OF *Z*-α-ACETAMIDOCINNAMIC ACID WITH Rh(I) COMPLEXES **2f** AND **4f**

Run	*Complex*	*Substrate/Rh ratio*	*Time (h)*	*Temperature (degrees)*	*Chemical yield (%)*[b]	*E.e. (%)*	*Configuration*
1	**2f**	100:1	24	25	100	4.8	*R*
2		50:1		25	100	6.9	*R*
3		20:1		25	97	2.5	*R*
4		100:1		40 ±1	100	3.1	*R*
5				60 ±1	100	1.5	*R*
6				80 ±1	100	2.1	*R*
7			7	−15–−20	92	12.1	*R*
8		20:1		−15–−20	93	9.5	*R*
9	**4f**	100:1	24	25	63	13.8	*R*
10		50:1		25	100	11.6	*R*
11		20:1		25	100	14.9	*R*
12		100:1		40 ±1	100	8.2	*R*
13				60 ±1	100	1.6	*S*
14				80 ±1	100	2.9	*S*
15			7	−15–−20	93	26.3	*R*
16		20:1		−15–−20	100	29.3	*R*

[a]At 1.48 atm. of H_2. [b]Based on ^{1}H-n.m.r. spectra.

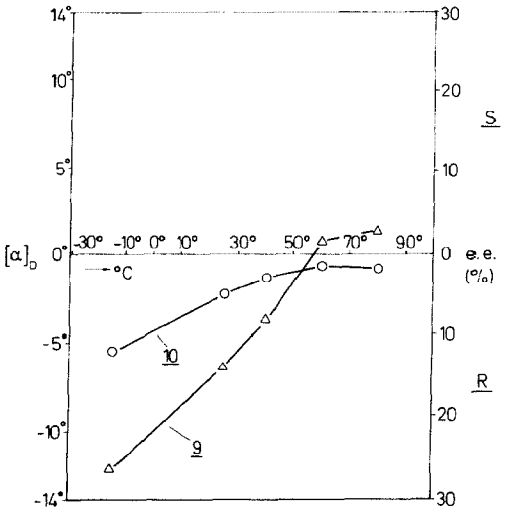

Fig. 6. Temperature dependence of % enantiomeric excess of *R*(*S*)-*N*-acetylphenylalanine in the hydrogenation of *Z*-α-acetamidocinnamic acid with the Rh(I) complex of **2f** (○—○—○) and **4f** (△—△—△). Substrate/Rh(I) ratio 100:1, 1.48 atm. of H_2.

substituents in **1a** and **3a**, both hydride complexes (**10** and **11**) of these glycols are cyclic. Two available hydrogens (H_a and H_b) in the 1:1 LAH–diol complex are diastereotopic and might show opposite enantioselectivities. However, relatively little perturbation by the tetrahydropyran rings seems to occur, and, because of the absence of shielding effect[33], these hydrogens have similar reactivities.

Enantioselective hydrogenation with Rh(I) complexes of diphenylphosphinites (**2f** *and* **4f**). — In continuing our work on the chiral bidentate diphenylphosphinite derivatives of monosaccharides[5], the Rh(I) complexes **2f** and **4f** were prepared and examined in the hydrogenation of *Z*-α-acetamidocinnamic acid. The results are presented in Table IV and Fig. 6.

The results revealed that both complexes are less enantioselective than the diphenylphosphinites **1e** and **3e**, which exhibited maximal enantioselectivities of 90.4 and 62.7%, respectively, though at low temperatures (−15°)[5]. The enantioselectivity with **2e** and **4e** was enhanced at lower temperatures, contrary to the general mechanistic scheme of Landis and Halpern[34], but similar to the recent results obtained by Salke and Pracejus[35]. Interestingly, the Rh(I) complex **4e** exhibited a small reversal of enantioselectivity at higher temperatures, although hydrogenation with both complexes preferentially afforded the *R* enantiomer of *N*-acetylphenylalanine. As already indicated above, these results could be explained by the flexibility and less well-defined chiroptical properties of the 7- and 8-membered chelate rings in the complexes **2e** and **4e** as compared with **1e** and **3e**.

EXPERIMENTAL

^{1}H-N.m.r. and ^{13}C-n.m.r. spectra were recorded with a Jeol FX 90Q F.t. spectrometer. T.l.c. was performed on Silica Gel 60 F (Merck) and column chromatography with granular silica gel (0.05–0.2 mm, Merck). Optical rotations were determined on a Perkin–Elmer 141 polarimeter in 1-dm cells. C.d. spectra were measured at room temperature with a Jobin–Yvon–ISA dichrograph Mark III, using 1–2mM solutions in acetonitrile. Data were collected on-line with a PDP/8-e (5 or 10 data points per nm), and curve smoothing made use of the Golay–Savitzky algorithm.

Preparation of the compounds **1a,d,e,f** and **3a,d,e,f** was described in ref. 5, while compound **2a** was described in ref. 36.

(2R,3R)-3-Acetoxy-2-acetoxymethyltetrahydropyran (**4g**). — To a solution of freshly distilled 3,4,6-tri-*O*-acetyl-D-galactal (2.32 g, 8.5 mmol) in dichloromethane (50 mL) were added triethylsilane (1.20 g, 10.2 mmol) and freshly distilled boron trifluoride etherate (1.45 g, 10.2 mmol) with stirring at ambient temperature[37]. After 15 min, the reaction was complete [t.l.c., ether–light petroleum (1:1.5)]. The mixture was poured into saturated aqueous sodium hydrogencarbonate (100 mL) and crushed ice, and extracted with chloroform (3 × 100 mL), and the combined extracts were washed with water to neutral pH, dried, and concentrated. Column chromatography [ether–light petroleum (1:1)] of the crude product (1.39 g) on silica gel (160 g) gave, in fractions 69–101 (5-mL fractions), **4g** (1.39 g, 76%), b.p. 90–100°/0.8 Torr, $[\alpha]_D^{25}$ −22.4° (*c* 2.64, chloroform); ν_{max} 3050, 2950, 2330, 1740, 1450, 1380, 1240, 1190, 1095, 1050, 1030, 955, 910, 860, 840, 820, 790, 735, 685, 650, 630, 610, and 600 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 2.09 (s, 6 H, 2 Ac), 3.79–3.96 (m, 1 H), 4.14–4.31 (m, 4 H), 5.09–5.16 (m, 1 H), 5.99–6.09 (m, 2 H).

Anal. Calc. for $C_{10}H_{14}O_5$ (214.22): C, 56.07; H, 6.59. Found: C, 55.94; H, 6.56.

(2R,3R)-2-Hydroxymethyltetrahydropyran-3-ol (**4a**). — Zemplén deacetylation of **4g** (23.13 g, 0.11 mol) and column chromatography (chloroform) of the crude product (17.1 g) on silica gel (400 g) gave, in fractions 129–280 (10-mL fractions), **4a** (9.98 g), b.p. 90–100°/1.2 Torr, $[\alpha]_D^{25}$ +7.2° (*c* 2.8, chloroform); ν_{max}^{KBr} 3400 (broad), 2950, 2860, 1650, 1465, 1445, 1370, 1345, 1220, 1190, 1095, 1060, 1035, 1020, 970, 940, 900, 880, 850, 810, 740, and 610 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.3–3.1 (m, 4 H), 3.35–4.15 (m, 6 H + 2 OH).

Anal. Calc. for $C_6H_{12}O_3$ (132.16): C, 54.53; H, 9.15. Found: C, 54.35; H, 9.12.

Dibenzoates **1b–4b**. — Diols **1a–4a** (2.80 mmol) were each stirred with freshly distilled benzoyl chloride (1.20 g, 8.6 mmol) in dry pyridine (5.0 mL) for 2 h at ~ −5° and then for 48 h at ~0°. Each mixture was poured into ice–water and extracted with dichloromethane (3 × 50 mL), and the combined extracts were washed (hydrochloric acid, 1:1; saturated aq. sodium carbonate; water), dried (Na_2SO_4), and concentrated. The crude products **1b–4b** were purified first by column chromatography (80 g of silica gel, dichloromethane) and then by distillation.

(3*R*,4*R*)-3,4-Dibenzoyloxytetrahydropyran (**1b**; 830 mg, 76.8%) had b.p. 205–212°/0.06 Torr, $[\alpha]_D^{25}$ −131.4° (*c* 2.55, chloroform); ν_{max}^{KBr} 2980, 2930, 2860, 1725, 1605, 1588, 1455, 1320, 1265, 1115, 1070, 1030, and 710 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 0.83–2.12 (m, 1 H), 2.20–2.44 (m, 1 H), 3.48–4.30 (m, 4 H), 5.14–5.52 (m, 2 H), 7.23–8.07 (m, 10 H); ^{13}C, δ 30.03 (C-5), 65.06 (C-6), 67.38 (C-3), 69.92 (C-4), 70.82 (C-2), 128.34, 129.63, 144.19, 165.58 (2 CO).

Anal. Calc. for $C_{19}H_{18}O_5$ (326.36): C, 69.91; H, 5.54. Found: C, 69.89; H, 5.63.

(3*S*,4*R*)-3,4-Dibenzoyloxytetrahydropyran (**2b**) had b.p. 230–235°/0.2–0.25 Torr, $[\alpha]_D^{25}$ +63.8° (*c* 2, chloroform); ν_{max}^{KBr} 1920–3000 (br), 1880, 1735, 1725, 1608, 1468, 1325, 1310, 1260–1290 (br), 1220, 1185, 1075, 1045, 980, 875, and 715 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 2.09–2.25 (m, 2 H), 3.6–4.1 (m, 4 H), 5.42–5.50 (m, 2 H), 7.22–7.56 (m, 6 H), 7.92–8.10 (m, 4 H); ^{13}C, δ 28.61 (C-5), 64.95 (C-6), 67.38 (C-3), 68.79 (C-4), 69.35 (C-2), 128.38, 129.69, 129.80, 130.03, 130.19, 133.12, 165.63 (C=O), 165.74 (C=O).

Anal. Calc. for $C_{19}H_{18}O_3$ (326.36): C, 69.63; H, 5.56. Found: C, 70.18; H, 5.76.

(2*R*,3*S*)-3-Benzoyloxy-2-benzoyloxymethyltetrahydropyran (**3b**; 763 mg, 80.1%) had b.p. 210–220°/0.006 Torr, $[\alpha]_D^{25}$ +75.8° (*c* 2.75, chloroform); ν_{max}^{KBr} 2960, 2860, 1725, 1605, 1455, 1308, 1275, 1100, 1070, 1028, and 710 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 1.5–1.7 (m, 3 H), 2.2–2.4 (m, 1 H), 3.4–5.2 (m, 6 H), 7.1–8.1 (m, 10 H); ^{13}C, δ 25.0 (C-5), 29.40 (C-4), 64.39 (C-6), 67.89 (C-2′), 69.29 (C-2), 77.70 (C-3), 128.27, 128.38, 129.62, 129.96, 132.90, 133.12, 165.40 (C=O), 166.37 (C=O).

Anal. Calc. for $C_{20}H_{20}O_5$ (340.38): C, 70.97; H, 5.92. Found: C, 70.74; H, 5.78.

(2*R*,3*R*)-3-Benzoyloxy-2-benzoyloxymethyltetrahydropyran (**4b**; 1.54 g, 90.2%) had b.p. 225–230°/0.2–0.25 Torr, $[\alpha]_D^{25}$ −66.2° (*c* 3, chloroform); ν_{max}^{KBr} 2960, 2860, 1725, 1608, 1455, 1320, 1270, 1180, 1110, 1095, 1060, 1028, and 712 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 1.5–2.1 (m, 4 H), 3.6–4.55 (m, 5 H), 5.29 (bs, 1 H), 7.25–7.50 (m, 6 H), 7.97–8.17 (m, 4 H); ^{13}C, δ 20.82 (C-5), 27.71 (C-4), 64.22 (C-6), 67.66 (C-2′), 68.00 (C-2), 75.79 (C-3), 128.27, 128.38, 129.68, 129.91, 130.19, 132.90, 133.07, 165.69 (C=O), 166.14 (C=O).

Anal. Calc. for $C_{20}H_{20}O_5$ (340.38): C, 70.97; H, 5.92. Found: C, 70.86; H, 5.66.

Ditosylates **1c–4c**. — To a cooled solution of each diol **1a–4a** (5.0 mmol) in pyridine (15 mL, freshly distilled over potassium hydroxide) was added portionwise toluene-*p*-sulphonyl chloride (12.8 g, 15.0 mmol; freshly crystallised from chloroform–light petroleum; m.p. 67–69°) whilst maintaining the temperature at −10 to −5°. The mixture was stirred for 6 h at this temperature, then stored for 72 h at ~5°, poured into crushed ice–water (200 mL), and extracted with chloroform (3 × 100 mL). The combined extracts were washed with dilute hydrochloric acid (1:4, 3 × 50 mL) and then water to pH 6, dried, and concentrated. The crude products **1c–4c** were obtained in yields of >90%.

(3*R*,4*R*)-3,4-Ditoluene-*p*-sulphonyloxytetrahydropyran (**1c**) had m.p. 126–128° (from methanol), $[\alpha]_D^{25}$ +12.9° (*c* 2.4, chloroform); ν_{max}^{KBr} 2980, 2930, 2870, 1600, 1500, 1465, 1370, 1360, 1330, 1310, 1300, 1225, 1190, 1125, 1095, 1045, 1010, 995, 950, 900, 835, 825, 710, 690, 670, and 650 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.16–2.30 (m, 2 H), 2.45 (s, 2 CH_3), 2.55–3.88 (m, 4 H), 3.95–5.16 (m, 2 H), 7.27–7.37 (m, 4 H), 7.65–7.89 (m, 4 H).

Anal. Calc. for $C_{19}H_{22}S_2O_7$ (426.51): C, 53.51; H, 5.20. Found: C, 53.30; H, 5.27.

(3*S*,4*R*)-3,4-Ditoluene-*p*-sulphonyloxytetrahydropyran (**2c**) had m.p. 102–104° (from methanol), $[\alpha]_D^{25}$ −5.6° (*c* 2.4, chloroform); ν_{max}^{KBr} 3100, 3060, 2460, 2440, 2370, 1945, 1920, 1600, 1500, 1450, 1405, 1380, 1360, 1340, 1330, 1310, 1250, 1185, 1160, 1140, 1095, 1085, 1000, 960, 915, 900, 840, 815, 800, 710, and 616 cm^{-1}; λ_{max}^{EtOH} 273 nm (log ε 2.98), 267 (3.03), 262 (3.09), 258.5 nm (2.95). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.58–2.28 (m, 2 H) 2.43 (s, 2 CH_3), 3.29–4.04 (m, 4 H), 4.25–4.69 (m, 2 H), 7.30–7.40 (m, 4 H), 7.42–7.79 (m, 4 H).

Anal. Calc. for $C_{19}H_{22}O_7S_2$ (426.51): C, 53.51; H, 5.20. Found: C, 53.68; H, 5.25.

Crude **3c** (94.7%) was purified by column chromatography on silica gel (110 g) with chloroform–ethyl acetate–light petroleum (1:1:3). Fractions 11–16 (10-mL fractions) contained (2*R*,3*S*)-2-hydroxymethyl-3-toluene-*p*-sulphonyloxytetrahydropyran (52.1 mg), m.p. 82–84° (from di-isopropyl ether); ν_{max}^{KBr} 3500, 2940, 2860, 1750, 1665, 1600, 1500, 1460, 1440, 1360, 1230, 1180, 1050, 970, 920, 820, and 670 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H, δ 1.37–1.67 (m, 5 H), 1.99 (s, CH_3), 2.45 (s, CH_3), 2.30–3.0 (m, 1 H), 3.4–3.6 (m, OH), 7.25–7.39 (m, 2 H), 7.75–7.84 (m, 2 H); ^{13}C, δ 21.63 (2 CH_3), 24.99 (C-5), 30.51 (C-4), 62.91 (C-2′), 67.83 (C-6), 74.99 (C-3), 76.51 (C-2), 127.72, 129.87, 133.46, 144.97.

Anal. Calc. for $C_{13}H_{18}O_5S$ (286.35): C, 54.53; H, 6.34. Found: C, 54.30; H, 6.19.

Fractions 24–41 contained (2*R*,3*S*)-3-toluene-*p*-sulphonyloxy-2-toluene-*p*-sulphonyloxymethyltetrahydropyran (**3c**, 2.05 g) as a yellow oil that solidified in the refrigerator; $[\alpha]_D^{25}$ +37.3° (*c* 2.7, chloroform); ν_{max}^{KBr} 3560, 3390, 2960, 2860, 1740, 1600, 1450, 1365, 1300, 1195, 1180, 1100, 1065, 980, 960, 880, 815, 795, and 670 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H, δ 1.51–1.65 (m, 6 H), 2.44 and 2.46 (2 s, 2 CH_3), 3.16–3.48 (m, 2 H), 3.70–3.89 (m, 2 H), 4.01–4.28 (m, 2 H), 7.28–7.29 (m, 4 H), 7.69–7.82 (m, 4 H); ^{13}C, δ 21.64 (2 CH_3), 24.75 (C-5), 30.21 (C-4), 67.39 (C-6), 68.51 (C-2′), 74.49 (C-3), 76.70 (C-2), 127.67, 127.96, 129.62, 130.31, 132.74, 133.33, 144.68, 145.26.

Anal. Calc. for $C_{20}H_{24}O_7S_2$ (440.54): C, 54.53; H, 5.49. Found: C, 54.51; H, 5.74.

(2*R*,3*R*)-3-Toluene-*p*-sulphonyloxy-2-toluene-*p*-sulphonyloxymethyltetrahydropyran (**4c**, 82.4%) had m.p. 118–120° (from methanol), $[\alpha]_D^{25}$ −14.8° (*c* 2.7, chloroform); ν_{max}^{KBr} 2970, 2860, 1605, 1375, 1365, 1198, 1180, 982, 960, 905, 825, 790, 700, 675, and 658 cm^{-1}; λ_{max}^{EtOH} 273 (log ε 2.96), 267 (3.02), 262 (3.03), 256.5 nm (2.94). N.m.r. data ($CDCl_3$): ^{1}H, δ 1.10–2.30 (m, 4 H), 2.45 (2 CH_3), 3.6–3.9 (m,

5 H), 4.61 (s, 1 H), 7.27–7.37 (m, 4 H), 7.37–7.80 (m, 4 H); ^{13}C, δ 19.81 (2 CH_3), 21.61 (C-5), 28.10 (C-4), 67.67 (C-2'), 68.96 (C-3), 74.66 (C-6), 75.79 (C-2), 127.66, 127.88, 127.97, 129.86, 132.90, 133.86, 144.93, 145.09.

Anal. Calc. for $C_{20}H_{24}O_7S_2$ (440.54): C, 54.53; H, 5.49. Found: C, 54.77; H, 5.76.

Cu(I) complexes of chiral diphenylphosphinites **2e** *and* **4e**. — The chiral diphosphinites **2e** and **4e** were prepared from diols **2a** and **4a** following the method[4] for **1e** and **3e**. Starting from 5 mmol of diol, chlorodiphenylphosphine (2.25 g, 10 mmol), and pyridine (0.8 g, 10.0 mmol), crude **2e** and **4e** were quantitatively isolated.

(3S,4R)-3,4-Bis(diphenylphosphinoxy)tetrahydropyran–copper(I) chloride complex (**2f**). — Crude **2e** was transformed[4] into **2f** with freshly prepared Cu(I)Cl in hot ethanol. Crude **2f** (90%), m.p. 124–130°, was recrystallised repeatedly from chloroform–ethanol to give material with m.p. 130–134°; ν_{max}^{KBr} 3450, 3080, 3060, 3010, 2960, 2930, 2860, 1965, 1900, 1820, 1640, 1590, 1575, 1485, 1435, 1390, 1370, 1335, 1315, 1285, 1240, 1215, 1180, 1160, 1100, 1050, 1010, 980, 935, 910, 870, 830, 795, 745, and 690 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H, δ 1.23 (t, J 7 Hz, ethanol CH_3), 1.75–2.03 (m, 2 H), 3.32–4.14 (m, 3 H), 4.8–4.9 (m, 3 H), 7.11–7.85 (m, 20 H, 4 Ph); ^{13}C, δ 16.78 (ethanol CH_3), 30.40 (C-5), 64.49 (C-6), 65.80 (ethanol CH_2), 67.74 (C-2), 75.09 (C-3), 75.28 (C-4), 77.04 ($CHCl_3$), 128.00, 128.34, 128.98, 129.56, 129.75, 130.14, 130.53, 131.21, 131.89, 132.52, 134.08, 134.91, 135.10, 135.49, 135.68, 136.22, 136.37, 136.61, 136.76, 137.05, 137.68, 137.87, 138.21.

Anal. Calc. for $C_{29}H_{28}O_3P_2 \cdot CuCl \cdot CHCl_3 \cdot C_2H_5OH$ (750.93): C, 51.20; H, 4.70. Found: C, 51.65; H, 4.42.

(2R,3R)-3-Diphenylphosphinoxy-2-diphenylphosphinoxymethyltetrahydropyran–copper(I) chloride complex (**4f**). — The crude product (31.5%) from the first crop had m.p. 105–110°. Repeated recrystallisation from chloroform–ethanol gave the pure product, m.p. 146–150°; ν_{max}^{KBr} 3460, 3080, 3060, 3010, 2960, 2930, 2850, 1970, 1900, 1820, 1670, 1590, 1575, 1485, 1465, 1435, 1380, 1360, 1345, 1330, 1310, 1285, 1270, 1215, 1180, 1160, 1095, 1045, 1025, 995, 970, 910, 850, 825, 795, 740, and 695 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H, δ 1.23 (t, J 6.9 Hz, EtOH CH_3), 1.4–4.0 (m, 10 H), 7.12–7.34 and 7.42–7.90 (20 H, 4 Ph); ^{13}C, δ 16.73 (ethanol CH_3), 20.47 (C-5), 28.99 (C-4), 65.70 (ethanol CH_2), 67.74 (C-6), 75.91 (C-2-CH_2), 77.04 ($CHCl_3$), 77.23, 78.49, 127.90, 128.34, 129.37, 129.95, 130.14, 130.34, 130.82, 131.06, 131.45, 135.01, 135.40, 135.59, 135.88, 136.12, 137.58, 137.82.

Anal. Calc. for $C_{30}H_{30}O_3P_2 \cdot CuCl \cdot 0.75\ CHCl_3 \cdot C_2H_5OH$ (735.11): C, 53.51; H, 5.04. Found: C, 53.49; H, 4.95.

Asymmetric reductions with LAH complexes. — These were conducted under argon, and anhydrous reagents were transferred through a rubber septum by oven-dried syringes. The formation of the LAH complexes **10** and **11**, as well as their interaction with achiral modifiers, was monitored on the basis of the volume of hydrogen evolved when the reaction was quenched with methanol. The reaction was monitored by t.l.c. 1-Phenylethanol was identified by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

Tetrahydrofuran was distilled from sodium metal and stored under argon. Solutions of LAH were filtered through dry Celite and the concentrations were assayed by determining the volume of hydrogen gas evolved by dropwise addition to water. Ethanol and 2-propanol were distilled from magnesium.

(*a*) *General procedure without a second modifier.* To 0.96–1.67M LAH (4.16 mmol) in tetrahydrofuran was added dropwise a solution of diol **1a** or **3a** (4.23 mmol) in tetrahydrofuran (2 mL). The resulting mixture was stirred for 30 min at room temperature, then cooled as appropriate in water–ice, solid CO_2–acetone, or liquid air–methanol. A solution of acetophenone (196 mg, 1.66 mmol) in tetrahydrofuran (1.5 mL) was added dropwise, the mixture was stirred for 3 h, then quenched with methanol (1 mL), and allowed to warm to room temperature, 2M HCl (10 mL) was added, and the mixture was extracted with dichloromethane. The extract was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography [dichloromethane–light petroleum (4:1)] of the residue afforded chromatographically and spectroscopically (^{1}H- and ^{13}C-n.m.r.) pure products.

(*b*) *General procedure with a second modifier.* The reducing agent was prepared by first adding 2M ethanol or 2-propanol in tetrahydrofuran (2.10 mL, 4.20 mmol) and then a solution of **1a** or **3a** (4.23 mmol) in tetrahydrofuran (2 mL) to the standardised 0.96–1.67M LAH (4.16 mmol) in tetrahydrofuran. After stirring for 30 min at room temperature, the reducing agent was cooled to the desired temperature, and a solution of acetophenone (98 mg, 0.83 mmol) in tetrahydrofuran (1 mL) was added dropwise. The mixture was stirred for 5 h at the same temperature and then quenched with methanol (1 mL). Acidic work-up, extraction with dichloromethane, and column chromatography yielded pure 1-phenylethanol; see Tables I and II.

Diols **1a** and **3a** were recovered from the aqueous layer by concentration and extraction (Soxhlet) of the residual solid with ethyl acetate and subsequent distillation.

Asymmetric hydrogenation of Z-α-acetamidocinnamic acid with di-μ-perchloratobis(norbornadiene)dirhodium and ligands **2f** *and* **4f**. — The catalytic system was prepared directly from the diphenylphosphinites **2e** and **4e**. These ligands (0.0125 mmol) were added to the deaerated solution of $[Rh(NBD)_2]ClO_4$ (0.01 mmol, prepared according to ref. 38). After stirring for 15 min at ambient temperature, triethylamine (5 mL, 0.015 mmol) and then *Z*-α-acetamidocinnamic acid (1.0 mmol) were added to the resulting orange-red solution. Hydrogenation, isolation of the product [*R*(*S*)-*N*-acetylphenylalanine], and determination of its chemical and optical purity were performed as described earlier[5].

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