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Stereocommunication through glycosidic linkages[1]

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Abstract

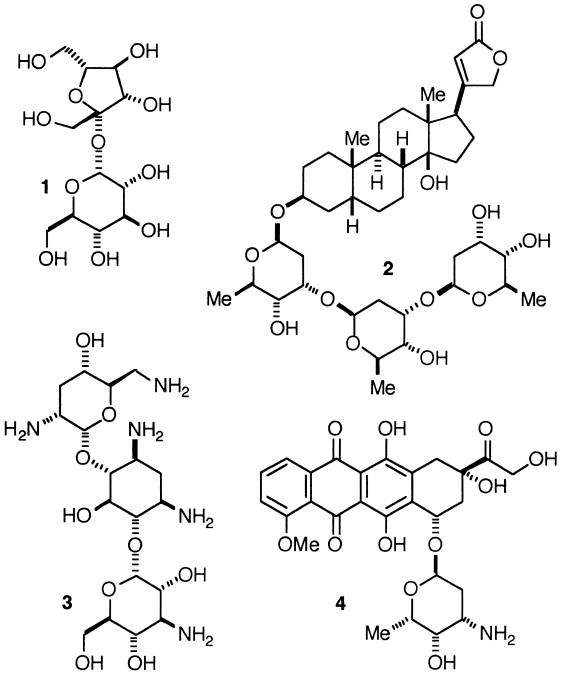
The olefinic units of glucosides of type **5** (R^1 = alkyl/alkoxy, R^2 = alkyl) display reasonable facial reactivities in oxidative additions, reacting with *N*-bromosuccinimide and alcohols to give mainly bromoalkoxy derivatives of type **12** and with dimethyldioxirane to give predominantly epoxides of type **26**. The major oxidation products can usually be isolated in near-stereopure states (d.e.s > 95%) and acceptable yields by fractional crystallization. Compounds of type **12** can be converted into novel chirons of type **16** (with e.e.s of 94–98%). They also undergo stereoselective intermolecular and intramolecular radical reactions leading, after auxiliary detachment, to chirons of types **22** (with e.e.s of 88–94%) and **25** (with e.e.s of 96%). Epoxides of type **26** can be transformed into dithianes of type **28** (with e.e.s of 93–98%) and alkenes of type **31** (with e.e.s of 91–99%).

Keywords: Glycosides; Stereocommunication; Oxidative additions

1. Introduction

Glycosides are of paramount importance in chemistry and biology. They are ubiquitous in nature and possess wide-ranging biological properties. Important low-molecular-weight representatives include sucrose **1** (a sweetening agent), digitoxin **2** (a cardionic agent), tobramycin **3** (an antibacterial agent) and adriamycin **4** (an anticancer agent). Heightened by the discovery that glycoside domains of glycoconjugates are involved in cell–cell, cell–bacterium and cell–virus interactions and the expectation that low-molecular-weight carbohydrate-related constructs may serve as drug-discovery leads (Musser, 1992), glycoside assembly is now a focus for synthetic chemists.

Glycosides with aglycones featuring stereogenic centres are traditionally assembled from sugars (in appropriately protected and anomerically activated forms) and aglycone alcohols. An alternative strategy, pursued in the author's group and the subject of this paper, is the synthesis of glycosides with aglycones that lack stereogenic centres and their subsequent elaboration into ones that possess them. Clearly, the success of such an approach depends critically on the ability of the sugar units to communicate stereoinformation to the diastereotopic faces (or ligands) of the aglycone units.



If diastereopure products emerge, an added opportunity becomes available. Because of their acetal nature, glycosidic linkages undergo hydrolysis under mildly acidic conditions. There is, therefore, the prospect of obtaining the free aglycone in a stereopure state. Overall, the sugar unit would fulfil a chiral auxiliary role and an enantioselective

[1] This paper is based on a lecture presented to the Second International Meeting of the Portuguese Carbohydrate Chemistry Group in Porto, Portugal, on 24 September 1997.

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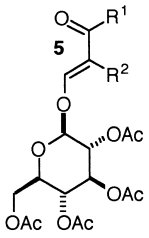
synthesis of the aglycone would be achieved. Because of the abundance, low cost and stereochemical variety of sugars, the technology could provide practical routes to enantiopure compounds—materials that are of particular importance to the fine-chemical industries (Collins et al., 1992; Sheldon, 1993).

2. Discussion

Glycosides derived from D-glucose—the cheapest monosaccharide available—will be the focus of this paper. Specifically, the ability of the 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl unit to direct the facial reactivity of vinylogous esters of type **5** ($R^1 = R^2 =$ alkyl) and vinylogous carbonates of type **5** ($R^1 =$ alkoxy, $R^2 =$ alkyl) in bromoalkoxylation and epoxidation reactions will be addressed; the conversion of the products into novel multifunctional chirons featuring tertiary bromide, quaternary carbon and tertiary alcohol stereocentres will also be considered.



2.1. Synthesis of glucosides

The assembly of vinylogous esters/carbonates of type **5** requires control of the anomeric configuration (β) and the olefinic geometry (*E*). Two routes have been developed in which this control is achieved; both employ the acetobromoglucose **8** (Fig. 1). In route *A*, which is used to prepare acyclic and cyclic vinylogous esters of type **5** ($R^1 =$ alkyl) and cyclic vinylogous carbonates of type **5** ($R^1 =$ alkoxy), a salt of type **7** (obtained by formylation of an α-methylene carbonyl compound of type **6**) is reacted with the acetobromoglucose **8**. The choice of solvent in the glucosidation reaction (which probably involves an S_N2-like displacement reaction at the anomeric centre) depends on the substituent R^2; dimethyl sulfoxide is usually more effective when $R^2 = H$ and aqueous acetone when $R^2 \neq H$. In route *B*, which is employed to make acyclic vinylogous carbonates of type **5** ($R^1 =$ alkoxy), the formyl ester **9** (prepared from **8** by the action of HCO_2Na) undergoes Wittig condensations with phosphoranes of type **11** ($R^1 =$ alkoxy) (derived from α-bromocarbonyl compounds of type **10** ($R^1 =$ alkoxy)).

Some examples of glucosides of type **5** prepared (which will feature in the oxidation reactions to be discussed) and their yields are shown in Table 1. Although the yields are often only moderate, the glucosides can be isolated in a pure state simply by crystallization.

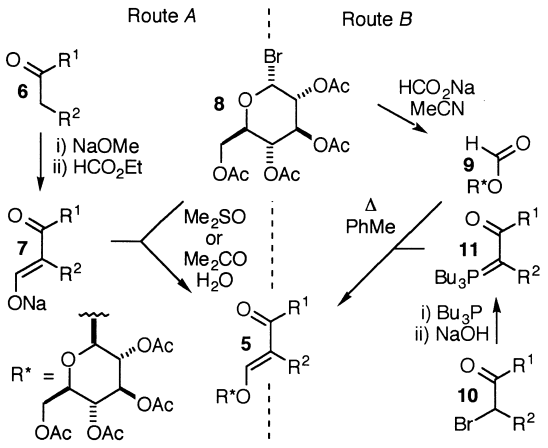


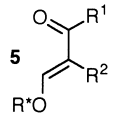
Fig 1.

2.2. Bromoalkoxylation reactions

At the outset of our studies (Idris et al., 1995), very little was known about bromoalkoxylation reactions of simple achiral vinylogous esters/carbonates. We hoped that high regioselectivity (dominated by vinyl ether character) and high stereoselectivity (dictated by *anti*-addition) would prevail. Accordingly, we expected that the bromoalkoxylation of glucosides of type **5** would be determined by facial reactivity issues, leading to adducts of type **12** and/or **13** (Fig. 2). Extrapolating from a model developed earlier to account for the *Re*-face reactivity of related dienyl glucosides in Diels–Alder reactions (Gupta et al., 1989), we predicted that adducts of type **12** would predominate. The clusters of reactive functionality present in such compounds should ensure synthetic versatility. Clearly, the yields and ease of isolation of bromoalkoxy derivatives of type **12** would determine the practicality of the technology.

Initial experiments with compound **5a**, summarized in Table 2, revealed that two bromoalkoxy derivatives were formed in ratios ranging from 2.7:1 to 8.1:1; moreover, in most cases the major product could be isolated in a near-stereopure state (d.e. $> 95\%$) by fractional crystallization. While methanol and a range of primary alcohols

Table 1
Examples and yields of glucosides of type **5**



Glucoside	R^1	R^2	Route	%Yield
5a	Me	Me	*A*	47
5b	OEt	Me	*B*	68
5c	Et	Me	*A*	35
5d	$CH_2CH_2CH_2$		*A*	30
5e	OCH_2CH_2		*B*	70
5f	Me	H	*A*	31
5g	OEt	H	*B*	53

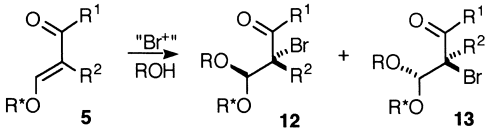


Fig 2.

participated in the reaction (better selectivities being observed with the larger alcohols), the best yield of the major adduct was realized in the bromopropoxylation reaction; in that instance, X-ray crystallographic analysis established that the material possessed the stereostructure **12a** (R = Pr), in accord with expectations.

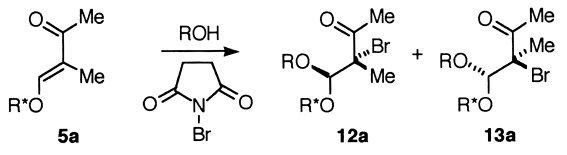
The bromopropoxylation reaction was applied to related glucosides, the results being summarized in Table 3. Better selectivities were observed with glucosides of type **5** (R^2 = alkyl) than with glucosides of type **5** (R^2 = H). In the former instances, it was possible to isolate the major products of type **12** (R = Pr) by fractional crystallization, usually in satisfactory yields.

An explanation for the observed facial reactivity of glucosides of type **5** in bromoalkoxylation reactions is suggested in Fig. 3. Thus, reaction is considered to occur by way of a conformer of type **14**, in which the planar vinylogous ester/carbonate unit is orthogonal to the C(1)–O(5) bond of the glucopyranosyl moiety (which adopts the preferred chair geometry). The orthogonal relationship is attributed to an *exo*-anomeric effect (in which an electron pair of the sp^2 hybridized anomeric O atom interacts with the σ^* orbital of the C(1)–O(5) bond). An electrophilic bromine atom is then delivered to the less-hindered *Re*-face of the alkene moiety to give a bromonium ion of type **15** preferentially. Attack by the alcohol in an S_N2-like manner affords the major product of type **12**.

2.3. Chirons with tertiary bromide stereocentres

Having shown that it was possible to prepare bromoalkoxy compounds of type **12** with reasonable efficiency,

Table 2
Outcome of bromoalkoxylation reactions of the glucoside **5a**



R	Ratio (**12a**:**13a**)	%Yield (**12a**)
Me	2.7:1	47
Et	4.0:1	38
Pr	5.3:1	57
Bu	8.1:1	41
$PhCH_2$	8.1:1	43
$^{i}PrCH_2$	8.1:1	55
$^{t}BuCH_2$	Little adduct	–
^{i}Pr	No adduct	–
^{t}Bu	No adduct	–

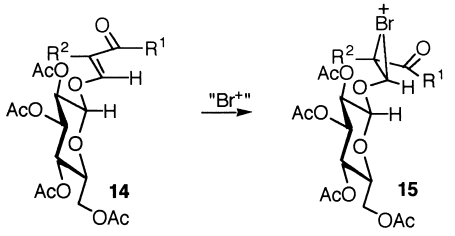


Fig 3.

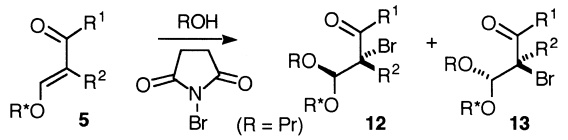
attention was directed at the removal of the sugar auxiliary. Initial efforts focused on the preparation of chirons of type **16**. In the presence of ethane-1,2-diol and trifluoroacetic acid, the desired transacetalization reaction occurred to give 1:1 mixtures of dioxolanes of type **16** and the tetraacetate **17** (as a mixture of anomers) (Fig. 4).

A simple procedure was developed, which led to the facile isolating of dioxolanes of type **16**. Thus, subjection of the product mixtures to the action of methanol containing *p*-toluenesulfonic acid led to the conversion of the tetraacetate **17** into D-glucose; after partitioning the product between water and dichloromethane, the dioxolane was isolated from the organic phase in a near-pure state. As the three examples shown in Table 4 illustrate, the protocol proceeded with acceptable efficiency and provided chirons of type **16** with high enantiomeric purities.

2.4. Chirons with quaternary carbon stereocentres

In principle, it should be possible to replace the bromine atom of bromocarbonyl compounds of type **12** by other substituents using free radical methodology. The prospects of achieving high stereoselectivity in intermolecular reactions did not appear to be good on the basis of the stereoinduction model **18** (in which a radical acceptor attacks from the direction of the small group associated with the adjacent methine stereogenic centre) proposed by Giese et al. (1991). Extrapolation of this model to our situation would lead to a radical of type **19**. Intuitively, the placement of the oxygen atoms between the small and large groups

Table 3
Outcome of bromopropoxylation reactions of glucosides of type **5**



Series	R^1	R^2	Ratio (**12**:**13**)	%Yield (**12**)
a	Me	Me	5.3:1	57
b	OEt	Me	5.7:1	73
c	Et	Me	6.7:1	51
d	$CH_2CH_2CH_2$		8.1:1	39
e	OCH_2CH_2		5.7:1	54
f	Me	H	2.6:1	–
g	OEt	H	3.1:1	–

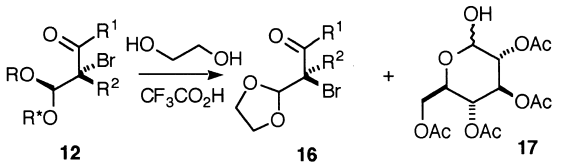
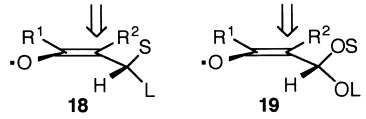


Fig 4.

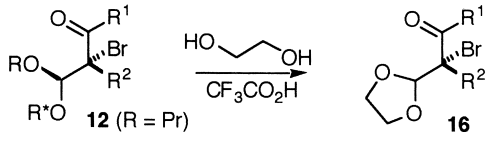
would be expected to lessen stereoinduction.



Because of high interest in the asymmetric synthesis of chirons featuring quaternary carbon stereogenic centres (Fuji, 1993), it was decided to examine the Keck allylation (Keck and Yates, 1982) of bromocarbonyl compounds of type **12**. In principle, such reactions may lead to allyl derivatives of type **20** and/or **21**. Initial studies, conducted with compounds of type **12a** by Peter Tiffin and Sum Idris, were encouraging; with allyltributyltin and AIBN in refluxing benzene, the allyl products were formed stereoselectively. In the case of compound **12a** (R = Me), the major allyl derivative (isolated in poor yield after several crystallizations) was shown to possess the stereostructure **20a** (R = Me) by X-ray crystallography, consistent with the stereoinduction model **19**.

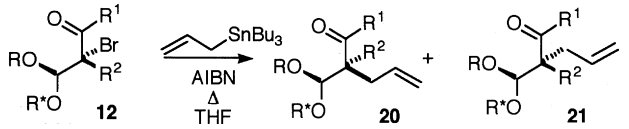
For the technology to be of value in the synthesis of chirons, it is necessary to isolate the major allyl products of type **20** in near-stereopure states and in acceptable yields by fractional crystallization. An alkoxy group 'tuning' study, carried out by Douglas Williamson and summarized in Table 5, showed that these requirements were difficult to achieve. In some instances, the products were inseparable; in others, several crystallizations were usually required to obtain allyl products of type **20** free of their diastereomers. Removal of the sugar auxiliary from appropriate allyl compounds of type **20** was achieved under transdithioacetalization conditions to give chirons of type **22** with reasonable e.e.s and in moderate yields (Table 6).

Table 4
Preparation of chirons of type **16**



Series	R^1	R^2	%Yield	%E.e.
a	Me	Me	63	97
b	OEt	Me	70	98
c	Et	Me	55	94

Table 5
Outcome of radical allylations of bromides of type **12**



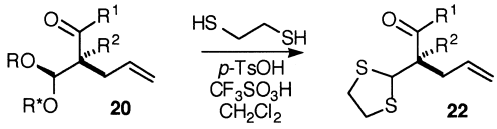
Series	R^1	R^2	Ratio (**20**:**21**)	%Yield (**20**)
a (R = Et)	Me	Me	8.5:1	a
a (R = Pr)	Me	Me	8.0:1	a
a (R = $PhCH_2$)	Me	Me	8.5:1	20
b (R = $PhCH_2$)	OEt	Me	–	40
c (R = Me)	Et	Me	9.0:1	16
c (R = Et)	Et	Me	10:1	19
c (R = Pr)	Et	Me	5.0:1	25
c (R = $PhCH_2$)	Et	Me	5.0:1	a

[a] Fractional crystallization failed to separate the diastereomers.

On the basis of the stereoinduction model **19**, it was anticipated that intramolecular radical reactions would display high stereoselectivity if the radical acceptor were to be appropriately located in the alkoxy substituent (OS). For example, an alkyne of type **12** (R = $HC{\equiv}CCH_2$) would be expected to afford a product of type **24** by way of a radical of type **23** (Fig. 5).

Douglas Williamson showed that it was possible to convert glucosides of type **5** into mainly alkynes of type **12** (R = $HC{\equiv}CCH_2$) by using *N*-bromosuccinimide and propargyl alcohol. Fractional crystallization afforded the representatives **12a** (R = $HC{\equiv}CCH_2$) and **12b** (R = $HC{\equiv}CCH_2$) in yields of 47 and 54%. Initial studies, conducted with compound **12b** (R = $HCC{\equiv}CH_2$), established that the desired cyclization reaction occurred in hot toluene containing tributyltin hydride and AIBN; following chromatography, compound **24a** was isolated in 35% yield (Table 7). The stereostructure of the material was deduced on the basis of an X-ray crystallographic analysis of its major hydrogenation product (which possessed a *cis*-arrangement of the ring methyl groups). After an extensive study of radical cyclization conditions, it was discovered that the use of *N*-methylpiperidinium hypophosphite (Barton et al., 1992) and

Table 6
Preparation of chirons of type **22**



Series	R^1	R^2	%Yield	%E.e.
a (R = $PhCH_2$)	Me	Me	58	94
b (R = $PhCH_2$)	OEt	Me	53	91
c (R = Pr)	Et	Me	54	88

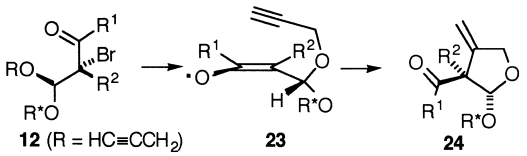


Fig 5.

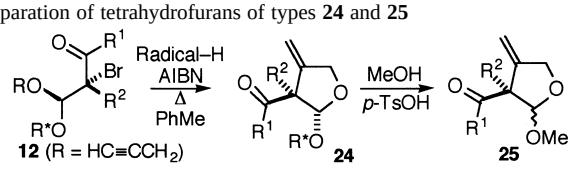
AIBN in refluxing toluene proved to be remarkably effective, providing compound **24b** in essentially quantitative yield in a chromatography-free process. Following auxiliary detachment under methanolysis conditions, the acetal **25b** (isolated as a 1:1 mixture of anomers) was shown to possess an e.e. of 96% (assessed on its γ-lactone oxidation product). Application of the technology to the alkyne **12a** (R = $HC{\equiv}CCH_2$) led to the isolation of the tetrahydrofuran derivative **25a** (isolated as a 2:1 mixture of anomers) in 79% overall yield with an e.e. of 96% (Table 7).

The excellent stereoselectivities achieved in the aforecited radical cyclization reactions provide strong support for the proposed stereoinduction model of type **23** and emphasize the importance of allylic strain considerations. The practicality of *N*-methylpiperidinium hypophosphite in the radical cyclizations is notable. Finally, the overall technology provides an effective route to chirons containing quaternary carbon stereogenic centres.

2.5. Epoxidation reactions

At the outset of our studies, it was known that simple achiral vinylogous esters could be epoxidized using dimethyldioxirane, although the products were reported to decompose below room temperature (Adam and Hadjiarapoglou, 1990). On the basis of the model used to account for the stereoselectivity of the bromoalkoxylation reactions (Fig. 3), we anticipated that glucosides of type **5** would display *Re*-face selectivity and give rise to epoxides of type **26** in preference to those of type **27**. The array of reactive functionality present in epoxides of type **26** should provide notable synthetic versatility (assuming stability and separation issues were not to be problems).

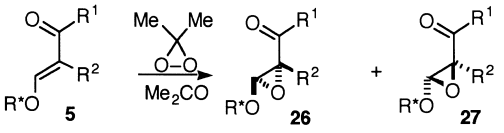
Table 7
Preparation of tetrahydrofurans of types **24** and **25**



Series	R^1	R^2	Radical-H	%Yield (**24**)	%Yield (**25**)	%E.e. (**25**)
b	Et	Me	Bu_3SnH	35	a	a
b	Et	Me	NMPHP[b]	100	84	96
a	Me	Me	NMPHP[b]	100	79	96

[a] Not determined.
[b] NMPHP = *N*-methylpiperidinium hypophosphite.

Table 8
Outcome of epoxidation reactions of glucosides of type **5**



Series	R^1	R^2	Ratio (**26**:**27**)	%Yield (**26**)
a	Me	Me	9:1	73
b	OEt	Me	10:1	74
c	Et	Me	9:1	52
d	$CH_2CH_2CH_2$		10:1	64
e	OCH_2CH_2		6.1:1	70
f	Me	H	2.2:1	–
g	OEt	H	2:1	–

The outcome of such reactions, first studied by Richard Lowe and recently published (Bhatia et al., 1997), is summarized in Table 8. In all cases, two epoxides were observed in ratios ranging from 2:1 to 10:1 (better selectivities being observed when R^2 was an alkyl substituent); moreover, the major epoxides could be isolated in acceptable yields and in near-stereopure states (d.e.s > 95%) by fractional crystallization. The major epoxide derived from the glucoside **5a** was shown to possess the stereostructure **26a** by X-ray crystallography, in accord with expectations.

2.6. Chirons with tertiary alcohol stereocentres

Having found that epoxides of type **26** were stable entities, efforts focused on the removal of the sugar auxiliary. It was envisaged that reaction with propane-1,2-dithiol under transdithioacetalization conditions would give dithianes of type **28** (Fig. 6). In initial studies conducted with the epoxide **26a**, Gurpreet Bhatia established that the desired dithiane **28a** could be prepared in acceptable yield (56%) when the reaction was performed in hot toluene containing *p*-toluenesulfonic acid (72°C, 1.5 h); however, the product was found to possess an e.e. of only 82% by HPLC analysis. Subsequent experiments revealed that the degree of racemization of the dithiane **28a** increased with time. It was presumed that the racemization was caused by a degenerate α-ketol rearrangement, involving an acid-catalysed

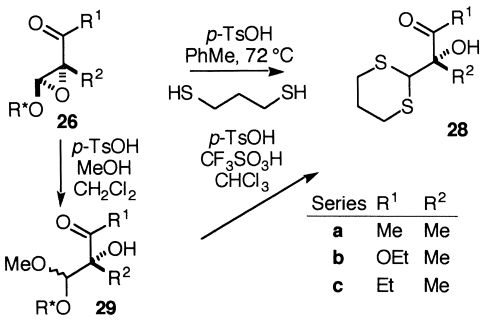


Fig 6.

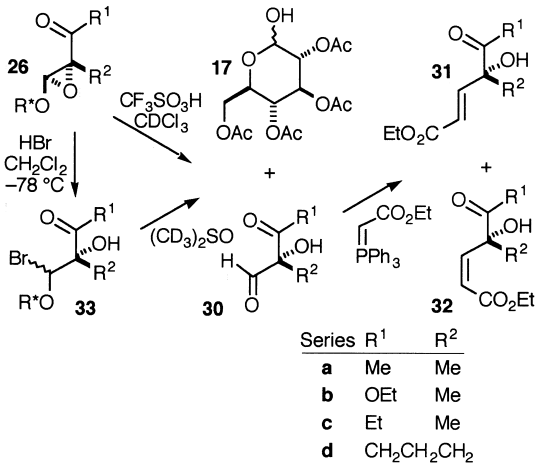


Fig 7.

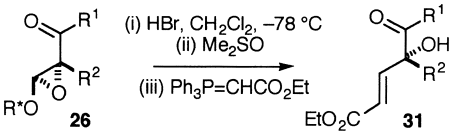
1,2-shift of the dithianyl group. In accord with this notion, no significant racemization accompanied the transformation of the epoxide **26b** into the dithiane **28b** (98% e.e.), isolated in 83% yield.

It was possible to avoid the partial racemization by the adoption of the two-step sequence shown in Fig. 6. Thus, treatment of the epoxide **26a** with methanol and a trace of *p*-toluenesulfonic acid gave the methoxy alcohol **29a** (as a 6:1 mixture of epimers), which underwent transdithioacetalization ($HSCH_2CH_2CH_2SH$, CF_3SO_3H, *p*-TsOH, $CHCl_3$) at room temperature to afford the dithiane **28a** with an e.e. of 98%; the overall yield for the sequence was 55%. Similarly, the epoxide **26c** was transformed into the dithiane **28c** (93% e.e.) in 48% overall yield.

Representing a new class of trifunctional chirons, compounds of type **28** are of obvious synthetic interest. However, their parent aldehydes would be expected to be of even wider synthetic utility (assuming that they can be generated and their aldehyde functions selectively manipulated). After considerable experimentation, Gurpreet Bhatia noted (by NMR monitoring) that addition of a catalytic amount of triflic acid ($\approx$ 1 mol%) to a deuteriochloroform solution of the epoxide **26a** resulted in the formation of a 1:1 mixture of the tetra-acetate **17** and the aldehyde **30a**. Although all work-up procedures led to the loss of the aldehyde **30a**, it was possible to intercept the material by the addition of ethoxycarbonylmethylenetriphenylphosphorane leading to the formation of a 2:1 mixture of the alkenes **31a** and **32a** (Fig. 7). In a preparative experiment conducted in chloroform, the (*E*)-alkene **31a** was isolated in 22% overall yield after chromatography.

Seeking a more efficient process, Gurpreet Bhatia examined the generation of intermediary aldehydes from bromohydrins of type **33** (readily prepared from epoxides of type **26** by the action of HBr). Gratifyingly, he found that the bromohydrin **33a** (isolated as a 9:1 mixture of epimers) underwent the desired reaction in deuteriodimethyl sulfoxide to give a 1:1 mixture of the tetra-acetate **17** and the aldehyde **30a**. When the phosphorane was added to the mixture, a 9:1 mixture of the alkenes **31a** and **32a** was produced (Fig. 7).

Table 9
Synthesis of chirons of type **31**



Series	R^1	R^2	%Yield (**31**)	%E.e. (**31**)
a	Me	Me	50	97
b	OEt	Me	59	97
c	Et	Me	59	91
d	$CH_2CH_2CH_2$		46	99

In a preparative experiment conducted in dimethyl sulfoxide, the (*E*)-alkene **31a** was isolated with an e.e. of 97% in 50% overall yield (based on the epoxide **26a**) (Table 9). Clearly, the intermediate aldehyde **30a** had been generated in a state of high enantiomeric purity and no significant racemization had accompanied the Wittig condensation reaction. The generality of the methodology was demonstrated by its application to the epoxides **26b**–**d** (Table 9).

In illustrating facets of the reactivity of epoxides of type **26**, the results exemplify technology for the assembly of compounds of type **31**; such multifunctional chirons are expected to have useful applications in synthesis.

3. Conclusions

The chemistry of simple α-alkyl-β-oxy-α,β-unsaturated ketones/esters has been notably expanded by the discovery that the facial reactivity of their alkene units can be directed by the attachment of the 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl auxiliary to the β-oxy group. In the case of alkenes with (*E*)-geometry, *Re*-face selectivity is observed in bromoalkoxylation reactions (which have also been shown to occur with high regioselectivity and *anti*-stereoselectivity) and in epoxidation reactions. The major products of such oxidation reactions, which can usually be isolated in near-stereopure states and in acceptable yields by fractional crystallization, can be converted into a range of novel multifunctional chirons featuring tertiary bromide, quaternary carbon and tertiary alcohol stereocentres.

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