Reactions of 1,3-Dioxolanes with Iodine Monochloride: Formation of Chlorohydrin Esters and Diol Monoesters

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2-Mono-substituted 1,3-dioxolanes are oxidised by iodine monochloride to the appropriate 2-substituted 1,3-dioxolan-2-ylium ions, whose stability is dependent upon the presence and nature of substituents on C-4 and C-5. Some dioxolanylium ions are labile and under the reaction conditions afford chlorohydrin esters, with inversion of configuration taking place at the ring carbon attacked by chloride. Others are stable under the reaction conditions and may be converted on aqueous workup to diol monoesters with retention of configuration at C-4 and C-5. The effect of substituents and reaction conditions on these competing reactions are described. The stereo- and regio-chemistry of both hydroxy- and chloro-ester formation was confirmed through NMR studies, which necessitated the prior detailed analysis of the ^1H and ^{13}C spectra associated with the acyloxy sidechains of the relevant esters.

We have reported [1,2] that 1,3-dioxolanes are oxidised by iodine monochloride to 1,3-dioxolan-2-ylium ions, some of which can be isolated as stable dichloroiodate(I) salts. Hydrolysis of these salts has been shown to afford 1,2-diol monoesters.[2] In contrast, certain dioxolanylium ions are labile and are converted under the reaction conditions to chlorohydrin esters. We now report on the scope of these reactions as a route to chlorohydrin esters and diol monoesters.

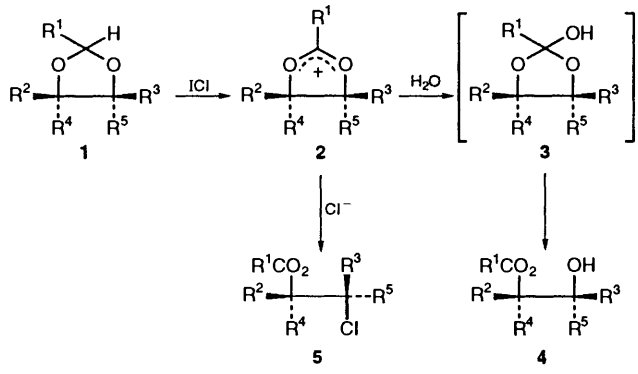
Results and Discussion

Product Studies.—A series of 2-mono-substituted 1,3-dioxolanes **1a–u** and the dioxane **1v** were treated with iodine monochloride under a variety of conditions and their products determined (Table 1).

At room temperature, those dioxolanes which are unsubstituted at the 4- and 5-positions (**1a–c**) or mono-substituted at one of these sites (**1d** and **1f**) are found to be rapidly converted under the reaction conditions to the appropriate 2-chloroalkyl esters **5a–f**. However, if the reactions are quenched with water within 3–5 min of completing the addition of iodine monochloride, predominantly 1,2-diol monoesters **4b–g** are obtained; only dioxolane **1a** failed to deliver any diol monoester. The unsymmetrical dioxolane **1f** forms the secondary hydroxy- and chloro-esters **4f** and **5f**, respectively, in preference to its primary isomers **4g** and **5g**. The dioxolane **1d** behaves similarly with respect to chloroester formation, while its primary hydroxyester **4e** is slightly preferred to the secondary isomer **4d**.

With the exception of **1k**, the 4,5-disubstituted dioxolanes **1h–m** do not produce chlorohydrin esters at room temperature, and upon aqueous workup afford only the diol monoesters **4h–m** in good yields. However, in refluxing chloroform, chlorohydrin esters **5h–m** are obtained in yields varying from moderate to near quantitative. In the case of the 4,4,5,5-tetramethyl-substituted dioxolanes **1o–u**, chlorohydrin ester formation is completely inhibited even at elevated temperatures and only pinacol monoesters are obtained after aqueous workup. The dioxane **1v** is found to react similarly to the dioxolane **1c**.

Mechanistic Studies.—A plausible mechanism for the formation of the hydroxy- and chloro-esters is outlined in Scheme 1. Hydrolysis of the dioxolanylium ion clearly proceeds *via* the hydrogen ortho ester **3** since we have established that conversion of dioxolane to hydroxyester occurs with retention of configuration at C-4 and C-5. For example, the dioxolanes **1j**, **1k** and **1m** were shown to afford exclusively the *erythro*-, *threo*- and *trans*-diol monobenzoates **4j**, **4k** and **4m**, respectively.



Scheme 1

	R^1	R^2	R^3	R^4	R^5
a	H	H	H	H	H
b	Me	H	H	H	H
c	Ph	H	H	H	H
d[a]	Ph	Me	H	H	H
e[b]	Ph	H	Me	H	H
f[a]	Ph	CH_2Cl	H	H	H
g[b]	Ph	H	CH_2Cl	H	H
h[c]	Pr	Me	Me	H	H
i[c]	Ph	Me	Me	H	H
o	H	Me	Me	Me	Me
p	Me	Me	Me	Me	Me
q	Pr	Me	Me	Me	Me
r	Ph	Me	Me	Me	Me
s	*p*-MeO-C_6H_4	Me	Me	Me	Me
t	*p*-O_2N-C_6H_4	Me	Me	Me	Me

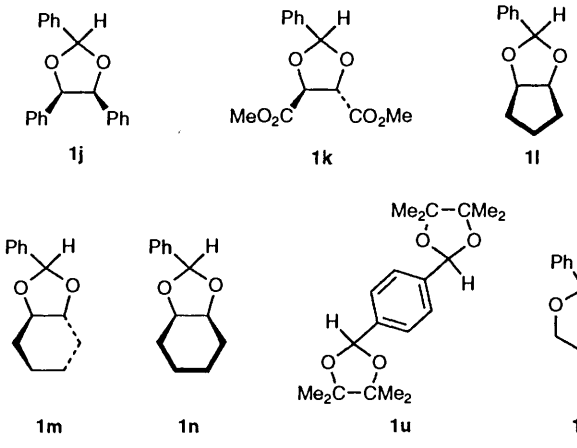
[a] Dioxolanes **1d** and **1f** consist of mixtures of *cis* and *trans* isomers. [b] Dioxolanes **1e** and **1g** are identical to **1d** and **1f**, respectively. [c] Dioxolane **1c** consists of a mixture of the *trans*, 4,5-*cis*-2-*syn* and 4,5-*cis*-2-*anti* isomers **6**, **7** and **8**, respectively.

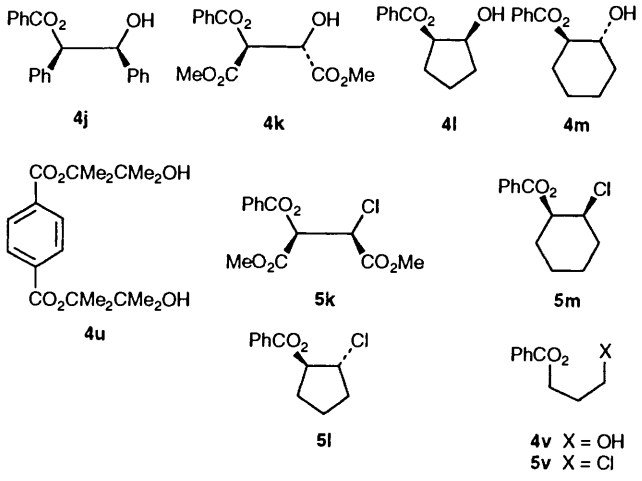
It is therefore possible to assign the configurations of hydroxyesters obtained in other cases. For example, dioxolane **1i** which consisted of an inseparable 69:31 mixture of the 4,5-*trans* and 4,5-*cis* isomers, afforded a 69:31 mixture of isomeric hydroxyesters. The major isomer is therefore assigned the *threo* configuration **1l** and the minor, *erythro* **4i**. Similarly, the

Table 1 Reaction of 2-mono-substituted 1,3-dioxolanes and related compounds with iodine monochloride: reaction conditions and product yields

Dioxolane	T/°C[a]	Time	Hydroxyester (%)	Chloroester (%)
1a		3 h	**4a**, 0	**5a**, 43
1b	0	3 min	**4b**, 26	**5b**, 7
1b		2 h		**5b**, 85
1c		5 min	**4c**, 84	**5c**, 5
1c		40 min	**4c**, 0	**5c**, 99
1d		5 min	**4d** + **4e**, 98[b,c]	**5d** + **5e**, 2[b]
1d	reflux	1 h		**5d** + **5e**, 92[b,d]
1f		5 min	**4f** + **4g**, 62[b,e]	**5f**, 30
1f		5 h	**4f** + **4g**, 12[b]	**5f**, 88
1h		1 h	**4h**, 97[f]	
1h	reflux	1 h		**5h**, 92[f]
1i		1 h	**4i**, 97[b,g]	
1i	reflux	1 h		**5i**, 94[b,h]
1j		1 h	**4j**, 54	
1k		1 h	**4k**, 20	**5k**, 29
1k	reflux	1 h	**4k**, 26	**5k**, 74
1l	55–60	1.5 h	**4l**, 52	**5l**, 26
1m		1 h	**4m**, 68	
1m	reflux	2 h	**4m**, 42	**5m**, 52
1o		1 h	**4o**, 75	**5o**, 0
1p		1 h	**4p**, 74	**5p**, 0
1q		1 h	**4q**, 100	**5q**, 0
1r		1 h	**4r**, 95	**5r**, 0
1r	reflux	1 h	**4r**, 80	**5r**, 0
1s		30 min	**4s**, 69	**5s**, 0
1t		1 h	**4t**, 81	**5t**, 0
1u		1 h	**4u**, 85	
1v	0	5 min	**4v**, 84	**5v**, 0
1v		2 h	**4v**, 0	**5v**, 96

[a] Room temp., unless specified otherwise (reflux reactions were carried out in $CHCl_3$). [b] Inseparable mixture. [c] **4d**:**4e** Isomer ratio 46:54. [d] **5d**:**5e** Isomer ratio 77:23. [e] **4f**:**4g** Isomer ratio 65:35. [f] Mixture of *threo* and *erythro* isomers, isomer ratio not determined. [g] **11**:**4i** isomer ratio 69:31. [h] **5i**:**12** isomer ratio 31:69.





hydroxyester **4l** resulting from the *cis*-fused dioxolane **1l** is assigned the *cis* configuration.

A degree of regioselectivity is observed in the formation of those hydroxyesters derived from the unsymmetrical dioxolanes **1d** and **1f**. Comparisons can be drawn between the ratios of the hydroxyester isomers **4d** and **4e** resulting from the dioxolane **1d** in our work, and those observed elsewhere for the conventional benzoylation of propane-1,2-diol. For example, treatment of propane-1,2-diol with benzoyl chloride in the presence of pyridine followed by phenyldimethylsilyl chloride has been reported[3] to give the silyl derivatives of **4d** and **4e** in a ratio of 9:91. Hydrolysis with dilute hydrochloric acid then results in a reversal of this ratio to 70:30.[3] The latter effect has been ascribed to acid-catalysed isomerisation of the diol monoesters[3,4] which proceeds *via* a hydrogen orthoester intermediate.[3,4,5] In our case the isomeric hydroxyesters are proposed to result from an identical intermediate, **3**, but interestingly, the isomer ratio resulting from the dioxolane **1d** is reversed.

We have established that chloroester formation takes place with inversion of configuration at the carbon atom attacked by chloride. The chloroester **5l** obtained from the *cis*-fused dioxolane **1l** was found to be identical with authentic *trans*-2-chlorocyclopentyl benzoate. Furthermore, the dioxolane **1i** afforded two isomeric chloroesters in the ratio 69:31. The same isomers were obtained except in a 35:65 ratio when the 31:69 mixture of *erythro*- and *threo*-butane-2,3-diol monobenzoate described earlier was treated with thionyl chloride. Since thionyl chloride is known[6] to convert alcohols to alkyl chlorides stereoselectively with retention of configuration, the major diastereoisomer obtained from the thionyl chloride reaction is therefore also *threo* **5i** and the minor, *erythro* **12**. However, since the major chloroester diastereoisomer obtained directly from this dioxolane with iodine monochloride is *erythro*, inversion of configuration on ring-opening of the dioxolanylium ion by chloride is clearly indicated.

The observed inhibition of chloroester formation with increasing substitution at the 4- and 5-positions of the dioxolane is also consistent with an S_N2-type reaction. The rate of chloride attack would be expected to be retarded by α-substituents as a result of steric hindrance.

However, the inhibition of chlorohydrin ester formation with increasing alkylation is apparently not exclusively steric in origin. Since the stability of a 1,3-dioxolan-2-ylium ion is highly sensitive to the electronic influences of substituents on the 4- and 5-positions,[2] the introduction of electron-releasing alkyl groups would be expected to stabilise the ion and consequently lower its reactivity towards chloride. The converse would be true of electron-withdrawing substituents, and hence it is found that at room temperature the 4,5-bis(methoxycarbonyl)dioxolane **1k** affords chlorohydrin ester more rapidly than its 4,5-dimethyl-substituted analogue **1i**, despite being less reactive.[2]

Also, it is evident that the 4-chloromethyldioxolane **1f** forms chloroester faster than the 4-methyldioxolane **1d** does (Fig. 1). In the early stages of these reactions the reverse is true, but this can be ascribed to a slower rate of formation of the 4-chloromethyldioxolanylium ion **2f** compared with **2d**; unreacted dioxolane **1f** was still apparent after 10 min whereas **1d** had reacted completely by the time the first aliquot was taken after 2 min, which confirms the sensitivity of dioxolanylium ion stability to the nature of substituents present on C-4 and C-5. Since an examination of space-filling models shows that the chloromethyl and methoxycarbonyl groups would offer at least as much steric hindrance to an approaching chloride ion as a

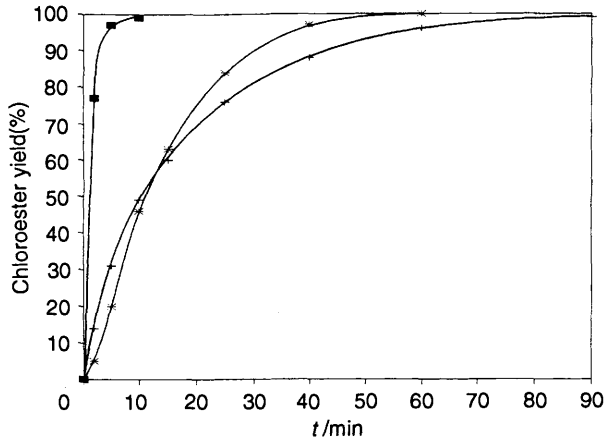


Fig. 1 Relative rates of chloroester formation from the reaction of dioxolanes **1c** (■) (at 0° C), **1d** (+) and **1f** (*) (both at 25 °C) with iodine monochloride

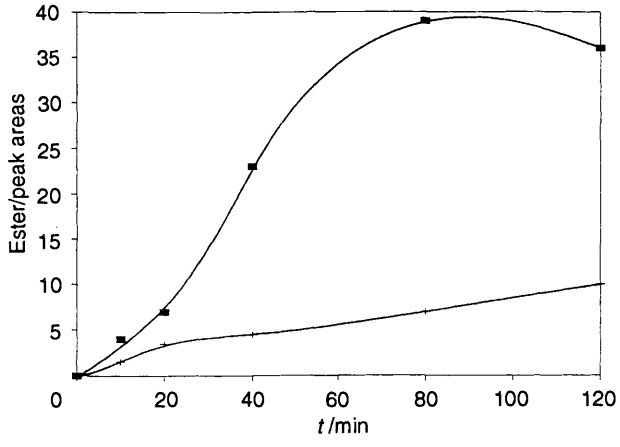


Fig. 2 Relative rates of hydroxy- (■) and chloroester (+) formation from the reaction of the *trans*-fused dioxolane **1m** with iodine monochloride

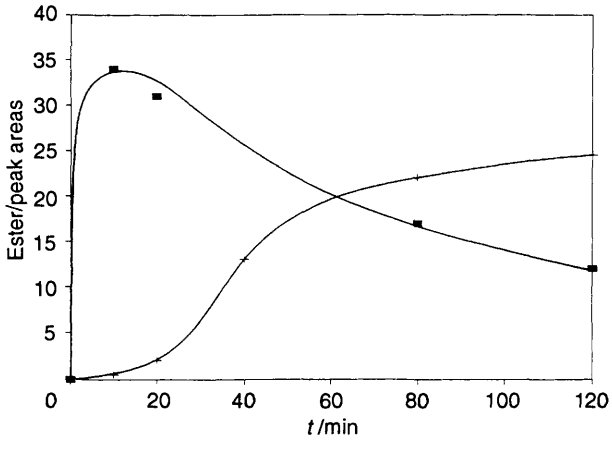


Fig. 3 Relative rates of hydroxy- (■) and chloro-ester (+) formation from the reaction of the *cis*-fused dioxolane **1n** with iodine monochloride

methyl group does, the greater reactivity of the dioxolanylium ions derived from **1f** and **1k** must be due to the destabilising effect of these electron-withdrawing substituents.

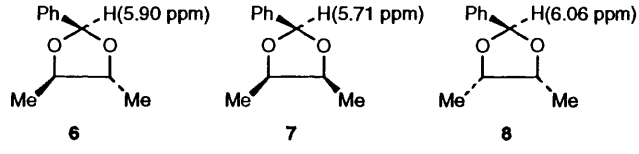
On comparing the relative rates of the reactions of the *trans*- and *cis*-fused bicyclic dioxolanes **1m** and **1n** (Figs. 2 and 3), two features become apparent. Firstly, as measured by the rate of combined ester formation, the *cis*-fused dioxolane **1n** is clearly oxidised faster than the *trans*-fused isomer **1m** to their respective dioxolanylium ions. Secondly, the *cis*-fused dioxolanylium ion is converted to chlorohydrin ester faster than the corresponding *trans*-fused ion is.

An examination of models shows that the accessibility of the 2-position towards the reagent is not likely to differ significantly between the two dioxolanes. There is abundant evidence[2] that 1,3-dioxolan-2-ylium ions are stabilised largely through mesomeric interactions with the oxygen atoms and these interactions are optimised when the dioxolane ring is planar, since overlap of the vacant p-orbital on C-2 and those containing lone pairs on the oxygen atoms is then maximised. This geometry is easily attainable in the conformationally flexible *cis*-fused system provided the cyclohexane ring adopts a half-chair or boat conformation, but not at all in the rigid *trans*-isomer. The activation energy of the oxidation process is consequently raised in the latter case, leading to a slower rate of formation of dioxolanylium ion.

Models also show that the C-4 and C-5 positions in the *trans*-fused dioxolanylium ion are sterically shielded against chloride attack by the transannular carbons of the cyclohexane ring, leading to a retarded rate of chlorohydrin ester formation. The same degree of steric hindrance is not apparent in the *cis*-isomer and, indeed, if the boat conformation is adopted by the cyclohexane ring, 'backside' attack by chloride on the C-4 and C-5 positions is unlikely to be significantly more hindered than in the dioxolanylium ion **2i**.

Elucidation of Stereochemistry.—The stereochemistry of hydroxyester formation was readily determined through characterisation of selected hydroxyesters such as **4j**, **4k** and **4m** whose properties had been reported previously in the chemical literature.

The inversion of configuration associated with chloroester formation was established initially by GLC comparison of the chloroester **5l** obtained from the *cis*-fused dioxolane **1l** with authentic *trans*-2-chlorocyclopentyl benzoate. However, confirmation of the stereochemistry of chloroester formation was afforded by the following NMR study. A mixture of (2*R*,3*R*)-, (2*S*,3*S*)- and *meso*-butane-2,3-diol was used in the synthesis of 4,5-dimethyl-2-phenyl-1,3-dioxolane **1i** and consequently three geometrical isomers, namely, *trans* **6***, 4,5-*cis*-2-*syn* **7** and 4,5-*cis*-2-*anti* **8** were obtained. These isomers were distinguished on the



basis of differences in the chemical shifts[7] of their C-2 protons, and from their integrals an isomer ratio for **6**:**7**:**8** of 69:20:11 was obtained.

Oxidation of this mixture of isomers with iodine monochloride would be expected to result in a 69:31 mixture of the *trans*-4,5-dimethyl- and *cis*-4,5-dimethyl-2-phenyl-1,3-dioxolanylium ions **9** and **10**, respectively. This was confirmed by a ^{1}H

NMR spectrum of the crude reaction mixture obtained shortly after adding iodine monochloride to the dioxolane **1i** and prior

* Only one enantiomer of the *trans* isomer **6** is shown.

Table 2 Selected ^{13}C chemical shifts (and intensities) for hydroxyesters **11** and **4i**

	11	**4i**
CH_3CHOH	18.05 (28.38)	16.51 (12.56)
CH_3CHOBz	20.78 (28.59)	19.73 (11.00)
CH_3CHOH	72.06 (35.55)	71.77 (14.64)
CH_3CHOBz	77.19 (36.68)	76.95 (16.51)

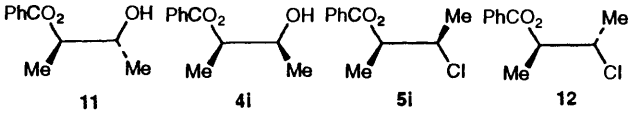
Table 3 Selected ^{13}C chemical shifts (and intensities) for chloroesters **12** and **5i**

	12	**5i**
CH_3CHCl	18.57 (29.26)[a] [17.41][b]	17.58 (17.67) [37.39]
CH_3CHOBz	22.75 (29.89)[c]	22.80 (19.17)[c]
CH_3CHCl	60.95 (16.32) [9.03]	61.36 (9.69) [20.53]
CH_3CHOBz	75.23 (19.72) [10.13]	75.65 (11.15) [23.32]

[a] Hydroxyesters **11** and **4i**, $SOCl_2$. [b] Dioxolane **1i**, ICl, heat. [c] Signals not resolved.

to workup. In addition to some chloroester and unreacted dioxolane, there was evidence for the presence of dioxolanylium ions. Two broad, ill-resolved doublets evident at 1.85 and 2.00 ppm (integral ratio 32:68) were assigned to the methyl groups in **10** and **9**, respectively, and two broad unresolved signals at 5.62 and 6.15 ppm (integral ratio 73:27) to the C-4 and C-5 protons in **9** and **10**, respectively. The phenyl protons were also shifted downfield with a triplet (2 H) at 7.78, triplet (1 H) at 8.09, and doublet (2 H) at 8.36 ppm assigned to the *meta-*, *para-* and *ortho*-protons, respectively.

Hydrolysis of this mixture of dioxolanylium ions was found to give a 69:31 mixture of two hydroxyesters. Since hydrolysis has been shown earlier to proceed with retention of configuration at C-4 and C-5, the major isomer was therefore assigned the *threo* **11** and the minor isomer the *erythro* **4i** configuration.



Small differences in the chemical shifts of the alkyl methine protons of these isomeric hydroxyesters were evident in a 200 MHz spectrum, but owing to overlap of the multiplets, the isomer ratio could not be accurately determined by integration. However, there were clear differences in the ^{13}C chemical shifts of the side-chains (Table 2) and the isomer ratio was determined from their integrals.[8] The validity of this approach was confirmed by capillary GLC analysis of the mixture which revealed two components in the same isomer ratio.

Treatment of this mixture of hydroxyesters with thionyl chloride afforded a 65:35 isomeric pair of chloroesters. The isomer ratio was also ascertained from the ^{13}C spectrum of the mixture (Table 3) and confirmed by GLC analysis. Since the configuration of an alcohol is retained when converted to an alkyl chloride with thionyl chloride, the major chloroester isomer is assigned the *threo* configuration **5i** and the minor isomer *erythro* **12**.

The same pair of chloroesters was obtained from a reaction of the dioxolane **1i** with iodine monochloride carried out under reflux. However, in this case the *threo* to *erythro* isomer ratio was found to be 31:69, which confirms that chloride attacks a dioxolanylium ion in an S_N^2-type process which leads to inversion of configuration on ring-opening.

In summary, since dioxolanes and dioxanes are easily synthesised from 1,2- and 1,3-diols, respectively, their reactions with iodine monochloride afford a convenient method for the stereoselective conversion of diols into either their monoesters (with retention of configuration) or chlorohydrin ester (with inversion of configuration), depending on the reaction conditions employed. The selective functionalisation of hydroxy groups in polyols is a topic of enduring interest, and the reactions we have described complement existing methodology.[9,10]

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on Pye Unicam SP1000 and Perkin Elmer 297 spectrophotometers. Unless otherwise specified, proton NMR spectra were recorded at 60 MHz on a Perkin Elmer R12A spectrometer with $SiMe_4$ as internal standard. 200 MHz proton and 50 MHz carbon-13 NMR spectra were recorded on a Varian Gemini 200 spectrometer. COSY and HETCOR 2D-techniques were used to aid chemical shift assignments where reaction products consisted of inseparable mixtures of isomers. *J*-Values are given in Hz. GLC analyses were conducted on a Becker–Packard 420 gas chromatograph equipped with an Autolab 6300 digital integrator and a column containing Silicon Dow 11 on Chromoport XXX 60–70 mesh, and a Varian 3300 gas chromatograph linked to a Varian 4290 integrator and containing a SBP-20 capillary column; both gas chromatographs were equipped with FID detectors. HPLC analyses were carried out on a Waters Analytical LC System containing a μ-Porasil column, using a model 440 Absorbance Detector (operating at 254 nm) linked to a Waters Data Module. Mass spectra were recorded at the CSIR in Pretoria on a Varian MAT-212 mass spectrometer equipped with a Varian SS-188 data system as well as an AEI MS 30 double beam mass spectrometer. Elemental analyses were determined in the Micro-Analytical Laboratories of the University of Cape Town.

Syntheses.—All the dioxolanes and the dioxane were synthesised as described previously.[2]

General Procedure for Reactions of 1,3-*Dioxolanes with Iodine Monochloride.*—Iodine monochloride (2.0 cm^3, 40 mmol) was added dropwise to an ice-cold, stirred solution of the dioxolane (8 mmol) in chloroform or dichloromethane (20 cm^3). The reaction mixtures were then either maintained at 0 °C, or allowed to warm to ambient temp., or brought to reflux for the periods specified in Table 1. The reactions were quenched by shaking with an aqueous solution of either sodium thiosulfate or sodium metabisulfite, containing sodium carbonate. Workup gave crude products whose yields (Table 1) were determined by NMR spectroscopy (internal standard method) before being purified by distillation or preparative TLC followed by distillation or recrystallisation.

1,3-*Dioxolane* **1a** gave after distillation 2-chloroethyl formate **5a**, b.p. 129 °C (lit.,[11] b.p. 130–131 °C); $\nu_{max}(CCl_4)/cm^{-1}$ 1742 and 1161; $\delta(CCl_4)$ 3.67 (2 H, t), 4.38 (2 H, t) and 8.05 (1 H, s).

2-*Methyl*-1,3-*dioxolane* **1b** gave 2-hydroxyethyl acetate **4b** and 2-chloroethyl acetate **5b** by comparison (NMR, IR and GLC) with authentic specimens.

2-*Phenyl*-1,3-*dioxolane* **1c** gave 2-hydroxyethyl benzoate **4c** and 2-chloroethyl benzoate **5c** by comparison (NMR, IR and GLC) with authentic specimens.

4-*Methyl*-2-*phenyl*-1,3-*dioxolane* **1d** gave the following after chromatography and distillation: firstly, an inseparable mixture of 1-hydroxyprop-2-yl benzoate **4d**; δ_H(200 MHz, $CDCl_3$), 1.36 (3 H, d, J_{XM} 6.45, Me), 2.40 (1 H*, br s, OH), 3.77 (1 H, d, J_{AM}

* Owing to coalescence of the hydroxy signals from the two isomers present, the integral represents the sum of the two isomers.

6.04, CH_2†), 3.78 (1 H, d, J_{BM} 4.03, CH_2†), 5.24 (1 H, q, d d, J_{MA} 6.04, J_{MB} 4.03, J_{MX} 6.45, 2-H), 7.37–7.63 (3 H, m, *m*-H and *p*-H) and 7.98–8.13 (2 H, m, *o*-H); δ_C(50 MHz, $CDCl_3$), 18.35 (Me), 67.99 (CH_2), 74.73 (C-2), 130.37–135.19‡ (Ph) and 168.64 or 168.71 (CO); and 2-hydroxypropyl benzoate **4e**; δ_H(200 MHz, $CDCl_3$) 1.30 (3 H, d, *J* 6.0, Me), 2.40 (1 H*, br s, OH) 4.12–4.27 (1 H, m, 2-H), 4.12–4.41 (2 H, m, CH_2), 7.37–7.63 (3 H, m, *m*-H and *p*-H) and 7.98–8.13 (2 H, m, *o*-H); δ_C(50 MHz, $CDCl_3$) 21.30 (Me), 68.21 (C-2), 72.09 (CH_2), 130.37–135.19‡ (Ph) and 168.71 or 168.64 (CO); mixture b.p. 146–148 °C/2 mmHg (Found: C, 67.0; H, 6.8. Calc. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%); ν_{max}($CHCl_3$)/cm^{-1} 3000 br (OH), 1716 (CO) and 1285 (CO–O) (the ratio of **4d** to **4e** was found to be 46:54 as measured from their NMR integrals); secondly, an inseparable mixture of 1-chloro-2-propyl benzoate **5d**; δ_H(200 MHz, $CDCl_3$), 1.47 (3 H, d, J_{XA} 6.37, Me), 3.72 (2 H, d, J_{MA} 5.13, CH_2), 5.36 (1 H, qd, J_{AX} 6.37, J_{AM} 5.13, 2-H) 7.40–7.63 (3 H, m, *m*-H and *p*-H) and 8.03–8.14 (2 H, m, *o*-H); δ_C(50 MHz, $CDCl_3$) 19.69 (Me), 49.01 (CH_2), 72.19 (C-2), 130.39–135.25¶ (Ph) and 167.76 (CO), and 2-chloropropyl benzoate **5e**; δ_H(200 MHz, $CDCl_3$) 1.61 (3 H, d, J_{XM} 6.39, Me), 4.34 (1 H, qdd, J_{MX} 6.39, J_{MA} 6.53, J_{MB} 5.39, C–2), 4.435 (1 H, d, J_{BM} 5.39, CH_2‡), 4.44 (1 H, d, J_{AM} 6.53, CH_2‡), 7.40–7.63 (3 H, m, *m*-H and *p*-H) and 8.03–8.14 (2 H, m, *o*-H); δ_C(50 MHz, $CDCl_3$) 23.63 (Me), 56.04 (C-2), 70.95 (CH_2), 130.39–135.25¶ (Ph) and 168.03 (CO); mixture b.p. 104–105 °C/0.5 mmHg (Found: C, 60.6; H, 5.6. $C_{10}H_{11}ClO_2$ requires C, 60.46; H, 5.58); *m*/*z* 198 (M^+); ν_{max}($CHCl_3$)/cm^{-1} 1724 (CO), 1716 (CO) and 1280 (CO–O) (the ratio of **5d** to **5e** was found to be 77:23 as measured from their NMR integrals).

4-*Chloromethyl*-2-*phenyl*-1,3-*dioxolane* **1f** gave after chromatography and distillation 1,3-dichloro-2-propyl benzoate **5f**, b.p. 187–189 °C/2.0 mmHg; *m*/*z* 232 (M^+) and 234 ($M^+ + 2$) (Found: C, 51.5; H, 4.35. $C_{10}H_{10}Cl_2O_2$ requires C, 51.53; H, 4.32%); ν_{max}(CCl_4)/cm^{-1} 1730 and 1278; δ_H(CCl_4) 3.81 (4 H, d), 5.31 (1 H, quint.), 7.30–7.63 (3 H, m), 7.90–8.15 (2 H, m), and an inseparable mixture of 1-chloro-3-hydroxy-2-propyl benzoate **4f**, δ_H(200 MHz, $CDCl_3$) 3.10 (1 H*, br s, OH), 3.67 [1 H, dd, J_{AB} 11.30, J_{AM} 4.93, CH_2OH (H_A)], 3.72 [1 H, dd, J_{BA} 11.30, J_{BM} 5.80, CH_2OH (H_B)], 4.21 [1 H, apparent quint., J_{MA} 4.93, J_{MB} 5.80, J_{MX} 5.21, 2-H (H_M)], 4.45 [2 H, d, J_{XM} 5.21, CH_2Cl (H_X)], 7.37–7.50 (2 H, m, *m*-ArH), 7.50–7.62 (1 H, m, *p*-ArH), 8.00–8.10 (2 H, m, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 47.99 (C-3), 67.70 (C-1), 71.65 (C-2), 130.35–135.62§ (Ph) and 168.67 (CO), and 3-chloro-2-hydroxypropyl benzoate **4g**, δ_H(200 MHz, $CDCl_3$) 3.10 (1 H*, br s, OH), 3.88 [2 H, d, J_{XM} 5.33, CH_2Cl (H_X)], 4.27 [1 H, apparent quint., J_{MA} 5.94, J_{MB} 5.38, J_{MX} 5.33, 2-H (H_M)], 4.57 [1 H, dd, J_{BA} 12.10, J_{BM} 5.38, CH_2OBz(H_B)], 4.61 [1 H, dd, J_{AB} 12.10, J_{AM} 5.94, CH_2OBz (H_A)], 7.37–7.50 (2 H, m, *m*-ArH), 7.50–7.62 (1 H, m, *p*-ArH), 8.00–8.10 (2 H, m, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 61.18 (C-2), 65.47 (C-3), 66.56 (C-1), 130.35–135.62§ (Ph) and 168.67 (CO); mixture b.p. 155–157 °C/1.00 mmHg; ν_{max}(CCl_4)/cm^{-1} 3500br, 1733 and 1275 (Found: C, 55.4; H, 5.1. $C_{10}H_{11}ClO_3$ requires C, 55.9; H, 5.2%). (The ratio of **4f** to **4g** was found to be 65:35 as measured from their NMR integrals.) This tentative assignment of the hydroxyester NMR signals to specific isomers was based on the following premise: both isomers contain two pairs of diastereotopic methylene protons. In each isomer, however, only one diastereotopic proton pair displays any discernible difference (at 200 MHz) in chemical shifts; the other pair shows none (together with the methine proton the five side-chain protons constitute an $ABMX_2$ spin system). We suggest that intramolecular hydrogen bonding could occur between the hydroxy hydrogen and either oxygen of the ester group thereby imparting a measure of rigidity to those bonds involved in the two possible cyclic structures. This could accentuate the chemical shift difference inherent in the protons of that methylene group involved in the cyclic structures. On the other hand, the chloromethylene group should remain relatively freely-rotating and hence its proton chemical shift differences could be minimised to the extent that its proton pair appears as a simple doublet at 200 MHz for both isomers. Accepting this assumption, consideration of chemical shift effects in the two possible isomers allows their structures to be assigned.

4,5-*Dimethyl*-2-*propyl*-1,3-*dioxolane* **1h** gave after distillation 3-hydroxy-2-butyl butyrate **4h**, b.p. 70 °C/1.5 mmHg; ν_{max}(CCl_4)/cm^{-1} 3505, 1740 and 1190; δ_H(CCl_4) 0.75–1.30 (9 H, m), 1.30–1.93 (2 H, m), 2.24 (2 H, t), 2.45 (OH), 3.64 (1 H, m) and 4.68 (1 H, m), and 3-chloro-2-butyl butyrate **5h**, b.p. 79–80 °C/1.0 mmHg (Found: C, 53.8; H, 8.35. $C_8H_{15}ClO_2$ requires C, 53.8; H, 8.45%); ν_{max}(CCl_4)/cm^{-1} 1751, 1256, 1190 and 920; δ_H(CCl_4) 0.95 (3 H, t), 1.20–2.00 (8 H, m), 2.02–2.41 (2 H, m), 3.80–4.20 (1 H, m) and 4.13–5.05 (1 H, m).

4,5-*Dimethyl*-2-*phenyl*-1,3-*dioxolane* **1i** gave after chromatography and distillation, firstly, an inseparable mixture of *threo*-3-hydroxybut-2-yl benzoate **11**, δ_H(200 MHz, $CDCl_3$) 1.24 [3 H, d, J_{XA} 6.42, 2-Me (H_X)], 1.34 [3 H, d, J_{YB} 6.42, 3-Me (H_Y)], 2.40 (1 H*, br s, OH), 3.90 [1 H, dq, J_{AB} 5.72, J_{AX} 6.42, 2-H (H_A)], 5.03 [1 H, dq, J_{BA} 5.72, J_{BY} 6.42, 3-H (H_B)], 7.42 (2 H, t, *m*-ArH), 7.56 (1 H, t, *p*-ArH) and 8.04 (2 H, d, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 18.05 (2-Me), 20.78 (3-Me), 72.06 (C-2), 77.19 (C-3), 130.36 (Ar), 131.59 (Ar), 132.33 (Ar), 135.00 (Ar) and 168.27 (CO), and *erythro*-3-hydroxy-2-butyl benzoate **4i**, δ_H(200 MHz, $CDCl_3$) 1.24 [3 H, d, J_{XA} 6.42, 2-Me (H_X)], 1.33 [3 H, d, J_{YB} 6.42, 3-Me (H_Y)], 2.40 (1 H*, br s, OH), 4.00 [1 H, dq, J_{AB} 3.48, J_{AX} 6.48, 2-H (H_A)], 5.11 [1 H, dq, J_{BA} 3.48, J_{BY} 6.48, 3-H (H_B)], 7.42 (2 H, t, *m*-ArH), 7.56 (1 H, t, *p*-ArH) and 8.04 (2 H, d, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 16.51 (2-Me), 19.73 (3-Me), 71.77 (2-H), 76.95 (3-H), 130.36 (Ar), 131.59 (Ar), 132.33 (Ar), 135.00 (Ar) and 168.27 (CO); mixture b.p. 167–170 °C (bulb temp.)/1.5 mmHg; *m*/*z* 194 (M^+) (Found: C, 67.9; H, 7.3. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.3%); ν_{max}(CCl_4)/cm^{-1} 3535, 1729, 1278 and 1121. [The ratio of **11** to **4i** was found to be 69:31 as measured from their ^{13}C NMR integrals (Table 2) and GLC]. Secondly was obtained an inseparable mixture of *threo*-3-chloro-2-butyl benzoate **5i**, δ_H(200 MHz, $CDCl_3$) 1.45 [3 H, d, J_{XA} 6.4, 2-Me (H_X)], 1.56 [3 H, d, J_{YB} 6.8, 3-Me (H_Y)], 4.19 [1 H, dq, J_{AB} 4.25, J_{AX} 6.8, 2-H (H_A)], 5.29 [1 H, dq, J_{BA} 4.25, J_{BY} 6.4, 3-H (H_B)], 7.45 (2 H, m, *m*-ArH), 7.59 (1 H, m, *p*-ArH) and 8.04 (2 H, m, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 18.57 (2-Me), 22.75 (3-Me), 60.95 (C-2), 75.23 (C-3), 130.42 (Ar), 131.71 (Ar), 132.14 (Ar), 135.13 (Ar) and 167.68 (CO), and *erythro*-3-chloro-2-butyl benzoate **12**, δ_H(200 MHz, $CDCl_3$) 1.45 [3 H, d, J_{XA} 6.4, 2-Me (H_X)], 1.57 [3 H, d, J_{YB} 6.8, 3-Me (H_Y)], 4.26 [1 H, dq, J_{AB} 4.3, J_{AX} 6.8, 2-H (H_A)], 5.25 [1 H, dq, J_{BA} 4.3, J_{BY} 6.4, 3-H (H_B)], 7.45 (2 H, m, *m*-ArH), 7.59 (1 H, m, *p*-ArH) and 8.04 (2 H, m, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 17.58 (2-Me), 22.80 (3-Me), 61.36 (C-2), 75.65 (C-3), 130.42 (Ar), 131.71 (Ar), 132.14 (Ar), 135.13 (Ar) and 167.68 (CO); b.p. of mixture 115–118 °C/1.0 mmHg; *m*/*z* 212 (M^+) and 214 ($M^+ + 2$) (Found: C, 62.0; H, 6.2. $C_{11}H_{13}ClO_2$ requires C, 62.1; H, 6.2%); ν_{max}(CCl_4)/cm^{-1} 1725, 1285, 1127, 1109 and 925. [The ratio of **5i** to **12** was found to be 31:69 and 30:70 as measured from their ^{13}C NMR integrals (Table 3) and GLC, respectively].

4,5-cis-2,4,5-*Triphenyl*-1,3-*dioxolane* **1j** gave after chromatography and recrystallisation *meso*-1,2-diphenyl-2-hydroxy-

* See footnote on p. 2178.

† The two protons of the methylene group are diastereotopic, constituting H_A and H_B of an $ABMX_3$ spin system. The reported coupling constants were confirmed by simulation of the spin system.

‡ Signals at 130.37, 130.44, 131.67, 131.85, 132.23, 135.08 and 135.19 were not assigned.

¶ Signals at 130.39, 131.69, 132.07, 135.13 and 135.25 were not assigned.

§ Signals at 130.35, 130.47, 131.45, 131.58, 131.69, 131.86, 131.99, 135.29, 135.37, 135.44 and 135.62 were not assigned.

ethyl benzoate **4j**, m.p. 160–161.5 °C (lit.,[12] m.p. 160–161 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 1720 and 1269; $\delta_H(CDCl_3)$ 2.20 (s, OH), 5.11 (1 H, d, *J* 5.7), 6.14 (1 H, d, *J* 5.7), 7.30–7.50 (13 H, m) and 7.85–8.10 (2 H, m).

(4R,5R)-4,5-*Bis*(*methoxycarbonyl*)-2-*phenyl*-1,3-*dioxolane* **1k** gave after chromatography (*R*,*R*)-2-hydroxy-1,2-bis(methoxycarbonyl)ethyl benzoate **4k**, m.p. 77–79 °C (lit.,[2] m.p. 78 °C); *m*/*z* 282 (M^+) (Found: C, 55.2; H, 5.0. $C_{13}H_{14}O_7$ requires C, 55.3; H, 5.0%); $\nu_{max}(CCl_4)/cm^{-1}$ 3550 (sharp), 1779, 1753 (shoulder at 1740) and 1260; $\delta_H(CCl_4)$ 3.34 (OH, d, *J* 7.7), 3.74 (3 H, s), 3.79 (3 H, s), 4.75 (1 H, dd, *J* 7.7, 2.7), 5.57 (1 H, d, *J* 2.7), 7.30–7.60 (3 H, m) and 7.90–8.15 (2 H, m), and (1*R*,2*S*)-2-chloro-1,2-bis(methoxycarbonyl)ethyl benzoate **5k**, b.p. 160 °C (bulb temp.)/0.3 mmHg; *m*/*z* 300 (M^+) and 302 ($M^+ + 2$) (Found: C, 52.15; H, 4.35. $C_{13}H_{13}ClO_6$ requires C, 51.9; H, 4.35%); $\nu_{max}(CCl_4)/cm^{-1}$ 1780, 1742 and 1253; $\delta_H(CCl_4)$ 3.77 (3 H, s), 3.81 (3 H, s), 4.87 (1 H, d, *J* 4.3), 5.75 (1 H, d, *J* 4.3), 7.20–7.63 (3 H, m) and 7.88–8.14 (2 H, m).

2-*Phenyl*-cis-*perhydrocyclopenta*[d][1,3]*dioxole* **1l** gave after chromatography and distillation *cis*-2-hydroxycyclopentyl benzoate **4l**, b.p. 137–145 °C (bulb temp.)/0.02 mmHg (Found: C, 69.4; H, 7.0. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%); ν_{max}(film)/cm^{-1} 3450, 1719 and 1280; $\delta_H(CCl_4)$ 1.5–2.1 (6 H, m), 2.2 (OH, s), 4.15 (1 H, m), 5.05 (1 H, m), 7.2–7.5 (3 H, m) and 7.8–8.1 (2 H, m), and *trans*-2-chlorocyclopentyl benzoate **5l**, b.p. 128–132 °C (bulb temp.)/0.02 mmHg (Found: C, 64.2; H, 6.0. $C_{12}H_{13}ClO_2$ requires C, 64.15; H, 5.8%); ν_{max}(film)/cm^{-1} 1729 and 1275; $\delta_H(CCl_4)$ 1.5–2.7 (6 H, m), 4.25 (1 H, m), 5.25 (1 H, m), 7.25–7.5 (3 H, m) and 7.8–8.05 (2 H, m), identical (GLC) to authentic *trans*-2-chlorocyclopentyl benzoate.

2-*Phenyl*-trans-*perhydro*-1,3-*benzodioxole* **1m** gave after chromatography *trans*-2-hydroxy cyclohexyl benzoate **4m**, m.p. 90–92 °C (lit.,[13] m.p. 89–91 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 3500, 1720 and 1281; $\delta_H(CDCl_3)$ 0.70–2.30 (8 H, m), 3.10 (OH, s), 3.40–3.90 (1 H, m), 4.55–5.07 (1 H, m), 7.15–7.68 (3 H, m) and 7.88–8.20 (2 H, m); and *cis*-2-chlorocyclohexyl benzoate **5m**, b.p. 145 °C (bulb temp.)/0.15 mmHg; *m*/*z* 238 (M^+) and 240 ($M^+ + 2$) (Found: C, 65.0; H, 6.35. $C_{13}H_{15}ClO_2$ requires C, 65.41; H, 6.33%); $\nu_{max}(CCl_4)/cm^{-1}$ 1725 and 1271; $\delta_H(CCl_4)$ 0.60–2.50 (8 H, m) 3.70–4.35 (1 H, m), 4.76–5.21 (1 H, m), 7.20–7.70 (3 H, m) and 7.91–8.22 (2 H, m).

Pinacol monoformate **4o**, pinacol monoacetate **4p** and pinacol monobutyrate **4q** which result from 4,4,5,5-tetramethyl-1,3-dioxolane **1o**, 2,4,4,5,5-pentamethyl-1,3-dioxolane **1p** and 2-propyl-4,4,5,5-tetramethyl-1,3-dioxolane **1q**, respectively, have been described previously.[2]

2-*Phenyl*-4,4,5,5-*tetramethyl*-1,3-*dioxolane* **1r** gave after distillation pinacol monobenzoate **4r**, b.p. 133–135 °C/1.5 mmHg (Found: C, 70.5; H, 8.2. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%); $\nu_{max}(CCl_4)/cm^{-1}$ 3620, 3450, 1722, 1699, 1288, 1166 and 1126; $\delta_H(CCl_4)$ 1.26 (6 H, s), 1.60 (6 H, s), 3.45 (OH, s), 7.20–7.60 (3 H, m) and 7.80–8.05 (2 H, m).

2-(p-*Methoxyphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolane* **1s** gave after chromatography pinacol mono-*p*-methoxybenzoate **4s** as a gum (Found: C, 66.5; H, 8.2. $C_{14}H_{20}O_4$ requires C, 66.65; H, 8.0%); $\nu_{max}(CCl_4)/cm^{-1}$ 3620, 3435, 1714, 1691, 1305 and 1170; $\delta_H(CCl_4)$ 1.23 (6 H, s), 1.57 (6 H, s), 3.50 (OH, s), 3.80 (3 H, s), 6.84 (2 H, d) and 7.82 (2 H, d).

2-(p-*Nitrophenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolane* **1t** gave after chromatography and recrystallisation (EtOH–EtOAc) pinacol mono-*p*-nitrobenzoate **4t**, m.p. 125–126 °C (Found: C, 58.6; H, 6.1; N, 5.4. $C_{13}H_{17}NO_5$ requires C, 58.4; H, 6.4; N, 5.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 1722 (shoulder at 1704), 1535, 1352, 1304 and 1127; $\delta_H(CDCl_3)$ 1.33 (6 H, s), 1.68 (6 H, s), 3.05 (OH, s), 8.12 (2 H, d) and 8.25 (2 H, d).

p-*Bis*(4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*yl*)*benzene* **1u** gave after recrystallisation (light petroleum) bis-(2-hydroxy-1,1,2-trimethylpropyl) terephthalate **4u**, m.p. 122–122.5 °C (Found: C, 66.65; H, 8.25. $C_{20}H_{30}O_6$ requires C, 65.55; H, 8.25%); $\nu_{max}(CCl_4)/cm^{-1}$ 3620, 3470, 1727 (shoulder at 1700) and 1280; $\delta_H(CDCl_3)$ 1.31 (12 H, s), 1.64 (12 H, s), 3.05 (OH, s) and 8.01 (4 H, s).

2-*Phenyl*-1,3-*dioxane* **1v** gave after chromatography and bulb-to-bulb distillation 3-hydroxypropyl benzoate **4v**, b.p. 130–135 °C (bulb temp.)/1.0 mmHg (Found: C, 66.4; H, 6.75. $C_{10}H_{12}O_3$ requires C, 66.65; H, 6.7%); $\nu_{max}(CCl_4)/cm^{-1}$ 3650, 3540, 1735 and 1280; $\delta_H(CCl_4)$ 1.93 (2 H, quint.), 3.07 (OH, s), 3.67 (2 H, t), 4.37 (2 H, t), 7.20–7.55 (3 H, m) and 7.80–8.10 (2 H, m) and 3-chloroprop-1-yl benzoate **5v**, b.p. 105–110 °C (bulb temp.)/1.3 mmHg (Found: C, 60.65; H, 5.75. $C_{10}H_{11}ClO_2$ requires C, 60.45; H, 5.9%); $\nu_{max}(CCl_4)/cm^{-1}$ 1735 and 1277; $\delta_H(CCl_4)$ 2.18 (2 H, quint.), 3.61 (2 H, t), 4.40 (2 H, t), 7.20–7.55 (3 H, m) and 7.83–8.12 (2 H, m).

Reaction of Hydroxyesters **11** *and* **4i** *with Thionyl Chloride*.—The unresolved 69:31 mixture *threo*- and *erythro*-3-hydroxy-2-butyl benzoate **11** and **4i**, respectively, was allowed to stand at room temp. for 4 h in the presence of excess thionyl chloride, before being refluxed for 30 min. The reaction mixture was then concentrated under reduced pressure, affording a mixture of *threo*-3-chloro-2-butyl benzoate **5i**, δ_H(200 MHz, $CDCl_3$) 1.45 [3 H, d, J_{XA} 6.4, 2-Me (H_X)], 1.56 [3 H, d, J_{YB} 6.8, 3-Me (H_Y)], 4.195 [1 H, dq, J_{AB} 4.25, J_{AX} 6.8, 2-H (H_A)], 5.295 [1 H, dq, J_{BA} 4.25, J_{BY} 6.4, 3-H (H_B)], 7.45 (2 H, m, *m*-ArH), 7.59 (1 H, m, *p*-ArH) and 8.18 (2 H, m, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 18.55 (2-Me), 22.73 (3-Me), 60.94 (C-2), 75.23 (C-3), 130.41 (Ar), 131.70 (Ar), 132.10 (Ar), 135.11 (Ar) and 167.69 (CO); and *erythro*-3-chloro-2-butyl benzoate **12**; δ_H(200 MHz, $CDCl_3$) 1.45 [3 H, d, J_{XA} 6.4, 2-Me (H_X)], 1.57 [3 H, d, J_{YB} 6.8, 3-Me (H_Y)], 4.26 [1 H, dq, J_{AB} 4.3, J_{AX} 6.8, 2-H (H_A)], 5.25 [1 H, dq, J_{BA} 4.3, J_{BY} 6.4, 3-H (H_B)], 7.45 (2 H, m, *m*-ArH), 7.59 (1 H, m, *p*-ArH) and 8.04 (2 H, m, *o*-ArH); δ_C(50 MHz, $CDCl_3$) 17.57 (2-Me), 22.79 (3-Me), 61.34 (C-2), 75.65 (C-3), 130.41 (Ar), 131.70 (Ar), 132.10 (Ar), 135.11 (Ar) and 167.69 (CO). The ratio of **5i** to **12** was found to be 64:36 and 65:35 as measured from their ^{13}C NMR integrals (Table 3) and GLC, respectively.

Procedure for Rate Studies.—(a) *Dioxolanes* **1c**, **d** *and* **f**. The appropriate dioxolane (3.74 mmol) was dissolved in chloroform (100 cm^3) in a 250 cm^3 round-bottom flask equipped with an overhead stirrer. The flask was then immersed in a constant-temperature bath maintained at 25.0 °C (± 0.1) (0 °C in the case of dioxolane **1c**). Once the solution had equilibrated, iodine monochloride (3.011 g, 18.55 mmol) was added in one portion to the stirred solution. Aliquots were withdrawn at intervals and quenched by shaking with a standard amount of aq. sodium thiosulfate. The organic layer was separated, dried (sodium sulfate) and analysed by GLC where the concentrations of the respective chloroesters were determined by calibration against standard solutions. The relative rates of formation of the chloroesters are shown in Fig. 1.

(b) *Dioxolanes* **1l** *and* **1m**. The appropriate dioxolane (0.500 g, 2.45 mmol) was dissolved in chloroform and the solution placed as described above in a constant-temperature bath maintained at 55 °C. A solution of iodine monochloride (2.360 g, 14.54 mmol) in chloroform (20 cm^3) was allowed to equilibrate to the bath temperature before being added in one portion to the dioxolane solution. Aliquots were withdrawn at intervals and worked-up as described above before being analysed by HPLC. The components of the reaction mixtures were identified by comparison with authentic samples and their variations with time are shown in Figs. 2 and 3. Note that the concentrations of the components were not standardised. Their relative concentrations are represented by their peak areas (the esters were detected through the benzoate chromophore and all are likely to evoke a similar detector response; the benzaldehyde response

could differ from that of the esters, but comparison of its variations between the graphs can be made).

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