Chemistry of Ketene Acetals. Part 8.[1] Stereochemistry of the Reaction of 1,1-Dimethoxypropene with Aldehydes

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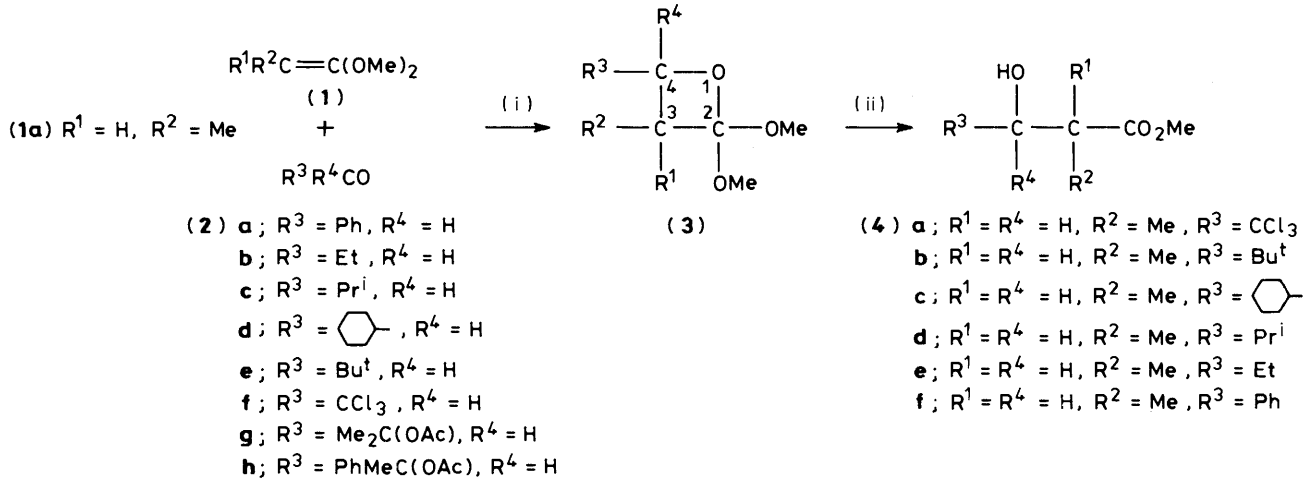
The Lewis acid-catalysed (2 + 2)cycloadditions of 1,1-dimethoxypropene with various aldehydes RCHO have been studied. These reactions, which are supposed to proceed *via* dipolar intermediates, yield 2,2-dimethoxyoxetanes, the formation of which is reversible in the presence of the catalyst used. The *cis*:*trans* ratio of the oxetanes was determined after short reaction times at low temperature ('kinetic' conditions) and after prolonged reaction times at room temperature (thermodynamic conditions). This was performed by stopping the reaction with triethylamine or by transforming the oxetanes at low temperature into β-hydroxy esters. The influence of the reaction conditions and the size of R on the stereochemistry of the reaction has been discussed. It appeared that under 'kinetic' conditions the *cis*:*trans* ratio of the oxetanes is not only determined by the most favourable transoid approach of the cycloaddends, but also by the rotation of the dipolar intermediate to a cisoid *gauche* conformation.

In previous papers[2-5] we have demonstrated the synthetic utility of cycloadditions between ketene acetals $R^1R^2C{=}C(OMe)_2$ (**1**) and carbonyl compounds R^3R^4CO (**2**). In the presence of a Lewis acid (*e.g.* $ZnCl_2$) a variety of carbonyl compounds can be converted in this way into 2,2-dimethoxyoxetanes (**3**) under mild conditions. These cycloadducts can easily be hydrolysed into β-hydroxy esters[2] (**4**), or into lactones[3,4] (*e.g.* γ-butyrolactones) when a suitably protected hydroxy group is present in R^3 (Scheme 1).



Scheme 1. *Reagents*: (i) $ZnCl_2$; (ii) H_3O^+

The chemical selectivity of the cycloadditions is rather high. Aldehydes can be converted selectively in the presence of other carbonyl compounds, olefinic double bonds, or substituents which are sensitive to nucleophilic attack. With α,β-unsaturated aldehydes an oxetane is in most cases the primary product when the reaction is performed at low temperature.[6]

The stereoselectivity of the cycloadditions is apparent in reactions of unsymmetrically substituted carbonyl compounds (*e.g.* aldehydes) with ketene acetals in which R^1 and R^2 are different, *e.g.* 1,1-dimethoxypropene (**1a**). In previous studies on these reactions, of the two possible *cis–trans* isomers of the oxetane one was favoured as the main product. We supposed that the *cis*-oxetane would always be formed in excess, because it arises *via* the more favourable transoid approach of the reactants leading to the *anti* conformation (**Figure**). Further experiments showed, however, that the stereochemistry of the reactions depends on the reaction conditions used. Therefore, the stereochemical course of the reactions of (**1a**) with several aldehydes has now been studied under different conditions.

Reactions of 1,1-*Dimethoxypropene* (**1a**) *with Benzaldehyde* (**2a**).—In the cycloadditions with benzaldehyde the *cis*:*trans* ratio in the product mixture can easily be determined from the

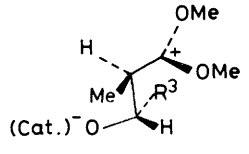


Figure.

^1H n.m.r. spectrum in which the 4-H absorptions are well separated ($\delta_{H(cis)}$ 5.27, $\delta_{H(trans)}$ 4.65). Equimolar solutions of benzaldehyde (**2a**) and (**1a**) (5.0 mmol) in di-isopropyl ether (15 ml) were treated at −78 °C with such an amount of $AlCl_2Et$ or $AlCl_2Obornyl$[7] that 20% conversion had been reached in 2 min.

At that time the reaction was stopped by the addition of triethylamine (TEA) and the product ratio was determined: *cis*:*trans* 80:20 with $AlCl_2$Obornyl, 70:30 with $AlCl_2$Et.

A similar experiment, using $ZnCl_2$ as the catalyst, was performed at −15 °C, because the reaction rate decreases substantially below −20 °C with this less acidic catalyst.[8] The *cis*:*trans* ratio in this experiment was 85:15. Apparently, the nature of the catalyst has no important influence on the product ratio.

It appeared, however, that the *cis*:*trans* ratio in these experiments is reduced when the product yield is increased by prolongation of the reaction time. Table 1 gives *cis*:*trans* ratios and percentages of conversion after several time intervals for the reaction of equimolar amounts (5.0 mmol) of benzaldehyde (**2a**) and (**1a**) at −78 °C in the presence of 1 mol% of $AlCl_2$Et. Ultimately the product ratio is completely reversed.

The results suggest that the *cis*-oxetane is the kinetically and the *trans*-oxetane the thermodynamically determined product. The latter can be expected to be the main product under circumstances which enable the catalyst to effect strong equilibration of the *cis*- and *trans*-oxetane.

Indeed, treatment of equimolar amounts of benzaldehyde (**2a**) and (**1a**) (5 mmol) dissolved in 1 ml of the polar solvent acetonitrile, at room temperature, for 2 h with a saturated solution of $ZnCl_2$ gave again a large excess of the *trans*-oxetane over the *cis*-oxetane (overall yield 75%, *cis*:*trans* ratio 1:4).

Preparation of the *cis*-oxetane in high yield is apparently not possible. Even at low temperature (−78 °C, using $AlCl_2$Et) and in a non-polar solvent the initially large *cis*:*trans* ratio is already reduced after relatively short reaction times, before the reaction has been completed.

Reactions of 1,1-*Dimethoxypropene* (**1a**) *with other Aldehydes* R^3CHO.—In order to establish a possible influence of the residue R^3 in the aldehyde on the *cis*:*trans* ratio, oxetane formation was investigated with a series of aldehydes (**2b—f**). The reactions were performed: (i) under thermodynamic conditions: equimolar (2.5M) solution of the reactants in acetonitrile, $ZnCl_2$ as the catalyst, 2 h at room temperature; (ii) under 'kinetic' conditions: an equimolar (0.3M) solution of the reactants in di-isopropyl ether, $AlCl_2$Et as the catalyst, 15 min at −35 °C. Because of the lower reactivity of some of the aldehydes in comparison with benzaldehyde (**2a**), standardization of the circumstances at lower temperature was not possible. In both cases the reactions were stopped by the addition of TEA.

In some cases (aldehydes without a proton at C-α) determination of the *cis*:*trans* ratio could be based on the difference between the doublets of the 4-H proton[5] in the ^{1}H n.m.r. spectrum of the *cis*:*trans* mixture (J_{cis} *ca.* 8 Hz, J_{trans} *ca.* 6 Hz). With the other aldehydes these signals cannot easily be assigned to the individual isomers either because of further splitting by protons in R^3 or because the 3-H and 4-H absorptions are hidden under other resonances.

Since separation of the isomers by distillation would change the *cis*:*trans* ratio, and separation by chromatography leads to hydrolysed products, the product mixture was then subjected to methanolysis at −78 °C and the resulting acyclic orthoesters were hydrolysed at room temperature with dilute hydrochloric acid into β-hydroxy esters $R^3CH(OH)CH(Me)CO_2Me$ (**4**; $R^1 = R^4 = H$, $R^2 = Me$). In this way the *cis*-oxetane gives an *erythro*-, the *trans*-oxetane a *threo*-β-hydroxy ester. Determination of the *erythro*:*threo* ratio from ^{1}H n.m.r. spectra can be based on the 2-H or 3-H signal because of the large difference between the 2-H–3-H coupling constants[9] (*J* 7—8 Hz for *threo*, 2—3 Hz for *erythro* compounds); the 2-H signal often appears as a quintet for *threo* compounds and as a double quartet for *erythro* compounds. The *erythro*:*threo* ratio in the β-hydroxy esters can also be determined by separation of the isomers by h.p.l.c. In those cases where *cis*:*trans* as well as *erythro*:*threo* ratios could be determined, agreement between the results showed that the hydrolytic procedure did not alter the product ratio seriously.

The results of these experiments are given in Table 2. Product ratios of cycloadditions with benzaldehyde (**2a**) have been included for comparison.

Table 2 reveals that under equilibrating conditions the *trans*-oxetane is always the main product. With most aldehydes the cycloaddition provides a useful procedure for the stereoselective preparation of *threo*-β-hydroxy esters in good yields. A low stereoselectivity is only found in the cycloaddition of EtCHO (**2b**). Because of the absence of branching at C-α the difference in thermodynamic stability of the *cis*- and *trans*-oxetane must be relatively small.

The *cis*:*trans* ratio, obtained with chloral (**2f**), is notable because for the bulky residue CCl_3 we expect an extreme preference for the *trans*-isomer on equilibration. Moreover, the ratio is equal to that found under 'kinetic' conditions. It appeared that the same product ratio (30:70) was obtained on treating chloral (**2f**) and (**1a**) in acetonitrile for 2 h without the addition of a catalyst. Besides, the ratio did not alter when the

Table 1. *cis*:*trans* Ratios and percentages of conversion as a function of time for the reaction of benzaldehyde (**2a**) and 1,1-dimethoxypropene (**1a**) at −78 °C in di-isopropyl ether, using $AlCl_2$Et as catalyst

Time (min)	0.5	5	20	60	120
cis:*trans* Ratio	80:20	65:35	60:40	45:55	30:70
Conversion (%)	40	50	60	70	70

Table 2. Product ratios of reactions between aldehydes (**2**) and 1,1-dimethoxypropene (**1a**) under different conditions

	Thermodynamic conditions				'Kinetic' conditions			
Aldehyde	*cis*:*trans* Ratio of oxetanes (**3**) (^{1}H n.m.r.)	*erythro*:*threo* Ratio of β-hydroxy esters (^{1}H n.m.r.)	*erythro*:*threo* Ratio of β-hydroxy esters (h.p.l.c.)	Yield of β-hydroxy ester (**4**) (%)	*cis*:*trans* Ratio of oxetanes (**3**) (^{1}H n.m.r.)	*erythro*:*threo* Ratio of β-hydroxy esters (^{1}H n.m.r.)	*erythro*:*threo* Ratio of β-hydroxy esters (h.p.l.c.)	Yield of β-hydroxy ester (**4**) (%)
(**2a**) PhCHO	20:80	20:80	15:85	70	60:40	60:40	65:35	60
(**2b**) EtCHO		45:55		70		50:50		65
(**2c**) Pr^iCHO		5:95		65		45:55		60
(**2d**) Cyclohexyl CHO	5:95	5:95	5:95	70		50:50	50:50	70
(**2e**) Bu^tCHO	5:95	5:95	5:95	50	50:50	45:55	40:60	50
(**2f**) CCl_3CHO	25:75	25:75	25:75	80	25:75	25:75	25:75	50

mixture was left at room temperature for a longer period. On the other hand heating of this mixture (with or without a catalyst) to 70 °C for 2 h gave the *trans*-oxetane as the sole product. Apparently, equilibration of the oxetane of chloral (**2f**) and (**1a**) proceeds very slowly, so that even in a polar solvent at room temperature the product ratio after long reaction times is mainly kinetically determined.

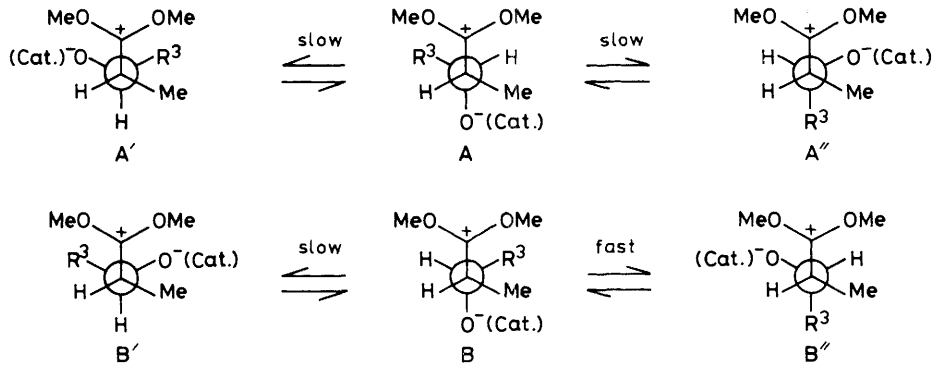
Under 'kinetic' conditions high stereoselectivity cannot easily be realised with most of the aldehydes. This can be ascribed to increasing equilibration during the progress of the reaction in those cycloadditions in which the kinetically and thermodynamically determined products are different, as was demonstrated in the experiments with benzaldehyde (**2a**). This is not always the case, however; the kinetically determined cycloadduct of chloral (**2f**) and (**1a**) appeared to be the more stable adduct. Therefore, in some cases the low stereoselectivity under kinetic conditions may be due to a small difference between the rate constants for the formation of the *cis*- and *trans*-adduct. In the next section it is argued that this can be expected in cycloadditions of aldehydes having large residues R^3.

Mechanistic Aspects.—It is generally accepted[2] that the oxetane formation from electron-donating ketene acetals and electron-accepting carbonyl compounds proceeds in two steps *via* a dipolar intermediate. In cycloadditions of ketene acetals like 1,1-dimethoxypropene (**1a**), in which the HOMO coefficient on C-β is much larger than on C-α, the preferred geometry of addend approach is according to FMO theory[10] as indicated in the Figure. The transoid approach of the reactants leads to a dipolar intermediate in which the charges are far apart,[11] and the oxetane formation requires, in a second step, rotation around the primary formed C–C bond to a cisoid *gauche* conformation.

The transoid approach of the unsymmetrically substituted alkene dimethoxypropene and an aldehyde will lead to two intermediates A and B (Scheme 2). Because of less crowding, stereoisomer A, having R^3 and Me in an *anti*-relationship, will be of lower energy. Therefore, the *cis*-oxetane resulting from A will be the kinetically determined product, when the formation of the intermediate is rate determining.

Bond rotation in the second step, leading to a cisoid *gauche* conformation, is possible in two directions. Starting from A both rotations are accompanied with an increase of crowding. With B, however, rotation into B″ leads to release of crowding. The formation of a *trans*-oxetane from B will, therefore, be easier than the conversion of A into a *cis*-oxetane. In those cases in which the second step is rate determining the *trans*-adduct may even become the kinetically determined product. The occurrence of the transition state of the overall reaction in the second step is more probable when R^3 is a large group. So the formation of the *trans*-oxetane as the main product for $R^3 = CCl_3$ under circumstances in which the cycloaddition is not reversible can be explained. The low stereoselectivity of the cycloadditions of aldehydes in which R^3 is a secondary or tertiary alkyl residue might also be due to a dependence of the product ratio on both reaction steps. The stereochemistry of product formation in the related reactions of ketene acetals with dicyanostyrene has previously been explained in a similar way.[12]

The incorrect supposition that the stereochemistry of oxetane formation is only determined by the more favourable transoid addend approach A has led in the past to erroneous conclusions about the stereochemical structure of oxetanes[4] obtained from α-acetoxyaldehydes and (**1a**). Because the reactions were performed under thermodynamic conditions (8 h; 30 °C; $ZnCl_2$; acetonitrile) it should now be expected that the main product is not a *cis*- but a *trans*-oxetane. Repeating the cycloadditions of aldehydes (**2g** and **h**) with (**1a**) we found that the vicinal coupling constants for the C-3 and C-4 protons is 6.5 Hz, in good agreement with the value for similar *trans*-oxetanes (*ca.* 6 Hz).[5]



Scheme 2. Newman projections of dipolar intermediates A and B

Experimental

General Methods.—M.p.s are uncorrected. ^1H N.m.r. spectra were recorded on a Bruker 90 Mz spectrometer in $CDCl_3$ solution with $SiMe_4$ as internal reference. All OH resonances could be exchanged with D_2O. Mass spectra were obtained with a VG 7070E mass spectrometer. Preparative h.p.l.c. was performed on a Miniprep L.C. Jobin Yvon apparatus using Merck silica gel 60H as stationary phase. Acetonitrile and diisopropyl ether were stored over CaH_2. Ether refers to diethyl ether. 1,1-Dimethoxypropene (**1a**) was prepared as described in the literature.[2] $AlCl_2Et$ was commercially available as a 25% standard solution in hexane (Alfa products) and was diluted with ether, previously dried over $LiAlH_4$, to a 0.3M ether–hexane solution before use. $AlCl_2O$bornyl was prepared as described in the literature.[7]

Preparation of β-*Hydroxy Esters,* $R^3CH(OH)CH(Me)CO_2Me$ *from Aldehydes* R^3CHO *and* (**1a**) via *the Corresponding Oxetanes.*—(a) *Experiments under 'kinetic conditions,' general procedure.* To a vigorously stirred mixture of the aldehyde (5 mmol) and 1,1-dimethoxypropene (**1a**) (0.56 g, 5.5 mmol) in diisopropyl ether (15 ml) was added $AlCl_2Et$ (1 ml of a 0.3M solution) at the temperature indicated in the text. After 15 min the reaction was terminated by the addition of triethylamine (0.5 ml) and the reaction mixture was allowed to come to room

temperature. After evaporation of the solvent n-pentane (*ca.* 30 ml) was added until a light precipitate was formed. The precipitate was filtered off. Evaporation of the solvent gave the crude oxetane.

To obtain the β-hydroxy esters (**4**; $R^1 = R^4 = H$, $R^2 = Me$) the crude oxetane was dissolved in di-isopropyl ether (15 ml) and stirred and cooled to −78 °C. A mixture of methanol (0.48 g, 15 mmol) and toluene-*p*-sulphonic acid monohydrate (pinpoint, *ca.* 10 mg) was added. The reaction mixture was kept at −78 °C for 1 h, and then allowed to come to room temperature. To the stirred mixture was added hydrochloric acid (10 ml of a 1M solution) and the mixture was stirred for 1 h. After addition of brine (25 ml) the di-isopropyl ether layer was separated and the aqueous layer was extracted with ether (3 × 25 ml). The combined ethereal extracts were dried ($MgSO_4$) and the solvent was evaporated to give the β-hydroxy ester as a faint yellow oil. Preparative h.p.l.c. using chloroform–acetonitrile (99 : 1) yielded the pure diastereoisomers.

In the case of chloral (**2f**) the aldehyde (5.0 mmol) was dissolved in di-isopropyl ether (15 ml) and the solution was cooled to −35 °C. 1,1-Dimethoxypropene (**1a**) (0.56 g, 5.5 mmol) was dissolved in di-isopropyl ether (1 ml) and the solution was added to the cooled solution of the aldehyde without a catalyst. Work-up was performed as described above.

(b) *Experiments under thermodynamic conditions, general procedure.* To a stirred mixture of the aldehyde (5.0 mmol) and 1,1-dimethoxypropene (**1a**) (0.56 g, 5.5 mmol) in acetonitrile (1 ml) was added $ZnCl_2$ (1 ml of a saturated solution in acetonitrile) at room temperature; in some cases immediate cooling with an ice-bath was necessary. After the addition of $ZnCl_2$ the mixture was left for 2 h whilst being vigorously stirred. Triethylamine (0.5 ml) was then added and the solvent was evaporated off. n-Pentane (*ca.* 30 ml) was added until a light precipitate was formed; the precipitate was filtered off. Evaporation of the solvent gave the crude oxetane. To obtain the β-hydroxy esters the same procedure as previously described was followed. In the case of chloral (**2f**) again no catalyst was used; a solution of the aldehyde (5.0 mmol) in acetonitrile (1 ml) was mixed at room temperature with a solution of 1,1-dimethoxypropene (**1a**) (0.56 g, 5.5 mmol) in acetonitrile (1 ml) and worked up as described above.

All β-hydroxy esters were characterized by ^1H n.m.r., mass spectroscopy, and C,H-analyses, or by comparison with literature data. The following esters were prepared.

Methyl 4,4,4-*trichloro*-3-*hydroxy*-2-*methylbutanoate* (**4a**), *threo*: m.p. 81—91 °C (Found: C, 30.75; H, 3.8%; $M^+ + 1$, 234.9692. $C_6H_9Cl_3O_3$ requires C, 30.60; H, 3.85%; $M + 1$, 234.9696); *m/z* 235 ($M + 1$, 48%), 203 (M − OMe, 24), 201 (37), 177 (100), and 117 ($M - CCl_3$, 30); $\delta_H(CDCl_3)$ 1.47 (3 H, d, *J* 7Hz, Me), 3.31 (1 H, dq, *J* 7 and 2 Hz,* 2-H), 3.73 (3 H, s, OMe), 4.06 (1 H, d, *J* 2 Hz, 3-H), and 5.39 (1 H, s, OH). *Erythro*: $\delta_H(CDCl_3)$ 1.40 (3 H, d, *J* 7 Hz, Me), 3.31 (1 H, dq, *J* 7 and 5 Hz,* 2-H), 3.23 (1 H, br s, OH), 3.73 (3 H, s, OMe), and 4.66 (1 H, d, *J* 5 Hz, 3-H).

Methyl 3-*hydroxy*-2,4,4-*trimethylpentanoate* (**4b**), *threo*: (Found: $M^+ + 1$, 175.1339. Calc. for $C_9H_{18}O_3$: $M + 1$, 175.1334); *m/z* 175 ($M + 1$, 100%), 174 (M, 1), 159 (M − Me, 40), 157 (M − OH, 100), 155 (16), 145 (15), and 143 (M − OMe, 50); δ_H, see supplementary material cited in ref. 13. We found, however, a smaller value for the 2-H–3-H coupling constant: *J* 2 Hz.* *Erythro*: $\delta_H(CDCl_3)$ 0.95 (9 H, s, Bu^t), 1.23 (3 H, d, *J* 7 Hz, Me), 2.22 (1 H, br s, OH), 2.75 (1 H, dq, *J* 7 Hz and 4.5 Hz,* 2-H), and 3.68 (3 H, s, OMe); 3-H resonance hidden under ester resonance.

Methyl 3-*cyclohexyl*-3-*hydroxy*-2-*methylpropanoate* (**4c**), *threo*: (Found: C, 65.75; H, 10.15%; $M^+ + 1$, 201.1494. Calc. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07%; $M + 1$, 201.1491); *m/z* 201 ($M + 1$, 100%), 200 (M, 1), 184 (50), 183 (M − OH, 100), 169 (M − OMe, 15), and 151 (47); δ_H see supplementary material cited in ref. 13. *Erythro*: $\delta_H(CDCl_3)$ 0.71—2.18 (11 H, m, −⬡), 1.16 (3 H, d, *J* 7 Hz, Me), 2.44 (1 H, br s, OH), 2.68 (1 H, dq, *J* 7 and 3.3 Hz, 2-H), 3.64 (1 H, dd, *J* 7.6 and 3.3 Hz, 3-H), and 3.69 (3 H, s, OMe).

Methyl 3-*hydroxy*-2,4-*dimethylpentanoate* (**4d**), *threo*: (Found $M^+ + 1$, 161.1168. Calc. for $C_8H_{16}O_3$: $M + 1$, 161.1178); *m/z* 161 ($M + 1$, 15%), 147 (24), 143 (M − OH, 82), 129 (M − OMe, 100), 127 (25), and 111 ($M - CO_2Me$, 13); δ_H see supplementary material cited in ref. 13.

Methyl 3-*hydroxy*-2-*methylpentanoate* (**4e**), Diastereoisomeric mixture: (Found: $M^+ + 1$, 147.1016. Calc. for $C_7H_{14}O_3$: $M + 1$, 147.1021); *m/z* 147 ($M + 1$, 100%), 129 (M − OH, 100), and 115 (M − OMe, 50); $\delta_H(CDCl_3)$ 0.97 (3 H, br t, *J* 7 Hz, 5-H_3), 1.18 and 1.21 (3H, 2 d, *J* 7 Hz, Me), 1.30—1.78 (2 H, m, 4-H_2), 2.46 (1 H, s, OH), 2.36—2.70 (1 H, m, 2-H), 3.43—3.90 (1 H, m, 3-H), and 3.70 (3 H, s, OMe).

Methyl 3-*hydroxy*-2-*methyl*-3-*phenylpropanoate* (**4f**), *threo*: m.p. 49—50 °C (lit.,[4] 52 °C) (Found: C, 68.1; H, 7.25%; $M^+ + 1$, 195.1028. Calc. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%; $M + 1$, 195.1021); *m/z* 195 ($M + 1$, 16%), 194 (M, 6), 177 (M − OH, 100), 163 (M − OMe, 7), and 121 (75); δ_H: see supplementary material cited in ref. 13. *Erythro*: $\delta_H(CDCl_3)$ 1.12 (3 H, d, *J* 7 Hz, Me), 2.78 (1 H, dq, *J* 7 and 3 Hz, 2-H), 2.94 (1 H, br s, OH), 3.66 (3 H, s, OMe), 5.08 (1 H, d, *J* 3 Hz, 3-H), and 7.30 (5 H, br s, Ph).

* These observed values for the *erythro* and *threo* coupling constants are a notable example in which the *threo* coupling constant is smaller than that of the *erythro* due to the presence of bulky tertiary groups [see ref. 9(*b*)].

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