Asymmetric Diels–Alder Reactions. Part 4.[1] Influence of Anomeric Configuration and 2'- and 6'-*O*-Benzyl Substitution on the Diastereofacial Reactivity of (*E*)-3-(t-Butyldimethylsiloxy)-1-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-buta-1,3-diene

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The 1-(2',3',4',6'-tetra-*O*-acetyl-α-D-glucopyranosyloxy), 1-(6'-*O*-benzyl-2',3',4'-tri-*O*-acetyl-α-D-glucopyranosyloxy), 1-(2'-*O*-benzyl-3',4',6'-tri-*O*-acetyl-α-D-glucopyranosyloxy), 1-(6'-*O*-benzyl-2',3',4'-tri-*O*-acetyl-β-D-glucopyranosyloxy), and 1-(2'-*O*-benzyl-3',4',6'-tri-*O*-acetyl-β-D-glucopyranosyloxy) derivatives of (*E*)-3-(t-butyldimethylsiloxy)buta-1,3-diene, *i.e.* (**8b–d**) and (**34a,b**) have been prepared and their diastereofacial reactivities towards *N*-phenylmaleimide assessed. Whereas the α-diene (**8b**) gave a 55:45 mixture of the cycloadducts (**11b**) and (**12b**) [the major product having the (1*S*,2*S*,3*R*)-configuration], its β-anomer, *i.e.* (**1b**), afforded an 85:15 mixture of the cycloadducts (**2b**) and (**3b**) [the major product having the (1*R*,2*R*,3*S*)-geometry]. Improved diastereoselections were displayed by the 6'-*O*-benzyl-α-diene (**8c**), which gave a 69:31 mixture of the cycloadducts (**11c**) and (**12c**), and by the 6'-*O*-benzyl-β-diene (**34a**), which yielded only the cycloadduct (**38a**). By contrast, reduced diastereofacial reactivities were exhibited by the 2'-*O*-benzyl-α-diene (**8d**), which afforded a 36:64 mixture of the cycloadducts (**11d**) and (**12d**) [the major product now having the (1*R*,2*R*,3*S*)-stereochemistry], and by the 2'-*O*-benzyl-β-diene (**34b**), which gave a 74:26 mixture of the cycloadducts (**38b**) and (**39b**).

Recently, we showed that the diene (**1a**)† displayed a useful diastereofacial reactivity in cycloadditions. Thus, it reacted[2] with *N*-phenylmaleimide in benzene to give an 86:14 mixture of the cycloadducts (**2a**) and (**3a**),‡ from which the former product was isolated by crystallisation in 58% yield. The reaction of the diene (**1a**) with tetracyanoethylene in benzene was less selective than that involving *N*-phenylmaleimide, affording[3] a 67:33 mixture of the cycloadducts (**4a**) and (**5a**).§ However, the major cycloadduct (**4a**) could again be obtained in a pure state (42% yield) by recrystallisation.

In corresponding Diels–Alder reactions, the dienes (**1b–e**) were shown[1] to exhibit diastereofacial reactivities that were comparable with those of the diene (**1a**) whereas the dienes (**1f–h**) were endowed[1,2] with superior selectivities. Thus, only the cycloadducts (**2f–h**) were detected in cycloadditions of the dienes (**1f–h**) with *N*-phenylmaleimide. Mixtures of the cycloadducts (**4f–h**) and (**5f–h**)—ranging from 78:22 to 89:11—arose from the reactions of the dienes (**1f–h**) with tetracyanoethylene.

To account for these results, it was suggested that the dienes (**1f-h**) reacted only by way of the conformers (**6f–h**) whereas the dienes (**1a–e**) reacted by way of both the conformers (**6a–e**) (the major pathway) and the conformers (**7a–e**). Thus, in the case of *N*-phenylmaleimide, the cycloadducts (**2a–h**) were postulated to arise by *endo*-addition to the least-hindered 'top' faces of the conformers (**6a–h**); the cycloadducts (**3a–c**) were presumed to originate by *endo*-addition to the least-hindered 'top' faces of the conformers (**7a–e**) [although the possibility that they arose by *endo*-addition to the more-hindered 'bottom' faces of the conformers (**6a–e**) could not be excluded]. With tetracyanoethylene (which was assumed to possess a lower steric requirement than *N*-phenylmaleimide), the cycloadducts (**4f–h**) and (**5f–h**) were believed to be formed by addition to the 'top' and 'bottom' faces of the conformers (**6f–h**), the cycloadducts (**4a–c**) by addition mainly to the 'top' faces of the conformers (**6a–e**), and the cycloadducts (**5a–e**) by addition to both the 'top' faces of the conformers (**7a–e**) and the 'bottom' faces of the conformers (**6a–e**).¶

In this paper, we describe the synthesis of five relatives of the diene (**1b**), its α-anomer, its 2'- and 6'-*O*-benzyl derivatives, and the 2'- and 6'-*O*-benzyl derivatives of its α-anomer—and we assess their diastereofacial reactivities towards *N*-phenylmaleimide.

Results and Discussion

To determine the effect of anomeric configuration on the diastereoselection process, the diene (**8a**) was sought. On the basis of our model,[1,3] it was expected that compound (**8a**) would undergo cycloaddition by way of the conformers (**9a**) and (**10a**) and that there would be a preference for dienophiles to add to the least-hindered 'top' face of the conformer (**9a**). Thus, the cycloadduct (**11a**) was expected to predominate over its diastereoisomer (**12a**) in the reaction of the diene (**8a**) with *N*-phenylmaleimide.

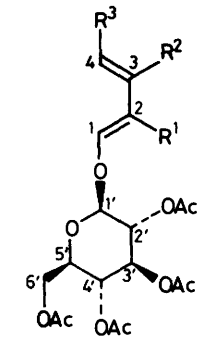
The initial preparation of the α-glucoside (**13a**)—the projected precursor of the diene (**8a**)—was unplanned. During attempts to introduce *C*-substituents at position 1, it was

† To facilitate comparisons, the dienes are numbered in the manner shown in structure (**1**).

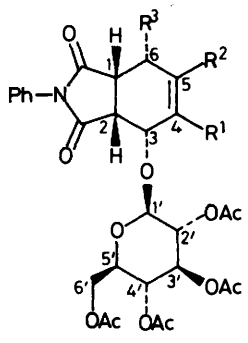
‡ The stereochemical outcome of this reaction has not been rigorously established; the major cycloadduct is assumed to possess the stereostructure (**2a**) by analogy with the result observed for *p*-benzoquinone which is unequivocal.[2] To facilitate comparisons, the cycloadducts are numbered in the manner shown in structure (**2**); derivatives of these compounds are numbered similarly. The αβ-notation is applied in the standard way to the aglycones of cycloadducts of type (**2**) and their derivatives; the descriptors are used in an opposite sense to describe the aglycones of cycloadducts of type (**3**) and their derivatives (because their absolute configuration is inverted).

§ The stereostructure of the major cycloadduct has not been rigorously defined. To facilitate comparisons, the cycloadducts are numbered as shown in structure (**4**).

¶ Of course, the ratio of the products is only equal to the population of the reacting conformers when the transition state energies of the two reactions are identical (see: J. I. Seeman, *J. Chem. Educ.*, 1986, **63**, 42).



(1)



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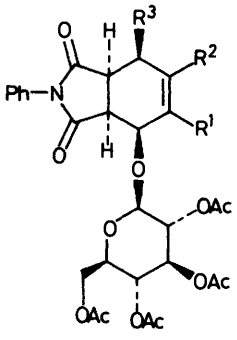

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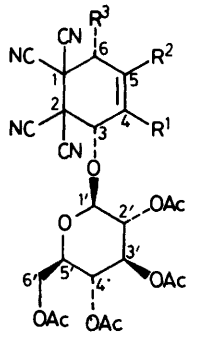

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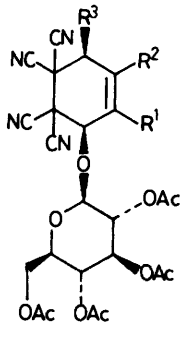

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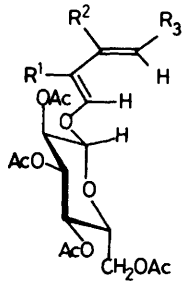

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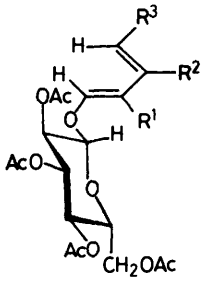


(7)

a; R^1 = H, R^2 = $OSiMe_3$, R^3 = H
b; R^1 = H, R^2 = $OSiMe_2Bu^t$, R^3 = H
c; R^1 = H, R^2 = $OSiMe_2Bu^t$, R^3 = OAc
d; R^1 = H, R^2 = H, R^3 = H
e; R^1 = H, R^2 = Me, R^3 = H
f; R^1 = Me, R^2 = $OSiMe_3$, R^3 = H
g; R^1 = Me, R^2 = $OSiMe_2Bu^t$, R^3 = Me
h; R^1 = Me, R^2 = Me, R^3 = H

discovered that the β-glucoside (**14a**)[4] reacted with sodium hydride in tetrahydrofuran (THF) to give a mixture of products. Following silica-gel chromatography, the penta-acetate (**15a**)[5] was isolated in 4% yield and the α-glucoside (**13a**) in 37% yield. The structure of compound (**13a**) followed from its analytical and spectroscopic properties. In particular, the 300 MHz ^{1}H NMR spectrum ($CDCl_3$) featured the 1′-hydrogen atom as a doublet (*J* 4 Hz) at δ 5.52 [in the β-glucoside (**14a**), the 1′-H absorbed as a doublet (*J* 8 Hz) at δ 4.91]. In accord with Hudson's rule,[6] the optical rotation of the α-glucoside (**13a**) {$[\alpha]_D$ +164° (CH_2Cl_2)} was substantially more positive than that of its β-counterpart (**14a**) {$[\alpha]_D$ −20° (EtOH)}.

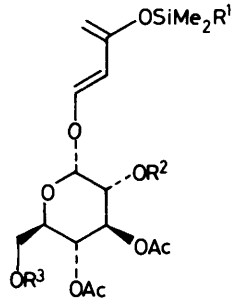
The anomerisation of glycosides under basic conditions is unusual.[7,8] A possible explanation is suggested in the Scheme in which a base (B) induces a β-elimination reaction of the β-glucoside (**14a**) to generate butynone and the species (**16**). The epimeric species (**18**), formed by way of the ring-opened intermediate (**17**), may then undergo a conjugate addition to butynone to give the α-glucoside (**13a**) and react with an acetyl-transfer species to give the penta-acetate (**15a**).

The methodology introduced by David and developed by Lubineau[9] was also applicable to the synthesis of the α-glucoside (**13a**). Thus, treatment of the tetra-acetate (**19a**)[10] (as a mixture of anomers) in THF with the tosylate (**20a**) [generated *in situ* by adding tosyl chloride to the salt (**20b**)[11]] and sodium hydride gave, after silica-gel fractionation, compound (**13a**) in 13% yield. A comparable yield of the β-glucoside (**14a**) was also isolated.

The best yield of the α-glucoside (**13a**), however, involved treating the tetra-acetate (**19a**) in dichloromethane with butynone and a catalytic amount of *N*-methylmorpholine.[12] Following chromatography, compound (**13a**) was isolated in 33% yield; the β-glucoside (**14a**) was also obtained (32% yield).

Under conditions in which the butenone (**14a**) was efficiently converted into the diene (**1a**) (Me_3SiCl–$ZnCl_2$–Et_3N in PhH at *ca.* 55 °C),[4] the butenone (**13a**) afforded a mixture of products from which the silyl glucoside (**21a**)[13] was isolated in 20% yield by crystallisation. However, treatment of the butenone (**13a**) in dichloromethane at −20 °C with t-butyldimethylsilyl triflate and triethylamine[14] gave, after rapid low-temperature silica-gel chromatography, the diene (**8b**) in excellent yield. The material, obtained in crystalline form, was analytically and spectroscopically characterised. In particular, its 300 MHz ^{1}H NMR spectrum ($CDCl_3$) featured the anomeric hydrogen atom as a doublet (*J* 4 Hz) at δ 5.35 [in the diene (**1b**), the 1′-H appeared as a doublet (*J* 8 Hz) at δ 4.80]. The optical rotation of the diene (**8b**) {$[\alpha]_D$ +141° (CH_2Cl_2)} was substantially larger than that of its relative (**1b**) {$[\alpha]_D$ −12° ($CHCl_2$)}.

The diene (**8b**) reacted with *N*-phenylmaleimide in benzene to give a 55:45 mixture of the cycloadducts (**11b**) and (**12b**) which were isolated in 47 and 34% yields after HPLC. The stereostructures of the cycloadducts were assigned by comparing their CD spectra (Figure 1) with those of the cycloadducts (**2a**) and (**3a**) (Figure 2). Thus, compound (**11b**) displayed (MeCN) negative dichroisms at 204sh (Δε −7.2), 214 (Δε −12.6), and 227sh nm (Δε −8.8) whereas compound (**3a**) showed negative dichroisms at 228 (Δε −3.8) and 248sh nm (Δε −2.8). Compound (**12b**) was characterised by the presence of a negative dichroism at 202 nm (Δε −6.5) and a positive one at 227 nm (Δε +10) whereas compound (**2a**) exhibited a negative dichroism at 212 nm (Δε −6.6) and positive dichroisms at 238sh (Δε +6.8) and 247 nm (Δε +7.4). In the 300 MHz ^{1}H NMR spectra ($CDCl_3$), the acetyl methyl groups of the major cycloadduct (**11b**) appeared at δ 1.32, 1.99, 2.04, and 2.09 whereas those of the minor cycloadduct (**12b**) absorbed at δ 1.95, 1.99 (6 H), and 2.09. Clearly, one of the acetyl methyl groups of the cycloadduct (**11b**) [probably that at the 2′-position (see later)] lay in the shielding zone of the phenyl ring. A similar



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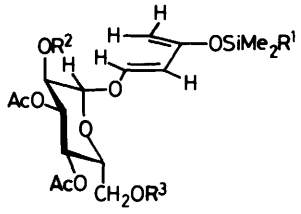
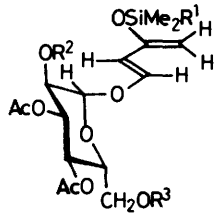


(9)



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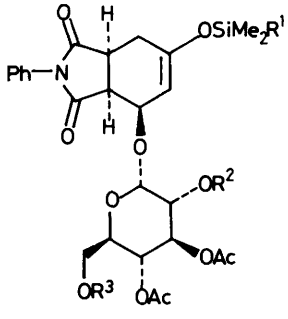

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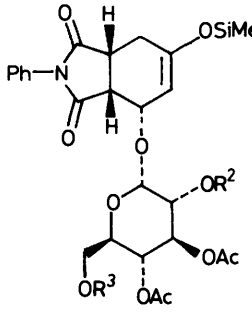
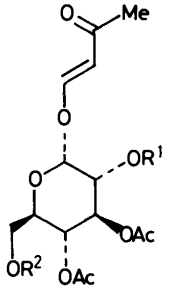
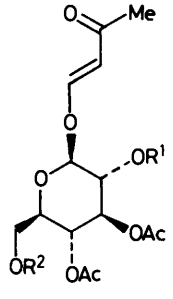


(12)

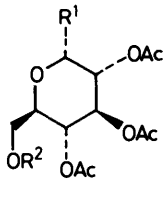
a: R^1 = Me, R^2 = Ac, R^3 = Ac
b: R^1 = Bu^t, R^2 = Ac, R^3 = Ac
c: R^1 = Bu^t, R^2 = Ac, R^3 = CH_2Ph
d: R^1 = Bu^t, R^2 = CH_2Ph, R^3 = Ac



(13)



(14)



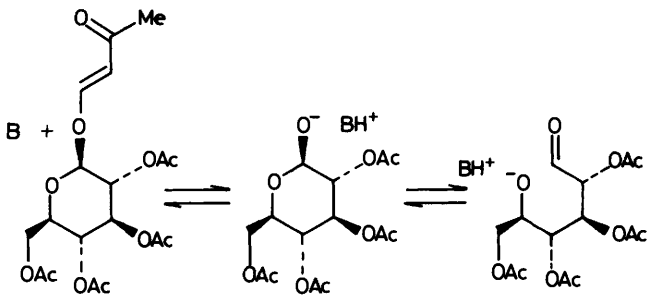
(15)

a: R^1 = Ac, R^2 = Ac
b: R^1 = Ac, R^2 = CH_2Ph
c: R^1 = CH_2Ph, R^2 = Ac

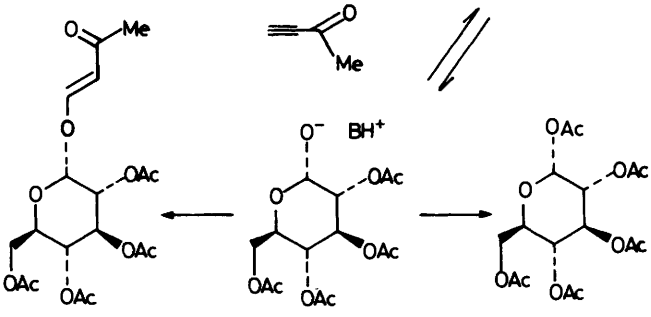
a: R^1 = OAc, R^2 = Ac
b: R^1 = Cl, R^2 = CH_2Ph

phenomenon was noted for the cycloadduct (**2a**) [and its relatives (**2b–h**)] but not for its counterpart (**3a**).

Acidic hydrolysis of the silyl enol ethers (**11b**) and (**12b**)

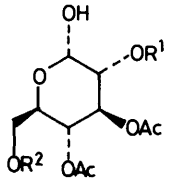


(14a) (16) (17)

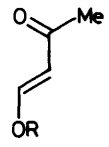


(13a) (18) (15a)

Scheme



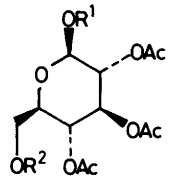
(19)



(20)

a: R^1 = Ac, R^2 = Ac
b: R^1 = Ac, R^2 = CH_2Ph
c: R^1 = CH_2Ph, R^2 = Ac

a: R = $SO_2C_6H_4Me$-*p*
b: R = Na



(21)

a: R^1 = $SiMe_3$, R^2 = Ac
b: R^1 = CHO, R^2 = CH_2Ph

afforded the ketones (**22a**) and (**23a**) in respective yields of 63 and 52%. Again, the CD spectrum (MeCN) of the ketone (**22a**) [237 (Δε −2.30), 287 (Δε +3.1), 297 (Δε +3.3), 304sh (Δε +2.6), and 315sh nm (Δε +1.2)] was comparable with that of its relative (**24a**) [284 (Δε +2.9), 297 (Δε +3.2), 305 (Δε +2.5), and 312sh nm (Δε +1.2)]. The CD spectrum (MeCN) of the ketone (**23a**) [235 (Δε +1.6), 286sh (Δε −3.1), 293 (Δε −3.3), 303 (Δε −2.7), and 313sh (Δε −1.3)] was also very similar to that of its counterpart (**25a**) [295 (Δε −4.4), 303 (Δε −3.6), and

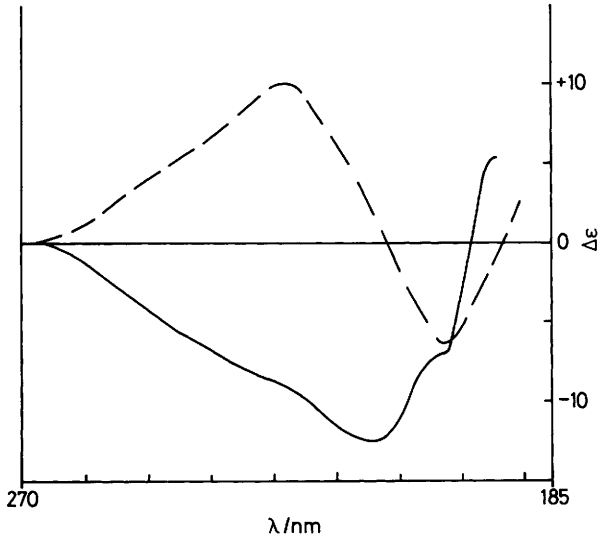


Figure 1. CD spectra (MeCN) of compounds (**11b**) (solid line) and (**12b**) (dashed line).

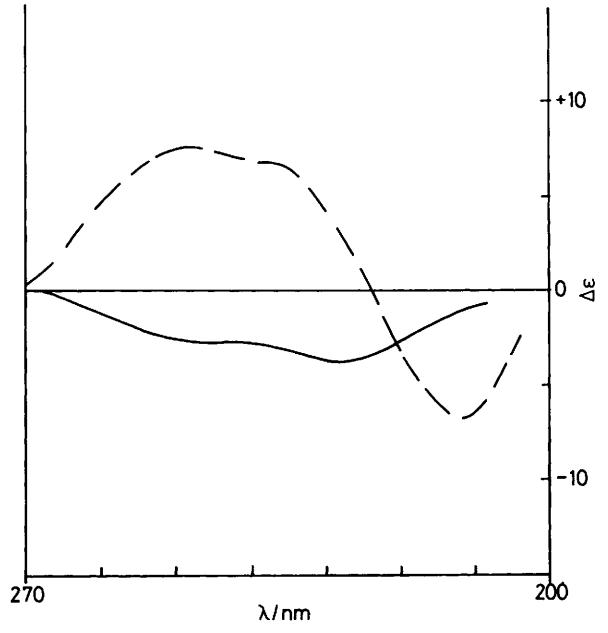


Figure 2. CD spectra (MeCN) of compounds (**2a**) (dashed line) and (**3a**) (solid line).

312sh ($\Delta\varepsilon$ −1.5)]. In the 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of the ketone (**22a**), one of the acetyl methyl groups appeared at much higher field (δ 1.37) than the others (δ 2.00, 2.05, and 2.12) [a similar shielding effect was noted for the ketones (**25a–c**)]; this effect was not observed in the case of the ketone (**23a**) [nor for its relative (**24a**)].

Although, as predicted, the diene (**8b**) had displayed a diastereofacial reactivity towards *N*-phenylmaleimide which was opposite to that of its epimer (**1b**), the magnitude of the discrimination was much smaller than expected. The conformation of compound (**8b**) was probed by NMR methods (the material was unsuitable for an X-ray analysis). On the basis of *J* values, the glucose moiety was shown to adopt the expected $^4C_1$ conformation with the oxy-group at position 1′ in the axial orientation. A mixture of the conformers (**26a**) and (**27a**), with a preference for the former species, was considered to exist in deuteriochloroform according to nuclear Overhauser effect difference (NOED) spectroscopy. Thus, irradiation of the anomeric hydrogen atom caused 20 and 8% enhancements of the 1- and 2-hydrogen atoms of the butadiene entity; the anomeric hydrogen atom was enhanced by 12 and 4% when the 1- and 2-hydrogen atoms of the butadiene moiety were irradiated. Clearly, the conformational behaviour of compound (**8b**) is very similar to that of its relative (**1b**), apart from the axial disposition of the anomeric substituent; in both cases, the results are in accord with expectations based upon the *exo*-anomeric effect.[15] On the basis of arguments presented earlier,[1,3] we believe that compound (**8b**) undergoes Diels–Alder reactions by way of the conformer (**9b**) (the major pathway) and the conformer (**10b**). Therefore, the poorer diastereofacial reactivity of compound (**8b**) compared with its epimer (**1b**) is unlikely to be due to major conformational differences in the reacting species.

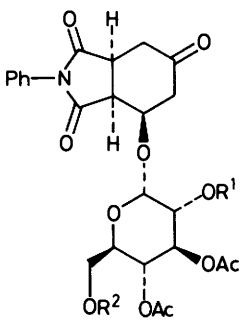
During the course of this work, Lubineau and Queneau[7] prepared the dienes (**1d**), (**28**), and (**29a,b**) and examined their diastereofacial reactivities towards 2-methylpropenal. In toluene, the diene (**1d**) yielded an 87:13 mixture of *endo*- and *exo*-cycloadducts [the *endo*-cycloadducts comprised a 62:38 mixture of (**30a**) and (**31a**)] whereas the diene (**29a**) gave rise to an 84:16 mixture of *endo*- and *exo*-cycloadducts [the *endo*-cycloadducts consisted of a 36:64 mixture of (**32a**) and (**33a**)]. In water, the diene (**28**) afforded only *endo*-cycloadducts [comprising a 60:40 mixture of (**30b**) and (**31b**)] whereas the diene (**29b**) yielded a 93:7 mixture of *endo*- and *exo*-cycloadducts [the *endo*-cycloadducts (**32b**) and (**33b**) were present in the ratio of 37:63]. Clearly, the stereochemical induction observed for the dienes (**1a–h**) and (**28**) is in the same direction; similarly, the diastereofacial selection observed for the dienes (**8b**) and (**29a,b**) is comparable.

According to our model, the nature of the 6′- and 2′-substituents on the glucose moiety could play a role in the diastereoselection process. Because of the possibility of a π-stacking interaction between the diene entity and a phenyl group,* it was decided to prepare the dienes (**34a,b**) and (**8c,d**) and to assess their reactivity towards *N*-phenylmaleimide.

The 6-*O*-benzyl derivative (**19b**) was prepared (89% yield after SiO_2 chromatography) from the tetra-acetate (**35**)[16] [obtained in 71% yield, as a 1:1 mixture of anomers, by acetylation (Ac_2O–pyridine) of 6-*O*-benzyl-D-glucose[17]] by selective deacetylation (NH_3 in MeOH–THF).[10] It reacted with butynone and *N*-methylmorpholine in dichloromethane to give, after chromatography, the α-glucoside (**13b**) in 85% yield and the β-glucoside (**14b**) in 5% yield. A more efficient route to the latter glucoside proceeded by way of the chloride (**15b**), obtained as a somewhat unstable gum (67% yield after SiO_2 chromatography) by treatment of compound (**19b**) with thionyl chloride in *N*,*N*-dimethylformamide (DMF) at 0 °C. When stirred with formic acid–silver(I) nitrate, the chloride (**15b**) was converted into an oily product [presumed to be mainly the formate (**21b**)], which reacted with acetylmethylenetriphenylphosphorane† in boiling ethyl acetate to yield the β-glucoside (**14b**) (60% yield after SiO_2 chromatography). In the α-glucoside (**13b**), the 1′-hydrogen atom resonated ($CDCl_3$) as a doublet (*J* 4 Hz) at δ 5.49; it appeared as a doublet (*J* 8 Hz) at δ 4.88 in the β-glucoside (**14b**). The α-glucoside (**13b**) displayed a much higher optical rotation {$[\alpha]_D$ +163° (CH_2Cl_2)} than its epimer (**14b**) {$[\alpha]_D$ +6.8° (CH_2Cl_2)}.

* Such an interaction was invoked (B. M. Trost, D. O'Krongly, and J. Belletire, *J. Am. Chem. Soc.*, 1980, **102**, 7595) to account for the diastereofacial reactivity of (*E*)-butadien-1-yl *O*-methylmandelate; recently, however, this explanation has been invalidated (C. Siegel and E. A. Thornton, *Tetrahedron Lett.*, 1988, **29**, 5225).

† The Wittig condensation of formyl esters with stabilised phosphoranes was first described by V. Subramanyam, E. H. Silver, and A. H. Soloway, *J. Org. Chem.*, 1976, **41**, 1972.



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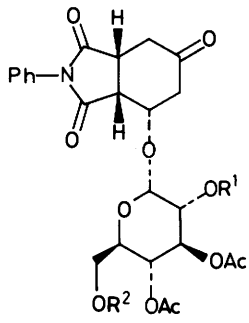

(23)

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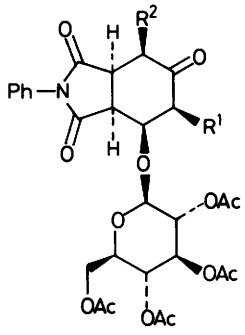
b: R^1 = Ac, R^2 = CH_2Ph
c: R^1 = CH_2Ph, R^2 = Ac



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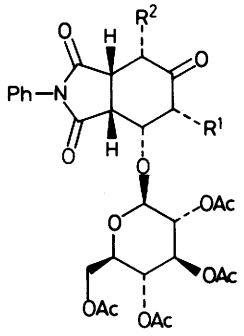

(25)

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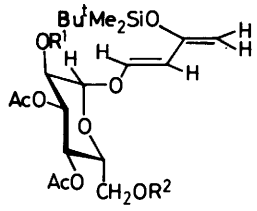
c: R^1 = Me, R^2 = Me



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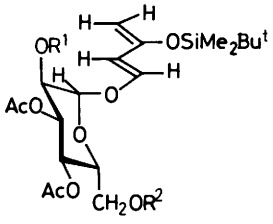
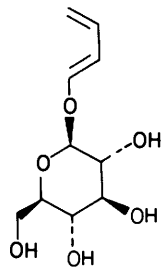


(27)

a: R^1 = Ac, R^2 = Ac
b: R^1 = Ac, R^2 = CH_2Ph
c: R^1 = CH_2Ph, R^2 = Ac



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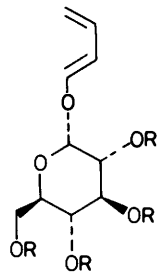

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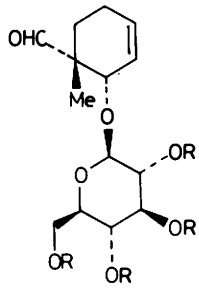
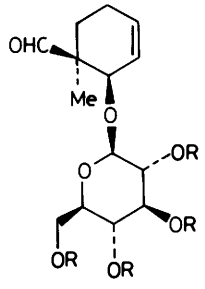


(30)

a: R = Ac
b: R = H



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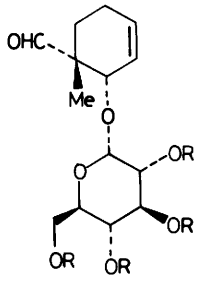

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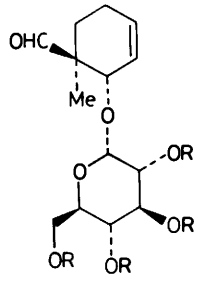
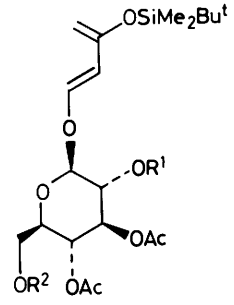


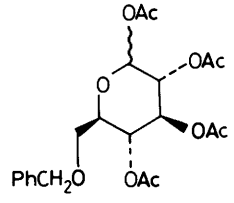
(33)

a: R = Ac
b: R = H



(34)

a: R^1 = Ac, R^2 = CH_2Ph
b: R^1 = CH_2Ph, R^2 = Ac

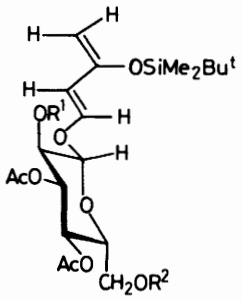


(35)

Under the usual silylating conditions, the butenones (**13b**) and (**14b**) were transformed into the corresponding dienes (**8c**) and (**34a**). After low-temperature chromatography, the former material was isolated as a somewhat impure syrup (93% yield) whereas the latter material was obtained in a crystalline state (72% yield). In the α-diene (**8c**), the 1′-hydrogen atom absorbed ($CDCl_3$) as a doublet (*J* 4 Hz) at δ 5.37; in the β-diene (**34a**), it was present as a doublet (*J* 8 Hz) at δ 4.80.

The 2-*O*-benzyl derivative (**19c**)[18] reacted with butynone and *N*-methylmorpholine in dichloromethane to afford, after chromatography, the α-glucoside (**13c**) in 26% yield and the β-glucoside (**14c**) in 29% yield. In the 300 MHz ^1H NMR spectra ($CDCl_3$), the 1′-hydrogen atom appeared as a doublet (*J* 4 Hz) at δ 5.12 in the case of the α-glucoside (**13c**) and as a doublet (*J* 8 Hz) at δ 4.90 in the case of the β-glucoside (**14c**). As in the previous examples, the α-glucoside (**13c**) {$[\alpha]_D$ +139° (CH_2Cl_2)} was much more dextrorotary than the β-glucoside (**14c**) {$[\alpha]_D$ +15° ($CHCl_2$)}. Under the usual silylating conditions, the butenones (**13c**) and (**14c**) were converted into the corresponding dienes (**8d**) and (**34b**). Following low-temperature chromatography, the dienes were isolated as syrups in near-quantitative yields; both dienes were somewhat unstable and they were used rapidly in cycloadditions. Again, the 1′-hydrogen atom appeared at lower field [as a doublet (*J* 4 Hz) at δ 5.05] in the α-anomer (**8d**) than in the β anomer (**34b**) [as a doublet (*J* 8 Hz) at δ 4.77].

On the basis of NOED spectroscopic studies, the 6′- and 2′-*O*-benzyl-α-dienes (**8c,d**) were considered to exist in deuter-



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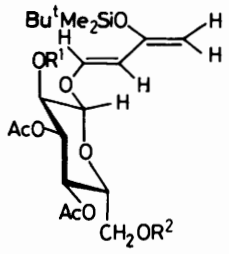
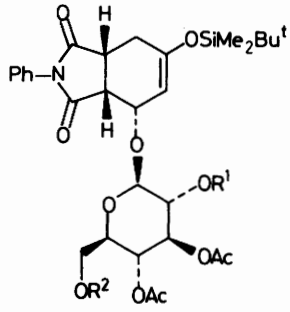


(37)

a: R^1 = Ac, R^2 = CH_2Ph
b: R^1 = CH_2Ph, R^2 = Ac



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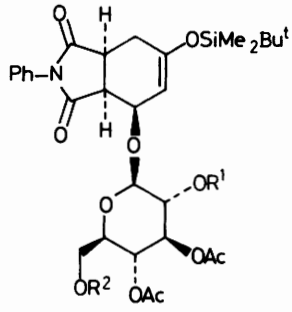

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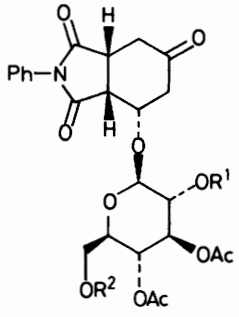


(40)

a: R^1 = Ac, R^2 = CH_2Ph
b: R^1 = CH_2Ph, R^2 = Ac

iochloroform as a mixture of the conformers (**26b,c**) and (**27b,c**) with a preference for the former species. Thus, irradiation of the anomeric hydrogen atom enhanced the 1- and 2-hydrogen atoms of the butadiene entity [by 11 and 20% in the case of (**8c**) and by 8 and 16% in the case of (**8d**)]; the anomeric hydrogen atom was enhanced [by 5 and 2.5% for both (**8c,d**)] when the 1- and 2-hydrogen atoms were irradiated. Similarly, the 6′- and 2′-*O*-benzyl-α-dienes (**34a,b**) were considered to adopt the conformers (**36a,b**) and (**37a,b**) with a preference for the former species. Thus, irradiation of the anomeric hydrogen atom caused enhancements of the 1- and 2-hydrogen atoms [by 5 and 11% in the case of (**34a**) and by 14 and 24% in the case of (**34b**)]; the anomeric hydrogen atom was enhanced [by 4 and 0% for (**34a**) and by 11 and 3% for (**34b**)] upon irradiation of the 1- and 2-hydrogen atoms.

The 6′-*O*-benzyl-α-diene (**8c**) reacted with *N*-phenylmaleimide in benzene to give a 69:31 mixture of the cycloadducts (**11c**) and (**12c**). Fractional crystallisation of the mixture led to the isolation of both the major cycloadduct (**11c**) (44% yield) and the minor cycloadduct (**12c**) (2% yield) in a pure state. The stereostructure of the major cycloadduct (**11c**) was assigned by CD spectroscopy; thus, it displayed (MeCN) negative dichroisms at 204 (Δε −8.7) and 213 nm (Δε −13.4). Furthermore, as noted for compound (**11b**), one of the acetyl methyl groups [probably that at position 2′ (see later)] of the major cycloadduct (**11c**) was substantially shielded (δ 1.32) compared with the others (δ 1.88 and 1.99). No such effect was observed for the minor cycloadduct (**12c**) [nor for its relative (**12b**)].

Acidic hydrolysis of the silyl enol ether (**11c**) gave the ketone (**22b**) (70% yield), in which again one of the acetyl methyl groups was notably shielded [a similar effect was observed for the ketone (**22a**) but not for its diastereoisomer (**23a**)]. Finally, when subjected to a hydrogenolysis–acetylation sequence, the benzyl derivative (**22b**) was transformed into the acetyl derivative (**22a**) (58% yield), confirming the stereochemical relationship between the cycloadducts (**11b,c**).

The 6′-*O*-benzyl-β-diene (**34a**) reacted with *N*-phenylmaleimide in benzene to give predominantly the cycloadduct (**38a**), isolated in 73% yield after recrystallisation [there was no evidence for the presence of the cycloadduct (**39a**) in the crude product]. The stereostructure of compound (**38a**) was assigned on the basis of its CD spectrum [λ_{max}(MeCN) 208 (Δε +4.8) and 224 nm (Δε +10.8)]. Moreover, in the 300 MHz ^{1}H NMR spectrum (recorded in CD_3COCD_3 because decomposition occurred in $CDCl_3$), one of the acetyl methyl groups appeared at higher field (δ 1.32) than the others (δ 1.58 and 1.60).

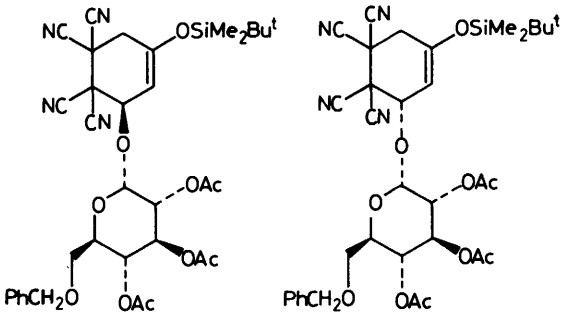
Acidic hydrolysis of the silyl enol ether (**38a**) afforded the ketone (**40a**) (95% yield), in which again one of the acetyl methyl groups was notably shielded. When subjected to a hydrogenolysis–acetylation sequence, the benzyl derivative was transformed into the acetyl derivative (**25a**) (81% yield), corroborating the stereochemical relationship between the cycloadducts (**38a**) and (**2b**).

On the basis of the aforecited results, it is clear that the diastereofacial reactivity of the 6′-*O*-benzyl-α-diene (**8c**) is better than that of its 6′-*O*-acetyl counterpart (**8b**) and the diastereofacial reactivity of the 6′-*O*-benzyl-β-diene (**34a**) is superior to that of its 6′-*O*-acetyl counterpart (**1b**). It was of interest, therefore, to compare the behaviour of the dienes (**8c**) and (**34a**) towards tetracyanoethylene.

The 6′-*O*-benzyl-α-diene (**8c**) reacted with tetracyanoethylene in benzene to give a 62:38 mixture of cycloadducts [tentatively, assigned the structures (**41**) and (**42**)], which was not separated. The corresponding reaction of the 6′-*O*-benzyl-β-diene (**34a**) afforded a 71:29 mixture of cycloadducts [tentatively, assigned the stereostructures (**43**) and (**44**)], from which the major cycloadduct was isolated by crystallisation in 54% yield.

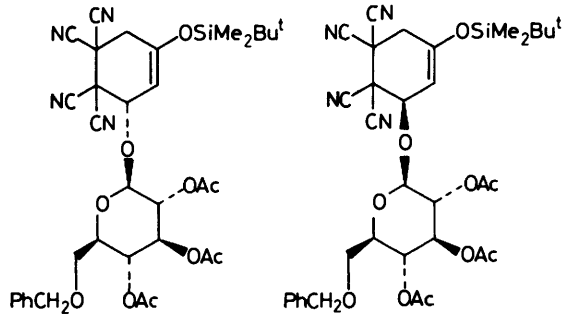
Although the reaction of the 6′-*O*-acetyl-α-diene (**8b**) with tetracyanoethylene was not examined, the 6′-*O*-benzyl (**34a**) is endowed with a slightly better diastereofacial reactivity towards tetracyanoethylene than its 6′-*O*-acetyl counterpart (**1b**).

The 2′-*O*-benzyl-α-diene (**8d**) reacted with *N*-phenylmaleimide to give a 36:64 mixture of the cycloadducts (**11d**) and (**12d**); following chromatography, the minor cycloadduct (**11d**) was isolated as a slightly impure syrup in 20% yield and the major cycloadduct (**12d**) as a crystalline solid in 31% yield. The stereostructure of the major cycloadduct (**12d**) was assigned by CD spectroscopy; thus, the spectrum (MeCN) featured a negative dichroism at 203 nm (Δε −3.8) and a positive one at 225 nm (Δε +10.4). In the 300 MHz ^{1}H spectra ($CDCl_3$), the acetyl methyl groups resonated at δ 1.93, 1.95, and 2.06 in the major cycloadduct (**12d**) and at δ 1.93, 1.98, and 2.06 in the minor cycloadduct (**11d**). Evidently, the acetyl group at the 2′-



(41)

(42)



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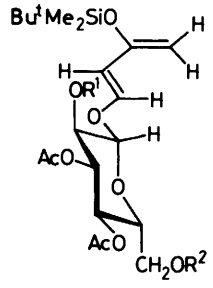
(44)



a: R^1 = Ac. R^2 = CH_2Ph
b: R^1 = CH_2Ph. R^2 = Ac

Table 1. Ratios of cycloadducts produced in the reactions of dienes with *N*-phenylmaleimide.

Diene	Possible cycloadducts	Ratio
(**1b**)	(**2b**) and (**3b**)	85:15
(**34a**)	(**38a**) and (**39a**)	>95:5
(**34b**)	(**38b**) and (**39b**)	76:26
(**8b**)	(**11b**) and (**12b**)	55:45
(**8c**)	(**11c**) and (**12c**)	69:31
(**8d**)	(**11d**) and (**12d**)	36:64

position of compounds (**11b,c**) is the one which lies in the shielding zone of the *N*-phenyl group.

Acidic hydrolysis of the silyl enol ether (**12d**) afforded the ketone (**23c**), in which the acetyl methyl groups appeared ($CDCl_3$) at δ 1.92, 2.00, and 2.03. When subjected to a hydrogenolysis–acetylation sequence, the 2′-*O*-benzyl derivative (**23c**) was converted into compound (**23a**), proving that the cycloadducts (**12b,c**) shared a common stereostructure.

Table 2. Chemical shifts (δ; $CDCl_3$) of the 1-, 2-, and 4-hydrogen atoms of dienes.

Diene	1-H	2-H	4-H_2
(**1b**)	6.75	5.65	*ca.* 4.15
(**34a**)	6.80	5.68	4.15 and 4.16
(**34b**)	6.83	5.73	4.19
(**8b**)	6.71	5.74	4.15 and 4.16
(**8c**)	6.73	5.75	4.14
(**8d**)	6.72	5.74	4.15

The reaction of the 2′-*O*-benzyl-β-diene (**34b**) with *N*-phenylmaleimide gave rise to a 74:26 mixture of the cycloadducts (**38b**) and (**39b**), from which the major cycloadduct (**38b**) was isolated in 63% yield by crystallisation. The stereostructure of compound (**38b**) was deduced from its CD spectrum (MeCN) [204 (Δε −8.7) and 213 nm (Δε −13.4)]. The acetyl methyl groups of the cycloadduct (**38b**) appeared in the 300 MHz ^1H NMR spectrum ($CDCl_3$) at δ 1.84, 1.99, and 2.06. This observation implies that the 2′-*O*-acetyl group of compounds (**2a–h**) and (**38a**) is the one which appears upfield.

Acidic hydrolysis of the silyl enol ether (**38b**) gave the ketone (**40b**) (64% yield), in which the acetyl methyl groups absorbed ($CDCl_3$) at δ 1.82, 2.01, and 2.12. Again, the result indicates that it is the 2′-*O*-acetyl group of compounds (**25a–c**) and (**40a**) which is shielded. By using a hydrogenolysis–acetylation sequence, the 2′-*O*-benzyl ketone (**40b**) was transformed into the 2′-*O*-acetyl ketone (**25a**) (27% yield), establishing the stereochemical relationship between the cycloadducts (**38b**) and (**2b**).

From the aforecited results, it is evident that the diastereofacial reactivity of the 2′-*O*-benzyl-α-diene (**8d**) is inverted compared with that of its 2′-*O*-acetyl counterpart (**8b**) and the diastereofacial reactivity of the 2′-*O*-benzyl-β-diene (**34b**) is inferior to that of its 2′-*O*-acetyl counterpart (**1b**).

The ratios of cycloadducts produced in the reactions of the dienes (**1b**), (**8b–d**), and (**34a,b**) with *N*-phenylmaleimide are summarised in Table 1. In the case of the β-dienes (**1b**) and (**34a,b**), the ratio increases when the 6′-*O*-acetyl group is replaced by a 6′-*O*-benzyl group and declines when the 2′-*O*-acetyl group is replaced by a 2′-*O*-benzyl group. A similar trend is observed for the α-dienes (**8b–d**). In terms of our model, the results are consistent with the notion that compounds (**1b**) and (**34a,b**) react mainly by way of the conformers (**6b**) and (**45a,b**) and that compounds (**8b–d**) react largely by way of the conformers (**9b–d**). Thus, assuming that the benzyl group acts as a more effective 'shield' than the acetyl group, the 'bottom' face of the conformer (**45a**) and the 'top' face of the conformer (**45b**) should be less accessible than the corresponding faces of the conformer (**6b**). Similarly, the 'bottom' face of the conformer (**9c**) and the 'top' face of the conformer (**9d**) should be more protected than the corresponding faces of the conformer (**9b**). Whether the 'shielding' effect is attributable to π-stacking or steric interactions must await further study. However, the chemical shifts of the 1-, 2-, and 4-hydrogen atoms of compounds (**1b**), (**8b–d**), and (**34a,b**), summarised in Table 2, were remarkably constant. Clearly, there is no evidence for interactions between the diene moiety and the phenyl group in compounds (**8c,d**) or (**34a,b**), at least in their conformers (**26b,c**) and (**27b,c**) or (**36a,b**) and (**37a,b**) which are believed to be adopted in deuteriochloroform solution.

Experimental

Dry solvents, referred to in the ensuing experiments, were prepared as follows: THF was distilled from sodium–benzo-

phenone immediately prior to use; dichloromethane was distilled from calcium chloride; benzene was stored over sodium wire; DMF was stored over 4 Å molecular sieves. Triethylamine was distilled from calcium hydride. Light petroleum refers to that fraction boiling in the range 40–60 °C. Deuteriochloroform was stored over tin granules when used as a solvent for the determination of NMR spectra of siloxyl compounds.

Optical rotations were measured at *ca.* 20 °C using either a Thorn Automation Type 243 polarimeter or an Optical Activity 1000 polarimeter. A Jasco J40-CS was employed to measure CD spectra. For other instrumental and for chromatographic details, see Parts 1,[1] 2,[3] and 3.[1]

Reaction of (*E*)-4-(2′,3′,4′,6′-*Tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**14a**) *with Sodium Hydride* (*with M.M.L. Crilley*).—Sodium hydride (0.300 g, 12.5 mmol) was added to a stirred solution of the butenone (**14a**)[4] (4.18 g, 10 mmol) in dry THF (50 cm^3). After 1 h, the mixture was concentrated and the residue was subjected to silica-gel column chromatography [light petroleum–EtOAc (3:1) as eluant] to give three fractions.

The first-eluted material (0.156 g, 4%), isolated as a white solid, was identified as 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose (**15a**). After recrystallisation from ethanol, the sample possessed m.p. 110–112 °C (lit.,[5] 112–113 °C); $[\alpha]_D$ +102° (1.2% in $CHCl_3$) [lit.,[5] +102° ($CHCl_3$)]; ν_{max}(KBr) 1 740 (ester C=O); δ(60 MHz; $CDCl_3$) 2.04, 2.11, and 2.19 (9, 3, and 3 H, each s, 5 × $MeCO_2$), 4.00–4.20 (3 H, m, 5-H and 6-H_2), 4.87–5.74 (3 H, m, 2-, 3-, and 4-H), and 6.28 (1 H, d, *J* 4 Hz, 1-H).

The second-eluted material (1.55 g, 37%), obtained as a crystalline solid, was (E)-4-(2′,3′,4′,6′-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**13a**). After recrystallisation from diethyl ether–light petroleum, the material displayed m.p. 125–126 °C; $[\alpha]_D$ +164° (0.3% in CH_2Cl_2); ν_{max}(KBr) 1 740 (ester C=O), 1 665 (vinylogous ester C=O), and 1 640 cm^{-1} (C=C); λ_{max}(EtOH) 238 nm (ε 15 900); δ(300 MHz; $CDCl_3$) 2.05 and 2.13 (each 6 H, s, 4 × $MeCO_2$), 2.22 (3 H, s, 1-H_3), 3.97 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.10 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.27 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 5.00 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.13 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.52 (1 H, d, *J* 4 Hz, 1′-H), 5.54 (1 H, t, *J* 10 and 10 Hz, 3-H), 5.96 (1 H, d, *J* 13 Hz, 3-H), and 7.45 (1 H, d, *J* 13 Hz, 4-H); *m/z* (CI) 331 ($C_{14}H_{19}O_9^+$, 53%) and 169 (100) (Found: C, 52.0; H, 5.7. $C_{18}H_{24}O_{11}$ requires C, 51.9. H, 5.75%).

The third-eluted material (0.353 g, 8%) was the starting butenone (**14a**) on the basis of 300 MHz ^{1}H NMR spectroscopy.

Reaction of 2,3,4,6-*Tetra*-O-*acetyl*-D-*glucopyranose* (**19a**) *with* (E)-4-(*Toluene*-p-*sulphonyloxy*)*but*-3-*en*-2-*one* (**20a**).—Toluene-*p*-sulphonyl chloride (4.10 g, 21.5 mmol) was added to a stirred suspension of the salt (**20b**)[11] (3.10 g, 28.7 mmol) in dry THF (30 cm^3). After 20 min, a solution of the glucopyranose (**19a**)[10] (5.00 g, 14.4 mmol) in dry THF (20 cm^3) was added followed by sodium hydride (0.680 g, 28.3 mmol). The mixture was poured into water (200 cm^3), after 1 h, and the solution extracted with ethyl acetate (× 2). The organic phase was then washed with water, dried ($MgSO_4$), and evaporated. Purification of the residue by silica-gel column chromatography [light petroleum–Et_2O (1:4) as eluant] gave two fractions.

The first-eluted material (0.760 g, 13%) was identified as the α-glucoside (**13a**) by 300 MHz ^{1}H NMR spectroscopy. After recrystallisation from diethyl ether–light petroleum, the sample showed m.p. 125–126 °C and $[\alpha]_D$ +164° (0.34%) in CH_2Cl_2).

The second-eluted material (0.900 g, 15%) was identified as the β-glucoside (**14a**) on the basis of 300 MHz ^{1}H NMR spectroscopy.

Reaction of 2′,3′,4′,6′-*Tetra*-O-*acetyl*-β-D-*glucopyranose* (**19a**) *with Butynone*.—A solution of the glucopyranose (**19a**)[10] (0.516 g, 1.48 mmol), butynone (0.116 cm^3, 1.57 mmol), and *N*-methylmorpholine (1 drop) in dry dichloromethane (5 cm^3) was stirred for 30 min. Evaporation and purification of the residue by silica-gel column chromatography [light petroleum–Et_2O (1:4) as eluant] gave two fractions.

The first-eluted material (0.203 g, 33%) was identified as the α-glucoside (**13a**) by 300 MHz ^{1}H NMR spectroscopy.

The second-eluted material (0.195 g, 32%) was identified as the β-glucoside (**14a**) by 300 MHz ^{1}H NMR spectroscopy.

Reaction of the Butenone (**13a**) *with Trimethylsilyl Chloride–Zinc Chloride–Triethylamine* (*with M. M. L. Crilley*).—A mixture of anhydrous zinc chloride (0.300 g, 2.2 mmol) and triethylamine (6 cm^3) was stirred until an even dispersion resulted. To the stirred mixture was added a solution of the butenone (**13a**) (2.60 g, 6.25 mmol) in dry benzene (4 cm^3) followed by trimethylsilyl chloride (3.5 cm^3, 28 mmol) whereupon a pink colouration developed. The mixture was heated at 55 °C for 26 h and concentrated. Addition of diethyl ether to the residue, removal of the insoluble material by filtration, and concentration of the filtrate left a syrup (3.47 g). Crystallisation of the syrup from diethyl ether–light petroleum gave trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**21a**) (0.513 g, 20%); m.p. 98–100 °C (lit.,[13] 98 °C); $[\alpha]_D$ +4° (1.3% in $CHCl_3$) (lit.,[13] +8° ($CHCl_3$)]; ν_{max}(KBr) 1 745 cm^{-1} (ester C=O); δ(300 MHz; $CDCl_3$) 0.16 (9 H, s, Me_3Si), 2.01, 2.03, 2.04, and 2.08 (each 3 H, s, 4 × $MeCO_2$), 3.62–3.76 (1 H, m, 5-H), 4.12 (1 H, dd, *J* 12 and 3 Hz, 6-H), 4.22 (1 H, dd, *J* 12 and 4 Hz, 6-H), 4.83 (1 H, d, *J* 8 Hz, 1-H), 4.90 (1 H, dd, *J* 9 and 8 Hz, 2-H), 5.06 (1 H, t, *J* 9 and 9 Hz, 4-H), and 5.19 (1 H, t, *J* 9 and 9 Hz, 3-H) (Found: C, 48.8; H, 6.5. Calc. for $C_{17}H_{28}O_{10}Si$: C, 48.55; H, 6.65%).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*) -1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*buta*-1,3-*diene* (**8b**).—t-Butyldimethylsilyl triflate (0.166 cm^3, 0.72 mmol) was added to a stirred, cooled (CCl_4–solid CO_2) solution of the butenone (**13a**) (0.250 g, 0.60 mmol) and dry triethylamine (0.169 cm^3, 1.21 mmol) in dry dichloromethane (5 cm^3). After 30 min, the mixture was allowed to warm to room temperature and concentrated. Subjection of the resultant residue to low-temperature silica-gel chromatography [light petroleum–Et_2O (1:1) as eluant] gave the *title diene* (**8b**) (0.309 g, 97%) as a colourless syrup which crystallised with time. The sample, after recrystallisation from diethyl ether–light petroleum, possessed m.p. 73–75 °C; $[\alpha]_D$ +141° (0.15% in CH_2Cl_2); ν_{max}(KBr) 1 750 (ester C=O), and 1 665 and 1 645 cm^{-1} (C=C); δ(300 MHz; $CDCl_3$) 0.18 (6 H, s, Me_2Si), 0.95 (9 H, s, Me_3C), 2.01, 2.02, 2.07, and 2.08 (each 3 H, s, 4 × MeCO), 3.93–4.08 (2 H, m, 5′- and 6′-H), 4.15 and 4.16 (each 1 H, s, 4-H_2), 4.26 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.94 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.10 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.35 (1 H, d, *J* 4 Hz, 1′-H), 5.53 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.74 (1 H, d, *J* 12 Hz, 2-H), and 6.71 (1 H, d, *J* 12 Hz, 1-H) (in a NOED spectroscopic study, irradiation of the signal at δ 5.35 enhanced the signals at δ 4.94, 5.74, and 6.71 by 20, 8, and 22%; irradiation of the signal at δ 5.74 caused a 4% enhancement of that at δ 5.35; irradiation of the signal at δ 6.71 resulted in a 12% enhancement of that at δ 5.35); *m/z* (FAB) 531 (MH^+, 3%), 331 ($C_{14}H_{19}O_9^+$, 46%), and 169 (100%) (Found: C, 54.5; H, 7.2. $C_{24}H_{38}O_{11}Si$ requires C, 54.3; H, 7.2%).

Reaction of the Diene (**8b**) *with* N-*Phenylmaleimide*.—A mixture of the diene (**8b**) (0.164 g, 0.31 mmol) and *N*-phenylmaleimide (0.054 g, 0.31 mmol) in dry benzene (1 cm^3) was stirred in the dark for 18 h. Evaporation of the solvent left a syrup (0.211 g) which comprised a 55:45 mixture of the cycloadducts (**11b**) and (**12b**) on the basis of 300 MHz ^{1}H NMR

spectroscopy [the ratio was estimated from the heights of the s at δ 0.93 and 0.94, ascribed to the t-butyl groups of compounds (**12b**) and (**11b**), and from the integrals of the s at δ 1.32 and 1.95 attributed to acetoxy groups of compounds (**11b**) and (**12b**)]. A portion of the residue (0.060 g) was fractionated by HPLC [C_6H_{14}–EtOAc (1:1) as eluant] to give two products.

The first-eluted material (0.029 g, 47%), isolated as a white foam, was (1S,2S,3R)-5-(*t-butyldimethylsiloxy*)-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**11b**) with $[\alpha]_D$ −50° (0.2% in CH_2Cl_2); CD (MeCN) 204sh (Δε −7.2), 214 (Δε −12.6), and 227sh nm (Δε −8.8); ν_{max}(KBr) 1 755 (ester C=O), 1 720 (imide C=O), and 1 655 cm^{-1} (C=C); λ_{max}(EtOH) 212 nm (ε 13 900); δ(300 MHz; $CDCl_3$) 0.19 and 0.20 (each 3 H, s, Me_2Si), 0.94 (9 H, s, Me_3C), 1.32, 1.99, 2.04, and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.60 (1 H, dd, *J* 17 and 10 Hz, 6-Hα), 2.89 (1 H, ddd, *J* 17, 7, and 2.5 Hz, 6-Hβ), 3.21 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.43 (1 H, dt, *J* 10, 10, and 7 Hz, 1-H), 3.87 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 3.97 and 4.25 (each 1 H, dd, *J* 12 and 3 Hz, 6′-H_2), 4.61 (1 H, dd, *J* 7 and 5 Hz, 3-H), 4.71 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.07br (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.15 (1 H, d, *J* 4 Hz, 1′-H), 5.24 (1 H, dd, *J* 7 and 2.5 Hz, 4-H), 5.32 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.30–7.50 (5 H, m, C_6H_5); *m/z* (FAB) 356 (70%) and 73 (100) (Found: C, 58.3; H, 6.6; N, 2.0. $C_{34}H_{45}NO_{13}Si$ requires C, 58.0; H, 6.45; N, 2.0%).

The second-eluted material (0.021 g, 34%), also isolated as a white foam, was (1R,2R,3S)-5-*t-butyldimethylsiloxy*)-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**12b**) with $[\alpha]_D$ +148° (0.1%) in CH_2Cl_2); CD (MeCN) 202 (Δε −6.5) and 227 nm (Δε +10); ν_{max}(KBr) 1 760 (ester C=O), 1 720 (imide C=O), and 1 650 cm^{-1} (C=C); λ_{max}(EtOH) 205 nm (ε 18 900); δ(300 MHz; $CDCl_3$) 0.19 and 0.20 (each 3 H, s, Me_2Si), 0.93 (9 H, s, Me_3C), 1.95, 1.99, and 2.09 (3, 6, and 3 H, each s, 4 × $MeCO_2$), 2.57 (1 H, dd, *J* 16 and 10 Hz, 6-Hα), 2.69 (1 H, ddd, *J* 16, 11, and 3 Hz, 6-Hβ), 3.23 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.45 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.91 (1 H, ddd, *J* 10, 4, and 3 Hz, 5′-H), 4.07 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.22 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.88 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 4.88 (1 H, dd, *J* 7 and 3 Hz, 3-H), 5.03 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.10 (1 H, dd, *J* 7 and 3 Hz, 4-H), 5.15 (1 H, d, *J* 4 Hz, 1′-H), 5.26 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.30–7.60 (5 H, m, C_6H_5); *m/z* (FAB) 356 (50%) and 73 (100) (Found: C, 57.7; H, 6.1; N, 1.8. $C_{34}H_{45}NO_{13}Si$ requires C, 58.0; H, 6.45; N, 2.0%).

Preparation of (1S,2S,3R)-5-*Oxo*-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**22a**).—0.1M Hydrochloric acid (1 cm^3) was added to a stirred solution of the cycloadduct (**11b**) (0.066 g, 0.094 mmol) in THF (4 cm^3). After 18 h, the mixture was partitioned between water and ethyl acetate. The organic phase was washed with water, dried ($MgSO_4$), and concentrated. Purification of the resultant syrup by silica-gel column chromatography [light petroleum–EtOAc (1:4) as eluant] gave the *title compound* (**22a**) (0.035 g, 63%) as a white solid. After recrystallisation from diethyl ether, the sample displayed m.p. 177–178 °C; $[\alpha]_D$ +91° (0.03% in CH_2Cl_2); CD (MeCN) 209 (Δε −5.2), 237 (Δε −2.3), 287 (Δε +3.1), 297 (Δε +3.3), 304sh (Δε +2.6), and 315 nm (Δε +1.2); ν_{max}(KBr) 1 755 (ester C=O) and 1 715 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 214sh nm (ε 12 000); δ(300 MHz; $CDCl_3$) 1.37, 2.00, 2.05, and 2.12 (each 3 H, s, 4 × $MeCO_2$), 2.43 (1 H, dd, *J* 19 and 3 Hz, 4-Hβ), 2.89 (1 H, dd, *J* 17 and 11 Hz, 6-Hα), 3.03–3.17 (2 H, m, 4-Hα and 6-Hβ), 3.22 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.48 (1 H, dt, *J* 11, 11, and 8 Hz, 1-H), 3.70 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′H), 4.07 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.13 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.65–4.74 (2 H, m, 2′- and 4-H), 4.96 (1 H, dd, *J* 11 and 10 Hz, 4′-H), 5.22 (1 H, d, *J* 4′-H), 5.27 (1 H, dd, *J* 10 and 9 Hz, 3′-H), and 7.36–7.50 (5 H, m, C_6H_5); *m/z* (FAB) 590 (MH^+, 21%) and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 56.7; H, 5.1; N, 2.3. $C_{28}H_{31}NO_{13}$ requires C, 57.05; H, 5.25; N, 2.4%).

Preparation of (1R,2R,3S)-5-*Oxo*-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**23a**).—0.1M Hydrochloric acid (1 cm^3) was added to a stirred solution of cycloadduct (**12b**) (0.048 g, 0.068 mmol) in THF (4 cm^3). After 23 h, the mixture was partitioned between water and ethyl acetate. The organic phase was washed with water, dried ($MgSO_4$), and concentrated. Purification of the resultant syrup by silica-gel column chromatography [light petroleum–EtOAc (1:4) as eluant] gave the *title compound* (**23a**) (0.021 g, 52%) as a white solid. After recrystallisation from diethyl ether–light petroleum, the sample displayed m.p. 191–193 °C; $[\alpha]_D$ +51° (0.1% in CH_2Cl_2); CD (MeCN) 235 (Δε +1.6), 286sh (Δε −3.1), 293 (Δε −3.3), 303 (Δε −2.7), and 313sh nm (Δε −1.3); ν_{max}(KBr) 1 760 (ester C=O) and 1 715 cm^{-1} (imide ketone C=O); λ_{max}(EtOH) 215sh (ε 7 500); δ(300 MHz; $CDCl_3$) 1.93, 1.99, 2.00, and 2.06 (each 3 H, s, 4 × $MeCO_2$), 2.36 (1 H, dd, *J* 19 and 2 Hz, 4-Hβ), 2.85 (1 H, dd, *J* 19 and 4 Hz, 4-Hα), 2.91 (1 H, dd, *J* 17 and 11 Hz, 6-Hα), 3.03 (1 H, dd, *J* 17 and 8 Hz, 6-Hβ), 3.40 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.52 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.85 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.00–4.12 (2 H, m, 6′-H_2), 4.88 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 4.90–4.95 (1 H, m, 3-H), 5.02 (1 H, dd, *J* 10 and 9 Hz, 4′-H), 5.02 (1 H, d, *J* 4 Hz, 1′-H), 5.25 (1 H, dd, *J* 10 and 9 Hz, 3′-H), and 7.40–7.58 (5 H, m, C_6H_5); *m/z* (FAB) 590 (MH^+, 3%) and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 56.7; H, 5.2; N, 2,3. $C_{28}H_{31}NO_{13}$ requires C, 57.05; H, 5.25; N, 2.4%).

Preparation of 6-O-*Benzyl*-1,2,3,4-*tetra*-O-*acetyl*-D-*glucose* (**35**).—A mixture of 6-*O*-benzyl-D-glucose[17] (3.40 g, 12.6 mmol) and acetic anhydride (25 cm^3) was cooled to 0 °C and pyridine (25 cm^3) was added. After 3 days in the refrigerator, the mixture was poured onto ice (250 g) and left overnight. The insoluble material was collected by filtration, dried, and crystallised from diethyl ether–light petroleum to give the title compound (**35**)[16] (3.80 g, 71%) as a 1:1 mixture of α- and β-anomers with m.p. 91–94 °C; $[\alpha]_D$ +59° (5.7% in CH_2Cl_2); ν_{max}(KBr) 1 740 cm^{-1} (ester C=O); λ_{max}(EtOH) 204 (ε 9 100), 250 (210), 255 (270), 261 (180), and 265 nm (100); δ(300 MHz; $CDCl_3$) 1.85, 1.88, 1.97, 1.98, 1.99, 2.06, and 2.13 (1.5, 1.5, 3, 1.5, 1.5, 1.5, and 1.5 H, each s, 4 × $MeCO_2$), 3.44–3.58 (2 H, m, 6-H_2), 3.72–3.78 and 4.00–4.06 (each 0.5, m, 5-H), 4.41, 4.43, 4.59, and 4.54 (each 0.5 H, d, *J* 13 Hz, PhCH_2), 5.03–5.22 and 5.42 [3.5 and 0.5 H, m and t (*J* 9 and 9 Hz), 2-, 3-, and 4-H], 5.67 and 6.30 [each 0.5 H, d (*J* 9 Hz) and d (*J* 3 Hz), 1-H], and 7.20–7.33 (5 H, m, C_6H_5); *m/z* (CI) 379 (55) and 91 ($C_7H_7^+$, 100) (Found: C, 57.3; H, 5.8. Calc. for $C_{20}H_{26}O_{11}$: C, 57.55; H, 6.0%).

Preparation of 6-O-*Benzyl*-2,3,4-*tri*-O-*acetyl*-D-*glucose* (**19b**).—Ammonia gas was bubbled into an ice-cooled mixture of THF (35 cm^3) and methanol (15 cm^3) for 10 min. The tetra-acetate (**35**) (3.00 g, 6.84 mmol) was then added and the mixture was stirred for 45 min. Evaporation left a residue which was purified by silica-gel column chromatography [Et_2O–light petroleum (3:2) as eluant] to give the title compound (**19b**) (2.40 g, 89%), comprising a 72:28 mixture of α- and β-anomers, as a clear oil with $[\alpha]_D$ +67° (0.65% in CH_2Cl_2); ν_{max}(film) 3 450 (OH) and 1 750 cm^{-1} (ester C=O); λ_{max}(EtOH) 205 nm (ε 9 200); δ(300 MHz; $CDCl_3$) 1.88, 1.90, 2.00, and 2.06 (0.84, 2.16, 3, and 3 H, each s, 3 × $MeCO_2$), 3.43–3.57 (2 H, m, 6-H_2), 3.62–3.70 and 4.17–4.26 (0.28 and 0.72 H, each m, 5-H), 3.87br and 4.02br (0.72 and 0.28 H, each s, OH), 4.52 (2 H, AB q, *J* 12 Hz, separation of inner lines 13 Hz, PhCH_2), 4.63–4.68 and 5.40–5.43 (0.28 and 0.72 H, each m, 1-H), 4.83–4.90 (1 H, m, 2-H), 5.02, 5.07, 5.18, and 5.50 (0.72, 0.28, 0.28, and 0.72 H, each t, *J* 9

and 9 Hz, 3- and 4-H), and 7.25–7.36 (5 H, m, C_6H_5); *m/z* (CI) 337 (2%) and 91 ($C_7H_7^+$, 100).

Reaction of 6-O-*Benzyl*-2,3,4-*tri*-O-*acetyl*-D-*glucopyranose* (**19b**) *with Butynone*.—A solution of the glucopyranose (**19b**) (0.150 g, 0.38 mmol), butynone (0.036 cm^3, 0.45 mmol), and *N*-methylmorpholine (0.042 cm^3, 0.38 mmol) in dry dichloromethane (2 cm^3) was stirred for 19 h. Evaporation and purification of the resultant dark oil by silica-gel column chromatography [light petroleum–EtOAc (7:3) as eluant] yielded two products.

The first-eluted material (0.150 g, 85%) was (E)-4-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**13b**). After recrystallisation from diethyl ether, the sample displayed m.p. 107–108 °C; $[\alpha]_D$ +163° (3% in CH_2Cl_2); ν_{max}(KBr) 1 740 (ester C=O), 1 680 and 1 660 (vinylogous ester C=O), and 1 640 cm^{-1} (C=C); λ_{max}(EtOH) 206 (ε 10 600) and 236 nm (17 800); δ(300 MHz; $CDCl_3$) 1.88, 2.01, and 2.04 (each 3 H, s, 3 × $MeCO_2$), 2.15 (3 H, s, 1-H_3), 3.47 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 3.52 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 3.88 (1 H, dt, *J* 10, 4, and 4 Hz, 5′-H), 4.49 (2 H, AB q, *J* 12 Hz, separation of inner lines 27 Hz, PhCH_2), 4.96 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.22 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.48 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.49 (1 H, d *J* 4 Hz, 1′-H), 5.91 (1 H, d, *J* 13 Hz, 3-H), 7.23–7.34 (5 H, m, C_6H_5), and 7.42 (1 H, d, *J* 13 Hz, 4-H); *m/z* (CI) 379 ($C_{19}H_{23}O_8^+$, 6%) and 91 ($C_7H_7^+$, 100) (Found: C, 59.5; H, 6.0. $C_{23}H_{28}O_{10}$ requires C, 59.45; H, 6.1%).

The second-eluted material (0.010 g, 5%) was (E)-4-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**14b**). After recrystallisation from diethyl ether, the sample showed m.p. 122–125 °C; $[\alpha]_D$ +6.8° (1.6% in CH_2Cl_2); ν_{max}(KBr) 1 750 (ester C=O), 1 690 and 1 670 (vinylogous ester C=O), and 1 640 cm^{-1} (C=C); λ_{max}(EtOH) 206 (ε 10 400) and 236 nm (18 300); δ(300 MHz; $CDCl_3$) 1.89, 1.98, and 2.02 (each 3 H, s, 3 × $MeCO_2$), 2.15 (3 H, s, 1-H_3), 3.53 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 3.58 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 3.73–3.78 (1 H, m, 5′-H), 4.50 (2 H, AB q, *J* 12 Hz, separation of inner lines 15 Hz, PhCH_2), 4.88 (1 H, d, *J* 8 Hz, 1′-H), 5.10–5.23 (3 H, m, 2′-, 3′-, and 4′-H), 5.82 (1 H, d, *J* 12 Hz, 3-H), 7.23–7.33 (5 H, m, C_6H_5), and 7.43 (1 H, d, *J* 12 Hz, 4-H); *m/z* (CI) 379 ($C_{19}H_{23}O_8^+$, 10%) and 91 ($C_7H_7^+$, 100) (Found: C, 59.6; H, 6.1. $C_{23}H_{28}O_{10}$ requires C, 59.45; H, 6.1%).

Preparation of 6-O-*Benzyl*-2,3,4-*tri*-O-*acetyl*-α-D-*glucopyranosyl Chloride* (**15b**).—Thionyl chloride (0.56 cm^3, 7.7 mmol) was added in drops to dry DMF (3 cm^3) at 0 °C and to the stirred solution was added a solution of the glucopyranose (**19b**) (0.610 g, 1.5 mmol) in dry DMF (2 cm^3). After 1 h at 0 °C, the mixture was stirred for 16 h at room temperature and then poured onto water (100 cm^3) and extracted with diethyl ether. The ethereal extract was washed with water, dried ($MgSO_4$), and concentrated to leave a yellow oil which was purified by silica-gel chromatography [light petroleum–Et_2O (7:3) as eluant] to give the title compound (**15b**) (0.430 g, 67%) as a somewhat unstable gum with $[\alpha]_D$ +157° (1.9% in CH_2Cl_2); ν_{max}(film) 1 750 cm^{-1} (ester C=O); λ_{max}(EtOH) 205 (ε 14 500) and 250 nm (ε 2 300); δ(300 MHz; $CDCl_3$) 1.90, 1.98, and 2.04 (each 3 H, s, together 3 × $MeCO_2$), 3.47–3.58 (2 H, m, 6-H_2), 4.18–4.25 (1 H, m, 5-H), 4.48 (2 H, AB q, *J* 12 Hz, separation of inner lines 24 Hz, PhCH_2), 4.97 (1 H, dd, *J* 10 and 4 Hz, 2-H), 5.20 (1 H, t, *J* 10 and 10 Hz, 4-H), 5.49 (1 H, t, *J* 10 and 10 Hz, 3-H), 6.28 (1 H, d, *J* 4 Hz, 1-H), and 7.13–7.34 (5 H, m, C_6H_5); *m/z* (CI) 416 and 414 (M^+, 1.6 and 4.4%), 371 (20), and 91 ($C_7H_7^+$, 100).

Preparation of (E)-4-(6′-O-*Benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**14b**).—Silver(I) nitrate (0.193 g, 1.14 mmol) was added to a stirred solution of the freshly prepared chloride (**15b**) (0.430 g, 1.04 mmol) in 98% formic acid (3 cm^3). After 45 min, the mixture was filtered and the filtrate partitioned between saturated aqueous sodium hydrogen carbonate and diethyl ether. The ethereal phase was washed with water, dried ($MgSO_4$), and concentrated to leave a pale-yellow oil (0.390 g). The oil was dissolved in ethyl acetate (10 cm^3), acetylmethylenetriphenylphosphorane (0.490 g, 1.54 mmol) added, and the mixture heated under reflux for 24 h. Evaporation and purification of the residue by silica-gel column chromatography [light petroleum–Et_2O (2:3) as eluant] gave a material (0.290 g, 60%) that was identified as the β-glucoside (**14b**) by 300 MHz ^1H NMR spectroscopy.

Preparation of (E)-1-(6′-O-*Benzyl*-(2′,3′,4′*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-3-(*t-butyldimethylsiloxy*)*buta*-1,3-*diene* (**8c**).—t-Butyldimethylsilyl triflate (0.089 cm^3, 0.39 mmol) was added to a stirred, cooled (CCl_4–solid CO_2) solution of the butenone (**13b**) (0.150 g, 0.32 mmol) and dry triethylamine (0.091 cm^3, 0.64 mmol) in dry dichloromethane (5 cm^3). After 15 min, the mixture was concentrated and the residue subjected to low-temperature column chromatography on silica-gel [light petroleum–diethyl ether (1:1) as eluant] to give the *title diene* (**8c**) (0.174 g, 93%) as a somewhat unstable syrup; ν_{max}(film) 1 755 (ester C=O) and 1 665 cm^{-1} (C=C); λ_{max}(EtOH) 209 (ε 14 300) and 239 nm (17 500); δ(300 MHz; $CDCl_3$) 0.16 and 0.17 (each 3 H, s, Me_2Si), 0.94 (9 H, s, Me_3C), 1.90, 2.02, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 3.48 (1 H, dd, *J* 11 and 4 Hz, 6′-H), 3.53 (1 H, dd, *J* 11 and 3 Hz, 6′-H), 3.92 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.14 (2 H, s, 4-H_2), 4.43 and 4.59 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.96 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.25 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.37 (1 H, d, *J* 4 Hz, 1′-H), 5.45 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.75 (1 H, d, *J* 12 Hz, 2-H), 6.73 (1 H, d, *J* 12 Hz, 1-H), and 7.25-7.35 (5 H, m, C_6H_5) (in a NOED spectroscopic study, irradiation of the signal at δ 5.37 enhanced the signals at δ 4.96, 5.75, and 6.73 by 17, 11, and 20%; irradiation of the signal at δ 6.73 caused a 2.5% enhancement of that at δ 5.37; irradiation of the signal at δ 6.73 resulted in a 5% enhancement of that at δ 5.37); *m/z* (FAB) 579 (MH^+, 1%), 379 (10), and 91 ($C_7H_7^+$, 100) (Found: C, 59.9; H, 7.2. $C_{29}H_{42}O_{10}Si$ requires C, 60.2; H, 7.3%).

Preparation of (E)-1-(6′-O-*Benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-3-(*t-butyldimethylsiloxy*)*buta*-1,3-*diene* (**34a**).—Dry triethylamine (0.135 cm^3, 0.97 mmol) followed by t-butyldimethylsilyl triflate (0.165 cm^3, 0.72 mmol) were added to a stirred cooled (CCl_4–solid CO_2) solution of the butenone (**14b**) (0.200 g, 0.43 mmol) in dry dichloromethane (5 cm^3). After 30 min, more triethylamine (0.5 cm^3) was added and the mixture was concentrated. The resultant orange oil was subjected to low-temperature silica-gel column chromatography [light petroleum–Et_2O (4:1) as eluant] to give the *title compound* (**34a**). After recrystallisation from diethyl ether–light petroleum, the sample (0.180 g, 72%) possessed m.p. 92–93 °C; $[\alpha]_D$ +3° (0.35%) in CH_2Cl_2); ν_{max}(KBr) 1 750 (ester C=O) and 1 650 cm^{-1} (C=C); λ_{max}(EtOH) 208 (ε 16 200) and 238 nm (20 000); δ(300 MHz; $CDCl_3$) 0.19 and 0.20 (each 3 H, s, Me_2Si), 0.97 (9 H, s, Me_3C), 1.95, 2.03, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 3.60 (2 H, d, separation 4 Hz, 6′-H_2), 3.78 (1 H, dt, *J* 9, 4, and 4 Hz, 5′-H), 4.15 and 4.16 (each 1 H, s, 4-H_2), 4.56 (2 H, AB q, *J* 12 Hz, separation of inner lines 10 Hz, PhCH_2), 4.80 (1 H, d, *J* 8 Hz, 1′-H), 5.10-5.18 (2 H, m, 2′-and 4′-H), 5.25 (1 H, t *J* 9 and 9 Hz, 3′-H), 5.68 (1 H, d, *J* 13 Hz, 2-H), 6.80 (1 H, d, *J* 13 Hz, 1-H), and 7.30–7.38 (5 H, m, C_6H_5) (in a NOED spectroscopic study, irradiation of the signal at δ 4.80 caused 9, 5, 5, and 11% enhancements of the signals at δ 3.78, 5.25, 5.68, and 6.80; irradiation of the signal at δ 5.68 enhanced that at δ 4.15 by 4%; irradiation of the signal at δ 6.80 resulted in a 3% enhancement of that at δ 4.80) (Found: C, 59.9; H, 7.3; Si, 4.7. $C_{29}H_{42}O_{10}Si$ requires C, 60.2; H, 7.3; Si, 4.85%).

Reaction of 2-O-*Benzyl*-3,4,6-*tri*-O-*acetyl*-D-*glucopyranose* (**19c**) *with Butynone*.—A solution of the glucopyranose (**19c**)[18] (0.300 g, 0.76 mmol), butynone (0.06 cm^3, 0.77 mmol), and *N*-methylmorpholine (1 drop) in dry dichloromethane (5 cm^3) was stirred for 30 min. Evaporation and subjection of the residue to silica-gel column chromatography [light petroleum–Et_2O (2:3→3:7) as eluant] gave two fractions.

The first-eluted material (0.091 g, 26%) was (E)-4-(2′-O-*benzyl*-3′,4′,6′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**13c**). After recrystallisation from diethyl ether–light petroleum, the sample displayed m.p. 93–94 °C; $[\alpha]_D$ +139° (0.23% in CH_2Cl_2); ν_{max}(KBr) 1 745 (ester C=O), 1 655 (vinylogous ester C=O), and 1 630 cm^{-1} (C=C); λ_{max}(EtOH) 210 (ε 8 500) and 240 nm (16 800); δ(300 MHz; $CDCl_3$) 2.02 and 2.05 (6 and 3 H, each s, 3 × $MeCO_2$), 2.19 (3 H, s, 1-H_3), 3.67 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.92 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.00 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.26 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.63 (2 H, AB q, *J* 12 Hz, separation of inner lines 25 Hz, PhCH_2), 5.02 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.12 (1 H, d, *J* 4 Hz, 1′-H), 5.47 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.90 (1 H, d, *J* 13 Hz, 3-H), and 7.25–7.42 (6 H, m, C_6H_5 and 4-H); *m/z* (CI) 465 (MH^+, 1%), 379 ($C_{19}H_{23}O_8^+$, 33), and 91 ($C_7H_7^+$, 100) (Found: C, 59.5; H, 5.8. $C_{23}H_{28}O_{10}$ requires C, 59.45; H, 6.1%).

The second-eluted material (0.101 g, 29%) was (E)-4-(2′-O-*benzyl*-3′,4′,6′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**14c**). After recrystallisation from diethyl ether–light petroleum, the sample showed m.p. 96–98 °C; $[\alpha]_D$ +15° (0.14% in CH_2Cl_2); ν_{max}(KBr) 1 755 (ester C=O), 1 690 (vinylogous ester C=O), and 1 610 cm^{-1} (C=C); λ_{max}(EtOH) 209 (ε 10 500), 239 (18 000), and 304 nm (1 300); δ(300 MHz; $CDCl_3$) 1.97, 2.05, and 2.11 (each 3 H, s, 3 × $MeCO_2$), 2.24 (3 H, s, 1-H_3), 3.65 (1 H, dd, *J* 10 and 8 Hz, 1′-H), 3.81 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.13 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.31 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.63 and 4.79 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.90 (1 H, d, *J* 8 Hz, 1′-H), 5.04 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.23 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.89 (1 H, d, *J* 12 Hz, 3-H), 7.25–7.41 (5 H, s, C_6H_5), and 7.50 (1 H, d, *J* 12 Hz, 4-H); *m/z* (CI) 392 (2%), 170 (41), 142 (75), and 91 ($C_7H_7^+$, 100) (Found: C, 59.2; H, 6.2. $C_{23}H_{28}O_{10}$ requires C, 59.45; H, 6.1%).

Preparation of (E)-1-(2′-O-*Benzyl*-3′,4′,6′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-3-(*t-butyldimethylsiloxy*)*buta*-1,3-*diene* (**8d**).—t-Butyldimethylsilyl triflate (0.072 cm^3, 0.31 mmol) was added to a stirred cooled (CCl_4–solid CO_2) solution of the butenone (**13c**) (0.122 g, 0.26 mmol) and dry triethylamine (0.074 cm^3, 0.52 mmol) in dry dichloromethane (2 cm^3). After 15 min, the mixture was concentrated and the residue purified by low-temperature silica-gel column chromatography [light petroleum–Et_2O (1:1) as eluant] to give the *title diene* (**8d**) (0.144 g, 98%) as a somewhat unstable syrup; ν_{max}(film) 1 755 (ester C=O) and 1 665 cm^{-1} (C=C); δ(300 MHz; $CDCl_3$) 0.18 and 0.19 (each 3 H, s, Me_2Si), 0.95 (9 H, s, Me_3C), 2.02 and 2.06 (6 and 3 H, each s, 3 × $MeCO_2$), 3.62 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.90–4.01 (2 H, m, 5′- and 6′-H), 4.15 (2 H, s, 4′-H_2), 4.29 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.63 (2 H, AB q, *J* 12 Hz, separation of inner lines 9 Hz, PhCH_2), 5.01 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.05 (1 H, d, *J* 4 Hz, 1′-H), 5.49 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.74 (1 H, d, *J* 13 Hz, 2-H), 6.72 (1 H, d, *J* 13 Hz, 1-H), and 7.26–7.40 (5 H, m, C_6H_5) (in a NOED spectroscopic study, irradiation of the signal at δ 5.05 enhanced the signals at δ 3.62, 5.74, and 6.72 by 14, 8, and 16%; irradiation of the signal at δ 5.74 caused a 2.5% enhancement of that at δ 5.05; irradiation of the signal at δ 6.72 resulted in a 5% enhancement of that at δ 5.05); *m/z* (FAB) 579 (MH^+, 1%) and 91 ($C_7H_7^+$, 100) (Found: C, 60.5; H, 7.6. $C_{29}H_{42}O_{10}Si$ requires C, 60.2; H, 7.3%).

Preparation of (E)-1-(2′-O-*Benzyl*-3′,4′,6′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-3-(*t-butyldimethylsiloxy*)*buta*-1,3-*diene* (**34b**).—t- Butyldimethylsilyl triflate (0.120 cm^3, 0.52 mmol) was added to a stirred, cooled (CCl_4–solid CO_2) solution of the butenone (**14c**) (0.200 g, 0.43 mmol) and dry triethylamine (0.121 cm^3, 0.86 mmol) in dry dichloromethane (5 cm^3). After 30 min, the mixture was allowed to warm to room temperature and the solvent removed by evaporation. The resultant residue was subjected to low-temperature silica-gel column chromatography [light petroleum–Et_2O (1:1) as eluant] to give the title compound (**34b**) (0.246 g, 98%) as a somewhat unstable syrup; ν_{max}(film) 1 750 (ester C=O) and 1 660 cm^{-1} (C=C); δ(300 MHz; $CDCl_3$) 0.22 (6 H, s, Me_2Si), 0.99 (9 H, s, Me_3C), 1.94, 2.03, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 3.57 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 3.77 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.10 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.19 (2 H, s, 4-H_2), 4.27 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.61 and 4.84 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.77 (1 H, d, *J* 8 Hz, 1′-H), 5.01 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.21 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.73 (1 H, d, *J* 12 Hz, 2-H), 6.83 (1 H, d, *J* 12 Hz, 1-H), and 7.26–7.36 (5 H, m, C_6H_5) (in a NOED spectroscopic study, irradiation of the signal at δ 4.77 caused enhancements of the signals at δ 3.77, 5.21, 5.73, and 6.83 by 13, 6, 24, and 14%; irradiation of the signal at δ 5.73 enhanced that at δ 4.19 by 4% and that at δ 4.77 by 3%; irradiation of the signal at δ 6.83 resulted in an 11% enhancement of that at δ 4.77).

Reaction of the 6′-O-*Benzyl*-α-*diene* (**8c**) *with* N-*Phenylmaleimide*.—A solution of the diene (**8c**) (0.160 g, 0.28 mmol) and *N*-phenylmaleimide (0.048 g, 0.28 mmol) in dry benzene (1 cm^3) was left in the dark for 20 h. Evaporation of the solvent left a pale-yellow syrup which comprised a 69:31 mixture of the cycloadducts (**11c**) and (**12c**) by 300 MHz ^1H NMR spectroscopy [the ratio was estimated from the heights of the s at δ 0.92 and 0.93, ascribed to the t-butyl group of compounds (**11c**) and (**12c**), and from the integrals of the s at δ 1.32 and 1.82, attributed to acetoxy groups of compounds (**11c**) and (**12c**)]. The syrup was dissolved in diethyl ether and the solution cooled to induce crystallisation. The filtered material (0.092 g, 44%), isolated as white needles, was (1S,2S,3R)-3-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-5-(*t-butyldimethylsiloxy*)-N-*phenylcyclohex*-4-*ene*-1,2-*dicarboximide* (**11c**) m.p. 146–148 °C; $[\alpha]_D$ −36° (0.2% in CH_2Cl_2); CD (MeCN) 204 (Δε −8.7) and 213 nm (Δε −13.4); ν_{max}(KBr) 1 750 (ester C=O), 1 720 and 1 710 (imide C=O), and 1 655 cm^{-1} (C=C); λ_{max}(EtOH) 202 nm (ε 24 500); δ(300 MHz; $CDCl_3$) 0.15 and 0.16 (each 3 H, s, Me_2Si), 0.92 (9 H, s, Me_3C), 1.32, 1.88, and 1.99 (each 3 H, s, 3 × $MeCO_2$), 2.55 (1 H, dd, *J* 17 and 10 Hz, 6-Hα), 2.88 (1 H, ddd, *J* 17, 8, and 3 Hz, 6-Hβ), 3.19 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.36–3.49 (3 H, m, 6′-H_2 and 1-H), 3.80 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.41 (1 H, d, *J* 12 Hz, PhC*H*H), 4.55–4.62 (2 H, m, 3-H, m, 3-H and PhCH*H*), 4.72 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.14–5.32 (4 H, m, 1′-, 3′- 4-, and 4′-H), and 7.26-7.45 (10 H, m, 2 × C_6H_5); *m/z* (FAB) 752 (MH^+, 1%) and 356 (100) (Found: C, 62.6; H, 6.6; N, 1.9. $C_{39}H_{49}NO_{12}Si$ requires C, 62.3; H, 6.55; N, 1.85%).

The filtrate from the above recrystallisation was treated with light petroleum and the resultant white solid recrystallised twice from cold diethyl ether and then from cold dichloromethane–diethyl ether. The filtered material (0.005 g, 2%), identified as (1R,2R,3S)-3-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-5-(t-*butyldimethylsiloxy*)-N-*phenylcyclohex*-4-*ene*-1,2-*dicarboximide* (**12c**), showed m.p. 157–160 °C; ν_{max}(KBr) 1 760 (ester C=O), 1 715 (imide C=O), and 1 640 cm^{-1} (C=C); λ_{max}204 nm (ε 28 000); δ(300 MHz; $CDCl_3$) 0.19 and 0.20 (each 3 H, s, Me_2Si), 0.93 (Me_3C), 1.82, 1.975, and 1.983 (each 3 H, s, 3 × $MeCO_2$), 2.55 (1 H, dd, *J* 17 and 10 Hz, 6-Hα), 2.68 (1 H, ddd, *J* 17, 8, and 2 Hz, 6-Hβ), 3.20 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.37–3.54 (3 H, m, 1-H and 6′-H_2), 3.87br (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.41 and 4.62 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.84–4.93 and 5.07–5.29 (2 and 4 H, each m, 1′-, 2′-, 3-, 3′-, 4-, and

4′-H), and 7.26–7.56 (10 H, m, 2 × C_6H_5); *m/z* (FAB) 866 ($MC_6H_{15}Si^+$, 8%), 694 ($M^+ - C_4H_9$, 8), and 356 (100) (Found: C, 62.0; H, 6.8; N, 1.9. $C_{39}H_{49}NO_{12}Si$ requires C, 62.3; H, 6.55; N, 1.85%).

Preparation of (1S,2S,3R)-3-(6′-O-*Benzyl*-2′,3′,4′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-5-*oxo*-N-*phenylcyclohexane*-1,2-*dicarboximide* (**22b**).—0.1M Hydrochloric acid (3 cm^3) was added to a stirred solution of the cycloadduct (**11c**) (0.250 g, 0.33 mmol) in THF (6 cm^3). After 22 h, the solution was poured into water and the mixture was extracted with ethyl acetate. The organic extract was washed with water, dried ($MgSO_4$), and concentrated. Recrystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave the *title compound* (**22b**) (0.150 g, 70%) as white crystals with m.p. 157–158 °C; $[\alpha]_D$ +81° (0.3% in CH_2Cl_2); ν_{max}(KBr) 1 755 (ester C=O) and 1 720 cm^{-1} (imide and ketone C=O); λ_{max}201 nm (ε 22 900); δ(300 MHz; $CDCl_3$) 1.35, 1.91, and 1.99 (each 3 H, s, 3 × $MeCO_2$), 2.41 (1 H, dd, *J* 19 and 2 Hz, 4-Hβ), 2.90 (1 H, dd, *J* 17 and 11 Hz, 6-Hα), 3.10 (1 H, dd, *J* 17 and 8 Hz, 6-Hβ), 3.16 (1 H, dd, *J* 19 and 3 Hz, 4-Hα), 3.31 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.40–3.53 (3 H, m, 1-H and 6′-H_2), 3.64 (1 H, dt, *J* 10, 4 and 4 Hz, 5′-H), 4.47 and 4.59 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.66–4.76 (2 H, m, 2′- and 3-H), 5.08 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.20–5.30 (2 H, m, 1′- and 3′-H), and 7.26–7.55 (10 H, m, 2 × C_6H_5); *m/z* (FAB) 379 (10%) and 136 (100) (Found: C, 61.9; H, 5.4; N, 2.1. $C_{33}H_{35}NO_{12}$ requires C, 62.15; H, 5.55; N, 2.2%).

Reaction of the 6′-O-*Benzyl Derivative* (**22b**) *with Hydrogen–Palladium followed by Acetic Anhydride*.—A mixture of the benzyl derivative (**22b**) (0.075 g, 0.12 mmol) and 10% palladium–charcoal (0.025 g, 0.33 mass equiv.) in ethyl acetate (5 cm^3) was stirred under an atmosphere of hydrogen for 4 days. The mixture was filtered through Celite and the filtrate was concentrated to leave a residue which was dissolved in pyridine (2 cm^3). Acetic anhydride (2 cm^3) was added to the stirred ice-cooled solution which, after 1 h, was allowed to warm up to room temperature. After 24 h, the mixture was diluted with dichloromethane and washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. Evaporation of the dried ($MgSO_4$) organic phase gave a syrup which was crystallised from cold dichloromethane–diethyl ether to give white needles (0.040 g, 58%), m.p. 177 °C, which were identified as the acetyl derivative (**22a**) by 300 MHz ^{1}H NMR spectroscopy.

Reaction of the 6′-O-*Benzyl*-β-*diene* (**34a**) *with* N-*Phenylmaleimide*.—A solution of the diene (**34a**) (0.115 g, 0.20 mmol) and *N*-phenylmaleimide (0.034 g, 0.20 mmol) in dry benzene (1 cm^3) was left overnight in the dark. Evaporation of the solvent gave an off-white solid which was mainly the cycloadduct (**38a**) by 300 MHz ^{1}H NMR spectroscopy. Crystallisation of the material from diethyl ether gave (1R,2R,3S)-3-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-5-(*t-butyldimethylsiloxy*)-N-*phenylcyclohex*-4-*ene*-1,2-*dicarboximide* (**38a**) (0.109 g, 73%) with m.p. 145–147 °C; $[\alpha]_D$ +88° (0.2% in CH_2Cl_2); CD (MeCN) 208 (Δε +4.8) and 224 nm (Δε +10.8); ν_{max}(KBr) 1 760 (ester C=O), 1 715 (imide C=O), and 1 660 cm^{-1} (C=C); λ_{max}(EtOH) 214sh (ε 15 600); δ(300 MHz; CD_3COCD_3) −0.18 and −0.16 (each 3 H, s, Me_2Si), 0.57 (9 H, s, Me_3C), 1.32, 1.58, and 1.60 (each 3 H, s, 3 × $MeCO_2$), 2.02 (1 H, d, *J* 17 and 10 Hz, 6-Hα), 2.95 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.09–3.20 (2 H, m, 6′-H_2), 3.27 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.54 (1 H, dt, *J* 10, 4, and 4 Hz, 5′-H), 4.12 (2 H, AB q, *J* 12 Hz, separation of inner lines 13 Hz, PhCH_2), 4.30 (1 H, d, *J* 10 and 8 Hz, 2′-H), 4.39br (1 H, t, *J* 5 and 5 Hz, 3-H), 4.54–4.65 (2 H, m, 1′- and 4′-H), 4.87 (1 H, t, *J* 10 and 10 Hz, 3′-H), 4.92 (1 H, dd, *J* 6 and 3 Hz, 4-H), and 6.85–7.25 (10 H, m, 2 × C_6H_5) (the signal for 6-Hβ was partly obscured by the solvent signals at δ 2.17–2.22); *m/z* (FAB) 752 (MH^+, 1%) and 356 (100) (Found: C, 62.5; H, 6.9; N, 1.9. $C_{39}H_{49}NO_{12}Si$ requires C, 62.3; H, 6.55; N, 1.85%).

Preparation of (1R,2R,3S)-3-(6′-O-*Benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-5-*oxo*-N-*phenylcyclohexane*-1,2-*dicarboximide* (**40a**).—0.1M Hydrochloric acid (5 cm^3) was added to a stirred solution of the cycloadduct (**38a**) (0.050 g, 0.07 mmol) in THF (10 cm^3). After 18 h, the solution was poured into water and the mixture was extracted with dichloromethane. The organic extract was washed with water, dried ($MgSO_4$), and concentrated. Recrystallisation of the residue from dichloromethane–diethyl ether gave the *title compound* (**40a**) (0.040 g, 95%) as white needles with m.p. 210–213 °C; $[\alpha]_D$ −41° (0.45% in CH_2Cl_2); ν_{max}(KBr) 1 745 (ester C=O) and 1 705 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 204sh nm (ε 23 000); δ(300 MHz; $CDCl_3$) 1.52, 1.93, and 1.96 (each 3 H, s, 3 × $MeCO_2$), 2.34 (1 H, dd, *J* 18 and 2 Hz, 4-Hβ), 2.92 (1 H, dd, *J* 16 and 12 Hz, 6-Hα), 2.98 (1 H, dd, *J* 16 and 8 Hz, 6-Hβ), 3.16 (1 H, dd, *J* 18 and 3 Hz, 4-Hα), 3.27 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.39 (1 H, dt, *J* 11, 11, and 8 Hz, 1-H), 3.50–3.58 (2 H, m, 6′-H_2), 3.66–3.73 (1 H, m, 5′-H), 4.53 (2 H, s, PhCH_2), 4.66 (1 H, d, *J* 8 Hz, 1′-H), 4.82 (1 H, apparent q, separation 3 Hz, 3-H), 4.89 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 4.99 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.16 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.28–7.56 (10 H, m, 2 × C_6H_5); *m/z* (CI) 379 (6%) and 91 ($C_7H_7^+$, 100) (Found: C, 62.0; H, 5.6; N, 2.2. $C_{33}H_{35}NO_{12}$ requires C, 62.15; H, 5.55; N, 2.2%).

Reaction of the 6′-O-*Benzyl Derivative* (**40a**) *with Hydrogen–Palladium followed by Acetic Anhydride*.—A mixture of the benzyl derivative (**40a**) (0.040 g, 0.063 mmol) and 10% palladium–charcoal (0.010 g, 0.25 mass equiv.) in ethyl acetate (5 cm^3) was stirred under an atmosphere of hydrogen for 20 h. The mixture was filtered through Celite and the filtrate was concentrated to leave a residue which was dissolved in pyridine (2 cm^3). Acetic anhydride (2 cm^3) was added to the stirred ice-cooled solution which, after 30 min, was allowed to warm up to room temperature. After 3 h, the solution was poured into water and the mixture was extracted with dichloromethane. The organic extract was washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. It was then dried ($MgSO_4$) and concentrated. Recrystallisation of the residue from dichloromethane–diethyl ether gave white crystals (0.032 g, 81%), m.p. 198–200 °C (lit.,[2] 205–207 °C), identified as the acetyl derivative (**25a**) (as a hemisolvate with CH_2Cl_2) by 300 MHz ^{1}H NMR spectroscopy.

Reaction of the 6′-O-*Benzyl*-α-*diene* (**8c**) *with Tetracyanoethylene*.—A mixture of the diene (**8c**) (0.160 g, 0.28 mmol) and tetracyanoethylene (0.035 g, 0.28 mmol) in dry benzene (1 cm^3) was stirred for 4 h. Evaporation left an off-white foam which comprised a 62:38 mixture of (3*R*)-3-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-5-(*t-butyldimethylsiloxy*)-*cyclohex*-4-*ene*-1,1,2,2-*tetracarbonitrile* (**41**) and its (3*S*)-isomer (**42**) by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the heights of the s at δ 0.92 and 0.93, attributed to the t-butyl groups of compounds (**41**) and (**42**), and from the integrals of the s at δ 2.04 and 2.12, ascribed to acetoxy groups of compounds (**42**) and (**41**)]; δ(300 MHz; $CDCl_3$) 0.16, 0.21, and 0.22 (1.86, 1.86, and 2.28 H, each s, Me_2Si), 0.92 and 0.93 (5.58 and 3.42 H, each s, Me_3C), 1.92, 1.93, 2.00, 2.02, 2.04, and 2.12 (1.14, 1.86, 1.86, 1.14, 1.14, and 1.86 H, each s, 3 × $MeCO_2$), 2.98 and 3.01 (0.62 and 0.38 H, each d, *J* 18 Hz, 6-H), 3.15 and 3.18 (0.38 and 0.62 H, each d, *J* 18 Hz, 6-H), 3.48, 3.54, and 3.62 [1.24, 0.38, and 0.38 H, d (separation 4 Hz), dd (*J* 11 and 4 Hz), and dd (*J* 11 and 2 Hz), 6′-H_2], 4.03 and 4.17 [0.62 and 0.38 H, dt (*J* 10, 4, and 4 Hz) and dt (*J* 10, 3, and 3 Hz), 5′-H], 4.45, 4.53, and 4.63

[0.38, 1.24, and 0.38 H, d (*J* 12 Hz), AB q (*J* 12 Hz, separation of inner lines 7 Hz), and d (*J* 12 Hz), PhCH_2], 4.84–4.90, 4.97–5.09, 5.14–5.27, and 5.39–5.51 (1, 2, 1, and 2 H, each m, 1′-, 2′-, 3-, 3′-, 4-, and 4′-H).

Reaction of the 6′-O-*Benzyl*-β-*diene* (**34a**) *with Tetracyanoethylene.*—A mixture of the diene (**34a**) (0.076 g, 0.13 mmol) and tetracyanoethylene (0.017 g, 0.13 mmol) in dry benzene (1 cm^3) was stirred overnight. Evaporation gave a white solid which was considered to be a 71:29 mixture of the cycloadducts (**43**) and (**44**) by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the heights of the s at δ 0.91 and 0.93, ascribed to the t-butyl groups of compounds (**43**) and (**44**), and of the s at δ 1.92 and 1.94, attributed to acetoxy groups of compounds (**43**) and (**44**)]. Crystallisation of the mixture from dichloromethane–diethyl ether–light petroleum gave (3S)-3-(6′-O-*benzyl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-5-(*t-butyldimethylsiloxy*)-*cyclohex*-4-*ene*-1,1,2,2-*tetracarbonitrile* (**43**) (0.050 g, 54%) with m.p. 129–132 °C; $[\alpha]_D$ +18° (0.2% in CH_2Cl_2); ν_{max}(KBr) 1 755 (ester C=O) and 1 670 cm^{-1} (C=C); λ_{max}(EtOH) 205 nm (ε 17 300); δ(300 MHz; $CDCl_3$) 0.19 and 0.21 (each 3 H, s, Me_2Si), 0.91 (9 H, s, Me_3C), 1.92, 2.01, and 2.11 (each 3 H, s, 3 × $MeCO_2$), 2.97 (1 H, d, *J* 18 Hz, 1-H), 3.13 (1 H, dt, *J* 18, 2, and 2 Hz, 1-H), 3.57 (2 H, d, separation 4 Hz, 6′-H_2), 3.73–3.78 (1 H, m, 5′-H), 4.52 (2 H, AB q, *J* 12 Hz, separation of inner lines 7 Hz, PhCH_2), 4.92 (1 H, d, *J* 8 Hz, 1′-H), 4.93–4.96 (1 H, m, 4-H), 5.08–5.17 (3 H, m, 2′-, 3-, and 4′-H), 5.25 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.26–7.40 (5 H, m, C_6H_5) (Found: C, 59.3; H, 6.1; N, 8.1. $C_{35}H_{42}N_4O_{10}Si$ requires C, 59.45; H, 6.0; N, 7.95%).

Reaction of the 2′-O-*Benzyl*-α-*diene* (**8d**) *with* N-*Phenylmaleimide.*—A mixture of the diene (**8d**) (0.130 g, 0.23 mmol) and *N*-phenylmaleimide (0.041 g, 0.24 mmol) in dry benzene (1 cm^3) was stirred in the dark overnight. Evaporation left a syrup which was considered to be mainly a 36:64 mixture of the cycloadducts (**11d**) and (**12d**) by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the integrals of the s at δ 0.92 and 0.94, attributed to the t-butyl groups of compounds (**12d**) and (**11d**), and of the s at δ 1.95 and 1.98, ascribed to acetoxy groups of compounds (**12d**) and (**11d**)]. Subjection of the material to silica-gel column chromatography [light petroleum–Et_2O (2:3) as eluant] gave two fractions.

The first-eluted material (0.034 g, *ca.* 20%), isolated as a syrup, was predominantly (1S,2S,3R)-3-(2′-O-*benzyl*-3′-,4′-,6′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-5-(*t-butyldimethylsiloxy*)-N-*phenylcyclohex*-4-*ene*-1,2-*dicarboximide* (**11d**); δ(300 MHz; $CDCl_3$) *inter alia* 0.190 and 0.194 (each 3 H, s, Me_2Si), 0.94 (9 H, s, Me_3C), 1.93, 1.98, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 2.60 (1 H, dd, *J* 17 and 10 Hz, 6-Hα), 2.91 (1 H, ddd, *J* 17, 9, and 2 Hz, 6-Hβ), 3.23 (1 H, dd, *J* 11 and 5 Hz, 2-H), 3.37 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.43 (1 H, q, separation 10 Hz, 1-H), 3.85–3.96 (2 H, m, 5′- and 6′-H), 4.10 (2 H, s, PhCH_2), 4.23 (1 H, dd, *J* 13 and 4 Hz, 6′-H), 4.73 (1 H, dd, *J* 7 and 5 Hz, 3-H), 4.90 (1 H, t, *J* 10 and 10 Hz, 4′-H), 4.97 (1 H, d, *J* 4 Hz, 1′-H), 5.17–5.27 (2 H, m, 3- and 3′-H), and 7.20–7.50 (10 H, m, 2 × C_6H_5).

The second-eluted material was recrystallised from diethyl ether–light petroleum to give (1R,2R,3S)-3-(2′-O-*benzyl*-3′-,4′-,6′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-5-*t-butyldimethylsiloxy*)-N-*phenylcyclohex*-4-*ene*-1,2-*dicarboximide* (**12d**) (0.053 g, 31%) with m.p. 159–161 °C; $[\alpha]_D$ +131° (0.3% in CH_2Cl_2); CD (MeCN) 203 (Δε −3.8) and 225 nm (Δε +10.4); ν_{max} 1 755 (ester C=O), 1 715 (imide C=O), and 1 650 cm^{-1} (C=C); λ_{max} 209sh nm (ε 19 200); δ(300 MHz; $CDCl_3$) 0.18 and 0.20 (each 3 H, s, Me_2Si), 0.92 (9 H, s, Me_3C), 1.93, 1.95, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 2.50br (1 H, dd, *J* 16 and 10 Hz, 6-Hα), 2.89 (1 H, ddd, *J* 16, 9, and 3 Hz, 6-Hβ), 3.23 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.42br (1 H, q, separation 10 Hz, 1-H), 3.56 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.92 (1 H, ddd, *J* 10, 4, and 2 Hz, 5′-H), 4.02 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.24 (1 H, dd, *J* 13 and 4 Hz, 6′-H), 4.50 (2 H, AB q, *J* 12 Hz, separation of inner lines 20 Hz, PhCH_2), 4.88–4.96 (2 H, m, 3- and 4′-H), 5.09 (1 H, d, *J* 4 Hz, 1′-H), 5.13–5.25 (2 H, m, 3′- and 4-H), and 7.15–7.60 (10 H, m, 2 × C_6H_5); *m/z* FAB) 356 (100%) (Found: C, 62.6; H, 6.7; N, 1.9. $C_{39}H_{49}NO_{12}Si$ requires C, 62.3; H, 6.55; N, 1.85%).

Preparation of (1R,2R,3S)-3-(2′-O-*benzyl*-3′,4′,6′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)-5-*oxo*-N-*phenylcyclohexane*-1,2-*dicarboximide* (**23c**).—A solution of the cycloadduct (**12d**) (0.010 g, 0.01 mmol) in THF (2 cm^3) was treated with 0.1M hydrochloric acid (1 cm^3) for 30 h. The mixture was then partitioned between water and dichloromethane and the organic layer was washed with water, dried ($MgSO_4$), and concentrated. The residue was predominantly the title compound (**23c**) on the basis of its ^{1}H NMR spectrum; δ(300 MHz; $CDCl_3$) *inter alia* 1.92, 2.00, and 2.03 (each 3 H, s, 3 × $MeCO_2$), 2.30 (1 H, dd, *J* 19 and 2 Hz, 4-Hβ), 2.82 (1 H, dd, *J* 19 and 3 Hz, 4-Hα), 2.96 (1 H, dd, *J* 17 and 8 Hz, 6-Hα), 3.13 (1 H, dd, *J* 17 and 11 Hz, 6-Hβ), 3.33 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.47 (1 H, ddd, *J* 11, 10, and 8 Hz, 1-H), 3.54 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.51 (1 H, ddd, *J* 10, 4, and 2 Hz, 5′-H), 3.96 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.13 (1 H, dd, *J* 13 and 4 Hz, 6′-H), 4.47 (2 H, AB q, *J* 12 Hz, separation of inner lines 17 Hz, PhCH_2), 4.75 (1 H, d, *J* 4 Hz, 1′-H), 4.86 (1 H, apparent q, separation 3 Hz, 3-H), 4.91 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.21 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.18–7.55 (5 H, m, C_6H_5).

Reaction of the 2-O-*Benzyl Ketone* (**23c**) *with Hydrogen–Palladium followed by Acetic Anhydride.*—The crude benzyl derivative (**23c**) from the aforecited experiment was dissolved in ethyl acetate (5 cm^3), 10% palladium–carbon (0.030 g) was added, and the mixture was stirred under an atmosphere of hydrogen for 24 h. The mixture was filtered through Celite and the filtrate was concentrated. The resultant residue was dissolved in pyridine (1 cm^3) and acetic anhydride (1 cm^3) was added to the ice-cooled solution which, after 1 h, was allowed to warm to room temperature. After 24 h, the mixture was diluted with dichloromethane and washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. Evaporation of the dried ($MgSO_4$) organic layer and purification of the residue by silica-gel column chromatography [light petroleum–EtOAc (1:4) as eluant] gave a solid (0.003 g, 35%) which was identified as the acetyl derivative (**23a**) by 300 MHz ^{1}H NMR spectroscopy.

Reaction of the 2′-O-*Benzyl*-β-*diene* (**34b**) *with* N-*Phenylmaleimide.*—A mixture of the diene (**34b**) (0.144 g, 0.25 mmol) and *N*-phenylmaleimide (0.043 g, 0.25 mmol) in dry benzene (1 cm^3) was stirred in the dark for 2.5 days. Evaporation of the solvent left a residue which comprised a 74:26 mixture of the cycloadducts (**38b**) and (**39b**) on the basis of 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the integrals of the s at δ 0.92 and 0.95, attributed to the t-butyl groups of compounds (**39b**) and (**38b**), and of the s at δ 1.81 and 1.84, ascribed to acetoxy groups of compounds (**39b**) and (**38b**)]. Trituration of the residue with dry diethyl ether and filtration gave (1R,2R,3S)-3-(2′-O-*benzyl*-3′,4′,6′-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-5-(*t-butyldimethylsiloxy*)-N-*phenylcyclohex*-4-*ene*-1,2-*dicarboximide* (**38b**) (0.177 g, 63%) as a crystalline solid. The sample, after recrystallisation from dichloromethane–diethyl ether–light petroleum, possessed m.p. 167–170 °C; $[\alpha]_D$ +98° (0.23% in CH_2Cl_2); CD (MeCN) 204 (Δε −8.7) and 213 nm (Δε −13.4); ν_{max}(KBr) 1 750 (ester C=O), 1 710 (imide C=O), and 1 645 cm^{-1} (C=C); λ_{max}(EtOH) 202 nm (ε 26 300); δ(300 MHz; $CDCl_3$) 0.19 and 0.20 (each 3 H, s, Me_2Si), 0.95 (9 H, s, Me_3C), 1.84, 1.99, and 2.06 (each 3 H, s, together 3 × $MeCO_2$), 2.52 (1 H, dd, *J* 17 and 10 Hz, 6-Hα), 2.89 (1 H, ddd, *J* 17, 8, and 3

Hz, 6-Hβ), 3.20 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.23 (1 H, dd, *J* 9 and 8 Hz, 2'-H), 3.45 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.54 (1 H, ddd, *J* 10, 4, and 2 Hz, 5'-H), 4.05 (1 H, dd, *J* 13 and 2 Hz, 6'-H), 4.19 (1 H, dd, *J* 13 and 4 Hz, 6'H), 4.33 and 4.58 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.61 (1 H, d, *J* 8 Hz, 1'-H), 4.92 (1 H, t, *J* 10 and 10 Hz, 4'-H), 4.98 (1 H, dd, *J* 6 and 4 Hz, 3-H), 5.12 (1 H, t, *J* 9 and 9 Hz, 3'-H), 5.18 (1 H, dd, *J* 6 and 2 Hz, 4-H), and 7.05–7.40 (10 H, m, 2 × C_6H_5); *m/z* (FAB) 774 (*M*Na^+, 10%) and 73 (100%) (Found: C, 62.0; H, 6.5; N, 1.8. $C_{39}H_{49}NO_{12}Si$ requires C, 62.3; H, 6.55; N, 1.85%).

Preparation of (1R,2R,3S)-3-(2'-O-*Benzyl*-3',4',6'-*tri*-O-*acetyl*-β-D-*glucopyranosyloxy*)-5-*oxo*-N-*phenylcyclohexane*-1,2-*dicarboximide* (**40b**).—A solution of the cycloadduct (**38b**) (0.135 g, 0.18 mmol) in THF (5 cm^3) was treated with 0.1M hydrochloric acid (2 cm^3) for 18 h. The mixture was then partitioned between water and dichloromethane and the organic layer was washed with water, dried ($MgSO_4$), and concentrated. Crystallisation of the residue from dichloromethane–diethyl ether gave the *title compound* (**40b**) (0.073 g, 64%) as a white solid with m.p. 199–201 °C; $[\alpha]_D$ −13° (0.2% in CH_2Cl_2); ν_{max}(KBr) 1 750 and 1 740 (ester C=O), and 1 710 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 213sh nm (ε 15 000); δ(300 MHz; $CDCl_3$) 1.82, 2.01, and 2.12 (each 3 H, s, 3 × $MeCO_2$), 2.41 (1 H, dd, *J* 20 and 3 Hz, 4-Hβ), 2.88–3.08 (3 H, m, 6-H_2 and 4-Hα), 3.30 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.38 (1 H, dd, *J* 10 and 8 Hz, 2'-H), 3.42–3.55 (1 H, m, 1-H), 3.70 (1 H, ddd, *J* 10, 5, and 2 Hz, 5'-H), 4.10 (1 H, dd, *J* 13 and 2 Hz, 6'-H), 4.18 (1 H, dd, *J* 13 and 5 Hz, 6'-H), 4.29 and 4.54 (each 1 H, d, *J* 12 Hz, PhCH_2), 4.70 (1 H, d, *J* 8 Hz, 1-H), 4.92 (1 H, t, *J* 10 and 10 Hz, 4'-H), 4.95–5.01 (1 H, m, 3-H), 5.17 (1 H, t, *J* 10 and 10 Hz, 3'-H), and 6.95–7.05, 7.15–7.25, and 7.30–7.40 (2, 3, and 5 H, each m, 2 × C_6H_5); *m/z* (CI) 290 (3%), 241 (50), and 91 ($C_7H_7^+$, 100) (Found: C, 61.9; H, 5.7, N.2.1. $C_{33}H_{35}NO_{12}$ requires C, 62.15; H, 5.55; N, 2.2%).

Reaction of the 2'-O-*Benzyl Ketone* (**40b**) *with Hydrogen–Palladium followed by Acetic Anhydride*.—A mixture of the ketone (**40b**) (0.062 g, 0.10 mmol) and 10% palladium–charcoal (0.006 g, 0.1 mass equiv.) in ethyl acetate (5 cm^3) was stirred under on atmosphere of hydrogen for 24 h. The mixture was filtered through Celite and the filtrate was concentrated. Fractionation of the resultant residue by silica-gel column chromatography [light petroleum–EtOAc (3:7) as eluant] gave two fractions.

The first-eluted material (0.032 g, 51%) was identified as the starting benzyl derivative (**40b**) on the basis of 300 MHz ^1H NMR spectroscopy.

The second-eluted material (0.016 g) was treated with pyridine (1 cm^3) and acetic anhydride (1 cm^3) for 18 h. The solution was then poured into water and the mixture extracted with dichloromethane. After being washed with saturated aqueous sodium hydrogen carbonate, dilute hydrochloric acid, and water, the organic phase was dried ($MgSO_4$) and concentrated. Recrystallisation of the residue from dichloromethane–diethyl ether gave a white solid (0.012 g, 27%), m.p. 195–197 °C (lit.,[2] 205–207 °C), which was identified as the tetra-acetate (**25a**) (as a hemisolvate with CH_2Cl_2) by 300 MHz ^1H NMR spectroscopy.

Note added in proof: The 6'-*O*-benzyl and 2'-*O*-benzyl derivatives of compounds (**28**) and (**29b**) have recently been reported (A. Lubineau and Y. Queneau, *Tetrahedron*, 1989, **45**, 6697). They showed trends in their diastereofacial reactivities [towards CH_2=C(Me)CHO in H_2O] which were similar to those observed for the related dienes of this study.

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