Stereoselective Radical Additions of γ-Oxy-α,β-unsaturated Ester Derivatives; 1,2-Asymmetric Induction in Acyclic and Cyclisation Systems

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Examination was made of 1,2-asymmetric induction in the addition of alkyl radicals to γ-oxy-α,β-unsaturated ester derivatives **1** and **2** prepared from ethyl lactate and (*R*)-2,3-*O*-isopropylideneglyceraldehyde **3**, respectively. The addition reactions of hexyl, cyclohexyl and 3-phenylpropyl radicals to (*Z*)-**2** derived from aldehyde **3** gave β-addition products with *syn*-stereoselectivity (*syn*:*anti* = 8.6:1—*syn* only). The reactions of (*E*)-**2** were non-stereoselective. Based on allylic strain, a transition-state model for the *syn*-stereoselectivity is proposed. 1,2-Asymmetric induction was carried out in radical cyclisation to synthesize optically active cyclohexane derivatives.

In recent years, there has been considerable effort devoted to controlling the stereochemistry of free-radical reactions.[1] Strategies based on auxiliary control have proven successful for conducting asymmetric radical additions of α,β-unsaturated carbonyl compounds.[1b,2] We have derived an alternative general approach to substrate-controlled stereoselective radical reaction for 1,2-asymmetric induction, where facial preference of radical addition to an acceptor double bond is determined by the chiral centre adjacent to the double bond (γ-asymmetric carbon in α,β-unsaturated carbonyl derivatives). γ-Oxy-α,β-unsaturated carbonyl derivatives are useful substrates for diastereoselective Michael reactions, and the stereoselectivities of reactions with various nucleophiles have been the object of experimental[3] and theoretical study.[4] Although additions of the nucleophilic alkyl radical to α,β-unsaturated ester derivatives are widely used in organic synthesis, stereoselectivity based on the γ-stereogenic centre has not been studied systematically.[5] Radicals are not cluttered with counter-ions, and radical-addition reactions to C=C double bonds are usually with early, reactant-like transition states. Thus, a comparison of the diastereoselectivity of the radical reactions of γ-oxy-α,β-unsaturated ester derivatives with those of ionic reactions should provide important data. Diastereoselective additions of alkyl radicals to γ-oxy-α,β-unsaturated ester derivatives to bring about 1,2-asymmetric induction in acyclic and cyclisation systems are discussed below.[6]

γ-Oxy-α,β-unsaturated ester derivatives **1** and **2** prepared from ethyl lactate (racemic) and (*R*)-2,3-*O*-isopropylideneglyceraldehyde **3**[7] were used as substrates. The reactions were carried out by the slow addition of a solution of tributyltin hydride (Bu_3SnH, 3 mol equiv.) and 2,2′-azoisobutyronitrile (AIBN, 0.2 mol equiv.) in benzene to a solution of ester **1** or **2** (1 mol equiv.) and alkyl iodide (3 mol equiv.) in benzene at reflux temperature for 4–5 h. The reaction mixture was then refluxed for 2 h. Addition products **4**, **5** and **8**, **9** were inseparable in most cases, and thus purified isomers were obtained as lactone derivatives, **6**, **7** and **10**, **11**, after treatment of the reaction mixtures with HCl in MeOH or boron tribromide (in the case of **1e**) (Schemes 1 and 2). Stereochemistries of the isomers *cis*-**6**, **10** and *trans*-**6**, **10** were determined by NOE experiments in ^1H NMR and X-ray crystallographic analysis {in the case of *cis*-**10** (R^1 = H, R^3 = $Ph[CH_2]_3$)}† and correlated to *syn*-**4**, **8** and *anti*-**4**, **8**, respectively. The results are summarised in Tables 1 and 2.

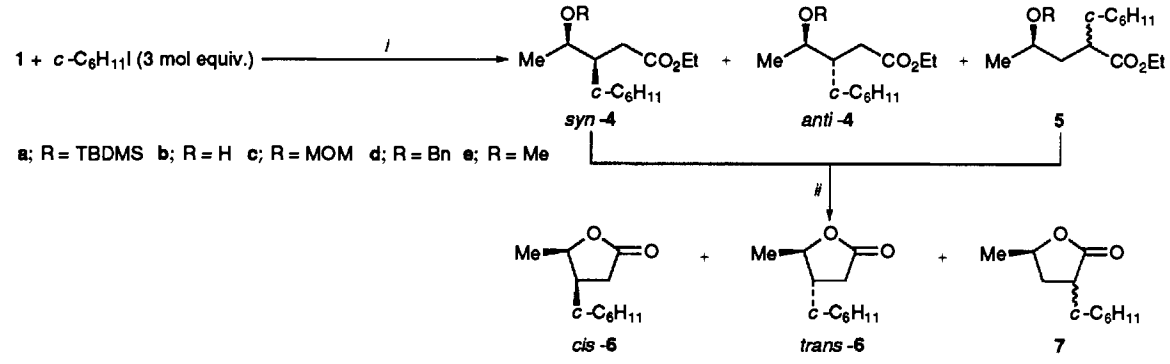
Table 1 Radical addition of compounds **1** with *c*-$C_6H_{11}I$

Entry	Substrate	Yield of **4** and **5** (%)	Ratio[a] (**4**:**5**[b])	Ratio[a] (*syn*-**4**:*anti*-**4**)
1	(*E*)-**1a**	35	1.9:1	1:1.9
2	(*E*)-**1b**	62[c]	2.6:1	1:1.6
3	(*E*)-**1c**	35	1:1.2	1.2:1
4	(*E*)-**1d**	N.R.[d]		
5	(*E*)-**1e**	35[c]	1:1.3	1:1
6	(*Z*)-**1a**	37[c]	1:1.3	10.2:1
7	(*Z*)-**1c**	49	1:2.0	15.8:1
8	(*Z*)-**1d**	N.R.[d]		
9	(*Z*)-**1e**	46[c]	1:1.2	1:14.3

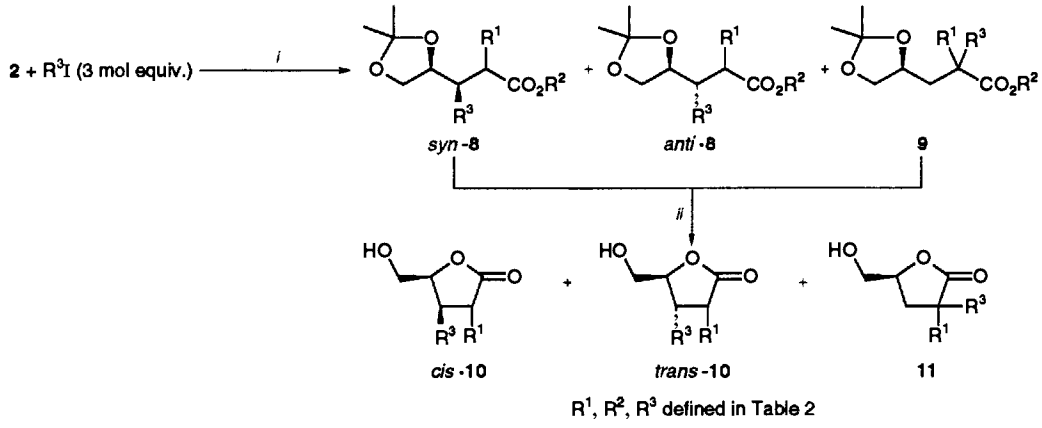
[a] Ratios were determined by isolation and/or GLC analysis of lactone derivatives (**6** and **7**). Yields of lactonisation: entry 1 (80%), entry 3 (83%), entry 7 (93%). [b] Ratios of the stereoisomers of **5** were not determined. [c] The yield after lactonisation. [d] 100% of (*E*)-**1d** and 38% of (*Z*)-**1d** were recovered, respectively.

For 4-oxypent-2-enoic acid ester derivatives **1** (Scheme 6 in Experimental section), the cyclohexyl radical added in 35–62% yield (except for the case of **1d**), but regioselectivity (4:**5**) was not observed (2.6:1–1:2.0). Stereoselectivity of β-addition pro-

† Since absolute stereochemistries of C-5 in compound *cis*-**10** (R^1 = H, R^3 = $Ph[CH_2]_3$) and C-4″ in compounds *syn*-**14a**, **b** (3*R*) are known (derived from compound **3**), other asymmetric centre(s) is/are automatically established by X-ray crystallographic analysis.



Scheme 1 *Reagents and conditions:* i, Bu_3SnH (3 mol equiv.) AIBN (cat.), benzene, reflux (slow addition); ii, HCl, MeOH or BBr_3



Scheme 2 *Reagents and conditions:* i, Bu_3SnH (3 mol equiv.), AIBN (cat.), benzene, reflux (slow addition); ii, HCl, MeOH

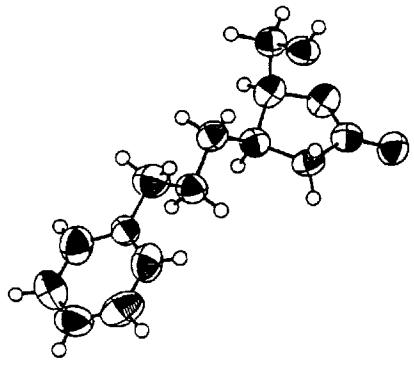
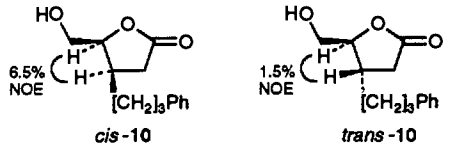
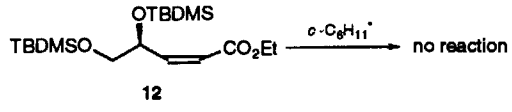


Fig. 1 X-Ray molecular structure of *cis*-**10** (R^1 = H, R^3 = Ph[CH_2]$_3$)



duct 4 was observed for (*Z*)-**1** depending on the protective group on the γ-oxygen (entries 6, 7 and 9). The TBDMS and MOM ethers, (*Z*)-**1a**, **c**, thus gave products *syn*-**4a**, **c** diastereoselectively (10.2:1 and 15.8:1, respectively). Methyl ether (*Z*)-**1e** induced reversal of stereoselectivity to give *anti*-4 (1:14.3). In the reaction of (*E*)- and (*Z*)-**1c**, replacement of the methyl group on the γ-carbon by the Bu^t group brought about recovery of the starting material.

Reactions of chiral substrates containing the 2,2-dimethyl-1,3-dioxolan-4-yl group derived from aldehyde **3** were carried out. In disubstituted compounds **2a–d** (entries 1–9), addition of hexyl, cyclohexyl and 3-phenylpropyl radicals proceeded in 54–quantitative yields to give β-addition products **8** preferentially (**8**:**9** = 2.8:1–7.3:1) (see Table 2). The *Z*-configuration for the acceptor double bond was crucial in attaining 1,2-asymmetric induction in the radical addition reaction. Thus, esters (*Z*)-**2a**, **b**, **c** gave the corresponding product *syn*-**8** stereoselectively in the ratio 8.6:1—*syn* only (entries 1–7). Reactions with cyclohexyl radicals showed higher *syn*-selectivity than those with sterically less hindered hexyl radicals. The alcohol moiety of the ester group in (*Z*)-**2a**, **b**, **c** had no effect on stereoselectivity. Compound (*E*)-**2d** expressed non-stereoselectivity (entries 8 and 9). The formation of α-addition products **9** was non-stereoselective. Ring opening of the dioxolane ring of (*Z*)-**2** and protection of hydroxy groups with TBDMS groups (conversion of **2** into **12**) reduced the



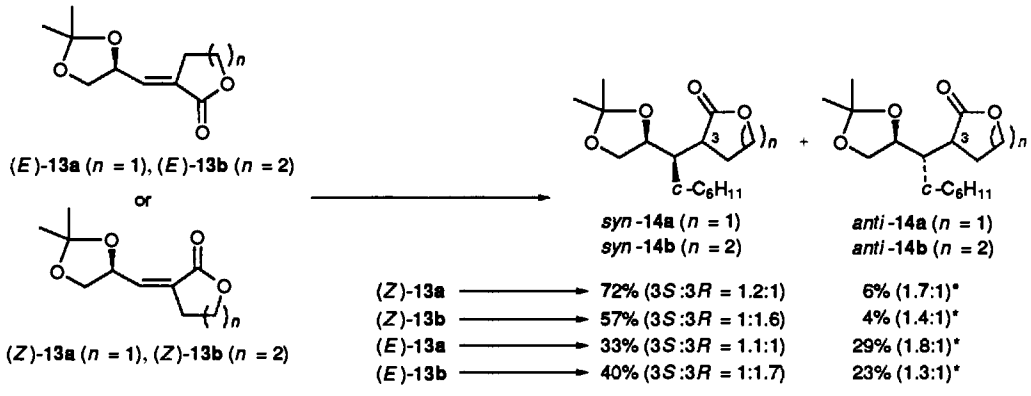
reactivity of the acceptor double bond, with consequent recovery of the starting material. In trisubstituted compounds (entries 10–12), ester (*Z*)-**2e** gave a ratio of 11.9:1 for *syn*-stereoselectivity in reaction with the cyclohexyl radical, and esters (*E*)-**2e**, **f** gave lower ratios (2.9:1 and 2.0:1, respectively). No stereoselectivity with respect to C-2 was observed in the reactions of compounds **2e**, **f** (1.8:1–1:1.3). In these cases, no α-addition products were detected.

Examination of radical additions of chiral unsaturated γ- and δ-lactone derivatives **13** obtained from aldehyde **3** (Scheme 3; Scheme 7 in Experimental section) indicated similar acyclic 1,2-asymmetric induction. Stereochemistries of products *syn*-**14a**, **b**

Table 2 Radical addition of compounds **2** with R^3I

Entry	2 R^1	2 R^2	R^3	Yield of **8** and **9** (%)	Ratio[a] (**8**:**9**[b])	Ratio[a] (*syn*-**8**:*anti*-**8**)
1 (*Z*)-**2a**	H	Me	*n*-C_6H_{13}	75	4.9:1	8.6:1
2			*c*-C_6H_{11}	82	3.8:1	16.2:1
3			$Ph[CH_2]_3$	54	7.3:1	*syn* only
4 (*Z*)-**2b**	H	Bn	*n*-C_6H_{13}	55	4.8:1	8.9:1
5			*c*-C_6H_{11}	79	3.9:1	*syn* only
6			$Ph[CH_2]_3$	58	5.6:1	14.5:1
7 (*Z*)-**2c**	H	Bu^t	*c*-C_6H_{11}	quant.	5.0:1	18.4:1
8 (*E*)-**2d**	H	Et	*n*-C_6H_{13}	55	3.8:1[c]	1.1:1[c]
9			*c*-C_6H_{11}	65	2.8:1	1.3:1
10 (*Z*)-**2e**	Me	Et	*c*-C_6H_{11}	51[d]	(**8** only)	11.9:1
11 (*E*)-**2e**	Me	Et	*c*-C_6H_{11}	32[d]	(**8** only)	2.9:1
12 (*E*)-**2f**	Pr^i	Et	*c*-C_6H_{11}	20[d]	(**8** only)	2.0:1

[a] Ratios were determined by isolation, ^1H NMR and/or GLC analysis of lactone derivatives (**10** and **11**). Yields of lactonisation: entry 1 (86%), entry 2 (quant.), entry 3 (88%), entry 4 (96%), entry 5 (95%), entry 6 (95%), entry 7 (80%), entry 9 (not determined). [b] Ratios of the stereoisomers of **9** were 2.3:1–1.1:1 (determined by analysis of **11**). Stereochemistry was not determined. [c] Ratios were determined by GLC analysis. [d] The yield after lactonisation.



* The ratio in parentheses indicates the distribution of stereoisomers with respect to C-3.

Scheme 3 *Reagents and conditions:* *c*-$C_6H_{11}I$ (3 mol equiv.), Bu_3SnH (3 mol equiv.), AIBN (cat.), benzene, reflux (slow addition)

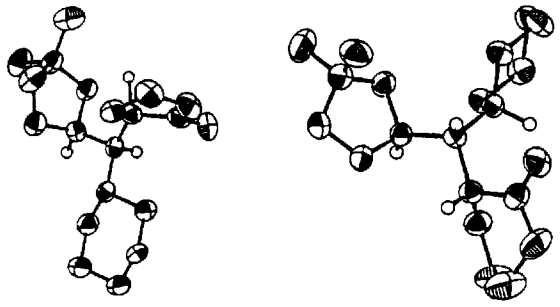
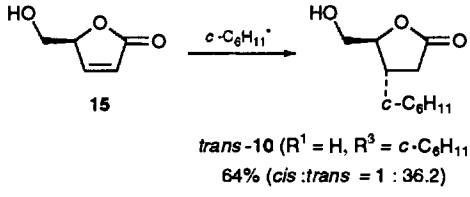


Fig. 2 X-Ray molecular structures of *syn*-**14a, b** (3*R*)

(3*R*) were established by X-ray crystallographic analysis.* Epimerisation of *syn*-**14a, b** (3*R*) at C-3 showed them to be correlated to (3*S*)-isomers. Addition products were obtained in 33–72% yield. The stereoselectivity of 1,2-asymmetric induction for lactones (*Z*)-**13a, b** was 12:1 and 14:1, respectively, with preference for *syn*-isomers. Lactones (*E*)-**13a, b** resulted in non-stereoselective addition. No stereoselectivity with respect to C-3 was observed.

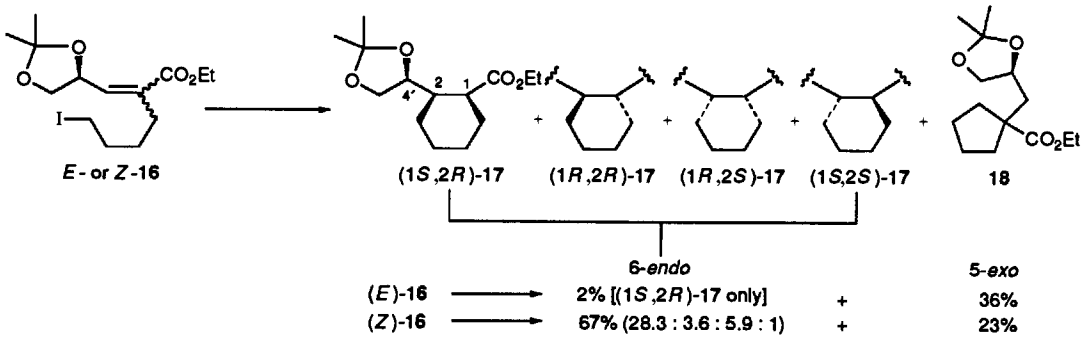
Acyclic stereocontrol of *syn*-selective 1,2-asymmetric induction was possible in radical additions of chiral compounds (*Z*)-**2** and **13** derived from aldehyde **3**. Owing to *trans*-selectivity (*trans*:*cis* = 36.2:1) of the addition of lactone



15 with cyclohexyl radical, the radical reaction of ester (*Z*)-**2** followed by lactonisation leading to *cis*-**10** also makes stereocontrol on the ring system possible.

Explanation for the above stereoselectivity can be obtained by conformational analysis of the substrate since the radical addition proceeds with an early, reactant-like transition state. The remarkable effect of the *Z*-configuration of the double bond in **2** on 1,2-asymmetric induction clearly indicates the dominant role of non-bonded steric interactions between the dioxolane ring and ester group on diastereoselectivity. Conformer **A** should be more favourable than **B** in which there is considerable allylic strain between the dioxolane ring and *cis*-ester group (Fig. 3). The alkyl radical attacks preferentially from the *re*-face (*anti* to the C–C bond of the dioxolane ring) of favoured conformer **A** to give product *syn*-**8**. The ester carbonyl group of ester (*Z*)-**2** may possibly have the s-*cis* conformation since diastereoselectivity was the same in reactions of esters (*Z*)-**2a, b, c** and conformationally locked lactones (*Z*)-**13a, b**. In esters (*E*)-**2**, energy differences among conformers with respect to the rotation of C-3–C-4 may be less than those in the case of geometric isomers (*Z*)-**2** due to relaxation of allylic

* See footnote † on p. 271.



Scheme 4 *Reagents and conditions:* Bu_3SnH (1.5 mol equiv.), AIBN (cat.), benzene, reflux (high dilution)

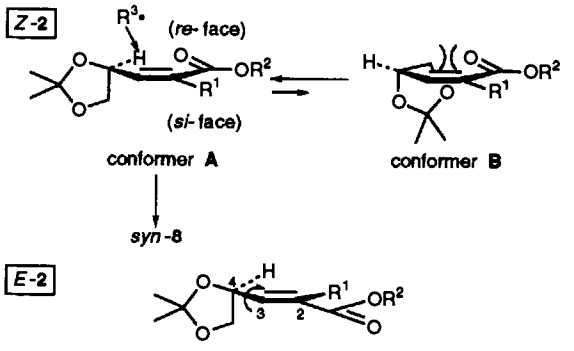
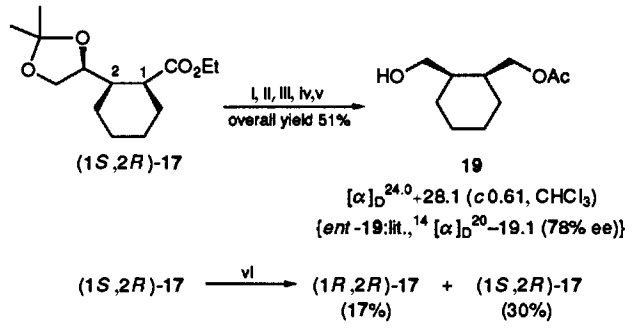


Fig. 3



Scheme 5 *Reagents:* i, $LiAlH_4$; ii, Ac_2O, pyridine; iii, dil. HCl; iv, $NaIO_4$; v, $NaBH_4$; vi, LDA; then aq. NH_4Cl

strain, thus preventing the facial selection.* Slight increase in *syn*-selectivity in esters (*E*)-**2e**, **f** compared with (*E*)-**2d** may be an indication of the importance of steric bulk of the substituent on C-2, in causing interaction with the dioxolane ring, for diastereoselectivity. Transition state model **A** can also be used to explain the *syn*-stereoselectivity of esters (*Z*)-**1a**, **c**. Diastereoselective ionic and concerted additions of compounds (*E*)- and (*Z*)-**2** have been extensively studied.[9] 2-[(Trimethylsilyl)methyl]prop-2-enyl acetate, cyclopentadiene, amines and diphenylsulfonium isopropylide add to esters (*E*)- and (*Z*)-**2** from the *re*-face, and the diastereoselectivity is explained by the transition-state models using conformation **A** for esters (*Z*)-**2** and the related conformation for (*E*)-**2**, respectively.[9,10] † AM 1 calculations for conformers of esters (*E*)- and (*Z*)-**2** with respect to the rotation of C-3–C-4 have been made by Ortuno and co-workers to obtain the lowest-energy conformer **A** for esters (*Z*)-**2**.[12]

1,2-Asymmetric induction based on the chiral centre derived from aldehyde **3** was examined in a radical cyclisation (Scheme 4).‡ Iodo esters (*E*)- and (*Z*)-**16** were prepared from aldehyde **3** with ethyl 6-(*tert*-butyldimethylsiloxy)hexanoate followed by separation of the stereoisomers and functional-group transformation, respectively (Scheme 8 in Experimental section). Bu_3SnH promoted the reaction of iodide (*E*)-**16** to give cyclised product **18** *via* 5-*exo* cyclisation along with a trace amount of a desired 6-*endo*-product **17** (1*S*,2*R*). With substrate (*Z*)-**16**, the cyclohexanecarboxylate **17** was obtained as a major product and the proportions of stereoisomers were 28.3:3.6:5.9:1. 1,2-Asymmetric induction was 4.6:1 with the same direction as in the acyclic system of compound *Z*-**2**. The absolute stereochemistry of product (1*S*,2*R*)-**17** was determined by conversion into diol derivative **19** and by comparison of the sign of the optical-rotation value with that in the literature[14] (Scheme 5). Treatment of (1*S*,2*R*)-**17** with lithium diisopropylamide (LDA) gave *trans* isomer (1*R*,2*R*)-**17** by epimerisation at C-1. Coupling constants (11.5, 10.7 and 3.7 Hz) in the ^1H NMR spectrum indicated two *trans*-diaxial relationships of vicinal hydrogens in the *trans*-configuration of the substituents of isomer (1*S*,2*S*)-**17**. Those of (1*R*,2*S*)-**17** (4.1, 4.1 and 4.1 Hz) corresponded to a *cis*-configuration of the substituents (Fig. 4). Stereoselectivity for the 1,2-aymmetric induction of compound (*Z*)-**16** *via* 6-*endo* cyclisation may be explained by a chair-like transition-state model **L** with the most stable conformation of the dioxolane ring and α,β-unsaturated ester for minimal allylic strain (Fig. 5). In compound (*E*)-**16**, deviation of regioselectivity to 5-*exo* cyclisation may be due to non-bonded interactions between the dioxolane ring and the radical site in transition-state model **M** for 6-*endo* cyclisation. Transition-state model **N** for 5-*exo* cyclisation is considered favourable.

In conclusion, significant stereoselectivity can be attained for additions of alkyl radicals with γ-oxy-α,β-unsaturated esters and lactones derived from (*R*)-2,3-*O*-isopropylideneglyceraldehyde **3**. The *Z*-configuration of the double bond in the substrate is important for *syn*-selective 1,2-asymmetric induction. A transition-state model in which allylic strain is a determining factor of conformational preference is proposed. In this study, a means was derived for stereochemical control of radical addition reactions in acyclic and cyclisation systems.

Experimental

M.p.s were determined on a Yanagimoto Micro-melting Point Apparatus MP-J13; IR spectra on a Perkin-Elmer FT-IR-1710 spectrophotometer; ^1H and ^{13}C NMR spectra on Bruker AM-

* During the course of this work, Smadja *et al.* reported the additions of silicon- and tin-centred radicals to (*E*)- and (*Z*)-**2** (R^1 = H, R^2 = Et), and attributed the observed stereoselectivity to steric and Felkin–Anh stereoelectronic control in the case of the *E*-one.[8]

† The diastereoselectivity of addition reactions of osmium tetraoxide, organocopper–boron trifluoride complexes and triphenylphosphonium isopropylide are highly dependent on the stereochemistry of the double bond of ester **2**. Reagents add to the *si*-face of the *E*-isomer, and *re*-face of the *Z*-isomer preferentially.[9,11]

‡ Recently, Warkentin reported 1,2-asymmetric induction (3.8:1) in aryl radical cyclisation to the aldimino double bond containing the adjacent 2,2-dimethyl-1,3-dioxolan-4-yl group.[13]

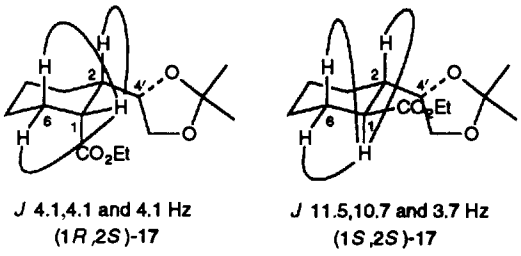


Fig. 4

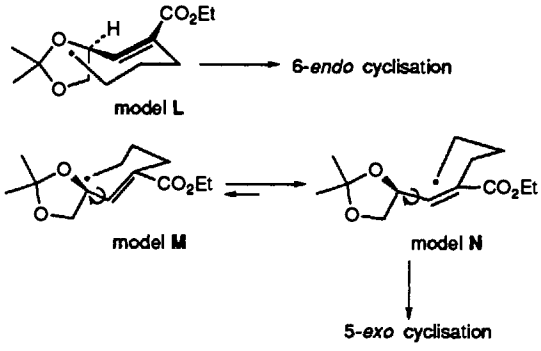


Fig. 5

400 and Varian Gemini-300 spectrometers for solutions of $CDCl_3$, with J values given in Hz; mass spectra on VG Auto Spec and Hitachi M-80 spectrometers; and optical rotations on a JASCO DIP-360 polarimeter, with $[\alpha]_D$ values given in units of 10^{-1} deg cm^2 g^{-1}. Column chromatography was on Wakogel C-200 (100–200 mesh). GLC analyses were carried out on a Hitachi G-3000 gas chromatograph (OV-1; 0.25 mm ID, 25 m). Medium-pressure liquid chromatography (MPLC) was performed with a KUSANO MPLC system (KPW-10, KU-331, Pre-Packed Columns-HS-101-1) and a Waters Differential Refractometer R403.

Preparation of Substrates.—Compounds **1**, **13** and **16** were prepared by standard methods as shown in Schemes 6–8. Compounds (*Z*)-**2a**,[15] (*E*)-**2d**,[15] (*Z*)-**2e**,[16] (*E*)-**2e**,[16] **3**[7] and **15**[17] were prepared by means of reported procedures. Compound (*Z*)-**2b** was prepared by a procedure similar to that used to prepare (*Z*)-**2a**. Compound (*Z*)-**2c** was prepared by the reaction of aldehyde **3** with *tert*-butyl (triphenylphosphoranylidene)acetate. Compound (*E*)-**2f** was prepared by the reaction of aldehyde **3** with triethyl 2-isopropylphosphonoacetate (ethyl 2-diethoxyphosphonyl-3-methylbutanoate) and sodium hydride.

Ethyl (E)-4-(tert-*butyldimethylsiloxy*)*pent*-2-*enoate* (E)-**1a**. Oil; δ_H(400 MHz; $CDCl_3$) 6.92 (1 H, dd, *J* 15.5 and 4.2, =CH), 5.98 (1 H, dd, *J* 15.5 and 1.8, =CH), 4.46 (1 H, qdd, *J* 6.5, 4.2 and 1.8, OCH), 4.20 (2 H, qd, *J* 7.1 and 2.7, OCH_2Me), 1.29 (3 H, t, *J* 7.1, CH_2Me), 1.26 (3 H, d, *J* 6.5, Me), 0.91 (9 H, s, Bu^t), 0.07 (3 H, s, SiMe) and 0.06 (3 H, s, SiMe); δ_C(100 MHz; $CDCl_3$) 166.85, 151.86, 121.70, 119.09, 67.77, 60.28, 25.84, 23.57, 18.23, 14.27, 3.26 and −4.82 (overlapping).

Ethyl (E)-4-*hydroxypent*-2-*enoate* (E)-**1b**. Oil; δ_H(400 MHz; $CDCl_3$) 6.95 (1 H, dd, *J* 15.7 and 4.7, =CH), 6.01 (1 H, dd, *J* 15.7 and 1.6, =CH), 4.48 (1 H, m, OCH), 4.19 (2 H, q, *J* 7.1, OCH_2Me), 1.96–1.60 (1 H, br s, OH), 1.33 (3 H, d, *J* 6.5, Me) and 1.28 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 166.67, 151.11, 119.50, 67.01, 60.42, 22.59 and 14.13.

Ethyl (E)-4-(*methoxymethoxy*)*pent*-2-*enoate* (E)-**1c**. Oil; δ_H(400 MHz; $CDCl_3$) 6.85 (1 H, dd, *J* 15.7 and 5.8, =CH), 5.98 (1 H, dd, *J* 15.7 and 1.5, =CH), 4.63 (2 H, s, OCH_2O), 4.35 (1 H, qdd, *J* 6.6, 5.8 and 1.5, OCH), 4.20 (2 H, q, *J* 7.1, OCH_2Me), 3.37 (3 H, s, OMe), 1.31 (3 H, d, *J* 6.6, Me) and 1.29 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 166.14, 148.64, 120.86, 94.37, 70.94, 60.24, 55.21, 20.42 and 14.08.

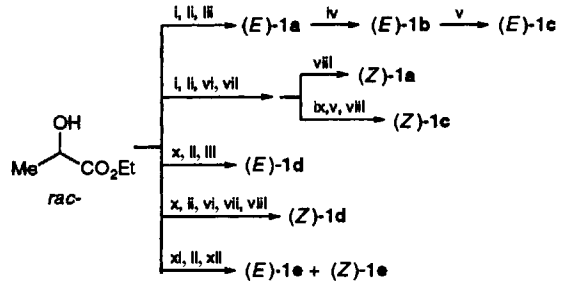
Ethyl (E)-4-*benzyloxypent*-2-*enoate* (E)-**1d**. Oil; δ_H(400 MHz; $CDCl_3$) 7.40–7.25 (5 H, m, Ph), 6.89 (1 H, dd, *J* 15.8 and 6.1, =CH), 6.02 (1 H, dd, *J* 15.8 and 1.3, =CH), 4.58 (1 H, d, *J* 11.9, PhC*H*), 4.44 (1 H, d, *J* 11.9, PhC*H*), 4.22 (2 H, q, *J* 7.1, OCH_2Me), 4.12 (1 H, qdd, *J* 6.5, 6.1 and 1.3, OCH), 1.33 (3 H, d, *J* 6.5, Me) and 1.31 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 166.14, 149.06, 138.11, 128.28, 127.50, 127.44, 121.22, 73.73, 70.57, 60.28, 20.50 and 14.12.

Ethyl (E)-4-*methoxypent*-2-*enoate* (E)-**1e**. Oil; δ_H(400 MHz; $CDCl_3$) 6.82 (1 H, dd, *J* 15.7 and 6.3, =CH), 5.97 (1 H, dd, *J* 15.7 and 1.3, =CH), 4.20 (2 H, q, *J* 7.1, OCH_2Me), 3.90 (1 H, qdd, *J* 6.6, 6.3 and 1.3, OCH), 3.31 (3 H, s, OMe), 1.29 (3 H, t, *J* 7.1, CH_2Me) and 1.27 (3 H, d, *J* 6.6, Me); δ_C(100 MHz; $CDCl_3$) 166.25, 148.94, 121.27, 76.15, 60.37, 56.60, 20.33 and 14.16.

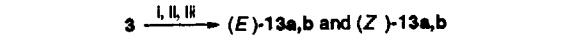
Ethyl (Z)-4-(tert-*butyldimethylsiloxy*)*pent*-2-*enoate* (Z)-**1a**. Oil; δ_H(400 MHz; $CDCl_3$) 6.19 (1 H, dd, *J* 11.7 and 7.8, =CH), 5.64 (1 H, dd, *J* 11.7 and 1.3, =CH), 5.44 (1 H, dqd, *J* 7.8, 6.3 and 1.3, OCH), 4.17 (2 H, q, *J* 7.1, OCH_2Me), 1.29 (3 H, t, *J* 7.1, CH_2Me), 1.25 (3 H, d, *J* 6.3, Me), 0.89 (9 H, s, Bu^t), 0.05 (3 H, s, SiMe) and 0.03 (3 H, s, SiMe); δ_C(100 MHz; $CDCl_3$) 165.87, 154.54, 116.94, 65.53, 60.60, 25.86, 23.53, 18.15, 14.24, −4.73 and −4.78.

Ethyl (Z)-4-(*methoxymethoxy*)*pent*-2-*enoate* (Z)-**1c**. Oil; δ_H(300 MHz; $CDCl_3$) 6.18 (1 H, dd, *J* 11.8 and 8.3, =CH), 5.78 (1 H, dd, *J* 11.8 and 1.4, =CH), 5.31 (1 H, dqd, *J* 8.3, 6.4 and 1.4, OCH), 4.64 (1 H, d, *J* 6.8, OCHO), 4.61 (1 H, d, *J* 6.8, OCHO), 4.17 (2 H, q, *J* 7.1, OCH_2Me), 3.36 (3 H, s, OMe), 1.31 (3 H, d, *J* 6.4, Me) and 1.28 (3 H, t, *J* 7.1, CH_2Me); δ_C(75 MHz; $CDCl_3$) 165.52, 151.38, 119.43, 94.97, 69.78, 60.06, 55.23, 20.43 and 14.05.

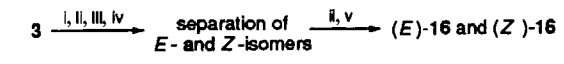
Ethyl (Z)-4-(*benzyloxy*)*pent*-2-*enoate* (Z)-**1d**. Oil; δ_H(400 MHz; $CDCl_3$) 7.38–7.23 (5 H, m, Ph), 6.23 (1 H, dd, *J* 11.7 and 8.3, =CH), 5.85 (1 H, dd, *J* 11.7 and 1.2, =CH), 5.16 (1 H, dqd, *J* 8.3, 6.4 and 1.2, OCH), 4.52 (1 H, d, *J* 11.6, PhC*H*), 4.45 (1 H, d, *J* 11.6, PhC*H*), 4.17 (2 H, q, *J* 7.1, OCH_2Me), 1.33 (3 H, d, *J* 6.4, Me) and 1.28 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 165.74, 151.90, 138.47, 128.27, 127.65, 127.47, 120.30, 71.50, 70.99, 60.13, 20.39 and 14.12.



Scheme 6 *Reagents:* i, TBDMSCl, imidazole; ii, DIBAL-H; iii, $(EtO)_2P(O)CH_2CO_2Et$; iv, TBAF; v, MOMCl, Pr^i_2NEt; vi, Ph_3P, CBr_4; vii, BuLi, $ClCO_2Et$; viii, H_2, Pd, $BaSO_4$, quinoline; ix, conc. HCl; x, BnBr, NaH; xi, MeI, NaH; xii, $Ph_3P{=}CHCO_2Et$



Scheme 7 *Reagents:* i, γ-butyrolactone or δ-valerolactone, LDA; ii, MsCl, Et_3N; iii, DBU



Scheme 8 *Reagents:* i, ethyl 6-(*tert*-butyldimethylsiloxy)hexanoate, LDA; ii, MsCl, Et_3N; iii, DBU; iv, TBAF; v, NaI

Ethyl (Z)-4-*methoxypent*-2-*enoate* (Z)-**1e**. Oil; δ_H(400 MHz; $CDCl_3$) 6.13 (1 H, dd, *J* 11.8 and 8.2, =CH), 5.84 (1 H, dd, *J* 11.8 and 1.2, =CH), 4.92 (1 H, dqd, *J* 8.2, 6.4 and 1.2, OCH), 4.18 (2 H, q, *J* 7.2, OCH_2Me), 3.30 (3 H, s, OMe), 1.29 (3 H, t, *J* 7.2, CH_2Me) and 1.27 (3 H, d, *J* 6.4, Me); δ_C(100 MHz; $CDCl_3$) 165.79, 152.02, 120.46, 73.23, 60.15, 56.55, 20.09 and 14.15.

Methyl (4'S,Z)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*prop*-2-*enoate* (Z)-**2a**. Oil; $[\alpha]_D^{27.8}$ +127.0 (*c* 2.00, $CHCl_3$) {lit.,[15] $[\alpha]_D$ +120.9 (*c* 3.54, $CHCl_3$)}; δ_H(400 MHz; $CDCl_3$) 6.37 (1 H, dd, *J* 11.9 and 6.7, =CH), 5.86 (1 H, dd, *J* 11.9 and 1.7, =CH), 5.50 (1 H, dddd, *J* 7.0, 6.7, 6.7 and 1.7, OCH), 4.38 (1 H, dd, *J* 8.3 and 7.0, OCH), 3.72 (3 H, s, OMe), 3.62 (1 H, dd, *J* 8.3 and 6.7, OCH), 1.45 (3 H, s, Me) and 1.39 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 166.05, 149.51, 120.34, 109.74, 73.52, 69.38, 51.46, 26.57 and 25.42.

Benzyl (4'S,Z)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*prop*-2-*enoate* (Z)-**2b**. Oil; $[\alpha]_D^{27.8}$ +104.2 (*c* 1.00, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 7.41–7.30 (5 H, m, Ph), 6.39 (1 H, dd, *J* 11.6 and 6.7, =CH), 5.90 (1 H, dd, *J* 11.6 and 1.7, =CH), 5.51 (1 H, dddd, *J* 7.0, 6.7, 6.7 and 1.7, OCH), 5.16 (2 H, s, OCH_2Ph), 4.35 (1 H, dd, *J* 8.3 and 7.0, OCH), 3.62 (1 H, dd, *J* 8.3 and 6.7, OCH), 1.45 (3 H, s, Me) and 1.38 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 165.36, 149.84, 135.68, 128.62, 128.36, 128.26, 120.47, 109.74, 73.51, 69.37, 66.31, 26.57 and 25.39.

tert-*Butyl* (4'S,Z)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*prop*-2-*enoate* (Z)-**2c**. Oil; $[\alpha]_D^{28.4}$ +87.20 (*c* 1.00, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.24 (1 H, dd, *J* 11.7 and 6.7, =CH), 5.75 (1 H, dd, *J* 11.7 and 1.7, =CH), 5.48 (1 H, dddd, *J* 7.0, 6.8, 6.7 and 1.7, OCH), 4.36 (1 H, dd, *J* 8.2 and 7.0, OCH), 3.60 (1 H, dd, *J* 8.2 and 6.8, OCH), 1.47 (9 H, s, Bu^t), 1.44 (3 H, s, Me) and 1.38 (3 H, s, Me); δ_C(75 MHz; $CDCl_3$) 164.79, 147.55, 122.47, 109.34, 80.53, 73.25, 69.19, 27.92, 26.43 and 25.28.

Ethyl (4'S,E)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*prop*-2-*enoate* (E)-**2d**. Oil; $[\alpha]_D^{27.2}$ +38.30 (*c* 2.00, $CHCl_3$) {lit.,[15] $[\alpha]_D^{23.0}$ +38.1 (*c* 2.94, $CHCl_3$)}; δ_H(400 MHz; $CDCl_3$) 6.87 (1 H, dd, *J* 15.6 and 5.7, =CH), 6.09 (1 H, dd, *J* 15.6 and 1.4, =CH), 4.66 (1 H, dddd, *J* 7.1, 6.6, 5.7 and 1.4, OCH), 4.21 (2 H, q, *J* 7.1, OCH_2Me), 4.18 (1 H, dd, *J* 8.2 and 6.6, OCH), 3.67 (1 H, dd, *J* 8.2 and 7.1, OCH), 1.45 (3 H, s, Me), 1.41 (3 H, s, Me) and 1.29 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 165.95, 144.58, 122.48, 110.16, 74.95, 68.82, 60.51, 26.44, 25.71 and 14.18.

Ethyl (4'S,Z)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)-2-*methylprop*-2-*enoate* (Z)-**2e**. Oil; $[\alpha]_D^{28.8}$ +50.20 (*c* 2.00, $CHCl_3$) {lit.,[16] $[\alpha]_D^{27.0}$ +64.64 (*c* 1.02, $CHCl_3$)}; δ_H(400 MHz; $CDCl_3$) 6.06 (1 H, dq, *J* 6.8 and 1.5, =CH), 5.25 (1 H, dddq, *J* 6.8, 6.8, 6.7 and 0.9, OCH), 4.29 (1 H, dd, *J* 8.2 and 6.8, OCH), 4.19 (2 H, q, *J* 7.1, OCH_2Me), 3.59 (1 H, dd, *J* 8.2 and 6.7, OCH), 1.92 (3 H, dd, *J* 1.5 and 0.9, Me), 1.44 (3 H, s, Me), 1.37 (3 H, s, Me) and 1.30 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 166.87, 142.15, 129.34, 109.28, 73.94, 69.57, 60.53, 26.57, 25.42, 19.86 and 14.12.

Ethyl (4'S,E)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)-2-*methylprop*-2-*enoate* (E)-**2e**. Oil; $[\alpha]_D^{29.6}$ +11.40 (*c* 2.00, $CHCl_3$) {lit.,[16] $[\alpha]_D^{21.0}$ +16.40 (*c* 1.01, $CHCl_3$)}; δ_H(400 MHz; $CDCl_3$) 6.68 (1 H, dq, *J* 8.0 and 1.3, =CH), 4.85 (1 H, ddd, *J* 8.0, 8.0 and 6.3, OCH), 4.20 (2 H, qd, *J* 7.1 and 1.0, OCH_2Me), 4.15 (1 H, dd, *J* 8.0 and 6.3, OCH), 3.62 (1 H, dd, *J* 8.0 and 8.0, OCH), 1.89 (3 H, d, *J* 1.3, Me), 1.45 (3 H, s, Me), 1.40 (3 H, s, Me) and 1.29 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 167.26, 138.06, 131.03, 109.72, 72.73, 68.69, 60.77, 26.57, 25.76, 14.15 and 12.91.

Ethyl (4'S,E)-3-(2'-2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)-2-*isopropylprop*-2-*enoate* (E)-**2f**. Oil; $[\alpha]_D^{26.8}$ +18.33 (*c* 1.20, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.48 (1 H, d, *J* 8.1, =CH), 4.92 (1 H, ddd, *J* 8.1, 7.8 and 6.3, OCH), 4.19 (2 H, qd, *J* 7.2 and 1.6, OCH_2Me), 4.13 (1 H, dd, *J* 7.8 and 6.3, OCH), 3.61 (1 H, dd, *J* 7.8 and 7.8, OCH), 2.84 (1 H, qq, *J* 7.0 and 7.0, CH), 1.45 (3 H, s, Me), 1.40 (3 H, s, Me), 1.30 (3 H, t, *J* 7.2, CH_2Me), 1.20 (3 H, d, *J* 7.0, Me) and 1.18 (3 H, d, *J* 7.0, Me); δ_C(75 MHz; $CDCl_3$) 166.44, 140.80, 136.68, 109.44, 71.98, 68.83, 60.06, 28.16, 26.37, 25.59, 21.15, 20.81 and 13.95.

(4'S,E)-3-(2',2'-*Dimethyl*-1',3'-*dioxolan*-4'-*ylmethylene*)*tetrahydrofuran*-2-*one* (E)-**13a**. Oil; $[\alpha]_D^{25.6}$ +14.81 (*c* 2.74, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.68 (1 H, dt, *J* 7.0 and 2.9, =CH), 4.74 (1 H, m, OCH), 4.38 (2 H, t, *J* 7.2, OCH_2), 4.19 (1 H, dd, *J* 8.2 and 6.4, OCH), 3.70 (1 H, dd, *J* 8.2 and 7.4, OCH), 3.11–2.90 (2 H, m, CH_2), 1.44 (3 H, s, Me) and 1.40 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 170.68, 135.83, 127.85, 110.28, 73.70, 68.55, 65.54, 26.37, 25.71 and 25.37.

(4'S,E)-3-(2',2'-*Dimethyl*-1',3'-*dioxolan*-4'-*ylmethylene*)*tetrahydro*-2H-*pyran*-2-*one* (E)-**13b**. Oil; $[\alpha]_D^{29.2}$ +12.10 (*c* 2.00, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.95 (1 H, ddd, *J* 8.1, 2.4 and 2.4, =CH), 4.79 (1 H, ddd, *J* 8.1, 7.4 and 6.3, OCH), 4.32 (2 H, t, *J* 5.3, OCH_2), 4.15 (1 H, dd, *J* 8.2 and 6.3, OCH), 3.67 (1 H, dd, *J* 8.2 and 7.4, OCH), 2.74 (1 H, dddd, *J* 16.7, 6.5, 6.5 and 2.4, CH), 2.50 (1 H, dddd, *J* 16.7, 6.8, 6.8 and 2.4, CH), 1.94 (2 H, m, CH_2), 1.42 (3 H, s, Me) and 1.39 (3 H, s, Me); δ_C(75 MHz; $CDCl_3$) 165.41, 141.57, 128.65, 110.13, 72.04, 68.68, 68.43, 26.52, 25.86, 23.98 and 22.55.

(4'S,Z)-3-(2',2'-*Dimethyl*-1',3'-*dioxolan*-4'-*ylmethylene*)*tetrahydrofuran*-2-*one* (Z)-**13a**. Needles, m.p. 33.0–34.0 °C (from hexane–AcOEt); $[\alpha]_D^{26.4}$ +73.03 (*c* 2.64, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.27 (1 H, dt, *J* 7.4 and 2.5, =CH), 5.70 (1 H, dddt, *J* 7.4, 6.7, 6.5 and 1.4, OCH), 4.37 (2 H, td, *J* 7.2 and 2.8, OCH_2), 4.32 (1 H, dd, *J* 8.3 and 6.7, OCH), 3.32 (1 H, dd, *J* 8.3 and 6.5, OCH), 2.99–2.92 (2 H, m, CH_2), 1.45 (3 H, s, Me) and 1.39 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 169.36, 141.33, 126.15, 109.72, 71.64, 69.14, 65.75, 28.57, 26.69 and 25.42.

(4'S,Z)-3-(2',2'-*Dimethyl*-1',3'-*dioxolan*-4'-*ylmethylene*)*tetrahydro*-2H-*pyran*-2-*one* (Z)-**13b**. Oil; $[\alpha]_D^{29.2}$ +122.80 (*c* 1.00, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.19 (1 H, ddd, *J* 6.4, 1.9 and 1.9, =CH), 5.33 (1 H, dddt, *J* 7.0, 6.6, 6.4 and 1.2, OCH), 4.39 (1 H, dd, *J* 8.4 and 7.0, OCH), 4.29 (2 H, m, OCH_2), 3.60 (1 H, dd, *J* 8.4 and 6.6, OCH), 2.59 (2 H, m, CH_2), 1.92 (2 H, m, CH_2), 1.43 (3 H, d, *J* 0.3, Me) and 1.35 (3 H, d, *J* 0.4, Me); δ_C(75 MHz; $CDCl_3$) 164.76, 147.20, 126.16, 109.46, 74.23, 69.54, 69.14, 28.89, 26.56, 25.23 and 22.97.

(4S)-5-(*Hydroxymethyl*)-2,5-*dihydrofuran*-2-*one* **15**.[17] Crystals; δ_H(400 MHz; $CDCl_3$) 7.48 (1 H, dd, *J* 5.8 and 1.5, =CH), 6.20 (1 H, dd, *J* 5.8 and 2.0, =CH), 5.15 (1 H, dddd, *J* 5.1, 3.8, 2.0 and 1.5, OCH), 3.99 (1 H, ddd, *J* 12.2, 6.8 and 3.8, OCH), 3.79 (1 H, ddd, *J* 12.2, 6.5 and 5.1, OCH) and 2.44–2.17 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 173.55, 154.14, 122.55, 84.29 and 61.93.

Ethyl (4'S,E)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)-2-(4-*iodobutyl*)*prop*-2-*enoate* (E)-**16**. Oil; $[\alpha]_D^{26.0}$ +3.80 (*c* 1.00, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.67 (1 H, d, *J* 8.5, =CH), 4.84 (1 H, ddd, *J* 8.5, 7.9 and 6.3, OCH), 4.22 (2 H, qd, *J* 7.1 and 1.6, OCH_2Me), 4.16 (1 H, dd, *J* 8.2 and 6.3, OCH), 3.65 (1 H, dd, *J* 8.2 and 7.9, OCH), 3.20 (2 H, t, *J* 6.7, ICH_2), 2.36 (2 H, m, CH_2), 1.84 (2 H, m, CH_2), 1.63–1.40 (2 H, m, CH_2), 1.46 (3 H, s, Me), 1.42 (3 H, s, Me) and 1.31 (3 H, t, *J* 7.1, CH_2Me); δ_C(75 MHz; $CDCl_3$) 166.85, 138.32, 135.27, 109.91, 72.34, 69.01, 60.88, 33.00, 30.47, 26.61, 26.10, 25.83, 14.21 and 6.35.

Ethyl (4'S,Z)-3-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)-2-(4-*iodobutyl*)*prop*-2-*enoate* (Z)-**16**. Oil; $[\alpha]_D^{26.8}$ +46.60 (*c* 2.91, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 6.02 (1 H, d, *J* 6.9, =CH), 5.21 (1 H, ddd, *J* 7.0, 6.9 and 6.8, OCH), 4.31 (1 H, dd, *J* 8.2 and 6.8, OCH), 4.22 (2 H, dq, *J* 7.1 and 2.3, OCH_2Me), 3.59 (1 H, dd, *J* 8.2 and 7.0, OCH), 3.18 (2 H, t, *J* 6.9, ICH_2), 2.40–2.21 (2 H, m, CH_2), 1.88–1.78 (2 H, m, CH_2), 1.61–1.52 (2 H, m, CH_2), 1.45 (3 H, s, Me), 1.38 (3 H, s, Me) and 1.32 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 166.75, 141.63, 133.56, 109.48, 74.06, 69.76, 60.71, 32.89, 32.70, 29.66, 26.65, 25.48, 14.25 and 6.12.

General Procedure for the Radical Addition.—Under argon, a solution of Bu_3SnH (873 mg, 3.0 mmol) and AIBN (90 mg, 0.55 mmol) in benzene (6 cm^3) was added to a refluxing solution of

the γ-oxy-α,β-unsaturated ester (**1** or **2**, 1.0 mmol) and the necessary alkyl iodide (3.0 mmol) in benzene (3.4 cm^3) during 4–5 h, and the reaction mixture was refluxed for 2 h. After removal of the solvent, the residue was treated with potassium fluoride (method A)[18] or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (method B)[19] to separate the organotin compounds. [Method A: the residue was dissolved in diethyl ether (10 cm^3) and 10% aq. KF (10 cm^3) was added to the stirred mixture. The precipitate was removed by filtration. The reaction mixture was extracted with diethyl ether, washed with saturated aq. NaCl, and dried over $MgSO_4$. Method B: the residue was dissolved in undried diethyl ether (20 cm^3), and DBU (685 mg, 4.5 mmol) was added. The reaction mixture was titrated with 0.1 mol dm^{-3} iodine in diethyl ether until the iodine colour just persisted, and was then transferred to a short-pad column (silica gel) and eluted with diethyl ether. The elutent was washed successively with 5% aq. $Na_2S_2O_3$ and saturated aq. NaCl, and dried over $MgSO_4$.] Column chromatography on silica gel gave the mixture of addition products 4 and **5**, or **8** and **9**.

General Procedure for the Conversion of the Addition Products into the Lactone Derivatives.—A solution of the mixture of radical-addition products (0.12 mmol) and 10% aq. HCl (6 cm^3) in MeOH (6 cm^3) was stirred for 2 h at room temperature. The reaction mixture was neutralised with saturated aq. $NaHCO_3$ and extracted with diethyl ether. The organic phase was washed with saturated aq. NaCl and dried over $MgSO_4$. Purification by column chromatography and MPLC on silica gel gave the lactone derivatives **6** and **7**, or **10** and **11**. In the case of compound **1e** (1.3 mmol), BBr_3 (1.0 mol dm^{-3} in CH_2Cl_2; 1.2 cm^3) was added to a solution of the mixture of radical-addition products **4e** and **5e** in CH_2Cl_2 (2 cm^3). The reaction mixture was stirred for 12 h at room temperature, and extracted with CH_2Cl_2. The organic phase was washed with saturated aq. NaCl and dried over $MgSO_4$. Purification by column chromatography and MPLC on silica gel gave the lactone derivatives **6** and **7**.

cis-4-*Cyclohexyl*-5-*methyltetrahydrofuran*-2-*one* cis-**6**. *Oil* (Found: M^+, 182.1300. $C_{11}H_{18}O_2$ requires M, 182.1307); ν_{max}(neat)/cm^{-1} 2981, 2927, 2853 and 1778; δ_H(400 MHz; $CDCl_3$) 4.74 (1 H, qd, *J* 6.6 and 6.6, OCH), 2.48–2.40 (1 H, m), 2.40–2.20 (2 H, m), 1.82–1.58 (6 H, m), 1.44–1.08 (3 H, m), 1.26 (3 H, d, *J* 6.6, Me) and 1.05–0.91 (2 H, m); δ_C(75 MHz; $CDCl_3$) 176.65, 78.67, 45.23, 37.48, 31.55, 31.30, 31.22, 26.10, 25.78, 25.57 and 14.97; *m*/*z* 182 (M^+), 167 (M^+ − Me) and 136.

trans-4-*Cyclohexyl*-5-*methyltetrahydrofuran*-2-*one* trans-**6**. *Oil* (Found: C, 72.1; H, 10.0. $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.95%); ν_{max}(neat)/cm^{-1} 2976, 2927, 2853 and 1774; δ_H(400 MHz; $CDCl_3$) 4.40 (1 H, dq, *J* 6.6 and 6.2, OCH), 2.60 (1 H, dd, *J* 17.8 and 9.1, COCH), 2.32 (1 H, dd, *J* 17.8 and 8.9, COCH), 1.91 (1 H, dddd, *J* 9.1, 8.9, 7.0 and 6.6, CH), 1.80–1.57 (5 H, m), 1.41–1.09 (4 H, m), 1.39 (3 H, d, *J* 6.2, Me) and 1.03–0.90 (2 H, m); δ_C(100 MHz; $CDCl_3$) 176.54, 80.21, 48.33, 40.61, 32.98, 31.17, 30.21, 26.16, 26.07, 25.99 and 21.64; *m*/*z* 182 (M^+), 167 (M^+ − Me) and 136.

3-*Cyclohexyl*-5-*methyltetrahydrofuran*-2-*one* **7**. More polar compound: oil; ν_{max}($CHCl_3$)/cm^{-1} 2976, 2927, 2853 and 1767; δ_H(400 MHz; $CDCl_3$) 4.49–4.40 (1 H, m, OCH), 2.56 (1 H, ddd, *J* 12.5, 8.8 and 5.2, CH), 2.27 (1 H, ddd, *J* 12.5, 8.8 and 5.6, CH), 1.93–1.50 (6 H, m), 1.40 (3 H, d, *J* 6.1, Me) and 1.38–0.99 (6 H, m); δ_C(100 MHz; $CDCl_3$) 178.11, 74.75, 46.84, 37.23, 32.79, 31.26, 28.43, 26.23, 26.13, 26.02 and 20.91.

Less polar compound: oil; ν_{max}($CHCl_3$)/cm^{-1} 2976, 2924, 2853 and 1769; δ_H(400 MHz; $CDCl_3$) 4.64–4.56 (1 H, m, OCH), 2.56 (1 H, ddd, *J* 9.7, 7.3 and 5.2, CH), 2.23 (1 H, ddd, *J* 13.0, 7.3 and 7.3, CH), 1.89–1.56 (5 H, m), 1.86 (1 H, ddd, *J* 13.0, 9.7 and 5.5, CH), 1.39–1.02 (6 H, m) and 1.36 (3 H, d, *J* 6.4, Me); δ_C(100 MHz; $CDCl_3$ 178.66, 75.20, 45.66, 38.46, 31.68, 30.98, 28.89, 26.17, 26.01 (overlapping) and 21.51.

(4R,5S)-4-*Hexyl*-5-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* cis-**10** (R^1 = H, R^3 = n-C_6H_{13}). *Oil* (Found: C, 65.7; H, 10.2. $C_{11}H_{20}O_3$ requires C, 65.97; H, 10.07%); $[\alpha]_D^{26.0}$ +19.72 (*c* 1.02, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3434, 2925, 2857 and 1780; δ_H(400 MHz; $CDCl_3$) 4.54 (1 H, ddd, *J* 7.6, 4.5 and 3.0, OCH), 3.88 (1 H, dd, *J* 12.5 and 3.0, OCH), 3.80 (1 H, dd, *J* 12.5 and 4.5, OCH), 2.62 (1 H, m, CH), 2.53 (1 H, dd, *J* 17.1 and 8.6, COCH), 2.41 (1 H, dd, *J* 17.1 and 10.5, COCH), 2.09 (1 H, br s, OH), 1.60–1.42 (2 H, m), 1.20–1.41 (8 H, m) and 0.88 (3 H, t, *J* 7.0, Me); δ_C(100 MHz; $CDCl_3$) 177.03, 82.52, 61.95, 38.03, 34.61, 31.64, 29.22, 28.90, 28.21, 22.55 and 13.98; *m*/*z* 201 (M^+ + 1), 183 (M^+ − OH) and 169.

(4S,5S)-4-*Hexyl*-5-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* trans-**10** (R^1 = H, R^3 = n-C_6H_{13}). *Oil* (Found: C, 65.8; H, 10.3%); $[\alpha]_D^{27.2}$ +52.62 (*c* 0.94, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3433, 2927, 2857 and 1781; δ_H(400 MHz; $CDCl_3$) 4.21 (1 H, ddd, *J* 7.0, 4.6 and 2.7, OCH), 3.91 (1 H, dd, *J* 12.6 and 2.7, OCH), 3.66 (1 H, dd, *J* 12.6 and 4.6, OCH), 2.74 (1 H, dd, *J* 17.5 and 8.7, CH), 2.41 (1 H, ddddd, *J* 8.7, 8.6, 8.6, 7.0 and 5.7, CH), 2.25 (1 H, dd, *J* 17.5 and 8.6, CH), 1.82 (1 H, br s, OH), 1.66–1.20 (10 H, m) and 0.89 (3 H, t, *J* 7.0, Me); δ_C(100 MHz; $CDCl_3$) 176.67, 86.00, 63.27, 36.28, 35.28, 33.39, 31.60, 29.11, 27.38, 22.51 and 13.97; *m*/*z* (CI) 201 (M^+ + 1), 183 (M^+ − OH) and 169.

(5S)-3-*Hexyl*-5-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* **11** (R^1 = H, R^3 = n-C_6H_{13}). More polar compound: powder, m.p. 62.5–63.5 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3345, 3264, 2954, 2923, 2856 and 1753; δ_H(400 MHz; $CDCl_3$) 4.50 (1 H, dddd, *J* 10.2, 6.2, 5.0 and 2.8, OCH), 3.92 (1 H, dd, *J* 12.6 and 2.8, OCH), 3.63 (1 H, dd, *J* 12.6 and 5.0, OCH), 2.65 (1 H, dddd, *J* 11.7, 9.1, 9.0 and 4.8, CH), 2.34 (1 H, ddd, *J* 12.6, 9.0 and 6.2, CH), 1.80 (1 H, ddd, *J* 12.6, 11.7 and 10.2, CH), 1.72 (1 H, br s, OH), 2.00–1.21 (10 H, m) and 0.88 (3 H, t, *J* 6.9, Me); δ_C(100 MHz; $CDCl_3$) 178.70, 78.64, 63.86, 40.67, 31.59, 30.36, 29.69, 28.98, 27.27, 22.55 and 14.01; *m*/*z* (CI) 201 (M^+ + 1), 183 (M^+ − OH) and 169.

Less polar compound: oil; ν_{max}($CHCl_3$)/cm^{-1} 3434, 2929, 2858 and 1768; δ_H(400 MHz; $CDCl_3$) 4.60 (1 H, dddd, *J* 8.0, 4.9, 4.8 and 3.1, OCH), 3.86 (1 H, dd, *J* 12.3 and 3.1, OCH), 3.65 (1 H, dd, *J* 12.3 and 4.9, OCH), 2.69 (1 H, dddd, *J* 9.5, 9.5, 8.0 and 4.8, CH), 2.29 (1 H, ddd, *J* 13.0, 9.5 and 4.8, CH), 2.01 (1 H, ddd, *J* 13.0, 8.0 and 8.0, CH), 1.64 (1 H, br s, OH), 1.90–1.20 (10 H, m) and 0.88 (3 H, t, *J* 6.9, Me); *m*/*z* (CI) 201 (M^+ + 1), 183 (M^+ − OH) and 169.

(4S,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* cis-**10** (R^1 = H, R^3 = c-C_6H_{11}). *Needles*, m.p. 81.0–81.5 °C (from hexane) (Found: C, 66.4; H, 9.2. $C_{11}H_{18}O_3$ requires C, 66.64; H, 9.15%); $[\alpha]_D^{23.0}$ +24.2 (*c* 1.00, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3502, 2973, 2924, 2852 and 1746; δ_H(400 MHz; $CDCl_3$) 4.58 (1 H, ddd, *J* 6.9, 4.2 and 2.7, OCH), 3.92 (1 H, dd, *J* 12.7 and 2.7, OCH), 3.82 (1 H, dd, *J* 12.7 and 4.2, OCH), 2.53–2.10 (4 H, m), 1.74–1.65 (5 H, m), 1.53 (1 H, m), 1.34–1.12 (3 H, m) and 1.04–0.91 (2 H, m); δ_C(100 MHz; $CDCl_3$) 177.36, 82.03, 61.66, 44.55, 37.42, 32.90, 32.05 (overlapping), 26.20, 25.78 and 25.54; *m*/*z* 198 (M^+), 167 (M^+ − CH_2OH) and 83.

(4R,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* trans-**10** (R^1 = H, R^3 = c-C_6H_{11}). *Oil* (Found: C, 66.55; H, 9.3%); $[\alpha]_D^{28.0}$ +44.61 (*c* 0.39, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3400, 2925, 2852 and 1772; δ_H(400 MHz; $CDCl_3$) 4.40 (1 H, ddd, *J* 6.3, 5.0 and 2.6, OCH), 3.91 (1 H, dd, *J* 12.5 and 2.6, OCH), 3.62 (1 H, dd, *J* 12.5 and 5.0, OCH), 2.68 (1 H, dd, *J* 18.0 and 9.6, CH), 2.36 (1 H, dd, *J* 18.0 and 7.7, CH), 2.23 (1 H, dddd, *J* 9.6, 7.7, 7.7 and 6.3, CH), 1.79–1.10 (10 H, m) and 1.03–0.94 (2 H, m); δ_C(100 MHz; $CDCl_3$) 176.74, 83.92, 64.62, 41.34, 41.03, 32.76, 30.70, 30.10, 29.69, 26.17 and 25.98; *m*/*z* (CI) 199 (M^+ + 1), 181 (M^+ − OH), 167 (M^+ − CH_2OH) and 154.

(5S)-3-*Cyclohexyl*-5-(*hydroxymethyl*)*tetrahydrofuran*-2-*one*

11 (R^1 = H, R^3 = c-C_6H_{11}). More polar compound: needles, m.p. 78.0–79.0 °C (from hexane–AcOEt); $\nu_{max}(CHCl_3)/cm^{-1}$ 3434, 2925, 2853 and 1759; δ_H(400 MHz; $CDCl_3$) 4.46 (1 H, dddd, *J* 11.3, 6.3, 5.2 and 2.8, OCH), 3.91 (1 H, br d, *J* 12.4, OCH), 3.64 (1 H, br d, *J* 12.4, OCH), 2.61 (1 H, ddd, *J* 12.6, 9.2 and 5.2, CH), 2.14 (1 H, ddd, *J* 12.6, 9.2 and 6.3, CH), 2.02–1.51 (8 H, m) and 1.37–1.00 (5 H, m); δ_C(100 MHz; $CDCl_3$) 177.73, 78.36, 63.91, 46.04, 37.56, 31.58, 28.45, 26.25, 26.14, 26.05 and 25.23; *m/z* (CI) 199 ($M^+ + 1$), 181 ($M^+ - OH$), 167 ($M^+ - CH_2OH$) and 153.

Less polar compound: needles, m.p. 61.0–62.5 °C (from hexane–AcOEt); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3322, 2927, 2852, 1748 and 1720; δ_H(400 MHz; $CDCl_3$) 4.53 (1 H, dddd, *J* 7.7, 6.1, 4.9 and 3.0, OCH), 3.84 (1 H, ddd, *J* 12.3, 6.7 and 3.0, OCH), 3.62 (1 H, ddd, *J* 12.3, 6.1 and 4.9, OCH), 2.64 (1 H, ddd, *J* 9.2, 7.7 and 5.0, CH), 2.20 (1 H, br t, *J* 6.1, OH), 2.18–2.07 (2 H, m), 1.86–1.54 (6 H, m) and 1.35–0.95 (5 H, m); δ_C(100 MHz; $CDCl_3$) 178.94, 78.85, 64.67, 45.24, 38.91, 30.82, 28.68, 26.21, 26.04 (overlapping) and 25.95; *m/z* (CI) 199 ($M^+ + 1$), 181 ($M^+ - OH$), 167 ($M^+ - CH_2OH$) and 135.

(4R,5S)-5-(*Hydroxymethyl*)-4-(3-*phenylpropyl*)*tetrahydrofuran*-2-*one* cis-**10** (R^1 = H, R^3 = Ph[CH_2]$_3$). *Crystal plates*, m.p. 78.0–79.0 °C (from hexane–AcOEt) (Found: C, 71.6; H, 7.6. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74%); $[\alpha]_D^{26.8}$ +12.5 (*c* 0.51, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400, 3086, 3063, 3030, 2934, 2920, 2893, 2863, 2850, 1776 and 1763; δ_H(400 MHz; $CDCl_3$) 7.31–7.15 (5 H, m, Ph), 4.52 (1 H, ddd, *J* 7.7, 4.2 and 2.9, OCH), 3.87 (1 H, dd, *J* 12.5 and 2.9, OCH), 3.76 (1 H, dd, *J* 12.5 and 4.2, OCH), 2.71–2.58 (3 H, m), 2.53 (1 H, dd, *J* 17.1 and 8.6, COCH), 2.43 (1 H, dd, *J* 17.1 and 10.8, COCH), 2.31 (1 H, br s, OH) and 1.78–1.50 (4 H, m); δ_C(100 MHz; $CDCl_3$) 177.05, 141.63, 128.44, 128.29, 126.00, 82.41, 61.81, 37.96, 35.77, 34.56, 30.05 and 28.46; *m/z* 234 (M^+), 216, 203 ($M^+ - CH_2OH$), 185 and 156.

(4S,5S)-5-(*Hydroxymethyl*)-4-(3-*phenylpropyl*)*tetrahydrofuran*-2-*one* trans-**10** (R^1 = H, R^3 = Ph[CH_2]$_3$). *Oil* (Found: C, 71.9; H, 7.7%); $[\alpha]_D^{25.8}$ +52.0 (*c* 0.25, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3433, 2932, 2859 and 1776; δ_H(400 MHz; $CDCl_3$) 7.31–7.13 (5 H, m, Ph), 4.19 (1 H, ddd, *J* 7.0, 4.5 and 2.7, OCH), 3.89 (1 H, br d, *J* 12.6, OCH), 3.64 (1 H, ddd, *J* 12.6, 4.5 and 4.5, OCH), 2.74 (1 H, dd, *J* 17.5 and 8.8, COCH), 2.64 (2 H, dt, *J* 7.2 and 2.8, PhCH_2), 2.43 (1 H, ddddd, *J* 8.8, 8.7, 8.5, 7.0 and 5.5, CH), 2.23 (1 H, dd, *J* 17.5 and 8.5, COCH), 1.97 (1 H, br s, OH) and 1.71–1.39 (4 H, m); δ_C(100 MHz; $CDCl_3$) 176.15, 141.48, 128.48, 128.33, 126.08, 85.65, 63.26, 36.21, 35.65, 35.23, 32.82 and 29.21; *m/z* 234 (M^+), 216, 203 ($M^+ - CH_2OH$) and 185.

(5S)-5-(*Hydroxymethyl*)-3-(3-*phenylpropyl*)*tetrahydrofuran*-2-*one* **11** (R^1 = H, R^3 = Ph[CH_2]$_3$). More polar compound: oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3437, 3085, 3061, 3026, 2935, 2861 and 1768; δ_H(400 MHz; $CDCl_3$) 7.34–7.14 (5 H, m, Ph), 4.48 (1 H, dddd, *J* 11.0, 6.2, 5.0 and 2.8, OCH), 3.90 (1 H, ddd, *J* 12.6, 6.4 and 2.8, OCH), 3.61 (1 H, ddd, *J* 12.6, 6.8 and 3.0, OCH), 2.74–2.56 (3 H, m), 2.32 (1 H, ddd, *J* 12.6, 9.0 and 6.2, CH), 2.02 (1 H, br t, *J* 6.0, OH), 2.00–1.89 (1 H, m), 1.80–1.62 (3 H, m) and 1.59–1.45 (1 H, m); δ_C(75 MHz; $CDCl_3$) 178.53, 141.75, 128.38, 128.35, 125.92, 78.69, 63.69, 40.62, 35.69, 29.98, 29.56 and 29.20; *m/z* 234 (M^+), 203 ($M^+ - CH_2OH$) and 129.

Less polar compound: oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3434, 3085, 3061, 3026, 2938, 2861 and 1766; δ_H(400 MHz; $CDCl_3$) 7.32–7.13 (5 H, m, Ph), 4.57 (1 H, dddd, *J* 7.8, 4.8, 4.6 and 3.1, OCH), 3.85 (1 H, ddd, *J* 12.3, 6.5 and 3.1, OCH), 3.63 (1 H, ddd, *J* 12.3, 5.8 and 4.8, OCH), 2.78–2.58 (3 H, m), 2.29 (1 H, ddd, *J* 13.0, 9.6 and 4.6, CH), 2.04–1.64 (5 H, m) and 1.58–1.45 (1 H, m); δ_C(75 MHz; $CDCl_3$) 179.44, 141.69, 128.40, 128.36, 125.93, 78.42, 64.59, 39.48, 35.61, 30.86, 29.58 and 29.05.

(3S,4R,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*methyltetrahydrofuran*-2-*one* cis-**10** (3S; R^1 = Me, R^3 = c-C_6H_{11}). *Plates*, m.p. 106.0–107.0 °C (from hexane) (Found: C, 67.7; H, 9.4. $C_{12}H_{20}O_3$ requires C, 67.89; H, 9.50%); $[\alpha]_D^{27.2}$ +1.99 (*c* 0.60, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3438, 2929, 2853 and 1772; δ_H(400 MHz; $CDCl_3$) 4.63 (1 H, ddd, *J* 8.0, 8.0 and 3.2, OCH), 3.89–3.76 (2 H, m, OCH_2), 2.66 (1 H, dq, *J* 8.7 and 7.7, COCH), 2.42 (1 H, ddd, *J* 10.8, 8.7 and 8.0, CH), 2.14 (1 H, dd, *J* 8.8 and 4.3, OH), 1.80–1.62 (6 H, m), 1.44–0.91 (5 H, m) and 1.27 (3 H, d, *J* 7.7, Me); δ_C(100 MHz; $CDCl_3$) 180.33, 83.46, 62.65, 46.62, 36.27, 34.44, 32.05, 31.43, 26.33, 25.77, 25.72 and 12.50; *m/z* (CI) 213 ($M^+ + 1$), 195 ($M^+ - OH$) and 181.

(3R,4R,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*methyltetrahydrofuran*-2-*one* cis-**10** (3R; R^1 = Me, R^3 = c-C_6H_{11}). *Oil* (Found, C, 67.6; H, 9.5%); $[\alpha]_D^{29.2}$ +34.88 (*c* 1.33, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3443, 2928, 2853 and 1770; δ_H(400 MHz; $CDCl_3$) 4.54 (1 H, ddd, *J* 8.0, 4.2 and 2.7, OCH), 3.89 (1 H, m, OCH), 3.78 (1 H, m, OCH), 2.60 (1 H, dq, *J* 11.0 and 7.1, COCH), 2.19 (1 H, m, OH), 1.74 (1 H, ddd, *J* 11.0, 10.9 and 8.0, CH), 1.86–1.49 (6 H, m), 1.35–0.97 (5 H, m) and 1.29 (3 H, d, *J* 7.1, Me); δ_C(100 MHz; $CDCl_3$) 180.94, 80.47, 61.56, 51.51, 38.28, 37.63, 32.68, 31.77, 26.14, 26.02, 25.75 and 17.85; *m/z* (CI) 213 ($M^+ + 1$), 195 ($M^+ - OH$) and 181.

(3S,4S,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*methyltetrahydrofuran*-2-*one* trans-**10** (3S; R^1 = Me, R^3 = c-C_6H_{11}). *Plates*, m.p. 64.5–66.0 °C (from hexane–AcOEt) (Found: C, 67.9; H, 9.75%); $[\alpha]_D^{27.2}$ +8.34 (*c* 1.03, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3477, 2927, 2852 and 1769; δ_H(400 MHz; $CDCl_3$) 4.29 (1 H, ddd, *J* 7.7, 5.1 and 2.4, OCH), 3.90 (1 H, ddd, *J* 12.6, 6.8 and 2.4, OCH), 3.57 (1 H, ddd, *J* 12.6, 6.1 and 5.1, OCH), 2.50 (1 H, dq, *J* 8.9 and 7.2, COCH), 1.92 (1 H, t, *J* 6.7, OH), 1.89–1.66 (6 H, m), 1.42 (1 H, m), 1.31 (3 H, d, *J* 7.2, Me) and 1.31–0.98 (5 H, m); δ_C(100 MHz; $CDCl_3$) 179.44, 81.95, 64.60, 48.84, 40.46, 38.66, 30.97, 30.68, 26.27 (overlapping), 26.22 and 17.01; *m/z* (CI) 213 ($M^+ + 1$), 195 ($M^+ - OH$) and 181.

(3R,4S,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*methyltetrahydrofuran*-2-*one* trans-**10** (3R; R^1 = Me, R^3 = c-C_6H_{11}). *Oil* (Found: C, 67.4; H, 9.6%); $[\alpha]_D^{29.2}$ +15.13 (*c* 0.37, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3429, 2927, 2853 and 1768; δ_H(400 MHz; $CDCl_3$) 4.40 (1 H, ddd, *J* 5.4, 5.4 and 3.0, OCH), 3.89 (1 H, ddd, *J* 12.3, 7.1 and 3.0, OCH), 3.66 (1 H, ddd, *J* 12.3, 5.4 and 5.4, OCH), 2.86 (1 H, dq, *J* 8.6 and 7.5, COCH), 2.19 (1 H, ddd, *J* 8.6, 5.4 and 5.4, CH), 1.91 (1 H, m, OH), 1.80–1.49 (6 H, m), 1.36–0.93 (5 H, m), 1.22 (3 H, d, *J* 7.5, Me); δ_C(100 MHz; $CDCl_3$) 179.76, 81.09, 64.84, 44.69, 37.24, 36.28, 31.81, 29.07, 26.24, 26.17, 25.93 and 10.63; *m/z* (CI) 213 ($M^+ + 1$), 195 ($M^+ - OH$) and 181.

(3S,4R,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*isopropyltetrahydrofuran*-2-*one* cis-**10** (3S; R^1 = Pr^i, R^3 = c-C_6H_{11}). Needles, m.p. 79.0–82.0 °C (from hexane); $\nu_{max}(CHCl_3)/cm^{-1}$ 3399, 2930, 2854 and 1769; δ_H(400 MHz; $CDCl_3$) 4.49 (1 H, ddd, *J* 9.3, 5.4 and 3.2, OCH), 4.09 (1 H, dd, *J* 12.0 and 9.3, OCH), 3.84 (1 H, br d, *J* 12.0, OCH), 2.46 (1 H, ddd, *J* 7.3, 5.4 and 5.2, CH), 2.28 (1 H, dd, *J* 9.3 and 7.3, COCH), 2.01–1.97 (2 H, m), 1.81–0.88 (11 H, m), 1.25 (3 H, d, *J* 6.5, Me) and 1.04 (3 H, d, *J* 6.5, Me); δ_C(100 MHz; $CDCl_3$) 177.08, 83.41, 62.60, 51.32, 46.71, 36.19, 32.36, 29.92, 26.96, 26.69, 26.34, 24.97, 23.47 and 20.56; *m/z* 209 ($M^+ - CH_2OH$) and 198.

(3R,4R,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*isopropyltetrahydrofuran*-2-*one* cis-**10** (3R; R^1 = Pr^i, R^3 = c-C_6H_{11}). *Oil* (Found: C, 69.7; H, 10.5. $C_{14}H_{24}O_3$ requires C, 69.96; H, 10.07%); $[\alpha]_D^{27.6}$ +25.65 (*c* 2.69, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3434, 2929, 2853 and 1766; δ_H(400 MHz; $CDCl_3$) 4.55 (1 H, ddd, *J* 7.3, 5.7 and 3.6, OCH), 3.88 (1 H, dd, *J* 12.3 and 5.7, OCH), 3.84 (1 H, dd, *J* 12.3 and 3.6, OCH), 2.41 (1 H, dd, *J* 6.4 and 4.7, COCH), 2.29 (1 H, br s, OH), 2.19 (1 H, ddd, *J* 7.3, 6.5 and 6.4, CH), 1.98 (1 H, qqd, *J* 6.9, 6.8 and 4.7, CH), 1.80–1.50 (6 H, m), 1.33–0.92 (5 H, m), 1.12 (3 H, d, *J* 6.9, Me) and 0.98 (3 H, d, *J* 6.8, Me); δ_C(100 MHz; $CDCl_3$) 178.46, 81.45, 61.87, 49.28, 45.98, 37.40, 32.25, 30.15, 29.37, 26.14 (overlapping), 26.05, 21.00 and 18.10; *m/z* 209 ($M^+ - CH_2OH$) and 198.

(3S,4S,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*isopropyltetrahydrofuran*-2-*one* trans-**10** (3S; R^1 = Pr^i, R^3 = c-C_6H_{11}). *Needles*, m.p. 72.0–74.5 °C (from hexane) (Found: C, 69.7; H, 10.2%); $[\alpha]_D^{27.6}$ +10.1 (*c* 0.99, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3442, 2927, 2853 and 1763; δ_H(400 MHz; $CDCl_3$) 4.29 (1 H, ddd, *J* 6.4, 6.4 and 2.8, OCH), 3.79 (1 H, dd, *J* 12.4 and 2.8, OCH), 3.60 (1 H, dd, *J* 12.4 and 6.4, OCH), 2.40 (1 H, dd, *J* 7.3 and 4.3, COCH), 2.10–1.95 (2 H, m), 1.92 (1 H, ddd, *J* 7.3, 6.5 and 6.4, CH), 1.83–1.60 (6 H, m), 1.38 (1 H, m), 1.30–0.93 (4 H, m), 1.09 (3 H, d, *J* 6.9, Me) and 1.01 (3 H, d, *J* 6.9, Me); δ_C(100 MHz; $CDCl_3$) 177.79, 81.73, 65.36, 49.13, 44.21, 41.23, 31.04, 30.27, 29.77, 26.37, 26.29, 26.21, 20.47 and 18.62.

(3R,4S,5S)-4-*Cyclohexyl*-5-(*hydroxymethyl*)-3-*isopropyltetrahydrofuran*-2-*one* trans-**10** (3R; R^1 = Pr^i, R^3 = c-C_6H_{11}). Crystals, m.p. 100.0–101.5 °C (from hexane); $[\alpha]_D^{27.6}$ +25.60 (*c* 0.50, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3428, 2927, 2853 and 1766; δ_H(400 MHz; $CDCl_3$) 4.35 (1 H, ddd, *J* 5.9, 5.9 and 3.0, OCH), 3.86 (1 H, br d, *J* 12.1, OCH), 3.62 (1 H, br dd, *J* 12.1 and 5.9, OCH), 2.49 (1 H, dd, *J* 8.7 and 6.0, COCH), 2.21 (1 H, ddd, *J* 8.7, 6.4 and 5.9, CH), 2.04 (1 H, qqd, *J* 6.7, 6.7 and 6.0, CH), 1.95 (1 H, br s, OH), 1.82–1.48 (6 H, m), 1.35–0.84 (5 H, m), 1.13 (3 H, d, *J* 6.7, Me) and 1.10 (3 H, d, *J* 6.7, Me); δ_C(100 MHz; $CDCl_3$) 177.32, 81.26, 64.84, 48.13, 44.36, 35.75, 32.51, 29.71, 26.15 (overlapping), 26.07, 25.50, 22.67 and 19.53; *m*/*z* 241 (M^+ + 1), 225 (M^+ − Me) and 209.

(3R,1′R,4″S)-3-[1′-*Cyclohexyl*-1′-(2″,2″-*dimethyl*-1″,3″-*dioxolan*-4″-*yl*)*methyl*]*tetrahydrofuran*-2-*one* syn-**14a** (3R). *Crystals*, m.p. 121.0–122.0 °C (from hexane) (Found: C, 68.0; H, 9.5. $C_{16}H_{26}O_4$ requires C, 68.06; H, 9.28%); $[\alpha]_D^{26.8}$ +40.37 (*c* 2.13, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 2977, 2929, 2891, 2854 and 1757; δ_H(400 MHz; $CDCl_3$) 4.45–4.37 (2 H, m, OCH × 2), 4.15 (1 H, ddd, *J* 10.2, 8.7 and 7.1, OCH), 3.97 (1 H, dd, *J* 8.2 and 6.6, OCH), 3.59 (1 H, dd, *J* 8.2 and 7.6, OCH), 2.89 (1 H, ddd, *J* 11.7, 9.5 and 2.2, COCH), 2.34 (1 H, ddd, *J* 6.4, 6.4 and 2.2, CH), 2.26–2.11 (2 H, m, CH_2), 1.79–1.49 (5 H, m), 1.42 (3 H, s, Me), 1.38–1.10 (6 H, m) and 1.36 (3 H, s, Me); δ_C(75 MHz; $CDCl_3$) 179.54, 108.47, 74.82, 66.24, 66.16, 44.51, 37.65, 37.47, 32.37, 30.89, 26.53, 26.46, 26.42, 26.15, 24.99 and 24.86; *m*/*z* (CI) 283 (M^+ + 1), 267 (M^+ − Me) and 225.

A solution of *syn*-**14a** (3*R*) (7.5 mg, 0.028 mmol) in THF (1 cm^3) was added to a solution of LDA (0.052 mmol) in THF (0.5 cm^3) at −78 °C and the whole was stirred for 2 h at the same temperature. The reaction mixture was then treated with saturated aq. NH_4Cl and extracted with diethyl ether. The organic layer was washed with saturated aq. NaCl and dried over $MgSO_4$. Purification by column chromatography on silica gel gave recovered *syn*-**14a** (3*R*) and the epimer *syn*-**14a** (3*S*) (7.5 mg, quantitative yield, 1 : 1.6 by ^1H NMR spectroscopy) (*vide infra*).

(3S,1′R,4″S)-3-[1′-*Cyclohexyl*-1′-(2″,2″-*dimethyl*-1″,3″-*dioxolan*-4″-*yl*)*methyl*]*tetrahydrofuran*-2-*one* syn-**14a** (3S). Needles, m.p. 101.0–103.0 °C (from hexane) (Found: C, 67.8; H, 9.3%); $[\alpha]_D^{28.0}$ −25.60 (*c* 0.50, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 2991, 2956, 2927, 2854 and 1755; δ_H(400 MHz; $CDCl_3$) 4.34 (1 H, ddd, *J* 9.0, 7.8 and 3.6, OCH), 4.19–4.09 (2 H, m, OCH × 2), 3.96 (1 H, dd, *J* 8.0 and 6.7, OCH), 3.66 (1 H, dd, *J* 8.0 and 8.0, OCH), 2.71 (1 H, ddd, *J* 10.7, 10.7 and 2.4, COCH), 2.38–2.23 (2 H, m), 2.11 (1 H, ddd, *J* 4.4, 4.4 and 2.4, CH), 1.90–1.58 (6 H, m), 1.49–0.98 (5 H, m), 1.39 (3 H, s, Me) and 1.31 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 179.51, 108.69, 75.55, 67.76, 66.39, 45.06, 39.23, 37.13, 32.39, 31.35, 26.65 (overlapping), 26.49, 26.42, 26.34 and 24.98.

(1′S,4″S)-3-[1′-*Cyclohexyl*-1′-(2″,2″-*dimethyl*-1″,3″-*dioxolan*-4″-*yl*)*methyl*]*tetrahydrofuran*-2-*one* anti-**14a** (*mixture of diastereoisomers*). δ_H(400 MHz; $CDCl_3$) 4.42–4.30 and 4.22–4.03 (4 H for both isomers, m, OCH × 4), 3.65 (1 H for minor isomer, dd, *J* 7.4 and 7.4, OCH), 3.58 (1 H for major isomer, dd, *J* 7.7 and 7.7, OCH), 2.84 (1 H, for major isomer, ddd, *J* 11.2, 9.4 and 1.7, COCH), 2.62 (1 H for minor isomer, m, COCH), 2.42–2.12 (2 H for both isomers and 1 H for minor isomer, m), 1.90 (1 H for major isomer, m), 1.81–1.53 (6 H for both isomers, m), 1.50–0.83 (5 H for both isomers, m), 1.39 (3 H for major isomer, s, Me), 1.33 (3 H for minor isomer, s, Me), 1.31 (3 H for major isomer, s, Me) and 1.29 (3 H for minor isomer, s, Me).

(3R,1′R,4″S)-3-[1′-*Cyclohexyl*-1′-(2″,2″-*dimethyl*-1″,3″-*dioxolan*-4″-*yl*)*methyl*]*tetrahydro*-2H-*pyran*-2-*one* syn-**14b** (3R). *Crystals*, m.p. 115.0–115.5 °C (from hexane) (Found: C, 68.5; H, 9.4. $C_{17}H_{28}O_4$ requires C, 68.89; H, 9.52%); $[\alpha]_D^{29.2}$ +37.80 (*c* 1.00, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2983, 2930, 2853 and 1730; δ_H(400 MHz; $CDCl_3$) 4.40–4.23 (3 H, m, OCH × 3), 3.96 (1 H, dd, *J* 8.0 and 6.3, OCH), 3.64 (1 H, dd, *J* 8.0 and 7.9, OCH), 2.63 (1 H, ddd, *J* 11.5, 6.7 and 2.4, CH), 2.46 (1 H, ddd, *J* 8.0, 5.8 and 2.4, CH), 1.97–1.10 (15 H, m), 1.41 (3 H, s, Me) and 1.35 (3 H, s, Me); δ_C(75 MHz; $CDCl_3$) 172.91, 108.52, 75.40, 69.00, 67.36, 46.11, 41.48, 38.65, 33.03, 30.85, 26.78, 26.60, 26.57, 26.22, 25.29, 23.09 and 22.33; *m*/*z* (CI) 297 (M^+ + 1), 281 (M^+ − Me) and 239.

By a procedure similar to that used to epimerise *syn*-**14a** (3*R*), *syn*-**14b** (3*R*) was treated with LDA to give recovered *syn*-**14b** (3*R*) and its epimer *syn*-**14b** (3*S*) (4.6 : 1, quantitative yield) (*vide infra*).

(3S,1′R,4″S)-3-[1′-*Cyclohexyl*-1′-(2″,2″-*dimethyl*-1″,3″-*dioxolan*-4″-*yl*)*methyl*]*tetrahydro*-2H-*pyran*-2-*one* syn-**14b** (3S). *Needles*, m.p. 91.0–92.0 °C (from hexane) (Found: C, 69.0; H, 9.6. $C_{17}H_{28}O_4$ requires C, 68.89; H, 9.52%); $[\alpha]_D^{29.2}$ +37.80 (*c* 0.50, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2985, 2926, 2853 and 1728; δ_H(400 MHz; $CDCl_3$) 4.37 (1 H, m, OCH), 4.32–4.25 (1 H, m, OCH), 4.23 (1 H, ddd, *J* 8.0, 7.0 and 4.9, OCH), 4.01 (1 H, dd, *J* 8.0 and 7.0, OCH), 3.73 (1 H, dd, *J* 8.0 and 8.0, OCH), 2.67 (1 H, ddd, *J* 11.7, 4.5 and 2.4, COCH), 2.33 (1 H, ddd, *J* 7.2, 4.9 and 2.4, CH), 2.05–0.98 (15 H, m), 1.43 (3 H, s, Me) and 1.32 (3 H, s, Me); δ_C(75 MHz; $CDCl_3$) 173.98, 108.47, 75.90, 68.99, 68.14, 45.54, 40.98, 36.50, 31.94, 31.55, 26.62, 26.46, 26.40 (overlapping), 24.76, 23.14 and 22.71; *m*/*z* 281 (M^+ − Me), 253 and 239.

(1′S,4″S)-3-[1′-*Cyclohexyl*-1′-(2″,2″-*dimethyl*-1″,3″-*dioxolan*-4″-*yl*)*methyl*]*tetrahydro*-2H-*pyran*-2-*one* anti-**14b**. More polar compound (major isomer): *crystals*, m.p. 103.0–105.0 °C (from hexane) (Found: C, 69.1; H, 9.7%); $[\alpha]_D^{27.6}$ −3.60 (*c* 0.50, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2982, 2928, 2854 and 1728; δ_H(400 MHz; $CDCl_3$) 4.33 (1 H, m, OCH), 4.25 (1 H, m, OCH), 4.13 (1 H, dd, *J* 8.0 and 5.8, OCH), 3.97 (1 H, ddd, *J* 8.8, 8.0 and 5.8, OCH), 3.62 (1 H, dd, *J* 8.0 and 8.0, OCH), 2.62 (1 H, m, CH), 2.43 (1 H, ddd, *J* 9.0, 9.0 and 2.4, CH), 1.92–0.85 (15 H, m), 1.34 (3 H, s, Me) and 1.31 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 174.12, 108.37, 76.29, 71.30, 68.88, 49.38, 40.40, 37.92, 31.80, 30.84, 26.43 (overlapping), 26.26, 25.88, 25.29, 23.67 and 21.82; *m*/*z* (CI) 297 (M^+ + 1), 281 (M^+ − Me) and 256. Less polar compound (minor isomer): solid, m.p. 69.0–71.0 °C (from hexane); ν_{max}(neat)/cm^{-1} 2984, 2929, 2853 and 1728; δ_H(400 MHz; $CDCl_3$) 4.41–4.33 (1 H, m, OCH), 4.30–4.21 (2 H, m, OCH × 2), 4.11 (1 H, dd, *J* 8.0 and 6.2, OCH), 3.59 (1 H, dd, *J* 8.0 and 7.6, OCH), 2.83 (1 H, m, COCH), 2.17–0.88 (16 H, m), 1.39 (3 H, s, Me) and 1.31 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 174.12, 108.37, 76.29, 71.30, 68.88, 49.38, 40.40, 37.92, 31.80, 30.84, 26.43 (overlapping), 26.26, 25.88, 25.29, 23.67 and 21.82; *m*/*z* 281 (M^+ − Me) and 239.

General Procedure for the Radical Cyclisation.—Under argon, a solution of iodo ester **16** (99.5 mg, 0.25 mmol), Bu_3SnH (109.1 mg, 0.38 mmol) and AIBN (21 mg, 0.13 mmol) in benzene (19 cm^3) was refluxed for 3 h. After removal of the solvent, the residue was treated with KF according to Method A (see above). Purification by column chromatography and MPLC on silica gel gave the cyclisation products **17** and **18**.

Ethyl (1S,2R,4′S)-2-(2′,2′-*dimethyl*-1′,3′-*dioxolan*-4′-*yl*)*cy*-

clohexanecarboxylate (1S, 2R)-**17**. *Oil* (Found: C, 65.4; H, 9.65. $C_{14}H_{24}O_4$ requires C, 65.60; H, 9.44%); $[\alpha]_D^{27.6}$ +35.60 (*c* 2.00, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2985, 2935, 2840 and 1732; δ_H(400 MHz; $CDCl_3$) 4.14–3.99 (1 H, overlapping, OCH), 4.11 (2 H, q, *J* 7.1, OCH_2Me), 4.02 (1 H, dd, *J* 7.6 and 5.8, OCH), 3.56 (1 H, dd, *J* 7.6 and 7.6, OCH), 2.53 (1 H, br ddd, *J* 4.0, 4.0 and 4.0, COCH), 2.00–1.91 (1 H, m, CH), 1.84–1.21 (8 H, m), 1.38 (3 H, s, Me), 1.34 (3 H, s, Me) and 1.25 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 174.10, 108.51, 77.64, 68.20, 60.12, 43.16, 41.77, 28.03, 26.92, 25.77, 25.67, 24.76, 22.41 and 14.23; *m*/*z* 241 (M^+ − Me) and 211.

By a procedure similar to that used to epimerise *syn*-**14a** (3*R*), (1*S*,2*R*)-**17** was treated with LDA to give recovered (1*S*,2*R*)-**17** and its 1-epimer (1*R*,2*R*)-**17** (46% yield; 1:1.8 by ^{1}H NMR spectroscopy) (*vide infra*).

Ethyl (1R,2R,4'S)-2-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*cyclohexanecarboxylate* (1R,2R)-**17**. Oil [Found: (M^+ − Me), 241.1448. $C_{13}H_{21}O_4$ requires *m*/*z* 241.1440]; $[\alpha]_D^{27.2}$ −41.42 (*c* 0.98, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2984, 2936, 2859 and 1731; δ_H(400 MHz; $CDCl_3$) 4.13 (2 H, qd, *J* 7.2 and 1.4, OCH_2Me), 4.00 (1 H, ddd, *J* 7.9, 6.5 and 4.1, OCH), 3.89 (1 H, dd, *J* 7.9 and 6.5, OCH), 3.62 (1 H, dd, *J* 7.9 and 7.9, OCH), 2.30 (1 H, ddd, *J* 11.8, 10.8 and 3.7, COCH), 1.96–1.70 (5 H, m), 1.51–1.09 (4 H, m), 1.37 (3 H, s, Me), 1.31 (3 H, s, Me) and 1.26 (3 H, t, *J* 7.2, CH_2Me); δ_C(100 MHz; $CDCl_3$) 175.98, 108.61, 77.48, 66.82, 60.17, 46.16. 40.80, 30.31, 26.20, 25.58, 25.35, 25.23, 25.17 and 14.21; *m*/*z* 241 (M^+ − Me) and 199.

Ethyl (1R,2S,4'S)-2-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*cyclohexanecarboxylate* (1R,2S)-**17**. *Oil* (Found: C, 65.6; H, 9.7. $C_{14}H_{24}O_4$ requires C, 65.60; H, 9.44%); $[\alpha]_D^{28.0}$ −14.41 (*c* 0.68, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2984, 2935, 2863 and 1730; δ_H(400 MHz; $CDCl_3$) 4.21 (1 H, ddd, *J* 9.0, 7.7 and 5.8, OCH), 4.19–4.06 (2 H, m, OCH_2Me), 4.02 (1 H, dd, *J* 7.7 and 5.8, OCH), 3.55 (1 H, dd, *J* 7.7 and 7.7, OCH), 2.88 (1 H, ddd, *J* 4.1, 4.1 and 4.1, COCH), 2.07–1.97 (1 H, m, CH), 1.77–1.62 (3 H, m), 1.62–1.45 (3 H, m), 1.41–1.22 (2 H, m), 1.37 (3 H, s, Me), 1.31 (3 H, s, Me) and 1.26 (3 H, t, *J* 7.2, CH_2Me); δ_C(100 MHz; $CDCl_3$) 174.34, 108.58, 68.78, 59.77, 43.01, 41.24, 28.01, 26.95, 25.69, 24.95, 24.87, 22.64 and 14.27 (a peak overlapped with those of $CDCl_3$); *m*/*z* 257 (M^+ + 1) and 239.

Ethyl (1S,2S,4'S)-2-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*yl*)*cyclohexanecarboxylate* (1S,2S)-**17**. Oil; ν_{max}($CHCl_3$)/cm^{-1} 2984, 2934, 2860 and 1735; δ_H(400 MHz; $CDCl_3$) 4.17–4.05 (2 H, m, OCH_2Me), 4.00 (1 H, dd, *J* 7.8 and 6.2, OCH), 3.89 (1 H, ddd, *J* 7.8, 7.6 and 6.2, OCH), 3.63 (1 H, dd, *J* 7.8 and 7.8, OCH), 2.13 (1 H, ddd, *J* 11.5, 10.7 and 3.7, COCH), 1.99–1.82 (2 H, m), 1.80–1.62 (2 H, m), 1.59–1.46 (1 H, m, CH), 1.40–1.13 (3 H, m), 1.35 (3 H, s, Me), 1.31 (3 H, s, Me), 1.26 (3 H, t, *J* 7.1, CH_2Me) and 0.99 (1 H, m); δ_C(100 MHz; $CDCl_3$) 175.82, 108.83, 78.89, 67.37, 60.11, 47.35, 42.28, 29.67, 26.64, 26.27, 25.66, 25.12, 24.75 and 14.18; *m*/*z* 241 (M^+ − Me), 227 (M^+ − Et) and 211 (M^+ − OEt).

Ethyl (4'S)-1-(2',2'-*dimethyl*-1',3'-*dioxolan*-4'-*ylmethyl*)*cyclopentanecarboxylate* **18**. Oil $[\alpha]_D^{28.0}$ +6.60 (*c* 1.00, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2983, 2940, 2874 and 1727; δ_H(400 MHz; $CDCl_3$) 4.11 (2 H, qd, *J* 7.2 and 1.8, OCH_2Me), 4.04 (1 H, m, OCH), 4.00 (1 H, dd, *J* 7.3 and 5.8, OCH), 3.43 (1 H, dd, *J* 7.3 and 7.3, OCH), 2.15 (2 H, m), 2.02 (1 H, dd, *J* 14.0 and 6.5, CH), 1.83 (1 H, dd, *J* 14.0 and 5.3, CH), 1.68–1.55 (5 H, m), 1.45 (1 H, m, CH), 1.36 (3 H, d, *J* 0.4, Me), 1.31 (3 H, d, *J* 0.5, Me) and 1.25 (3 H, t, *J* 7.2, CH_2Me); δ_C(100 MHz; $CDCl_3$) 177.29, 108.49, 74.13, 70.03, 60.44, 52.53, 42.47, 36.52, 36.23, 26.82, 25.81, 24.63, 24.57 and 14.15; *m*/*z* 241 (M^+ − Me), 211 (M^+ − OEt) and 199.

[(1S,2R)-2-(*Hydroxymethyl*)*cyclohexyl*]*methyl acetate* **19**. *Oil* (Found: C, 64.3; H, 10.0. $C_{10}H_{18}O_3$ requires C, 64.49; H, 9.74%); $[\alpha]_D^{24.0}$ +28.09 (*c* 0.61, $CHCl_3$) {lit.,[14] *ent*-**19**: $[\alpha]_D^{20.0}$ −19.1 (78%ee)} ν_{max}(neat)/cm^{-1} 3422, 2928, 2860 and 1739; δ_H(400 MHz; $CDCl_3$) 4.16 (1 H, dd, *J* 11.1 and 6.5, OCH), 4.03 (1 H, dd, *J* 11.1 and 7.6, OCH), 3.62 (1 H, dd, *J* 11.0 and 7.6, OCH), 3.55 (1 H, dd, *J* 11.0 and 7.1, OCH), 2.10 (1 H, m, CH), 2.05 (3 H, s, COMe), 1.88 (1 H, m, CH), 1.79 (1 H, br s, OH) and 1.68–1.21 (8 H, m, CH_2 × 4); δ_C(100 MHz; $CDCl_3$) 171.21, 64.73, 63.83, 40.54, 35.66, 27.09, 25.72, 24.07, 22.95 and 21.00; *m*/*z* 143 (M^+ − CH_3CO) and 125.

X-Ray Crystallography.—*Compound* cis-**10** (R^1 = H, R^3 = Ph[CH_2]$_3$): $C_{14}H_{18}O_3$, *M* = 234.29, orthorhombic, space group $P2_12_12_1$, *a* = 7.865(6), *b* = 30.50(2), *c* = 5.434(2) Å, *Z* = 4, *V* = 1304(1) Å^3, D_c = 1.194 g cm^{-3}, μ(Cu-Kα) = 6.35 cm^{-1}, crystal size = 0.50 × 0.20 × 0.05 mm, number of reflections ($2\theta \leqslant 120.3°$) = 1201, *R* = 0.033 for 702 reflections with $I > 3.00\sigma(I)$.

Compound syn-**14a** (3R): $C_{16}H_{26}O_4$, *M* = 282.38, orthorhombic, space group $P2_12_12$, *a* = 15.060(2), *b* = 18.75(1), *c* = 5.48(1) Å, *Z* = 4, *V* = 1549(2) Å^3, D_c = 1.211 g cm^{-3}, μ(Cu-Kα) = 6.92 cm^{-1}, crystal size = 0.50 × 0.10 × 0.10 mm, number of reflections ($2\theta \leqslant 120.2°$) = 1390, *R* = 0.045 for 952 reflections with $I > 3.00\sigma(I)$.

Compound syn-**14b** (3R): $C_{17}H_{28}O_4$, *M* = 296.41, orthorhombic, space group $P2_12_12_1$, *a* = 15.244(2), *b* = 16.682(2), *c* = 6.447(2) Å, *Z* = 4, *V* = 1639.5(4) Å^3, D_c = 1.201 g cm^{-3}, μ(Cu-Kα) = 6.76 cm^{-1}, crystal size = 0.30 × 0.15 × 0.05 mm, number of reflections ($2\theta \leqslant 120.1°$) = 1463, *R* = 0.043 for 1218 reflections with $I > 3.00\sigma(I)$.

Intensity data were collected on a Rigaku AFC-5R diffractometer in ω–2θ scan mode using Cu-Kα radiation. Full lists of fractional atomic coordinates, bond lengths and angles, and thermal parameters have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.*

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* See Instructions for Authors, in the January issue.

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