Regio- and stereo-selectivity issues in radical brominations of allylic units of vinylogous esters/carbonates bearing the 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl auxiliary and in nucleophilic displacements of the derived allylic bromides †

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Under radical conditions, *N*-bromosuccinimide effects bromination of the methyl group of the 1-oxyallyl unit of (*E*)-3-methyl-4-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one **1a**, (*E*)-2-methyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)pent-1-en-3-one **1b** and methyl/ethyl (*E*)-2-methyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)prop-2-enoate **1c/1d** to give the bromoethyl derivatives **14a**–**14d**.

Displacement of the bromine atom of compounds **14a**–**c** occurs without allylic rearrangement (in Me_2CO under reflux and/or in MeCN at ambient temperature) with sodium azide (to give the azidomethyl derivatives **15a**–**c**), potassium *O*-ethyl dithiocarbonate [to give the ethoxy(thiocarbonyl)thiomethyl derivatives **16a**–**c**] and with potassium thiocyanate (to give the thiocyanatomethyl derivatives **17a**–**c**). Silver(I) thiocyanate in acetonitrile also effects the **14a** ⟶ **17a** conversion.

Compounds **14a**, **14b** and **14d** react with sodium acetate in boiling acetonitrile to give largely the rearranged acetates **19a/20a**, **19b/20b** and **19d/20d** with a moderate degree of stereoselection under kinetically controlled conditions. However, equilibration slowly occurs under the reaction conditions (requiring the presence of NaOAc) to give mainly the unrearranged acetates **18a**, **18b** and **18d**. With silver(I) acetate in acetonitrile, the bromides **14a** and **14d** are transformed into the rearranged acetates **19a/20a** and **19d/20d** with a good degree of stereoselection and without appreciable equilibration. The reaction of the bromide **14a** with silver(I) oxide and acetic acid parallels that observed with sodium acetate, the equilibration of the acetates **18a**, **19a** and **20a** being induced by acetic acid.

The bromide **14a** reacts with alcohols at ambient temperature in the presence of silver(I) oxide to give, in kinetically controlled reactions, mixtures of rearranged alkoxy derivatives of types **24/25** and unrearranged alkoxy derivatives of type **23**. Although the former products predominate, their proportion in the mixture declines as the size of the alcohol increases. Similar results are observed for the bromides **14b** and **14d**.

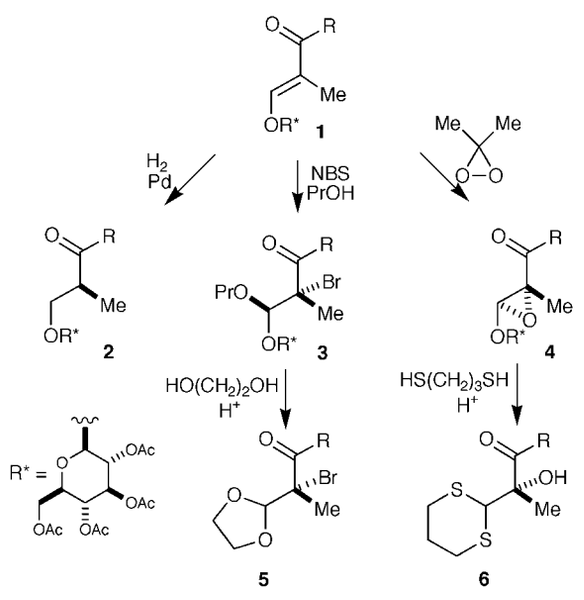
The ambident reactivity of allylic bromides of type **14** towards nucleophiles is consistent with the principle of hard and soft acids and bases.

Introduction

Over the past few years, we have demonstrated that β-oxy α,β-unsaturated carbonyl compounds incorporating the 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl auxiliary are versatile intermediates in asymmetric synthesis.[2] For example, compounds of type **1** exhibit reasonable *Re*-face selectivity in hydrogenation,[3] bromopropoxylation[4] and epoxidation reactions,[5] affording predominantly products of types **2**–**4**; in the case of compounds of types **3** and **4**, it is possible to remove the auxiliary and to generate chirons featuring tertiary carbon stereogenic centres, *e.g.* of types **5** and **6** (Scheme 1).

Furthermore, the dienes **7a** and **7b**, obtained by enol silylation of the vinylogous esters **1a** and **1b**, display excellent *Re*-face selectivity in Diels–Alder reactions[6] affording, for instance, the *endo*-cycloadducts **8a** and **8b** with *N*-phenylmaleimide (Scheme 2).

In this paper, we describe our efforts to effect the allylic functionalisation of systems of type **1**. As outlined in Scheme 3, such a process could, in principle, lead to products of types **9**–**12**. Hopefully, compounds of type **9** would react similarly to their methyl counterparts (*cf*. Schemes 1 and 2), permitting



Scheme 1

† For preliminary communication, see ref. 1.

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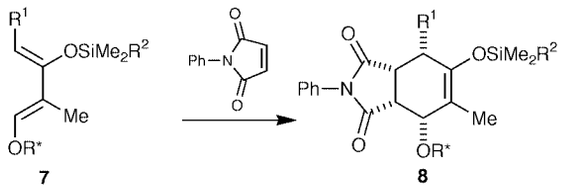
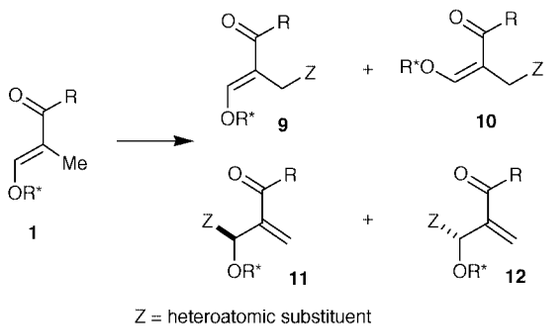


a R^1 = H, R^2 = Me **b** R^1 = Me, R^2 = Bu^t

Scheme 2



Z = heteroatomic substituent

Scheme 3

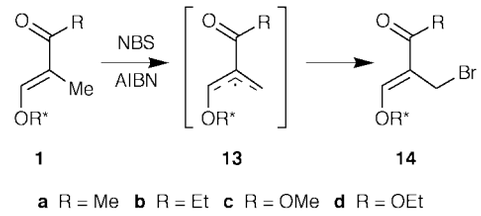
access to related products with additional functionality. If allylic rearrangements were to occur, the products of type **11** or **12** would be of interest in the synthesis of novel chirons.

Results and discussion

In the hope that we would be able to derive the bromide **14a** and subsequently replace its halogen atom by *N*-, *S*- and *O*-nucleophiles under S_N2-like conditions, we decided to investigate the reaction of the butenone **1a**[7] with *N*-bromosuccinimide (NBS). Although the reagent (in CCl_4 in the presence of a radical initiator) has been widely used as an allylic brominating agent,[8] we are unaware of any studies involving its application to α-methyl β-oxy α,β-unsaturated carbonyl compounds.‡

When heated with NBS in carbon tetrachloride in the presence of 2,2′-azoisobutyronitrile (AIBN), the butenone **1a** was converted into one main product (72% yield after crystallisation) that was formulated as the bromide **14a**. That the product had been formed without (*E*) ⟶ (*Z*) isomerisation of the double bond was suggested by its olefinic proton chemical shift (δ 7.47) [which was very similar to that of the reactant **1a** (δ 7.36)] and corroborated by a nuclear Overhauser enhancement difference (NOED) spectroscopic study (in which mutual enhancements were observed between the olefinic proton and the ketonic methyl protons). Similarly, the pentenone **1b**[6] was transformed into the bromide **14b** (79% yield after crystallisation), the propenoate **1c**[3] into the bromide **14c** (61% yield after crystallisation) and the propenoate **1d**[3] into the bromide **14d** (63% yield after crystallisation).

Clearly, the foregoing bromination reactions were highly regioselective, with attack occurring at the unsubstituted primary carbon of the presumed allylic radical intermediates **13a**–**d** (Scheme 4). It is also worth noting that high site selectivity was realised in the case of the reactants **1a** and **1b** (no products arising from bromination of the methyl/methylene



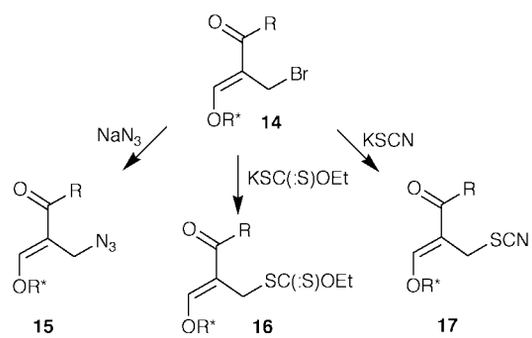
a R = Me **b** R = Et **c** R = OMe **d** R = OEt

Scheme 4

groups adjacent to the vinylogous ester carbonyl functions being detected).

With bromides of type **14** in hand, attention was directed at defining the regio- and stereo-selectivities of their reactions with representative heteroatomic nucleophiles. In principle, attack may occur to give products of type **9** (and **10** if olefinic isomerisation occurs) and products of types **11** and **12**. Clearly, several mechanisms are feasible for such substitution reactions. Thus, products of type **9** may arise by S_N2 or S_N1 pathways, products of type **10** by S_N1 processes, and products of types **11** and **12** by S_N2', S_N1' or conjugate addition–elimination pathways.

The outcomes of the reactions of the bromides **14a**–**c** with sodium azide, potassium *O*-ethyl dithiocarbonate and potassium thiocyanate are summarised in Scheme 5.



a R = Me **b** R = Et **c** R = OMe

Scheme 5

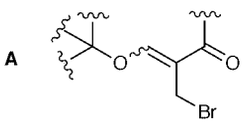
In boiling acetone, sodium azide reacted with the bromides **14a**–**c** to give the azides **15a**–**c** (in respective yields of 64, 74 and 50% after crystallisation); the reaction involving the bromide **14a** was also conducted in acetonitrile at ambient temperature to give the azide **15a** (68% yield after crystallisation).

Potassium *O*-ethyl dithiocarbonate (in MeCN at ambient temperature) effected the conversion of the bromides **14a**–**c** into the dithiocarbonates **16a**–**c** (in respective yields of 54, 65 and 78% after chromatography and/or crystallisation).

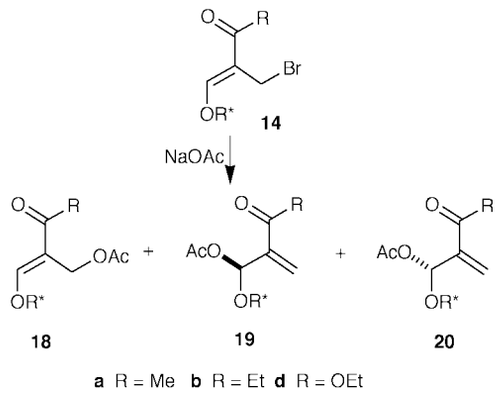
In the presence of potassium thiocyanate (in MeCN at ambient temperature), the bromides **14a**–**c** were transformed into the thiocyanates **17a**–**c** (in respective yields of 76, 72 and 60% after crystallisation). In accord with the thiocyanate formulation (rather than the isothiocyanate alternative), compounds **17a**–**c** showed characteristic sharp but weak IR absorptions at ≈2150 cm^{-1} (alkyl isothiocyanates display broad intense absorptions in the 2106–2084 cm^{-1} region).[9] Furthermore, the ^{13}C NMR spectrum of compound **17a** displayed a signal at δ_C 112.2 typical of an alkyl thiocyanate carbon (alkyl isothiocyanate carbons resonate in the δ_C 128.6–132.3 region).[10]

Presumably, the reactions summarised in Scheme 5 take place by S_N2 pathways. The use of silver(I) thiocyanate in place of potassium thiocyanate would be expected to increase the S_N1-character of such reactions; it was hoped therefore to produce alkyl isothiocyanates in preference to alkyl thiocyanates.[11] However, when treated with the reagent in acetonitrile at ambient temperature, the bromide **14a** was slowly transformed into the thiocyanate **17a**.

‡ Searches of databases (STN International, Beilstein Crossfire) using the substructure **A** failed to provide any representative compounds.



The outcome of the reaction of the bromide **14a** with sodium acetate (in MeCN under reflux) is summarised in Scheme 6.



Scheme 6

Three substitution products, formulated as the unrearranged acetoxy derivative **18a** and the rearranged acetoxy derivatives **19a** and **20a**, resulted; their proportion varied with time. In the early stages of the reaction, mainly a 6:79:15 mixture of compounds **18a**, **19a** and **20a** was produced;§ after 48 h, the proportion of compounds **18a**, **19a** and **20a** changed to 75:12:13.

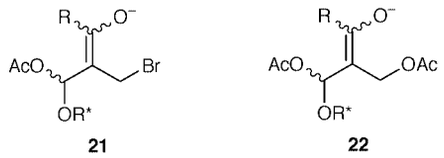
From a preparative-scale experiment (which gave a 17:67:16 mixture of compounds **18a**, **19a** and **20a**), two fractions were isolated after HPLC. The first-eluted fraction, obtained in 59% yield, was an 80:20 mixture of the acetoxy derivatives **19a** and **20a**; after two crystallisations, the product comprised an 86:14 mixture of compounds **19a** and **20a**. The second fraction, obtained in 15% yield, was the acetoxy derivatives **18a**.

A 74:12:14 mixture of compounds **18a**, **19a** and **20a** was produced when the acetoxy derivative **18a** was subjected to the action of sodium acetate in boiling acetonitrile, establishing the equilibrium nature of the reaction. Equilibration did not occur in boiling acetonitrile alone, revealing that the isomerisation was not simply a thermal process.

The bromides **14b** and **14d** reacted in an analogous manner with sodium acetate (Scheme 6). Thus, the former reaction led to the acetoxy derivatives **18b**, **19b** and **20b** (initially as a 10:71:19 mixture and as a 73:12:15 mixture after 96 h) and the latter reaction to the acetoxy derivatives **18d**, **19d** and **20d** (the proportions changing from 22:58:20 after 6 h to 56:26:18 after 180 h).§

From a preparative-scale experiment involving the bromide **14b** (which gave a 10:75:15 mixture of compounds **18b**, **19b** and **20b** together with ≈30% of starting material recovered), one main fraction (50% yield) was isolated after chromatography; it was identified as an 84:16 mixture of the acetoxy derivatives **19b** and **20b**. A similar experiment involving the bromide **14d** (which led to a 32:50:16 mixture of the acetoxy derivatives **18d**, **19d** and **20d** together with ≈25% unchanged starting material) resulted in the isolation, after chromatography, of only one homogeneous fraction (8% yield); it was identified as the acetoxy derivative **18d**.

Clearly, in the early stages, the reactions of the bromides **14a**, **14b** and **14d** with sodium acetate are under kinetic control, and afford mainly the rearranged acetoxy derivatives **19a/20a**, **19b/20b**, and **19d/20d** (with selectivities of ≈4:1). With time, the products interconvert to give equilibrium mixtures (with a preponderance of compounds **18a** and **18b** in the case of the bromides **14a** and **14b**). Although the kinetic products are formally the result of S_N2'-like processes, intermediates of type **21** (formed by conjugate addition reactions) may intervene.



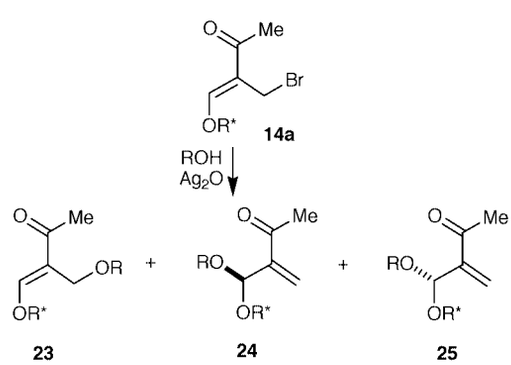
Related intermediates of type **22** may also be involved in the equilibration reactions.

The bromides **14a** and **14d** were also subjected to the action of silver(I) acetate in acetonitrile at ambient temperature. After *ca.* 3 h (when the starting materials were depleted), a 3:86:11 mixture of the acetoxy derivatives **18a**, **19a** and **20a** was present in the former reaction and a 5:87:8 mixture of the acetoxy derivatives **18d**, **19d** and **20d** in the latter reaction. From the reaction involving the bromide **14d**, it was possible to isolate compound **19d** in 41% yield after crystallisation. The proportion of the acetoxy derivatives **18a**, **19a** and **20a** changed with time and, after 48 h, it was 23:64:13. Evidently, partial equilibration occurs under the reaction conditions.

The reaction of the bromide **14a** with silver(I) acetate in acetic acid (generated by adding Ag_2O to stirred HOAc) was also examined.¶ Within 10 min, a 5:71:24 mixture of the acetoxy derivatives **18a**, **19a** and **20a** was produced; the proportions altered to 26:52:22 after 3 h and to 72:12:16 after 18 h. The product obtained from an 18 h reaction was fractionated by HPLC to give a 50:50 mixture of compounds **19a** and **20a** in 23% yield and compound **18a** in 51% yield. In parallel experiments, the bromide **14a** and a 3:90:7 mixture of the acetoxy derivatives **18a**, **19a** and **20a** were subjected, respectively, to the actions of silver(I) oxide and acetic acid and of acetic acid for 96 h. The mixture of the acetoxy derivatives **18a**, **19a** and **20a** was produced in each case, the proportions being 78:8:14 and 81:8:11.

Clearly, there is a close parallel in the reactions of the bromides **14a** and **14d** with silver(I) acetate and sodium acetate. However, with the former reagent in acetonitrile, it is possible to largely avoid product equilibration and to generate the kinetic acetoxy derivatives **19a/20a** and **19d/20d** with high stereoselection (≈10:1).

A study was undertaken of the reaction of the bromide **14a** with alcohols in the presence of silver(I) oxide (Scheme 7). In



Scheme 7

the case of methanol,¶ a 7:67:26 mixture of the methoxy derivatives **23a**, **24a** and **25a**‖ was produced within 2 h. Although the proportions did not change, two new products,

§ The evidence for the assignment of the stereostructures **19a**, **19b** and **19d** to the major rearranged acetoxy derivatives, which is tentative, will be discussed elsewhere.

¶ In acetic acid or methanol alone, the bromide **14a** decomposed within 3 h with formation of the tetraacetate **27**.

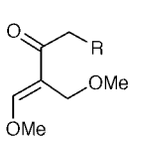
‖ The evidence for the assignment of the stereostructures **24a–e**, **29a–c** and **32a–c** to the major rearranged alkoxy derivatives will be discussed elsewhere.

Table 1 Outcome of the reaction of the bromides **14a**, **14b** and **14d** with alcohols in the presence of silver(I) oxide

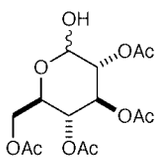
Substrate	Alcohol	Products	Composition	Ratio of regioisomers[a]	Ratio of stereoisomers[b]
14a	MeOH	**23a**, **24a**, **25a**	7:67:26	7:93	72:28
	EtOH	**23b**, **24b**, **25b**	11:72:17	11:89	81:19
	PrOH	**23c**, **24c**, **25c**	13:62:25	13:87	71:29
	Pr^{i}OH	**23d**, **24d**, **25d**	15:67:18	15:85	79:21
	Bu^{t}OH	**23e**, **24e**, **25e**	29:61:10	29:71	86:14
14b	MeOH	**28a**, **29a**, **30a**	7:63:30	7:93	68:32
	Pr^{i}OH	**28b**, **29b**, **30b**	20:52:28	20:80	65:35
	Bu^{t}OH	**28c**, **29c**, **30c**	29:49:22	29:71	69:31
14c	MeOH	**31a**, **32a**, **33a**	12:67:21	12:88	76:24
	Pr^{i}OH	**31b**, **32b**, **33b**	26:61:13	26:74	82:18
	Bu^{t}OH	**31c**, **32c**, **33c**	35:53:12	35:65	82:18

[a] Ratio of unrearranged alkoxy compounds to rearranged alkoxy compounds. [b] Ratio of rearranged (*R*)- to (*S*)-alkoxy compounds.

identified as the dimethoxy derivative **26a** and the tetraacetate **27** (as a 2:1 mixture of α- and β-anomers), were in evidence after 24 h. After 120 h, their relative concentrations had doubled (≈20% of compound **26a** was present in the mixture of compounds **23a**, **24a**, **25a** and **26a**).



26a R = H
b R = Me



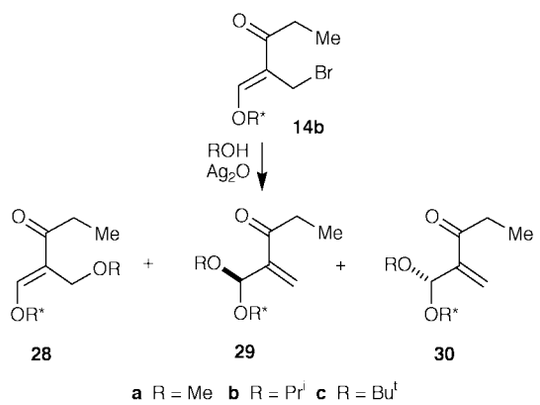
27

In a preparative-scale experiment, conducted for 24 h, the product was separated into three fractions by HPLC. The first-eluted fraction (66% yield) consisted of a 70:30 mixture of the rearranged methoxy derivatives **24a** and **25a**; fractional crystallisation provided compound **24a** in a pure state (26% yield). The second-eluted fraction (6% yield) was the unrearranged methoxy derivative **23a**. The third-eluted fraction (≈7% yield) was mainly the dimethoxy derivative **26a**. When resubjected to the action of silver(I) oxide and methanol, compounds **23a** and **24a** were both partially converted (≈10%) into the dimethoxy compound **26a** (no change occurred in MeOH alone); there was no evidence for the interconversion of the reactants.

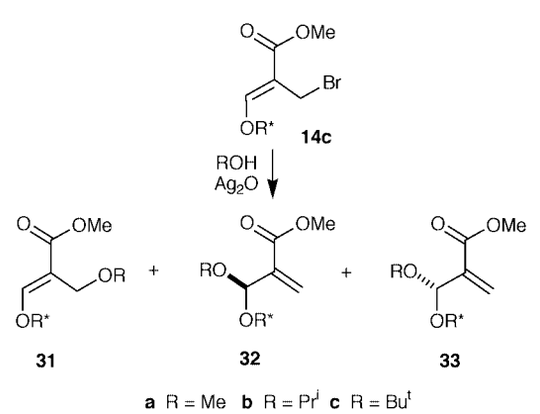
Evidently, the methoxy derivatives **23a**, **24a** and **25a** are formed from the bromide **14a** in kinetically controlled reactions; the products are then slowly transformed into compounds **26a** and **27**.

Having established that the methanolysis of the bromide **14a** occurred with a high degree of regioselection and a modest degree of stereoselection, it was of interest to extend the study to other alcoholysis reactions (see Scheme 7). The results involving ethanol, propan-1-ol, isopropyl alcohol and *tert*-butyl alcohol are summarised in Table 1 (and compared with those observed for MeOH). In all instances, mixtures of unrearranged alkoxy derivatives of type **23** and rearranged alkoxy derivatives of types **24** and **25**‖ were produced. Although the rearranged products also predominated, their percentage composition of the mixture declined as the size of the alcohol increased. The stereoisomeric ratios of the rearranged alkoxy derivatives were modest and they were not substantially influenced by the nature of the alcohol.

The study (using MeOH, Pr^{i}OH and Bu^{t}OH) was extended to the bromide **14b** (Scheme 8) and to the bromide **14c** (Scheme 9). As noted in Table 1, the substrates showed reactivities that were similar to those observed for the bromide **14a**. In the reaction of the substrate **14b** with methanol (in which there was ^{1}H NMR spectral evidence for the production of ≈10% of the dimethoxy derivative **26b**), a 69:31 mixture of the methoxy derivatives **29a** and **30a**‖ was isolated (59% yield after chromatography). Similarly, the reaction of the bromide **14b** with isopropyl alcohol gave rise to 66:34 mixture of the isopropoxy derivatives **29b** and **30b**‖ (43% yield after chromatography) and with *tert*-butyl alcohol to a 69:31 mixture of the *tert*-butoxy derivatives **29c** and **30c**‖ (52% yield after chromatography). From the reaction of the bromide **14c** with methanol, it was possible to isolate (after HPLC) a 74:26 mixture of the methoxy derivatives **32a** and **33a** (64% yield) and the methoxy derivative **31a** (8% yield). The reaction with isopropyl alcohol gave rise (after HPLC) to an 82:18 mixture of the isopropoxy derivatives **32b** and **33b** (55% yield) and compound **31b** (22% yield). Finally, the bromide **14c** underwent reaction with *tert*-butyl alcohol in the presence of silver(I) oxide to afford (after chromatography) an 82:18 mixture of the *tert*-butoxy derivatives **32c** and **33c** (48% yield) and compound **31c** (32% yield).



Scheme 8



Scheme 9

The contrasting behaviour of bromides of type **14** towards azide/*O*-ethyl dithiocarbonate/thiocyanate anions and acetate anions/alcohols is of interest. It remains to be established

whether the unrearranged products arise by S_N2 routes and the rearranged products by S_N2' processes (or conjugate addition–elimination variants) or whether both products originate from delocalised carbenium ion intermediates (paired with bromide anions) formed by S_N1 pathways. However, it is worth noting that the outcomes are consistent with the principle of hard and soft acids and bases.[12] Thus, bromides of type **14** are attacked only at the softer allylic site by two soft nucleophiles [EtOC(:S)S^- and NCS^-] and one borderline nucleophile (N_3^-) and preferentially at the harder allylic site by two hard nucleophiles (AcO^- and ROH).

In conclusion, we consider our findings to be of synthetic and mechanistic note. Compounds of type **14** appear to be the first representatives of α-bromomethyl β-oxy α,β-unsaturated compounds to be described and their formation provides an opening insight into the regiochemical behaviour of 2-acyl/alkoxycarbonyl 1-oxy allylic radicals. The substitution reactions, involving a new class of allylic bromides, highlight the contrasting behaviour of soft/borderline nucleophiles compared with hard nucleophiles and contribute to an understanding of ambident allylic reactivity.[13] Finally, the methodology makes compounds of types **14**–**17**, of notable synthetic potential, accessible by practical routes.

Experimental

Dry solvents, referred to in the ensuing experiments, were prepared as follows: carbon tetrachloride was refluxed over phosphorus pentaoxide and distilled from it; acetone was refluxed over magnesium sulfate, decanted, stirred overnight with calcium chloride, decanted, refluxed over fresh magnesium sulfate, distilled from it and stored over 4 Å molecular sieves; acetonitrile was refluxed over phosphorus pentaoxide, distilled from it and stored over 4 Å molecular sieves. Light petroleum refers to that fraction boiling in the range 40–60 °C; NBS was recrystallised from ten times its weight of water, dried *in vacuo* (over P_2O_5) and stored in the dark; sodium acetate was dried in an oven at ≈150 °C.

The progress of reactions was monitored by TLC, using Merck plastic or aluminium sheets coated with silica gel (60 F_{254}); chromatograms were initially examined under UV light (Mineralight UVG2-58 lamp) and visualised with a *p*-anisaldehyde stain [plates were sprayed with *p*-$MeOC_6H_4CHO$–conc. H_2SO_4–EtOH (1:4:95) and heated]. Column chromatography was effected, under positive pressure from a compressed air line, with Crossfield Sorbsil C60 flash silica or Merck Kieselgel 60. Preparative HPLC was carried out using a column (25 × 0.8 cm) of Spherisorb S10 silica, a Kontron 420 pump, a Rheodyne 7125 injector and Kontron 742 UV and ERC-7515A RI detectors.

Evaporations were conducted under reduced pressure (using a water-pump) at ≤40 °C with a Büchi rotary evaporator (fitted with a water condenser). Mps were determined with a either an Electrothermal Digital or a Büchi 512 melting point apparatus and are uncorrected. Specific rotations, given in 10^{-1} deg cm^2 g^{-1}, were measured at ≈20 °C using a Thorn Automation Type 243 or an Optical Activity 1000 polarimeter with a cell of path length 0.1 dm. Carbon, hydrogen, nitrogen and sulfur contents were determined with a Carlo Erba Model 1108 analyser; bromine content was measured by oxygen combustion followed by automatic argentometric titration on a Mettler DL25 titrator. A Perkin-Elmer Lambda 15 or a JASCO 7800 spectrometer was used to determine UV spectra; extinction coefficients (ε) are presented in cm^2 $mmol^{-1}$. IR spectra were recorded using a Perkin-Elmer 783, a Perkin-Elmer FTIR-1600 or a Shimadzu IR-345 spectrometer. NMR spectra were measured using a Bruker AC 300, a Varian Unity Plus 300 or a Bruker AM 400 [with distortionless enhancement by polarisation transfer (DEPT) editing for ^{13}C spectra]; *J*-values and separations are given in Hz. FAB mass spectra (*m*-$NO_2C_6H_4CH_2OH$ as matrix) were measured using a Kratos MS 50 spectrometer.

Allylic bromination studies

General procedure. Recrystallised NBS (0.890 g, 5 mmol) and a catalytic quantity of AIBN were added to a stirred suspension of the vinylogous ester/carbonate **1a**–**d** (4 mmol) in dry carbon tetrachloride (60 cm^3) and the mixture was heated under reflux. When the reaction was complete [it was best to monitor the progress by ^1H NMR spectroscopy (samples were removed and worked up as described below); depletion of the allylic bromide generally took 1–4 h], the mixture was concentrated and the residue partitioned between methylene dichloride and aq. sodium metabisulfite. After having been washed with water and dried ($MgSO_4$), the organic phase was concentrated and the product was purified by crystallisation.

(*E*)-3-Bromomethyl-4-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one 14a. The butenone **1a** (6.71 g, 15.6 mmol) gave the *title compound* **14a** (5.51 g, 72%) (after crystallisation from EtOAc–hexanes); mp 137–138 °C; $[\alpha]_D$ +30 (*c* 0.4, $CHCl_3$) (Found: C, 44.8; H, 4.9; Br, 15.9. $C_{19}H_{25}BrO_{11}$ requires C, 44.8; H, 4.9; Br, 15.7%); λ_{max} (EtOH)/nm 245 (ε 13 100); ν_{max} (KBr)/cm^{-1} 1750 (ester C=O), 1675 (vinylogous ester C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 2.045, 2.051 and 2.10 (3, 3 and 6 H, each s, 4 × $MeCO_2$), 2.31 (3 H, s, 1-H_3), 3.87 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 4.16–4.21 (3 H, m, 6′-H and 3-CH_2Br), 4.31 (1 H, dd, *J* 4.5 and 12.5, 6′-H), 5.02 (1 H, d, *J* 7.5, 1′-H), 5.15–5.32 (3 H, m, 2′-, 3′- and 4′-H) and 7.47 (1 H, s, 4-H) (in an NOED spectroscopic experiment, irradiation at δ 2.31 enhanced the s at δ 7.47 at 7.9%; irradiation at δ 4.18 caused a 0.7% enhancement of the s at δ 2.31; irradiation at δ 7.47 caused a 3.7% enhancement of the d at δ 5.02 and a 1.3% enhancement of the s at δ 2.31); *m*/*z* (FAB) 841 and 839 [$M(C_{14}H_{19}O_9)^+$, each 25%], 643 and 641 (65 and 55), 511 and 509 (MH^+, 28 and 35), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (40).

(*E*)-2-Bromomethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)pent-1-en-3-one 14b. The pentenone **1b** (1.89 g, 4.1 mmol) gave the *title compound* **14b** (1.70 g, 79%) (after crystallisation from Et_2O–light petroleum); mp 92–94 °C; $[\alpha]_D$ +29 (*c* 0.4, $CHCl_3$) (Found: C, 45.6; H, 5.1; Br, 15.1. $C_{20}H_{27}BrO_{11}$ requires C, 45.9; H, 5.2; Br, 15.3%); λ_{max} (EtOH)/nm 245 (ε 13 800); ν_{max} (KBr)/cm^{-1} 1750 and 1740 (ester C=O), 1670 (vinylogous ester C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 1.13 (3 H, *J* 7.5, 5-H_3), 2.04, 2.05, 2.09 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 2.59–2.67 (2 H, m, 4-H_2), 3.86 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 4.17 and 4.31 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.19 (2 H, s, 2-CH_2Br), 5.01 (1 H, d, *J* 7.5, 1′-H), 5.15–5.32 (3 H, m, 2′-, 3′- and 4′-H) and 7.48 (1 H, s, 1-H); *m*/*z* (FAB) 525 and 523 (MH^+, each 1%), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (35).

Methyl (*E*)-2-bromomethyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)prop-2-enoate 14c. The propenoate **1c** (1.70 g, 3.8 mmol) gave the *title compound* **14c** (1.18 g, 61%) (after crystallisation from EtOAc–hexanes); mp 108–109 °C; $[\alpha]_D$ +59 (*c* 0.4, $CHCl_3$) (Found: C, 43.7; H, 4.7; Br, 15.5. $C_{19}H_{25}BrO_{12}$ requires C, 43.4; H, 4.8; Br, 15.2%); λ_{max} (EtOH)/nm 236 (ε 13 700); ν_{max} (KBr)/cm^{-1} 1755 (ester C=O), 1715 (vinylogous carbonate C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 2.038, 2.043, 2.09 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.79 (3 H, s, MeO_2C), 3.84 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 4.17 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.18 (2 H, AB q, *J* 10, separation of inner lines 10, 2-CH_2Br), 4.96 (1 H, d, *J* 7.5, 1′-H), 5.13–5.30 (3 H, m, 2′-, 3′- and 4′-H) and 7.54 (1 H, s, 3-H); *m*/*z* (FAB) 527 and 525 (MH^+, 9 and 10%), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (70).

Ethyl (*E*)-2-bromomethyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)prop-2-enoate 14d. The propenoate **1d** (1.38 g, 2.9 mmol) gave the *title compound* **14d** (0.985 g, 63%) (after crystallisation from Et_2O–light petroleum); mp 98–99 °C; $[\alpha]_D$ +45 (*c* 0.3, $CHCl_3$) (Found: C, 44.8; H, 4.9; Br, 15.0. $C_{20}H_{27}BrO_{12}$ requires C, 44.5; H, 5.0; Br, 14.8%); λ_{max} (EtOH)/nm 236 (ε 14 600); ν_{max} (KBr)/cm^{-1} 1760 (ester C=O), 1710 (vinylogous carbonate C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 1.31 (3 H, t, *J* 7, *Me*CH_2), 2.03, 2.04, 2.09 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.85 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.13–4.33 (6 H, m, 2-CH_2Br, 6′-H_2 and OCH_2Me), 4.97 (1 H, d, *J* 7.5, 1′-H), 5.13–5.30 (3 H, m, 2′-, 3′- and 4′-H) and 7.52 (1 H, s, 3-H); *m*/*z* (FAB) 541 and 539 (MH^+, each 6%), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (95).

Reactions of allylic bromides with sodium azide

General procedure. A mixture of the allylic bromide (0.5 mmol), sodium azide (0.033 g, 0.5 mmol) and dry acetone (25 cm^3) was heated under reflux. When the reaction was complete (TLC), the mixture was partitioned between water and methylene dichloride. Evaporation of the dried ($MgSO_4$) organic phase gave a material that was purified in the manner described.

(*E*)-3-Azidomethyl-4-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one 15a. *Method (a)*.—The material obtained from the reaction of the allylic bromide **14a** (0.102 g, 0.2 mmol) for 1.5 h was crystallised from ethyl acetate–light petroleum to give the *title compound* **15a** (0.060 g, 64%); mp 153–154 °C; $[\alpha]_D$ +14 (*c* 0.25, CH_2Cl_2) (Found: C, 48.5; H, 5.3. $C_{19}H_{25}N_3O_{11}$ requires C, 48.4; H, 5.3%); λ_{max} (EtOH)/nm 240 (ε 16 200); ν_{max} (KBr)/cm^{-1} 2140, 2100 and 2080 (N_3), 1750 (ester C=O), 1665 (vinylogous ester C=O) and 1650 (C=C); δ_H (300 MHz; $CDCl_3$) 2.03, 2.05, 2.06 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.30 (3 H, s, 1-H_3), 3.86 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 3.95 and 4.07 (each 1 H, d, *J* 13, 3-CH_2N), 4.18 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 5.01 (1 H, *J* 7.5, 1′-H), 5.13–5.31 (3 H, m, 2′-, 3′- and 4′-H) and 7.59 (1 H, s, 4-H); *m*/*z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 75%) and 169 (100).

Method (b).—A mixture of the allylic bromide **14a** (0.026 g, 0.05 mmol), sodium azide (0.003 g, 0.05 mmol) and dry acetonitrile (2.5 cm^3) was stirred for 6 h and then concentrated. The residue was partitioned between water and methylene dichloride. Evaporation of the dried ($MgSO_4$) organic phase left the azide **15a** (0.022 g, 93%) [0.016 g, 68% (after crystallisation from EtOAc–hexanes)].

(*E*)-2-Azidomethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)pent-1-en-2-one 15b. The material obtained from the reaction of the allylic bromide **14b** (0.157 g, 0.3 mmol) for 1.5 h was crystallised from ethyl acetate–hexanes to give the *title azide* **15b** (0.108 g, 74%); mp 72–74 °C; $[\alpha]_D$ + 10 (*c* 0.25, CH_2Cl_2) (Found: C, 49.6; H, 5.4; N, 8.4. $C_{20}H_{27}N_3O_{11}$ requires C, 49.5; H, 5.6; N, 8.7%); λ_{max} (EtOH)/nm 240 (ε 12 100); ν_{max} (KBr)/cm^{-1} 2120, 2100 and 2080 (N_3), 1755 (ester C=O), 1665 (vinylogous ester C=O) and 1650 (C=C); δ_H (300 MHz; $CDCl_3$) 1.13 (3 H, t, *J* 7.5, 5-H_3), 2.03, 2.05, 2.06 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.57–2.67 (2 H, m, 4-H_2), 3.85 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 3.96 and 4.09 (each 1 H, d, *J* 13, 2-CH_2N), 4.17 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.99 (1 H, d, *J* 7.5, 1′-H), 5.13–5.31 (3 H, m, 2′-, 3′- and 4′-H) and 7.60 (1 H, s, 1-H); *m*/*z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 100%), 169 (69) and 43 ($C_2H_3O^+$, 72) {(after addition of KI) 524 [$M(K)^+$, 9%]}.

Methyl (*E*)-2-azidomethyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)prop-2-enoate 15c. The material obtained from the reaction of the allylic bromide **14c** (0.263 g, 0.5 mmol) for 3.2 h was crystallised from methylene dichloride–diethyl ether–light petroleum to give the *title compound* **15c** (0.122 g, 50%) as a pale yellow solid; mp 117–118 °C; $[\alpha]_D$ +8 (*c* 0.3, $CHCl_3$) (Found: C, 46.6; H, 5.1; N, 8.3. $C_{19}H_{25}N_3O_{12}$ requires C, 46.8; H, 5.2; N, 8.6%); λ_{max} (EtOH)/nm 229 (ε 14 000); ν_{max} (KBr)/cm^{-1} 2140, 2100 and 2080 (N_3), 1750 (ester C=O), 1710 (vinylogous carbonate C=O) and 1650 (C=C); δ_H (300 MHz; $CDCl_3$) 2.03, 2.04, 2.05 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 3.78 (3 H, s, MeO_2C), 3.83 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 3.90 and 4.10 (each 1 H, d, *J* 13, 2-CH_2N), 4.15 and 4.29 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.95 (1 H, d, *J* 7.5, 1′-H), 5.11–5.29 (3 H, m, 2′-, 3′- and 4′-H) and 7.66 (1 H, s, 3-H); *m*/*z* (FAB) 510 [$M(Na)^+$, 30%], 331 ($C_{14}H_{19}O_9^+$, 95) and 169 (100).

Reactions of allylic bromides with potassium *O*-ethyl dithiocarbonate

General procedure. A mixture of the allylic bromide (0.25 mmol) and potassium *O*-ethyl dithiocarbonate (0.040 g, 0.25 mmol) in dry acetonitrile (12.5 cm^3) was stirred at room temperature for 15 min and then concentrated. The residue was partitioned between methylene dichloride and water and the organic phase was washed sequentially with 1% aq. sodium metabisulfite and water. Evaporation of the dried ($MgSO_4$) organic phase left a product that was purified in the matter specified.

(*E*)-3-Ethoxy(thiocarbonyl)thiomethyl-4-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one 16a. The reaction of the allylic bromide **14a** (0.127 g, 0.25 mmol) gave rise to a product that was subjected to column chromatography [EtOAc–hexanes (2:1) as eluent]. Crystallisation of the chromatographed material (0.088 g, ≈64%) from diethyl ether–hexanes gave the *title compound* **16a** (0.074 g, 54%); mp 104–106 °C; $[\alpha]_D$ −6 (*c* 0.25, CH_2Cl_2) (Found: C, 47.7; H, 5.8; S, 11.4. $C_{22}H_{30}O_{12}S_2$ requires C, 48.0; H, 5.5; S, 11.6%); λ_{max} (EtOH)/nm 207 (ε 12 300), 240 (14 400) and 282 (10 500); ν_{max} (KBr)/cm^{-1} 1755 and 1740 (ester C=O), 1670 (vinylogous ester C=O) and 1650 (C=C); δ_H (300 MHz; $CDCl_3$) 1.42 (3 H, t, *J* 7, *Me*CH_2), 2.03, 2.05, 2.08 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 2.28 (3 H, s, 1-H_3), 3.85 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 3.96 and 4.11 (each 1 H, d, *J* 12.5, 3-CH_2S), 4.17 and 4.30 [each 1 H, dd (*J* 2 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.65 (2 H, q, *J* 7, OCH_2Me), 4.99 (1 H, d, *J* 7.5, 1′-H), 5.13–5.30 (3 H, m, 2′-, 3′- and 4′-H) and 7.49 (1 H, s, 4-H); *m*/*z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 65%), 169 (100) and 109 (62) {(after addition of KI) 589 [$M(K)^+$, 35%]}.

(*E*)-2-Ethoxy(thiocarbonyl)thiomethyl-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)pent-1-en-3-one 16b. The reaction of the allylic bromide **14b** (0.131 g, 0.25 mmol) gave rise to a product that was subjected to column chromatography [EtOAc–hexanes (2:1) as eluent]. The chromatographed material (0.092 g, 65%), isolated as a foam, was identified as the *title compound* **16b**; $[\alpha]_D$ −2 (*c* 0.5, CH_2Cl_2) (Found: C, 48.4; H, 6.2; S, 10.8. $C_{23}H_{32}O_{12}S_2$ requires C, 48.9; H, 5.7; S, 11.3%); ν_{max} (film)/cm^{-1} 1755 (ester C=O), 1670 (vinylogous ester C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 1.11 (3 H, t, *J* 7.5, 5-H_3), 1.42 (3 H, t, *J* 7, *Me*CH_2O), 2.03, 2.04, 2.08 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 2.55–2.65 (2 H, m, 4-H_2), 3.84 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 3.99 and 4.12 (each 1 H, d, *J* 12.5, 2-CH_2S), 4.17 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.65 (2 H, q, *J* 7, OCH_2Me), 4.98 (1 H, d, *J* 7.5, 1′-H), 5.13–5.30 (3 H, m, 2′-, 3′- and 4′-H) and 7.50 (1 H, s, 1-H); *m*/*z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 73%) and 169 (100) {(after addition of KI) 603 [$M(K)^+$, 100%]}.

Methyl (*E*)-2-ethoxy(thiocarbonyl)thiomethyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)prop-2-enoate 16c. The reaction of the allylic bromide **14c** (0.131 g, 0.25 mmol) gave

rise to a product that was crystallised from methylene dichloride–diethyl ether–light petroleum to give the *title compound* **16c** (0.110 g, 78%); mp 105.5–107 °C; $[\alpha]_D$ −4 (*c* 0.46, CH_2Cl_2) (Found: C, 46.6; H, 5.3; S, 10.9. $C_{22}H_{30}O_{13}S_2$ requires C, 46.6; H, 5.3; S, 11.3%); ν_{max} (KBr)/cm^{-1} 1780, 1760 and 1745 (ester C=O), 1720 (vinylogous carbonate C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 1.43 (3 H, t, *J* 7, *Me*CH_2), 2.03, 2.04, 2.08 and 2.11 (each 3 H, s, 4 × $MeCO_2$), 3.76 (3 H, s, MeO_2C), 3.83 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.04 (2 H, AB q, *J* 12.5, separation of inner lines 13, 2-CH_2S), 4.16 and 4.20 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.66 (2 H, q, *J* 7, OCH_2Me), 4.94 (1 H, d, *J* 7.5, 1′-H), 5.12–5.29 (3 H, m, 2′-, 3′- and 4′-H) and 7.56 (1 H, s, 3-H); δ_C (75 MHz; $CDCl_3$) 14.1 (*C*H_3CH_2), 20.9 and 21.0 (4 × *C*H_3CO), 29.8 (2-CH_2), 52.3 (CH_3O), 61.8 (6′-CH_2), 68.1, 70.8, 72.5 and 73.1 (2′-, 3′-, 4′- and 5′-CH), 70.2 (O*C*H_2Me), 101.0 (1′-CH), 109.2 (2-C), 155.7 (3-CH), 166.9, 169.4, 169.6, 170.5 and 170.9 (*C*O_2Me and 4 × Me*C*O) and 214.1 (CS); *m/z* (FAB) 567 (MH^+, 2%), 331 ($C_{14}H_{19}O_9^+$, 70), 169 ($C_9H_{13}O_3^+$, 95), 109 (70) and 43 (100) {(after addition of KI) 605 [$M(K)^+$, 15%]}.

Reactions of allylic bromides with potassium thiocyanate

General procedure. A mixture of the allylic bromide (0.5 mmol), potassium thiocyanate (0.049 g, 0.5 mmol) and dry acetonitrile (25 cm^3) was stirred until the reaction was complete (TLC). Evaporation of the solvent left a residue, which was partitioned between methylene dichloride and 1% aq. sodium metabisulfite. After having been washed with water, the organic phase was dried ($MgSO_4$) and concentrated. The product was analysed by 300 or 400 MHz ^{1}H NMR spectroscopy and then purified in the manner described.

(*E*)-4-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3-(thiocyanatomethyl)but-3-en-2-one 17a. The product obtained from the reaction of the allylic bromide **14a** (0.255 g, 0.5 mmol) for 6 h was predominantly the thiocyanate **17a**. Crystallisation of the material from ethyl acetate–light petroleum gave the *title compound* **17a** (0.185 g, 76%); mp 152–152.5 °C; $[\alpha]_D$ +33 (*c* 0.4, $CHCl_3$) (Found: C, 49.4; H, 5.5; N, 2.7; S, 6.8. $C_{20}H_{25}NO_{11}S$ requires C, 49.3; H, 5.2; N, 2.9; S, 6.6%); λ_{max} (EtOH)/nm 242 (ε 12 400), ν_{max} (Nujol)/cm^{-1} 2153 (C≡N), 1748 (ester C=O), 1668 (vinylogous ester C=O) and 1642 (C=C); δ_H (300 MHz; $CDCl_3$) 2.03, 2.04, 2.09 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 2.31 (3 H, s, 1-H_3), 3.64 and 3.93 (each 1 H, d, *J* 12.5, 3-CH_2S), 3.86 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.17 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 5.05 (1 H, d, *J* 7.5, 1′-H), 5.15 (1 H, t, *J* 10, 4′-H), 5.20 (1 H, dd, *J* 7.5 and 9, 2′-H), 5.29 (1 H, t, *J* 9.5, 3′-H) and 7.63 (1 H, s, 4-H); δ_C (75 MHz; $CDCl_3$) 20.43, 20.58 and 20.61 (4 × *C*H_3CO), 25.17 (1-CH_3), 26.09 (3-CH_2S), 61.28 (6′-CH_2), 67.61, 70.23, 71.84 and 72.73 (2′-, 3′-, 4′- and 5′-CH), 100.2 (1′-CH), 112.2 (SCN), 119.2 (3-C), 156.4 (4-CH), 169.2, 169.4, 169.9 and 170.4 (4 × Me*C*O) and 194.0 (2-CO); *m/z* (FAB) 510 [$M(Na)^+$, 4%], 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (90).

(*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2-(thiocyanatomethyl)pent-1-en-3-one 17b. The product obtained from the reaction of the allylic bromide **14b** (0.262 g, 0.5 mmol) for 7 h was predominantly the thiocyanate **17b**. Crystallisation of the material from ethyl acetate–light petroleum gave the *title compound* **17b** (0.180 g, 72%); mp 151–152 °C; $[\alpha]_D$ +33 (*c* 0.4, $CHCl_3$) (Found: C, 50.5; H, 5.7; N, 2.7; S, 6.8. $C_{21}H_{27}NO_{11}S$ requires C, 50.3; H, 5.4; N, 2.8; S, 6.4%); λ_{max} (EtOH)/nm 243 (ε 17 200); ν_{max} (Nujol)/cm^{-1} 2153 (C≡N), 1756 (ester C=O), 1670 (vinylogous ester C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 1.15 (3 H, t, *J* 7.5, 5-H_3), 2.04, 2.05, 2.10 and 2.11 (each 3 H, s, 4 × $MeCO_2$), 2.64 (2 H, q, *J* 7.5, 4-H_2), 3.66 and 3.96 (each 1 H, d, *J* 12.5, 2-CH_2S), 3.86 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.18 and 4.31 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 5.04 (1 H, d, *J* 7.5, 1′H), 5.13–5.33 (3 H, m, 2′-, 3′- and 4′-H) and 7.65 (1 H, s, 1-H); *m/z* (FAB) 524 [$M(Na)^+$, 5%], 502 (MH^+, 1) and 331 ($C_{14}H_{19}O_9^+$, 100).

Methyl (*E*)-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2-(thiocyanatomethyl)prop-2-enoate 17c. The product obtained from the reaction of the allylic bromide **14c** (0.210 g, 0.4 mmol) for 15 h was predominantly the thiocyanate **17c**. Crystallisation of the material from ethyl acetate–light petroleum gave the *title compound* **17c** (0.121 g, 60%); mp 131–132.5 °C; $[\alpha]_D$ +42 (*c* 0.35, $CHCl_3$) (Found: C, 47.6; H, 5.3; N, 2.7; S, 6.8. $C_{20}H_{25}NO_{12}S$ requires C, 47.7; H, 5.0; N, 2.8; S, 6.4%); λ_{max} (EtOH)/nm 234 (ε 15 600); ν_{max} (Nujol)/cm^{-1} 2149 (C≡N), 1752 and 1733 (ester C=O), 1700 (vinylogous carbonate C=O) and 1648 (C=C); δ_H (300 MHz; $CDCl_3$) 2.03, 2.04 and 2.09 (3, 3 and 6 H, each s, 4 × $MeCO_2$), 3.63 and 4.03 (each 1 H, d, *J* 13, 2-CH_2S), 3.80 (3 H, s, MeO_2C), 3.83 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 4.16 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.99 (1 H, d, *J* 7.5, 1′H), 5.14 (1 H, t, *J* 9.5, 4′-H), 5.18 (1 H, dd, *J* 7.5 and 9.5, 2′-H), 5.27 (1 H, t, *J* 9, 3′-H) and 7.69 (1 H, s, 3-H); *m/z* (FAB) 526 [$M(Na)^+$, 11%], 331 ($C_{14}H_{19}O_9^+$, 75) and 169 (100).

Reaction of the allylic bromide 14a with silver(I) thiocyanate

A mixture of the allylic bromide **14a** (0.051 g, 0.1 mmol), silver(I) thiocyanate (0.0166 g, 0.1 mmol) and dry acetonitrile (5 cm^3) was stirred. At intervals, aliquots (≈1 cm^3) were removed and concentrated; the residue was then partitioned between methylene dichloride and water. The material, obtained after evaporation of the dried ($MgSO_4$) organic phase, was analysed by 300 MHz ^{1}H NMR spectroscopy. After 3 h, mainly an 89 : 11 mixture of compounds **14a** and **17a** was present; the ratio changed to 74 : 26 after 6 h, 25 : 75 after 24 h and 3 : 97 after 48 h.

Reactions of allylic bromides with sodium acetate

General procedure. A mixture of the allylic bromide (0.5 mmol), dry sodium acetate (0.369 g, 1.5 mmol) and dry acetonitrile (25 cm^3) was heated under reflux for the time specified. The solvent was then evaporated and the residue was partitioned between methylene dichloride and water. After having been washed with water, the organic phase was dried ($MgSO_4$) and concentrated. The product was analysed by 300 or 400 MHz ^{1}H NMR spectroscopy and then purified in the manner described.

Reaction involving the allylic bromide 14a. *Method (a).*—A mixture of the allylic bromide **14a** (0.102 g, 0.2 mmol), dry sodium acetate (0.016 g, 0.2 mmol) and dry acetonitrile (10 cm^3) was heated under reflux. At intervals, aliquots (≈1 cm^3) were removed, worked up and analysed. After 3 h (when ≈60% of unchanged **14a** remained), the product comprised mainly a 6 : 79 : 15 mixture of compounds **18a**, **19a** and **20a** [the proportions were estimated from the integrals of the signals at δ 7.53 (attributed to the 4-H of **18a**), 6.79 (assigned to the 1″-H of **19a**) and 6.85 (ascribed to the 1″-H of **20a**)]. After 6 h (when ≈35% of unchanged **14a** was present), the proportions were unaltered. After 24 h (when no **14a** was detected), the proportions of compounds **18a**, **19a** and **20a** were 60 : 26 : 14. Finally, after 48 h, the product comprised mainly a 75 : 12 : 13 mixture of compounds **18a**, **19a** and **20a**.

Method (b).—(i) The reaction involving the allylic bromide **14a** (0.255 g, 0.5 mmol) using the general procedure gave rise, after 3 h, to a product that comprised mainly a 17 : 67 : 16 mixture of the acetoxy derivatives **18a**, **19a** and **20a**. Subjection of the mixture to HPLC [EtOAc–hexanes (2 : 1) as eluent] gave two fractions.

The first-eluted fraction (0.144 g, 59%), isolated as a colourless syrup, was identified as an 80 : 20 mixture of *(1″S)-3-[1″-acetoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)-*

methyl]but-3-en-2-one **19a** and its *(1″R)-isomer* **20a**. After two crystallisations from diethyl ether–hexanes, the sample (0.104 g, 43%) (now as an 86:14 mixture of **19a** and **20a**) showed mp 123–124 °C; $[a]_D$ −50 (*c* 0.2, $CHCl_3$) (Found: C, 51.3; H, 5.8. $C_{21}H_{28}O_{13}$ requires C, 51.6; H, 5.8%); λ_{max} (EtOH)/nm 210 (ε 8900); ν_{max} (Nujol)/cm^{-1} 1750 and 1737 (ester C=O) and 1676 (enone C=O); δ_H (300 MHz; $CDCl_3$) 2.00, 2.01, 2.02, 2.04, 2.08, 2.10 and 2.11 (0.4, 3, 3, 2.6, 5.2, 0.4 and 0.4 H, each s, 5 × $MeCO_2$), 2.34 and 2.35 (0.4 and 2.6 H, each s, 1-H_3), 3.66 and 3.72 [0.14 and 0.86 H, dt (*J* 10 and 3) and ddd (*J* 2.5, 5 and 10), 5′-H], 4.09, 4.13–4.15 and 4.27 [0.86, 0.28 and 0.86 H, dd (*J* 2.5 and 12.5), m and dd (*J* 5 and 12.5), 6′-H_2], 4.89 and 4.96 (0.86 and 0.14 H, each d, *J* 8, 1′-H), 5.00–5.10 (2 H, m, 2′- and 4′-H), 5.22 (1 H, t, *J* 9.5, 3′-H), 6.23, 6.30, 6.33 and 6.38 (0.14, 0.86, 0.14 and 0.86 H, each s, 4-H_2) and 6.79 and 6.85 (0.86 and 0.14 H, each s, 1″-H); *m/z* (FAB) 511 [M(Na)$^+$, 7%], 331 ($C_{14}H_{19}O_9^+$, 60) and 169 (100).

The second-eluted fraction (0.036 g, 15%), isolated as a colourless syrup, was identified as *(E)-3-acetoxymethyl-4-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one* **18a**. After crystallisation from ethyl acetate–hexanes, the sample (0.026 g, 11%) showed mp 103–104 °C; $[a]_D$ −8 (*c* 0.5, CH_2Cl_2) (Found: C, 51.4; H, 5.8. $C_{21}H_{28}O_{13}$ requires C, 51.6; H, 5.8%); λ_{max} (EtOH)/nm 201 (ε 1900), 239 (20 200) and 311 (1500); ν_{max} (KBr)/cm^{-1} 1755 and 1740 (ester C=O), 1670 (vinylogous ester C=O) and 1650 (C=C); δ_H (300 MHz; $CDCl_3$) 2.02, 2.03, 2.04, 2.06 and 2.10 (each 3 H, s, 5 × $MeCO_2$), 2.28 (3 H, s, 1-H_3), 3.86 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.17 and 4.30 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.73 and 4.87 (each 1 H, d, *J* 11.5, 3-CH_2O), 5.00 (1 H, d, *J* 7.5, 1′-H), 5.13–5.29 (3 H, m, 2′-, 3′- and 4′-H) and 7.53 (1 H, s, 4-H); δ_C (75 MHz; $CDCl_3$) 20.62, 20.68, 20.82, 20.97 and 21.19 (5 × *C*H_3CO), 26.27 (1-CH_3), 55.67 (3-CH_2), 61.57 (6′-CH_2), 67.79, 70.65, 72.20 and 72.93 (2′-, 3′-, 4′- and 5′-CH), 100.7 (1′-CH), 119.2 (3-C), 157.0 (4-CH), 169.1, 169.4, 170.3, 170.6 and 170.8 (5 × Me*C*O) and 195.9 (2-CO); *m/z* (FAB) 527 [M(K)$^+$, 1%], 511 [M(Na)$^+$, 7], 489 (MH^+, 1) and 331 ($C_{14}H_{19}O_9^+$, 100).

(ii) The aforecited reaction was repeated and the product was subjected to column chromatography (Et_2O as eluent). One main fraction (0.105 g, 43%) was collected which was an 80:20 mixture of compounds **19a** and **20a**.

Reaction involving the allylic bromide 14b. *Method (a).*—A mixture of the allylic bromide **14b** (0.105 g, 0.2 mmol), dry sodium acetate (0.033 g, 0.4 mmol) and dry acetonitrile (10 cm^3) was heated under reflux. At intervals, aliquots (≈1 cm^3) were removed, worked up and analysed. After 3 h (when ≈30% of **14b** remained), the product comprised mainly a 10:71:19 mixture of the acetoxy derivatives **18b**, **19b** and **20b** [the proportions were estimated from the integrals of the signals at δ 7.53 (ascribed to the 1-H of **18b**), 6.80 (attributed to the 1″-H of **19b**) and 6.86 (assigned to the 1″-H of **20b**)]. After 6 h (when **14b** was absent), the proportions were 18:64:18. After 24 h, the proportions were 49:35:16. Finally, after 96 h, the product comprised mainly a 73:12:15 mixture of compounds **18b**, **19b** and **20b**.

Method (b).—The reaction involving the allylic bromide **14b** (0.262 g, 0.5 mmol) using the general procedure gave rise, after 3 h, to a product that contained mainly a 10:75:15 mixture of compounds **18b**, **19b** and **20b** (≈30% of **14b** remained). Subjection of the mixture to column chromatography (Et_2O as eluent) led to the isolation of one main fraction (0.126 g, 50%), identified as an 84:16 mixture of *(1″S)-2-[1″-acetoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)-methyl]pent-1-en-3-one* **19b** and its *(1″R)-isomer* **20b**. After crystallisation from diethyl ether–light petroleum, the sample (0.080 g, 32%) (still as an 84:16 mixture of **19b** and **20b**) showed mp 104–106 °C; $[a]_D$ −37 (*c* 0.25, $CHCl_3$) (Found: C, 52.9; H, 5.9. $C_{22}H_{30}O_{13}$ requires C, 52.6; H, 6.0%); λ_{max} (EtOH)/nm 211 (ε 8900); ν_{max} (Nujol)/cm^{-1} 1744 (ester C=O), 1677 (enone C=O) and 1638 (C=C); δ_H (300 MHz; $CDCl_3$) 1.07 and 1.09 (0.48 and 2.52 H, each t, *J* 7.5, 5-H_3), 1.99, 2.00, 2.01, 2.020, 2.024, 2.04, 2.07, 2.09 and 2.11 (0.48, 2.52, 0.48, 2.52, 0.48, 2.52, 5.04, 0.48 and 0.48 H, each s, 5 × $MeCO_2$), 2.64–2.80 (2 H, m, 4-H_2), 3.66 and 3.72 [0.16 and 0.84 H, dt (*J* 10 and 3) and ddd (*J* 2.5, 5 and 10), 5′-H], 4.08, 4.12–4.15 and 4.27 [0.84, 0.32 and 0.84 H, dd (*J* 2.5 and 12.5), m and dd (*J* 5 and 12.5), 6′-H_2], 4.88 (0.84 H, d, *J* 8, 0.84 × 1′-H), 4.97–5.10 (2.16 H, m, 2′- and 4′-H and 0.16 × 1′-H), 5.22 (1 H, t, *J* 9.5, 3′-H), 6.21, 6.27, 6.28 and 6.33 (0.16, 0.16, 0.84 and 0.84 H, each s, 1-H_2) and 6.80 and 6.86 (0.84 and 0.16 H, each s, 1″-H); *m/z* (FAB) 525 [M(Na)$^+$, 5%), 331 ($C_{14}H_{19}O_9^+$, 50) and 169 (100).

Reaction involving the allylic bromide 14d. *Method (a).*—A mixture of the allylic bromide **14d** (0.054 g, 0.1 mmol), sodium acetate (0.0164 g, 0.2 mmol) and dry acetonitrile (5 cm^3) was heated under reflux. At intervals, aliquots (≈1 cm^3) were removed, worked up and analysed. After 6 h (when 22% of **14d** remained), the product comprised mainly a 22:58:20 mixture of the acetoxy derivatives **18d**, **19d** and **20d** [the composition was estimated from the integrals of the signals at δ 7.60 (attributed to the 3-H of **18d**), 6.20 (assigned to an olefinic H of **19d**) and 6.14 (ascribed to an olefinic H of **20d**)]. After 180 h, the proportions of compounds **18d**, **19d** and **20d** were 56:26:18.

Method (b).—The reaction involving the allylic bromide **14d** (0.269 g, 0.5 mmol) using the general procedure gave rise, after 6.5 h, to a product comprising 25% unchanged **14d** and a 32:52:16 mixture of compounds **18d**, **19d** and **20d**. Subjection of the mixture of column chromatography (Et_2O as eluent) gave three main fractions.

The first-eluted fraction (0.090 g) comprised 23% unchanged **14d** and an 80:20 mixture of the acetoxy derivatives **19d** and **20d**.

The second-eluted fraction (0.120 g) comprised 27% unchanged **14d** and a 32:49:19 mixture of the acetoxy derivatives **18d**, **19d** and **20d**.

The third-eluted fraction (0.020 g, 8%) was ethyl (*E*)-2-acetoxymethyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)prop-2-enoate **18d**; $[a]_D$ −16 (*c* 0.5, CH_2Cl_2); ν_{max} (film)/cm^{-1} 1750 (ester C=O), 1720 (vinylogous carbonate C=O) and 1660 (C=C); δ_H (300 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7, *Me*CH_2), 2.04, 2.05, 2.08 and 2.12 (6, 3, 3 and 3 H, each s, 5 × $MeCO_2$), 3.86 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.18 and 4.31 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.24 (2 H, q, *J* 7, O*C*H_2Me), 4.76 and 4.86 (each 1 H, d, *J* 11.5, 2-CH_2O), 4.97 (1 H, d, *J* 7.5, 1′-H), 5.13–5.30 (3 H, m, 2′-, 3′- and 4′-H) and 7.60 (1 H, s, 3-H); *m/z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 65%), 169 (85) and 109 (100) {(after addition of KI) 557 [M(K)$^+$, 100%]}.

Equilibration of the allylic acetates 18a, 19a and 20a. *Method (a).*—A mixture of the acetoxy compound **18a** (0.005 g, 0.01 mmol), sodium acetate (0.0008 g, 0.01 mmol) and dry acetonitrile (1 cm^3) was heated under reflux for 18 h and then the solvent was evaporated. The residue was partitioned between water and methylene dichloride and the organic phase was dried ($MgSO_4$) and concentrated to leave mainly a 74:12:14 mixture of compounds **18a**, **19a** and **20a**.

Method (b).—A solution of a 3:90:7 mixture of the allylic acetates **18a**, **19a** and **20a** (0.015 g, 0.03 mmol) in acetic acid (1.5 cm^3) was stirred in the dark. At intervals, aliquots (≈0.5 cm^3) were removed, worked up [CH_2Cl_2 was added to the solution which, after having been washed successively with aq. $NaHCO_3$ and water, was dried ($MgSO_4$) and concentrated] and analysed. Compounds **18a**, **19a** and **20a** were present in proportions of 60:35:5 after 24 h, 77:16:7 after 48 h and 81:8:11 after 96 h.

The reaction of allylic bromide **14a** (0.015 g, 0.03 mmol) with silver(I) oxide and acetic acid was conducted simultaneously under similar conditions. The products comprised compounds

18a, **19a** and **20a** in proportions of 55:28:17 after 24 h, 71:15:14 after 48 h and 78:8:14 after 96 h.

Reactions of allylic bromides with silver(I) acetate

General procedure. A mixture of the allylic bromide (0.5 mmol), silver(I) acetate (0.084 g, 0.5 mmol) and dry acetonitrile (25 cm^3) was stirred for the time specified. The solvent was then evaporated and the residue was partitioned between methylene dichloride and water. After having been washed with water, the organic phase was dried ($MgSO_4$) and concentrated. The product was analysed by 300 or 400 MHz ^1H NMR spectroscopy and then purified in the manner described.

Reaction involving the allylic bromide 14a. (i) From the reaction involving the allylic bromide **14a** (0.051 g, 0.1 mmol), aliquots (≈1 cm^3) were removed, worked up and analysed at intervals. After 3 h (when no **14a** remained), mainly a 3:86:11 mixture of compounds **18a**, **19a** and **20a** was present. After 6 h, the proportions of compounds **18a**, **19a** and **20a** were 6:83:11. After 24 h, a 14:75:11 mixture of compounds **18a**, **19a** and **20a** was present. Finally, after 48 h, the proportions of compounds **18a**, **19a** and **20a** were 23:64:13.

(ii) The reaction involving the allylic bromide **14a** (0.255 g, 0.5 mmol) for 3 h gave rise to a product that, after crystallisation from diethyl ether–hexanes, comprised a 5:91:4 mixture of compounds **18a**, **19a** and **20a** (0.098 g, 40%).

Reaction involving the allylic bromide 14d. (*With A. Schofield.*)—The reaction involving the allylic bromide **14d** (0.270 g, 0.5 mmol) for 2.5 h gave rise to a product that comprised mainly a 5:87:8 mixture of the acetoxy derivatives **18d**, **19d** and **20d**. Crystallisation of the mixture from diethyl ether gave *ethyl (1″S)-2-[1″-acetoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]prop-2-enoate* **19d** (0.107 g, 41%); mp 96–98 °C; $[\alpha]_D$ −48 (*c* 0.77, CH_2Cl_2) (Found: C, 50.7; H, 5.7. $C_{22}H_{30}O_{14}$ requires C, 51.0; H, 5.8%); ν_{max} (KBr)/cm^{-1} 1765 and 1750 (ester C=O) and 1715 (unsat. ester C=O); δ_H (400 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7, *Me*CH_2), 2.01, 2.02, 2.03, 2.08 and 2.09 (each 3 H, s, 5 × $MeCO_2$), 3.73 (1 H, ddd, *J* 2, 4.5 and 10, 5′-H), 4.11 (1 H, dd, *J* 2 and 12, 6′-H), 4.15–4.31 (3 H, m, 6′-H and OCH_2Me), 4.86 (1 H, d, *J* 8, 1′-H), 5.05 (1 H, dd, *J* 8 and 9.5, 2′-H), 5.09 (1 H, t, *J* 10, 4′-H), 5.22 (1 H, t, *J* 9.5, 3′-H), 6.20 and 6.46 (each 1 H, s, 3-H_2) and 6.78 (1 H, s, 1″-H); δ_C (100 MHz; $CDCl_3$) 14.4 (CH_3CH_2), 20.9, 21.0 and 21.2 (4 × CH_3CO), 61.3 and 62.0 (OCH_2Me and 6′-CH_2), 68.6, 71.3, 72.5 and 73.0 (2′-, 3′-, 4′- and 5′-CH), 90.0 (1″-CH), 98.3 (1′-CH), 129.4 (3-CH_2), 136.3 (2-C), 164.6 (1-CO) and 169.6, 169.8, 170.5 and 171.0 (5 × Me*C*O); *m/z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 55), 169 (100) and 109 (70) {(after addition of KI) 557 [$M(K)^+$, 85%]}.

Reaction of the allylic bromide 14a with acetic acid in the presence of silver(I) oxide

(i) Silver(I) oxide (0.025 g, 0.11 mmol) was added to stirred acetic acid (5 cm^3) in the dark followed, after 1.5 h, by the allylic bromide **14a** (0.051 g, 0.1 mmol). At intervals, aliquots (≈1 cm^3) were removed, worked up [the sample was diluted with CH_2Cl_2 and filtered through a pad of Celite®; the filtrate was then washed successively with saturated aq. $NaHCO_3$ and water, dried ($MgSO_4$) and concentrated] and analysed. After 10 min, a 5:71:24 mixture of compounds **18a**, **19a** and **20a** was present. The proportions changed to 9:67:24 after 30 min, 26:52:22 after 3 h and 72:12:16 after 18 h.

(ii) The aforecited reaction of the allylic bromide **14a** (0.255 g, 0.5 mmol) was repeated and the product, obtained after 18 h, was subjected to HPLC [EtOAc–hexanes (2:1) as eluent] to give two fractions.

The first-eluted fraction (0.056 g, 23%), isolated as a colourless syrup, was identified as a 50:50 mixture of compounds **19a** and **20a**; δ_C (75 MHz; $CDCl_3$) 20.69, 20.72, 20.83, 20.90, 21.01, 21.18 and 21.29 (5 × CH_3CO), 26.24 and 26.29 (1-CH_3), 61.78 and 61.83 (6′-CH_2), 68.19, 68.42, 71.03, 71.08, 72.29, 72.38, 72.66 and 72.75 (2′-, 3′-, 4′- and 5′-CH), 89.81 and 92.24 (1″-CH), 98.44 and 102.5 (1′-CH), 127.5 and 128.9 (4-CH_2), 143.6 and 143.7 (3-C), 169.51, 169.54, 169.63, 169.66, 169.8, 170.2, 170.3 and 170.8 (5 × Me*C*O), and 197.0 (2-CO). After crystallisation from diethyl ether–hexanes, the sample (0.042 g, 17%) (now as a 44:56 mixture of **19a** and **20a**) showed mp 99–100 °C; $[\alpha]_D$ −36 (*c* 0.25, CH_2Cl_2).

The second-eluted fraction (0.124 g, 51%), isolated as a colourless syrup, was identified as the acetoxy derivative **18a**. After crystallisation from ethyl acetate–hexanes, the sample (0.104 g, 43%) showed mp 103–104 °C; $[\alpha]_D$ −8 (*c* 0.5, CH_2Cl_2).

Reactions of allylic bromides with alcohols in the presence of silver(I) oxide

General procedure. A suspension of silver(I) oxide (0.255 g, 1.1 mmol) in the alcohol (50 cm^3) was stirred in the dark for 1.5 h and then the allylic bromide (1 mmol) was added. After 24 h, the mixture was diluted with methylene dichloride and filtered through a pad of Celite®. The filtrate was washed successively with brine and water, dried ($MgSO_4$) and concentrated. Following analysis by 300 or 400 MHz ^1H NMR spectroscopy, the product was purified in the manner described.

Reaction involving the allylic bromide 14a and methanol. (i) From the reaction involving the allylic bromide **14a** (0.102 g, 0.2 mmol), aliquots (≈1 cm^3) were removed, worked up and analysed at intervals. After 2 h, compound **14a** was essentially depleted and mainly a 7:67:26 mixture of compounds **23a**, **24a** and **25a** was present [the proportions were estimated from the integrals of the signals at δ 7.50 (attributed to the 4-H of **23a**), 5.42 (assigned to the 1″-H of **24a**) and 5.70 (ascribed to the 1″-H of **25a**)]. Although the proportions remained unaltered over 120 h, new signals attributable to the dimethoxy derivative **26a** [δ 7.39 (4-H)] and to the tetraacetate **27** {as a 2:1 mixture of α- and β-anomers [δ 5.23 (3-H of α-anomer) and 5.53 (3-H of β-anomer)]} grew in intensity (the ratio of **23a** and **26a** was ≈1:1 after 24 h and ≈1:3 after 120 h).

(ii) The product obtained from the reaction of the allylic bromide **14a** (0.509 g, 1.0 mmol) was subjected to HPLC [EtOAc–hexanes (2:1) as eluent] to give three fractions.

The first-eluted fraction (0.302 g, 66%), isolated as a colourless syrup, was identified as a 70:30 mixture of compounds **24a** and **25a**; δ_H (300 MHz; $CDCl_3$ (*inter alia* for **25a**) 2.35 (3 H, s, 1-H_3), 3.25 (3 H, s, MeO), 4.82 (1 H, d, *J* 8, 1′-H), 5.70 (1 H, s, 1″-H) and 6.24 and 6.29 (each 1 H, s, 4-H_2). Crystallisation of the mixture from diethyl ether–hexanes gave *(1″R)-1″-methoxy-3-[1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]-but-3-en-2-one* **24a** (0.118 g, 26%); mp 113–114 °C; $[\alpha]_D$ −68 (*c* 0.5, CH_2Cl_2) (Found: C, 52.5; H, 5.8. $C_{20}H_{28}O_{12}$ requires C, 52.2; H, 6.1%); λ_{max} (EtOH)/nm 211 (ε 6800); ν_{max} (KBr)/cm^{-1} 1740 (ester C=O) and 1670 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.992, 1.993, 2.02 and 2.07 (each 3 H, s, 4 × $MeCO_2$), 2.34 (3 H, s, 1-H_3), 3.46 (3 H, s, MeO), 3.68 (1 H, ddd, *J* 3, 5 and 9.5, 5′-H), 4.14 and 4.19 [each 1 H, dd (*J* 3 and 12) and dd (*J* 5 and 12), 6′-H_2], 4.69 (1 H, d, *J* 8, 1′-H), 4.99–5.09 (2 H, m, 2′- and 4′-H), 5.19 (1 H, t, *J* 9.5, 3′-H), 5.42 (1 H, s, 1″-H) and 6.16 and 6.19 (each 1 H, s, 4-H_2); δ_C (75 MHz; $CDCl_3$) 20.72 and 20.82 (4 × CH_3CO), 26.51 (1-CH_3), 56.17 (CH_3O), 62.17 (6′-CH_2), 68.55, 71.35, 72.09 and 73.06 (2′-, 3′-, 4′- and 5′-CH), 97.62 and 100.0 (1′- and 1″-CH), 126.4 (4-CH_2), 145.4 (3-C), 169.2, 169.6, 170.4 and 170.7 (4 × Me*C*O) and 197.9 (2-CO); *m/z* (FAB) 483 [$M(Na)^+$, 5%], 385 ($C_{17}H_{21}O_{10}^+$, 5), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (25).

The second-eluted fraction (0.026 g, 6%), isolated as a colourless syrup, was identified as *(E)-3-methoxymethyl-4-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)-but-3-en-2-one* **23a**. After crystallisation from ethyl acetate–hexanes, the sample

(0.020 g, 4%) showed mp 121–122 °C; $[\alpha]_D$ −16 (*c* 0.25, CH_2Cl_2) (Found: C, 52.1; H, 5.8%); λ_{max} (EtOH)/nm 239 nm (ε 15 300); ν_{max} (Nujol)/cm^{-1} 1755 and 1742 (ester C=O), 1662 (vinylogous ester C=O) and 1645 (C=C); δ_H (300 MHz; $CDCl_3$) 2.03, 2.041, 2.043 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.28 (3 H, s, 1-H_3), 3.28 (3 H, s, MeO), 3.84 (1 H, ddd, *J* 2, 4.5 and 10, 5′-H), 4.14 (2 H, s, 3-CH_2O), 4.15 and 4.29 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.94 (1 H, d, *J* 7.5, 1′-H), 5.12–5.30 (3 H, m, 2′-, 3′- and 4′-H) and 7.50 (1 H, s, 4-H); *m/z* (FAB) 791 [$M(C_{14}H_{19}O_9)^+$, 12%], 483 [$M(Na)^+$, 78], 462 (MH_2^+, 24), 461 (MH^+, 95), 331 ($C_{14}H_{19}O_9^+$, 100), 169 (90) and 109 (64).

The third-eluted fraction (0.010 g, ≈7%), isolated as a colourless syrup, was mainly *(E)-4-methoxy-3-(methoxymethyl)-but-3-en-2-one* **26a**; λ_{max} (EtOH)/nm 249 (ε 11 400); δ_H (300 MHz; $CDCl_3$) *inter alia* 2.26 (3 H, s, 1-H_3), 3.33 (3 H, s, *Me*OCH_2), 3.92 (3 H, s, 4-MeO), 4.17 (2 H, s, 3-CH_2O) and 7.39 (1 H, s, 4-H); *m/z* (FAB) 146 (MH_2^+, 46%), 129 [$(M - CH_3)^+$, 100] and 113 [$(M - CH_3O)^+$, 94].

(iii) The product obtained from the reaction of the allylic bromide **14a** (0.509 g, 1.0 mmol) was subjected to column chromatography [EtOAc–light petroleum (2:1) as eluent] to give two fractions.

The first-eluted fraction (0.253 g, 55%), isolated as a colourless syrup, was a 65:35 mixture of the methoxy derivatives **24a** and **25a**. Crystallisation of the mixture from diethyl ether–light petroleum gave compound **24a** (0.115 g, 25%).

The second-eluted fraction (0.032 g, 7%) [0.019 g, 4% (after crystallisation from EtOAc–light petroleum)] was compound **23a**.

Reaction involving the allylic bromide 14a and ethanol. (i) The reaction involving the allylic bromide **14a** (0.509 g, 1.0 mmol) gave rise to a product that comprised mainly an 11:72:17 mixture of the ethoxy derivatives **23b**, **24b** and **25b** [the proportions were estimated from the integrals of the signals at *δ* 7.47 (attributed to the 4-H of **23b**), 5.51 (assigned to the 1″-H of **24b**) and 5.72 (ascribed to the 1″-H of **25b**)]. Subjection of the mixture to HPLC [EtOAc–hexanes (2:1) as eluent] led to the isolation of two fractions.

The first-eluted fraction (0.334 g, 70%), isolated as a colourless syrup, was identified as an 81:19 mixture of compounds **24b** and **25b**; δ_H (300 MHz; $CDCl_3$) (*inter alia* for **25b**) 2.34 (3 H, s, 1-H_3), 4.82 (1 H, d, *J* 8, 1′-H), 5.72 (1 H, s, 1″-H) and 6.24 and 6.25 (each 1 H, s, 4-H_2). Crystallisation of the mixture from diethyl ether–hexanes gave *(1″R)-1″-ethoxy-3-[1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]but-3-en-2-one* **24b** (0.104 g, 22%); mp 105–106 °C; $[\alpha]_D$ −56 (*c* 0.25, CH_2Cl_2) (Found: C, 52.9; H, 6.3. $C_{21}H_{30}O_{12}$ requires C, 53.2; H, 6.4%); λ_{max} (EtOH)/nm 211 (ε 6900); ν_{max} (KBr)/cm^{-1} 1745 (ester C=O) and 1675 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.21 (3 H, t, *J* 7, *Me*CH_2), 1.987, 1.990, 2.02 and 2.08 (each 3 H, s, 4 × $MeCO_2$), 2.34 (3 H, s, 1-H_3), 3.56 and 3.87 (each 1 H, dq, *J* 9.5 and 7, O*C*H_2Me), 3.67 (1 H, dt, *J* 10 and 3.5, 5′-H), 4.14–4.16 (2 H, m, 6′-H_2), 4.69 (1 H, d, *J* 8, 1′-H), 4.98–5.08 (2 H, m, 2′- and 4′-H), 5.19 (1 H, t, *J* 9.5, 3′-H), 5.51 (1 H, s, 1″-H) and 6.15 and 6.21 (each 1 H, s, 4-H_2); δ_C (75 MHz; $CDCl_3$) 15.02 (*C*H_3CH_2), 20.67, 20.69 and 20.79 (4 × *C*H_3CO), 26.53 (1-CH_3), 62.22 (6′-CH_2), 64.34 (O*C*H_2Me), 68.56, 71.34, 72.05 and 73.07 (2′-, 3′-, 4′- and 5′-CH), 97.51 and 98.53 (1′- and 1″-CH), 126.2 (4-CH_2), 145.7 (3-C), 169.2, 169.5, 170.3 and 170.6 (4 × Me*C*O) and 198.0 (2-CO); *m/z* (FAB) 601 [$M(C_7H_{11}O_2)^+$, 2%], 497 [$M(Na)^+$, 2], 331 ($C_{14}H_{19}O_9^+$, 34), 169 (66), 127 ($C_7H_{11}O_2^+$, 89), 109 (50), 99 ($C_5H_7O_2^+$, 79) and 43 ($C_2H_3O^+$, 100).

The second-eluted fraction (0.046 g, 10%), isolated as a colourless syrup, was identified as *(E)-3-ethoxymethyl-4-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one* **23b**. After crystallisation from ethyl acetate–hexanes, the sample (0.032 g, 7%) showed mp 102–104 °C; $[\alpha]_D$ −12 (*c* 0.25, CH_2Cl_2) (Found: C, 53.2; H, 6.4%); λ_{max} (EtOH)/nm 239 (ε 17 100); ν_{max} (KBr)/cm^{-1} 1760 and 1740 (ester C=O), 1690 (vinylogous ester C=O) and 1610 (C=C); δ_H (300 MHz; $CDCl_3$) 1.17 (3 H, t, *J* 7, *Me*CH_2), 2.03, 2.040, 2.042 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.29 (3 H, s, 1-H_3), 3.45 (2 H, q, *J* 7, O*C*H_2Me), 3.83 (1 H, ddd, *J* 2, 4.5 and 10, 5′-H), 4.14 and 4.29 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.19 (2 H, s, 3-CH_2O), 4.94 (1 H, d, *J* 7.5, 1′-H), 5.11–5.29 (3 H, m, 2′-, 3′- and 4′-H) and 7.47 (1 H, s, 4-H); δ_C (75 MHz; $CDCl_3$) 15.28 (*C*H_3CH_2), 20.59, 20.65 and 20.78 (4 × *C*H_3CO), 26.75 (1-CH_3), 61.30, 61.57 and 65.79 (6′-CH_2, 3-CH_2 and O*C*H_2Me), 67.82, 70.63, 72.23 and 72.77 (2′-, 3′-, 4′- and 5′-CH), 100.9 (1′-CH), 120.6 (3-C), 156.0 (4-CH), 169.1, 169.4, 170.2 and 170.6 (4 × Me*C*O) and 197.4 (2-CO); *m/z* (FAB) 497 [$M(Na)^+$, 6%], 475 (MH^+, 18), 331 ($C_{14}H_{19}O_9^+$, 100), 169 (53), 109 (22) and 43 ($C_2H_3O^+$, 53).

(ii) The product obtained from the reaction of the allylic bromide **14a** (0.255 g, 0.5 mmol) was subjected to column chromatography [EtOAc–light petroleum (2:1) as eluent]. One main fraction (0.142 g, 60%) was obtained; it comprised largely a 67:33 mixture of the ethoxy derivatives **24b** and **25b**.

Reaction involving the allylic bromide 14a and propan-1-ol. (i) The reaction involving the allylic bromide **14a** (0.509 g, 1.0 mmol) gave rise to a product that comprised mainly a 13:62:25 mixture of the propoxy derivatives **23c**, **24c** and **25c** [the proportions were estimated from the integrals of the signals at *δ* 7.47 (attributed to the 4-H of **23c**), 5.50 (assigned to the 1″-H of **24c**) and 5.73 (ascribed to the 1″-H of **25c**)]. Subjection of the mixture to HPLC [EtOAc–hexanes (2:1) as eluent] led to the isolation of two fractions.

The first-eluted fraction (0.322 g, 66%), isolated as a colourless syrup, was identified as a 72:28 mixture of *(1″R)-3-[1″-propoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)-methyl]but-3-en-2-one* **24c** and its *(1″S)-isomer* **25c**. After crystallisation from diethyl ether–hexanes, the sample (0.176 g, 36%) (still as a 72:28 mixture of **24c** and **25c**) showed mp 98–100 °C; $[\alpha]_D$ −46 (*c* 0.5, CH_2Cl_2) (Found: C, 54.3; H, 6.9. $C_{22}H_{32}O_{12}$ requires C, 54.1; H, 6.6%); λ_{max} (EtOH)/nm 211 (ε 6600); ν_{max} (KBr)/cm^{-1} 1745 (ester C=O) and 1675 (enone C=O); δ_H (300 MHz; $CDCl_3$) 0.89 and 0.91 (0.84 and 2.16 H, each t, *J* 7.5, *Me*CH_2), 1.52–1.66 (2 H, m, MeCH_2), 1.99, 2.01, 2.02, 2.03, 2.07 and 2.08 (4.32, 0.84, 3.00, 0.84, 0.84 and 2.16 H, each s, 4 × $MeCO_2$), 2.33 and 2.34 (2.16 and 0.84 H, each s, 1-H_3), 3.36–3.48 and 3.73–3.81 [each 1 H, m and dt (*J* 9.5 and 6.5), O*C*H_2Et], 3.63–3.71 (1 H, m, 5′-H), 4.08, 4.14–4.16 and 4.21 [0.28, 1.44 and 0.28 H, dd (*J* 2 and 12), m and dd (*J* 5 and 12), 6′-H_2], 4.70 and 4.83 (0.72 and 0.28 H, each d, *J* 8, 1′-H), 4.98–5.10 (2 H, m, 2′- and 4′-H), 5.19 and 5.23 (0.72 and 0.28 H, each t, *J* 9.5, 3′-H), 5.50 and 5.73 (0.72 and 0.28 H, each s, 1″-H) and 6.14, 6.20, 6.23 and 6.25 (0.72, 0.72, 0.28 and 0.28 H, each s, 4-H_2); δ_C (75 MHz; $CDCl_3$) 10.66 and 10.71 (*C*H_3CH_2 of **24c** and **25c**), 20.73 and 20.83 (4 × *C*H_3CO), 22.80 and 22.90 (CH_3CH_2 of **24c** and **25c**), 26.56 and 26.59 (1-CH_3 of **25c** and **24c**), 61.99 and 62.22 (6′-CH_2 of **25c** and **24c**), 67.80 and 70.55 (O*C*H_2Et of **25c** and **24c**), 68.51, 68.55, 71.24, 71.35, 72.06, 72.98 and 73.11 (2′-, 3′-, 4′- and 5′-CH), 95.83, 96.32, 97.48 and 98.76 (1′- and 1″-CH), 126.1 and 128.2 (4-CH_2 of **24c** and **25c**), 144.5 and 145.7 (3-C of **25c** and **24c**), 169.2, 169.3, 169.6, 170.4, 170.7 and 170.8 (4 × Me*C*O) and 197.7 and 198.0 (2-CO of **25c** and **24c**); *m/z* (FAB) 628 [$M(C_8H_{12}O_2)^+$, 8%], 527 [$M(K)^+$, 3], 511 [$M(Na)^+$, 8], 489 (MH^+, 1), 331 ($C_{14}H_{19}O_9^+$, 23), 169 (37), 141 ($C_8H_{13}O_2^+$, 46), 109 (25) and 99 ($C_5H_7O_2^+$, 100).

The second-eluted material (0.054 g, 11%), isolated as a colourless syrup, was identified as *(E)-3-propoxymethyl-4-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one* **23c**. After crystallisation from ethyl acetate–hexanes, the sample (0.038 g, 8%) showed mp 81–82 °C; $[\alpha]_D$ +4 (*c* 0.25, CH_2Cl_2) (Found: C, 53.8; H, 6.5%); λ_{max} (EtOH)/nm 239 (ε 17 200); ν_{max} (KBr)/cm^{-1} 1760 and 1735 (ester C=O), 1690 (vinylogous ester C=O) and 1610 (C=C); δ_H (300 MHz; $CDCl_3$) 0.89 (3 H, t, *J* 7.5,

MeCH_2), 1.50–1.60 (2 H, m, MeCH_2), 2.03, 2.04 and 2.09 (3, 6 and 3 H, each s, 4 × $MeCO_2$), 2.29 (3 H, s, 1-H_3), 3.34 (2 H, t, *J* 6.5, OCH_2Et), 3.82 (1 H, ddd, *J* 2.5, 5 and 10, 5′-H), 4.08–4.23 (3 H, m, 6′-H and 3-CH_2O), 4.29 (1 H, dd, *J* 5 and 12.5, 6′-H), 4.93 (1 H, d, *J* 7.5, 1′-H), 5.11–5.29 (3 H, m, 2′-, 3′- and 4′-H) and 7.47 (1 H, s, 4-H); δ_C (75 MHz; $CDCl_3$) 10.74 (CH_3CH_2), 20.64, 20.68 and 20.81 (4 × CH_3CO), 22.98 (CH_3CH_2), 26.91 (1-CH_3), 61.59 and 61.63 (6′-CH_2 and 3-CH_2), 67.89, 70.71, 72.20 and 72.83 (2′-, 3′-, 4′- and 5′-CH), 72.31 (O*C*H_2Et), 101.0 (1′-CH), 120.5 (3-C), 155.8 (4-CH), 169.1, 169.4, 170.2 and 170.7 (4 × Me*C*O) and 197.6 (2-CO); *m/z* (FAB) 511 [M(Na)$^+$, 7%], 489 (MH^+, 7), 331 ($C_{14}H_{19}O_9^+$, 62), 169 (100), 109 (68) and 43 (88).

(ii) The product obtained from the reaction of the allylic bromide **14a** (0.153 g, 0.3 mmol) was subjected to column chromatography [EtOAc–light petroleum (2:1) as eluent]. One main fraction (0.083 g, 56%) was obtained; it comprised largely a 55:45 mixture of the propoxy derivatives **24c** and **25c**.

Reaction involving the allylic bromide 14a and isopropyl alcohol. (i) The reaction involving the allylic bromide **14a** (0.509 g, 1.0 mmol) gave rise to a product that comprised mainly a 15:67:18 mixture of the isopropoxy derivatives **23d**, **24d** and **25d** [the proportions were estimated from the integrals of the signals at δ 7.44 (attributed to the 4-H of **23d**), 5.61 (assigned to the 1″-H of **24d**) and 5.72 (ascribed to the 1″-H of **25d**)]. Subjection of the mixture to HPLC [EtOAc–hexanes (2:1) as eluent] led to the isolation of two fractions.

The first-eluted fraction (0.316 g, 65%), isolated as a colourless syrup, was identified as a 79:21 mixture of compounds **24d** and **25d**; δ_H (300 MHz; $CDCl_3$) (*inter alia* for **25d**) 2.34 (3 H, s, 1-H_3), 4.80 (1 H, d, *J* 8, 1′-H), 5.72 (1 H, s, 1″-H) and 6.22 and 6.25 (each 1 H, s, 4-H_2). Crystallisation of the mixture from diethyl ether–hexanes gave *(1″R)-3-[1″-isopropoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]but-3-en-2-one* **24d** (0.104 g, 21%); mp 113–114 °C; $[\alpha]_D$ −76 (*c* 0.25, CH_2Cl_2) (Found: C, 53.9; H, 6.6. $C_{22}H_{32}O_{12}$ requires C, 54.1; H, 6.6%); λ_{max} (EtOH)/nm 212 (ε 6900); ν_{max} (KBr)/cm^{-1} 1740 (ester C=O) and 1670 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.14 and 1.22 (each 3 H, d, *J* 6, *Me*$_2$CH), 1.988, 1.992, 2.02 and 2.08 (each 3 H, s, 4 × $MeCO_2$), 2.33 (3 H, s, 1-H_3), 3.66 (1 H, dt, *J* 10 and 4, 5′-H), 4.04 (1 H, sept, *J* 6, OC*H*Me$_2$), 4.15 (2 H, d, separation 4, 6′-H_2), 4.68 (1 H, d, *J* 8, 1′-H), 4.98–5.07 (2 H, m, 2′- and 4′-H), 5.18 (1 H t, *J* 9.5, 3′-H), 5.61 (1 H, s, 1″-H) and 6.13 and 6.20 (each 1 H, s, 4-H_2); δ_C (75 MHz; $CDCl_3$) 20.71, 20.73 and 20.83 (4 × CH_3CO), 21.37 and 23.23 [(CH_3)$_2$CH], 26.66 (1-CH_3), 62.30 (6′-CH_2), 68.63, 70.22, 71.39, 72.05 and 73.18 (2′-, 3′-, 4′- and 5′-CH and O*C*HMe$_2$), 96.24 and 97.17 (1′- and 1″-CH), 126.1 (4-CH_2), 146.3 (3-C), 169.2, 169.6, 170.4 and 170.7 (4 × Me*C*O) and 198.2 (2-CO); *m/z* (FAB) 489 (MH^+, 1%), 331 ($C_{14}H_{19}O_9^+$, 45), 169 (100) and 141 ($C_8H_{13}O_2^+$, 60).

The second-eluted fraction (0.064 g, 13%), isolated as a colourless syrup, was identified as *(E)-3-isopropoxymethyl-4-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one* **23d**. After crystallisation from ethyl acetate–hexanes, the sample (0.044 g, 9%) showed mp 99–100 °C; $[\alpha]_D$ +8 (*c* 0.25, CH_2Cl_2) (Found: C, 54.1; H, 6.6%); λ_{max} (EtOH)/nm 239 (ε 15 600); ν_{max} (KBr)/cm^{-1} 1760 and 1735 (ester C=O), 1690 (vinylogous ester C=O) and 1610 (C=C); δ_H (300 MHz; $CDCl_3$) 1.14 and 1.15 (each 3 H, d, *J* 6, *Me*$_2$CH), 2.02, 2.038, 2.043 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.29 (3 H, s, 1-H_3), 3.58 (1 H, sept, *J* 6, OC*H*Me$_2$), 3.82 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 4.11–4.16 and 4.29 [each 1 H, m and dd (*J* 4.5 and 12.5), 6′-H_2], 4.14 and 4.22 (each 1 H, d, *J* 10.5, 3-CH_2O), 4.93 (1 H, d, *J* 7.5, 1′-H), 5.11–5.29 (3 H, m, 2′-, 3′- and 4′-H) and 7.44 (1 H, s, 4-H); δ_C (75 MHz; $CDCl_3$) 20.61 and 20.75 (4 × CH_3CO), 22.08 and 22.16 [(CH_3)$_2$CH], 26.86 (1-CH_3), 59.05 and 61.56 (3-CH_2 and 6′-CH_2), 67.80, 70.66, 71.16, 72.29 and 72.72 (2′-, 3′-, 4′- and 5′-CH and O*C*HMe$_2$), 100.8 (1′-CH), 120.8 (3-C), 155.6 (4-CH), 169.0, 169.4, 170.2 and 170.6 (4 × Me*C*O) and 197.5 (2-CO); *m/z* (FAB) 511 [M(Na)$^+$, 6%], 489 (MH^+, 17), 331 ($C_{14}H_{19}O_9^+$, 93), 169 (100) and 109 (71).

(ii) The product from the reaction of the allylic bromide **14a** (0.382 g, 0.75 mmol) was subjected to column chromatography [EtOAc–light petroleum (2:1) as eluent] to give three fractions.

The first-eluted fraction (0.070 g, 19%) was identified as a 58:42 mixture of the isopropoxy derivatives **24d** and **25d**.

The second-eluted fraction (0.025 g, ≈7%) was mainly a 70:30 mixture of the isopropoxy derivatives **24d** and **25d**. Crystallisation of the mixture from diethyl ether–light petroleum gave compound **24d** (0.011 g, 3%) {mp 114–115 °C; $[\alpha]_D$ −78 (*c* 0.2, $CHCl_3$)}.

The third-elution fraction (0.020 g, 5%) was mainly compound **23d**.

Reaction involving the allylic bromide 14a and *tert*-butyl alcohol. (i) The reaction involving the allylic bromide **14a** (0.102 g, 0.2 mmol) [in the presence of CH_2Cl_2 (2 cm^3)] gave rise to a product that comprised mainly a 29:61:10 mixture of the *tert*-butoxy derivatives **23e**, **24e** and **25e** [the proportions were estimated from the integrals of the signals at δ 7.40 (attributed to the 4-H of **23e**), 5.84 (assigned to the 1″-H of **24e**) and 5.79 (ascribed to the 1″-H of **25e**)]. Subjection of the mixture to HPLC [EtOAc–hexanes (2:1) as eluent] led to the isolation of two fractions.

The first-eluted fraction (0.050 g, 50%), isolated as a colourless syrup, was identified as a 84:16 mixture of the *tert*-butoxy derivatives **24e** and **25e**. Crystallisation of the mixture from diethyl ether–hexanes gave *(1″R)-3-[1″-(tert-butoxy)-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]but-3-en-2-one* **24e** (0.016 g, 16%); mp 137–138 °C; $[\alpha]_D$ −79 (*c* 0.3, $CHCl_3$) (Found: C, 54.7; H, 6.7. $C_{23}H_{34}O_{12}$ requires C, 55.0; H, 6.8%); λ_{max} (EtOH)/nm 207 (ε 7100); ν_{max} (Nujol)/cm^{-1} 1755 (ester C=O) and 1670 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.25 (9 H, s, Me_3C), 1.99, 2.02 and 2.08 (3, 6 and 3 H, each s, 4 × $MeCO_2$), 2.33 (3 H, s, 1-H_3), 3.59 (1 H, dt, *J* 10 and 4, 5′-H), 4.13 (2 H, d, separation 4, 6′-H_2), 4.69 (1 H, d, *J* 8, 1′-H), 4.96–5.06 (2 H, m, 2′- and 4′-H), 5.17 (1 H, t, *J* 9.5, 3′-H), 5.84 (1 H, s, 1″-H) and 6.11 and 6.16 (each 1 H, s, CH_2C); *m/z* (FAB) 525 [M(Na)$^+$, 10%], 503 (MH^+, 4), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (45).

The second-eluted fraction (0.016 g, 16%), isolated as a colourless syrup, was identified as *(E)-3-(tert-butoxymethyl)-4-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)but-3-en-2-one* **23e**. After crystallisation from ethyl acetate–hexanes, the sample (0.012 g, 12%) showed mp 92–93 °C; $[\alpha]_D$ +14 (*c* 0.25, CH_2Cl_2) (Found: C, 54.8; H, 6.8%); λ_{max} (EtOH)/nm 240 (ε 15 300); ν_{max} (Nujol)/cm^{-1} 1756 (ester C=O), 1687 (vinylogous ester C=O) and 1605 (C=C); δ_H (300 MHz; $CDCl_3$) 1.19 (9 H, s, Me_3C), 2.00, 2.01, 2.02 and 2.06 (each 3 H, s, 4 × $MeCO_2$), 2.26 (3 H, s, 1-H_3), 3.81 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.05 and 4.15 (each 1 H, d, *J* 9.5, CH_2OCMe$_3$), 4.11 and 4.26 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.92 (1 H, d, *J* 7.5, 1′-H), 5.09–5.26 (3 H, m, 2′-, 3′- and 4′-H) and 7.40 (1 H, s, 4-H); *m/z* (FAB) 525 [M(Na)$^+$, 9%], 503 (MH^+, 8), 331 ($C_{14}H_{19}O_9^+$, 60) and 169 (100).

(ii) The product obtained from the reaction of the allylic bromide **14a** (0.255 g, 0.5 mmol) [in the presence of CH_2Cl_2 (5 cm^3)] was subjected to column chromatography [EtOAc–light petroleum (2:1) as eluent] to give two fractions.

The first-eluted fraction (0.099 g, 39%) was a 73:27 mixture of the *tert*-butoxy derivatives **24e** and **25e**. Crystallisation of the mixture from diethyl ether–hexanes gave compound **24e** (0.065 g, 26%).

The second-eluted fraction (0.049 g, 20%) [0.025 g, 10% (after crystallisation from EtOAc–light petroleum)] was compound **23e**.

Reaction involving the allylic bromide 14b and methanol. The reaction involving the allylic bromide **14b** (0.314 g, 0.6 mmol) gave rise to a product that comprised mainly a 7:63:30 mixture

of the methoxy derivatives **28a**, **29a** and **30a** [the proportions were estimated from the integrals of the signals at δ 7.50 (attributed to the 1-H of **28a**), 5.44 (ascribed to the 1″-H of **29a**) and 5.72 (assigned to 1″-H of **30a**)]. There was also evidence for the presence of the dimethoxy derivative **26b** [δ 7.40 (1-H), 3.93 (1-MeO) and 3.35 (*Me*OCH$_2$)] (the ratio of **28a** and **26b** was ≈1:2) and the tetraacetate **27**. Subjection of the mixture to column chromatography [EtOAc–light petroleum (2:1) as eluent] led to the isolation of one major fraction (0.167 g, 59%) identified as a 69:31 mixture of *(1″R)-2-[1″-methoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]pent-1-en-3-one* **29a** and its *(1″S)-isomer* **30a**. After crystallisation from diethyl ether–light petroleum, the sample (0.117 g, 41%) (still as a 69:31 mixture of **29a** and **30a**) showed mp 57–58 °C; $[\alpha]_D$ −3 (*c* 0.4, $CHCl_3$) (Found: C, 53.3; H, 6.2. $C_{21}H_{30}O_{12}$ requires C, 53.2; H, 6.4%); λ_{max} (EtOH)/nm 212 (ε 7100); ν_{max} (KBr)/cm^{-1} 1750 (ester C=O) and 1680 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.09 and 1.10 (2.07 and 0.93 H, each t, *J* 7, 5-H$_3$), 1.99, 2.01, 2.02, 2.04 and 2.07 (4.14, 0.93, 4.14, 0.93 and 1.86 H, each s, 4 × $MeCO_2$), 2.61–2.80 (2 H, m, 4-H$_2$), 3.25 and 3.46 (0.93 and 2.07 H, each s, MeO), 3.67–3.71 (1 H, m, 5′-H), 4.06–4.26 (2 H, m, 6′-H$_2$), 4.69 and 4.84 (0.69 and 0.31 H, each d, *J* 8, 1′-H), 5.00–5.12 (2 H, m, 2′- and 4′-H), 5.19 and 5.24 (0.69 and 0.31 H, each t, *J* 9.5, 3′-H), 5.44 and 5.72 (0.69 and 0.31 H, each s, 1″-H), and 6.14, 6.18 and 6.26 (1.38, 0.31 and 0.31 H, each s, 1-H$_2$); *m/z* (FAB) 497 [M(Na)$^+$, 1%], 331 ($C_{14}H_{19}O_9^+$, 65) and 169 (100).

Reaction involving the allylic bromide 14b and isopropyl alcohol. The reaction involving the allylic bromide **14b** (0.314 g, 0.6 mmol) gave rise to a product that comprised mainly a 20:52:28 mixture of the isopropoxy derivatives **28b**, **29b** and **30b** [the proportions were estimated from the integrals of the signals at δ 7.44 (attributed to the 1-H of **28b**), 5.62 (ascribed to the 1″-H of **29b**) and 5.72 (assigned to the 1″-H of **30b**)]. Subjection of the mixture to column chromatography [EtOAc–light petroleum (2:1) as eluent] led to the isolation of one major fraction (0.131 g, 43%), identified as a 66:34 mixture of *(1″R)-2-[1″-isopropoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]pent-1-en-3-one* **29b** and its *(1″S)-isomer* **30b**. After crystallisation from diethyl ether–light petroleum, the sample (0.095 g, 31%) (now as a 69:31 mixture of **29b** and **30b**) showed mp 84–85 °C; $[\alpha]_D$ −61 (*c* 0.5, $CHCl_3$) (Found: C, 54.7; H, 7.0. $C_{23}H_{34}O_{12}$ requires C, 55.0; H, 6.8%); λ_{max} (EtOH)/nm 210 (ε 8500); ν_{max} (Nujol)/cm^{-1} 1744 (ester C=O) and 1680 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.06–1.25 (9 H, m, 5-H$_3$ and Me_2CH), 1.976, 1.988, 1.992, 2.005, 2.02, 2.03, 2.06 and 2.08 (0.93, 2.07, 2.07, 0.93, 2.07, 0.93, 0.93 and 2.07 H, each s, 4 × $MeCO_2$), 2.58–2.84 (2 H, m, 4-H$_2$), 3.66 (1 H, ddd, *J* 3, 4.5 and 10, 5′-H), 3.88 (0.31 H, sept, *J* 6, 0.31 × C*H*Me$_2$), 3.98–4.22 (2.69 H, m, 0.69 × C*H*Me$_2$ and 6′-H$_2$), 4.68 and 4.81 (0.69 and 0.31 H, each d, *J* 8, 1′-H), 4.98–5.09 (2 H, m, 2′- and 4′-H), 5.18 and 5.22 (0.69 and 0.31 H, each t, *J* 9.5, 3′-H), 5.62 and 5.72 (0.69 and 0.31 H, each s, 1″-H) and 6.12, 6.16, 6.20 and 6.21 (0.69, 0.69, 0.31 and 0.31 H, each s, CH_2C); *m/z* (FAB) 525 [M(Na)$^+$, 12%], 503 (MH$^+$, 3), 331 ($C_{14}H_{19}O_9^+$, 65), 169 (40) and 113 (100).

Reaction involving the allylic bromide 14b and *tert*-butyl alcohol. The reaction involving the allylic bromide **14b** (0.262 g, 0.5 mmol) [in the presence of CH_2Cl_2 (5 cm^3)] gave rise to a product that comprised mainly a 29:49:22 mixture of the *tert*-butoxy derivatives **28c**, **29c** and **30c** [the proportions were estimated from the integrals of the signals at δ 7.41 (attributed to the 1-H of **28c**), 5.86 (ascribed to the 1″-H of **29c**) and 5.80 (assigned to the 1″-H of **30c**)]. Subjection of the mixture to column chromatography [EtOAc–light petroleum (2:1) as eluent] led to the isolation of one main fraction (0.132 g, 52%), identified as a 69:31 mixture of *(1″R)-2-[1″-(tert-butoxy)-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]pent-1-en-3-one* **29c** and its *(1″S)-isomer* **30c**. After two crystallisations from diethyl ether–light petroleum, the sample (0.038 g, 15%) (now as an 86:14 mixture of **29c** and **30c**) showed mp 123–125 °C; $[\alpha]_D$ −70 (*c* 0.35, $CHCl_3$) (Found: C, 55.8; H, 6.9. $C_{24}H_{36}O_{12}$ requires C, 55.8; H, 7.0%); λ_{max} (EtOH)/nm 209 (ε 5900); ν_{max} (Nujol)/cm^{-1} 1748 (ester C=O) and 1678 (enone C=O); δ_H (300 MHz; $CDCl_3$) 1.08 (3 H, t, *J* 7.5, 5-H$_3$), 1.24 and 1.26 (1.3 and 7.7 H, each s, Me_3C), 1.99, 2.00, 2.01, 2.02, 2.03, 2.06 and 2.09 (2.58, 0.42, 0.42, 3.00, 2.58, 0.42 and 2.58 H, each s, 4 × $MeCO_2$), 2.57–2.85 (2 H, m, 4-H$_2$), 3.62 (1 H, ddd, *J* 3, 4.5 and 10, 5′-H), 4.09–4.19 (2 H, m, 6′-H$_2$), 4.69 and 4.76 (0.86 and 0.14 H, each d, *J* 8, 1′-H), 4.96–5.08 (2 H, m, 2′- and 4′-H), 5.17 and 5.19 (0.86 and 0.14 H, each t, *J* 9.5, 3′-H), 5.80 and 5.86 (0.14 and 0.86 H, each s, 1″-H) and 6.10, 6.125, 6.133 and 6.15 (0.86, 0.86, 0.14 and 0.14 H, each s, 1-H$_2$); *m/z* (FAB) 539 [M(Na)$^+$, 35%], 517 (MH$^+$, 5), 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (15).

Reaction involving the allylic bromide 14c and methanol. (i) The reaction involving the allylic bromide **14c** (0.210 g, 0.4 mmol) gave rise to a product that comprised mainly a 12:67:21 mixture of the methoxy derivatives **31a**, **32a** and **33a** [the ratio was estimated from the integrals of the signals at δ 7.60 (attributed to the 3-H of **31a**), 5.40 (assigned to the 1″-H of **32a**) and 5.70 (ascribed to the 1″-H of **33a**)]. Subjection of the mixture to HPLC [EtOAc–hexanes (2:1) as eluent] led to the isolation of two fractions.

The first-eluted fraction (0.122 g, 64%) was identified as a 74:26 mixture of *methyl (1″R)-2-[1″-methoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]propenoate* **32a** and its *(1″S)-isomer* **33a**. After crystallisation from diethyl ether–hexanes, the sample (0.064 g, 35%) (now as an 84:16 mixture of **32a** and **33a**) showed mp 87–89 °C; $[\alpha]_D$ −60 (*c* 0.4, $CHCl_3$) (Found: C, 50.1; H, 5.8. $C_{20}H_{28}O_{13}$ requires C, 50.4; H, 5.9%); ν_{max} (KBr)/cm^{-1} 1760 (ester C=O), 1725 (unsat. ester C=O) and 1650 (C=C); δ_H (300 MHz; $CDCl_3$) 2.00, 2.01, 2.02, 2.024, 2.03, 2.04, 2.08 and 2.09 (2.68, 2.68, 0.32, 2.68, 0.32, 0.32, 0.32 and 2.68 H, each s, 4 × $MeCO_2$), 3.25 and 3.46 (0.32 and 2.68 H, each s, MeO), 3.64 (1 H, ddd, *J* 2.5, 5 and 10, 5′-H), 3.78 and 3.79 (2.68 and 0.32 H, each s, MeO_2C), 4.10, 4.11, 4.20 and 4.26 [0.84, 0.16, 0.84 and 0.16 H, dd (*J* 2.5 and 12.5), dd (*J* 2.5 and 12.5), dd (*J* 5 and 12.5) and dd (*J* 5 and 12.5), 6′-H$_2$], 4.71 and 4.85 (0.84 and 0.16 H, each d, *J* 8, 1′-H), 5.03–5.11 (2 H, m, 2′- and 4′-H), 5.20 and 5.23 (0.84 and 0.16 H, each t, *J* 9.5, 3′-H), 5.40 and 5.70 (0.84 and 0.16 H, each s, 1″-H) and 6.08, 6.10, 6.32 and 6.46 [0.84, 0.16, 0.84 and 0.16 H, t (*J* 1), t (*J* 1), d (*J* 1) and d (*J* 1), 3-H$_2$]; *m/z* (FAB) 807 [M($C_{14}H_{19}O_9$)$^+$, 2%], 499 [M(Na)$^+$, 12], 477 (MH$^+$, 2), 331 ($C_{14}H_{19}O_9^+$, 50), 169 (70) and 129 ($C_6H_9O_3^+$, 100).

The second-eluted fraction (0.016 g, 8%) was *methyl (E)-2-methoxymethyl-3-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)propenoate* **31a**; δ_H (300 MHz; $CDCl_3$) 2.02, 2.04 and 2.09 (3, 6 and 3 H, each s, 4 × $MeCO_2$), 3.28 (3 H, s, MeO), 3.75 (3 H, s, MeO_2C), 3.82 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.12 (2 H, s, 2-CH_2O), 4.14 and 4.29 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H$_2$], 4.92 (1 H, d, *J* 7.5, 1′-H), 5.11–5.28 (3 H, m, 2′-, 3′- and 4′-H) and 7.60 (1 H, s, 3-H).

(ii) The product from the reaction of the allylic bromide **14c** (0.368 g, 0.7 mmol) was subjected to column chromatography [EtOAc–light petroleum (2:1) as eluent] to give two fractions.

The first-eluted fraction (0.182 g, 52%) was a 75:25 mixture of the methoxy derivatives **32a** and **33a**.

The second-eluted fraction (0.029 g, ≈9%) was mainly compound **31a**.

Reaction involving the allylic bromide 14c and isopropyl alcohol. (i) The reaction involving the allylic bromide **14c** (0.210 g, 0.4 mmol) gave rise to a product that comprised mainly a 26:61:13 mixture of the isopropoxy derivatives **31b**, **32b** and

33b [the proportions were estimated from the integrals of the signals at δ 7.54 (attributed to the 3-H of **31b**), 5.58 (ascribed to the 1″-H of **32b**) and 5.70 (assigned to the 1″-H of **33b**)]. Subjection of the mixture to HPLC [EtOAc–hexanes (1 : 1) as eluent] gave two fractions.

The first-eluted fraction (0.110 g, 55%) was identified as an 82 : 18 mixture of the isopropoxy derivatives **32b** and **33b**. Crystallisation of the mixture from diethyl ether–hexanes gave *methyl (1″R)-2-[1″-isopropoxy-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)methyl]propenoate* **32b** (0.034 g, 17%); mp 108–109 °C; $[\alpha]_D$ −58 (*c* 1.54, $CHCl_3$) (Found: C, 52.2; H, 6.2. $C_{22}H_{32}O_{13}$ requires C, 52.4; H, 6.4%); λ_{max} (EtOH)/nm 206 (ε 6200); δ_H (300 MHz; $CDCl_3$) 1.16 and 1.23 [each 3 H, d (*J* 6) and d (*J* 6.5), Me_2CH], 2.00, 2.01, 2.02 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 3.62 (1 H, ddd, *J* 2.5, 5 and 10, 5′-H), 3.77 (3 H, s, MeO_2C), 4.00–4.10 (2 H, m, OC*H*Me_2 and 6′-H), 4.18 (1 H, dd, *J* 5 and 12, 6′-H), 4.71 (1 H, d, *J* 8, 1′-H), 5.02–5.09 (2 H, m, 2′- and 4′-H), 5.19 (1 H, t, *J* 9.5, 3′-H), 5.58 (1 H, s, 1″-H) and 6.11 and 6.29 (each 1 H, s, 3-H_2); *m/z* (FAB) 661 (5%), 505 (MH^+, 2), 331 ($C_{14}H_{19}O_9^+$, 20), 169 (35) and 115 (100).

The second-eluted fraction (0.044 g, 22%) was compound **31b**.

(ii) The product from the reaction of the allylic bromide **14c** (0.525 g, 1.0 mmol) was subjected to column chromatography [EtOAc–light petroleum (1 : 1) as eluent] to give two fractions.

The first-eluted fraction (0.341 g, 67%) was an 83 : 17 mixture of the isopropoxy derivatives **32b** and **33b**. Crystallisation of the mixture from diethyl ether–light petroleum gave compound **32b** (0.213 g, 42%).

The second-eluted fraction (0.020 g, 5%) [0.013 g, 3% (after crystallisation from EtOAc–light petroleum)] was identified as *methyl (E)-2-isopropoxymethyl-3-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)propenoate* **31b**; mp 88–89.5 °C; $[\alpha]_D$ −19 (*c* 0.22, $CHCl_3$) (Found: C, 52.4; H, 6.5. $C_{22}H_{32}O_{13}$ requires C, 52.4; H, 6.4%); λ_{max} (EtOH)/nm 227 (ε 16 300); δ_H (300 MHz; $CDCl_3$) 1.14 and 1.16 (each 3 H, d, *J* 6, Me_2CH), 2.03, 2.04, 2.05 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.60 (1 H, sept, *J* 6, OC*H*Me_2), 3.75 (3 H, s MeO_2C), 3.82 (1 H, ddd, *J* 2.5, 4.5 and 9.5, 5′-H), 4.12–4.18 and 4.30 [each 1 H, m, and dd (*J* 4.5 and 12.5), 6′-H_2], 4.15 (2 H, AB q, *J* 10.5, separation of inner lines 12.5, 2-CH_2O), 4.92 (1 H, d, *J* 7, 1′-H), 5.12–5.21 (2 H, m, 2′- and 4′-H), 5.26 (1 H, t, *J* 9, 3′-H) and 7.54 (1 H, s, 3-H); *m/z* (FAB) 527 [$M(Na)^+$, 30%], 505 (MH^+, 5), 331 ($C_{14}H_{19}O_9^+$, 84), 169 (100) and 109 (77).

Reaction involving the allylic bromide 14c and *tert*-butyl alcohol. The reaction involving the allylic bromide **14c** (0.368 g, 0.7 mmol) [in the presence of CH_2Cl_2 (5 cm^3)] gave rise to a product that comprised mainly a 35 : 53 : 12 mixture of the *tert*-butoxy derivatives **31c**, **32c** and **33c** [the proportions were estimated from the integrals of the signals at δ 7.51 (attributed to the 3-H of **31c**), 5.79 (ascribed to the 1″-H of **32c**) and 5.77 (assigned to the 1″-H of **33c**)]. Subjection of the mixture of column chromatography [EtOAc–light petroleum (1 : 1) as eluent] led to the isolation of two fractions.

The first-eluted fraction (0.171 g, 48%) was identified as an 82 : 18 mixture of the *tert*-butoxy derivatives **32c** and **33c**; δ_H (300 MHz; $CDCl_3$) (*inter alia* for **33c**) 4.77 (1 H, d, *J* 8, 1′-H), 5.77 (1 H, s, 1″-H) and 6.14 and 6.35 (each 1 H, s, 3-H_2). Crystallisation of the mixture from diethyl ether–light petroleum gave *methyl (1″R)-2-[1″-(tert-butoxy)-1″-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)propenoate* **32c** (0.122 g, 34%); mp 135–136 °C; $[\alpha]_D$ −53 (*c* 0.4, $CHCl_3$) (Found: 53.5; H, 6.3. $C_{23}H_{34}O_{13}$ requires C, 53.3; H, 6.6%); λ_{max} (EtOH)/nm 205 (ε 7200); ν_{max} (Nujol)/cm^{-1} 1748 (ester C=O), 1714 (enone C=O) and 1633 (C=C); δ_H (300 MHz; $CDCl_3$) 1.26 (9 H, s, Me_3C), 1.99, 2.01, 2.03 and 2.08 (each 3 H, s, 4 × $MeCO_2$), 3.56 (1 H, ddd, *J* 2.5, 5 and 10, 5′-H), 3.75 (3 H, s, MeO), 4.05 and 4.16 [each 1 H, dd (*J* 2.5 and 12) and dd (*J* 5 and 12), 6′-H_2], 4.73 (1 H, d, *J* 8, 1′-H), 5.00–5.08 (2 H, m, 2′- and 4′-H), 5.17 (1 H, t, *J* 9.5, 3′-H), 5.79 (1 H, s, 1″-H) and 6.09 and 6.27 (each 1 H, s, 3-H_2); *m/z* (FAB) 541 [$M(Na)^+$, 10%], 519 (MH^+, 2) and 331 ($C_{14}H_{19}O_9^+$, 100).

The second-eluted fraction (0.115 g, 32%) was identified as *methyl (E)-2-(tert-butoxymethyl)-3-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)propenoate* **31c**. After crystallisation from ethyl acetate–light petroleum, the sample (0.047 g, 13%) showed mp 106–107 °C; $[\alpha]_D$ −19 (*c* 0.22, $CHCl_3$) (Found: C, 53.5; H, 6.6%); λ_{max} (EtOH)/nm 227 (ε 16 300); ν_{max} (Nujol)/cm^{-1} 1758 and 1736 (ester C=O), 1709 (vinylogous carbonate C=O) and 1643 (C=C); δ_H (300 MHz; $CDCl_3$) 1.21 (9 H, s, Me_3C), 2.02, 2.03, 2.04 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 3.73 (3 H, s, MeO_2C), 3.80 (1 H, ddd, *J* 2.5, 4.5 and 10, 5′-H), 4.03 and 4.10 (each 1 H, d, *J* 9.5, 2-CH_2O), 4.13 and 4.28 [each 1 H, dd (*J* 2.5 and 12.5) and dd (*J* 4.5 and 12.5), 6′-H_2], 4.90 (1 H, d, *J* 7, 1′-H), 5.11–5.27 (3 H, m, 2′-, 3′- and 4′-H) and 7.51 (1 H, s, 3-H); *m/z* (FAB) 541 [$M(Na)^+$, 2%], 519 (MH^+, 1) 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (65).

Stability studies involving the methoxy compounds 23a and 24a with methanol in the presence of silver(I) oxide

The methoxy compounds **23a** and **24a** (0.009 g, 0.02 mmol) were each added to suspensions of silver(I) oxide (0.005 g, 0.02 mmol) in methanol (2 cm^3) that had been stirred in the dark for 1.5 h. Work-up after 24 h yielded residues that contained 90% unchanged compounds **23a** and **24a** and 10% of the dimethoxy compound **26a**.

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