Asymmetric Diels–Alder Reactions. Part 3.[1] Influence of Butadiene Structure upon the Diastereofacial Reactivity of (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)buta-1,3-dienes

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(*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)buta-1,3-diene (**1c**), its 3-methyl derivative (**1d**), its 2,3-dimethyl derivative (**1e**), its (3*Z*)-4-acetoxy-3-(t-butyldimethylsilyloxy) derivative (**1f**), its 3-(t-butyldimethylsilyloxy) derivative (**1g**), and its (3*Z*)-3-(t-butyldimethylsilyloxy)-2,4-dimethyl derivative (**1h**) have been prepared and their diastereofacial reactivities towards *N*-phenylmaleimide and tetracyanoethylene assessed. With the former dienophile in benzene at ambient temperature, the dienes (**1c, d, f, g**) gave *ca.* 87:13 mixtures of the cycloadduct pairs (**2c**) and (**3c**), (**2d**) and (**3d**), (**2f**) and (**3f**), and (**2g**) and (**3g**); however, the dienes (**1e, h**) afforded only the cycloadducts (**2e, h**). With tetracyanoethylene in benzene at ambient temperature, the aforecited dienes reacted to give mixtures of cycloadducts, ranging from a 69:31 mixture of the cycloadducts (**6c**) and (**7c**) in the case of the diene (**1c**) to an 89:11 mixture of the cycloadducts (**6h**) and (**7h**) in the case of the diene (**1h**).

Recently, we showed[2] that the diene (**1a**)† exhibited notable diastereofacial reactivity towards a range of cyclic dienophiles, including *p*-benzoquinone, 2-methoxycarbonyl-*p*-benzoquinone, 2-acetyl-*p*-benzoquinone, and *N*-phenylmaleimide. Although mixtures of cycloadducts—ranging from 75:25 to 89:11—were produced, the major cycloadducts were readily isolated in a pure state by recrystallisation. For example, the diene (**1a**) reacted with *N*-phenylmaleimide in benzene to give an 86:14 mixture of the cycloadducts (**2a**)‡ and (**3a**) from which the former product was isolated in 52% yield; it was also possible to obtain the minor cycloadduct (**3a**) pure (6% yield) by chromatographic fractionation of the mother liquor.§

Significantly, the methylated diene (**1b**) displayed[1] an improved diastereoselection over its counterpart (**1a**), reacting with the aforementioned dienophiles to give essentially single cycloadducts. Thus, with *N*-phenylmaleimide in benzene, it afforded the cycloadduct (**2b**) in 87% yield.

To explain the results, it was suggested[1] that the methylated diene (**1b**) reacted only by way of the conformer (**4b**) in which the s-*cis*-diene entity and the anomeric C–O bond were *anti*-disposed; the dienophiles then underwent *endo*-additions to the least-hindered 'top' face of this conformer. In the case of the diene (**1a**), two reacting conformers were postulated. The major and minor cycloadducts were considered to arise by *endo*-additions to the least-hindered 'top' faces of the conformers (**4a**) and (**5a**) in which the s-*cis*-diene moiety and the anomeric C–O bond possessed *anti*- and *syn*-orientations, respectively.

The selectivities of the reactions of the dienes (**1a, b**) with tetracyanoethylene in benzene were poorer than those involving the cyclic dienophiles.[1] However, the methylated diene (**1b**) did display a higher diastereofacial reactivity than its counterpart. Thus, a 67:33 mixture of the cycloadducts (**6a**)¶ and (**7a**) was produced in the case of the diene (**1a**) whereas an 80:20 mixture of the cycloadducts (**6b**) and (**7b**) arose with the diene (**1b**); the major cycloadducts (**6a, b**) were isolated in respective yields of 42 and 69%.

The difference in behaviour between tetracyanoethylene and the cyclic dienophiles was attributed to steric effects. It was assumed that tetracyanoethylene, because of its low steric volume, showed a small tendency to react with the diene (**1b**) from the 'bottom' face of the conformer (**4b**). Presumably, it also underwent addition to the diene (**1a**) from the 'top' and 'bottom' faces of the conformers (**4a**) and (**5a**).

In this paper, we describe the preparation of six relatives of compounds (**1a, b**), modified in the butadiene entity, and we assess their diastereofacial reactivities towards *N*-phenylmaleimide and tetracyanoethylene.

Results and Discussion

Our initial objective was to prepare the diene (**1c**) and to examine its behaviour. Oxygenated butadienes of type (**8**; R = achiral ligand) have been well studied[3] and have found application in natural product synthesis, *e.g.* vernolepin.[4] Moreover, at the outset of our studies, three examples of dienes of type (**8**; R = homochiral ligand) had been described. These were the D-glucose-derived dienes (**8a, b**), developed by David's group,[5] and the mandelic acid-derived diene (**8c**), introduced by Trost and his co-workers.[6] Only hetero-Diels–Alder reactions of the dienes (**8a, b**) had been examined and the selectivities were modest. For example, the diene (**8b**) reacted with diethyl oxomalonate to give a 68:32 mixture of the cycloadducts (**9**) and (**10**). Trost's diene (**8c**) underwent reaction with acrolein in the presence of boron trifluoride–diethyl ether complex to give an 82:18 mixture of the cycloadducts (**11**) and (**12**) and with juglone in the presence of tetra-acetyl diborate to give only the cycloadduct (**13**).

It was hoped that the diene (**1c**) would be accessible from the butenone (**14a**)[7] by a reduction-dehydration sequence. Al-

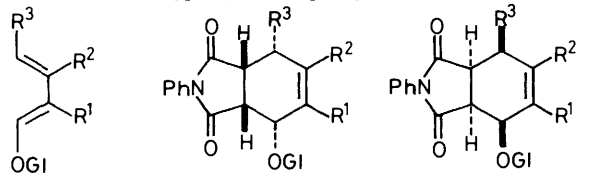
† To facilitate comparisons, the dienes are numbered in the manner shown in structure (**1**).

‡ To faciliate comparisons, the cycloadducts of diene of type (**1**) with *N*-phenylmaleimide are numbered as shown in structure (**2**); derivatives of these compounds are numbered in an analogous manner.

§ 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.

¶ To facilitate comparisons, the numbering shown in structure (**6**) is used to describe the cycloadducts of dienes of type (**1**) with tetracyanoethylene.

Table 1. Ratios of cycloadducts of types (**2**) and (**3**) produced in the reactions of dienes of type (**1**) with *N*-phenylmaleimide

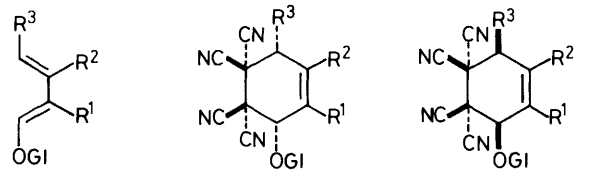


(**1**) (**2**) (**3**)

R^1	R^2	R^3	Diene	Possible cycloadducts	Ratio
H	$OSiMe_3$	H	(**1a**)	(**2a**) and (**3a**)	86:14
Me	$OSiMe_3$	H	(**1b**)	(**2b**) and (**3b**)	>95:5
H	H	H	(**1c**)	(**2c**) and (**3c**)	86:14
H	Me	H	(**1d**)	(**2d**) and (**3d**)	88:12
Me	Me	H	(**1e**)	(**2e**) and (**3e**)	>95:5
H	$OSiMe_2Bu^t$	OAc	(**1f**)	(**2f**) and (**3f**)	89:11
H	$OSiMe_2Bu^t$	H	(**1g**)	(**2g**) and (**3g**)	85:15
Me	$OSiMe_2Bu^t$	Me	(**1h**)	(**2h**) and (**3h**)	>95:5

Gl = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl

Table 2. Ratios of cycloadducts of types (**6**) and (**7**) produced in the reactions of dienes of type (**1**) with tetracyanoethylene



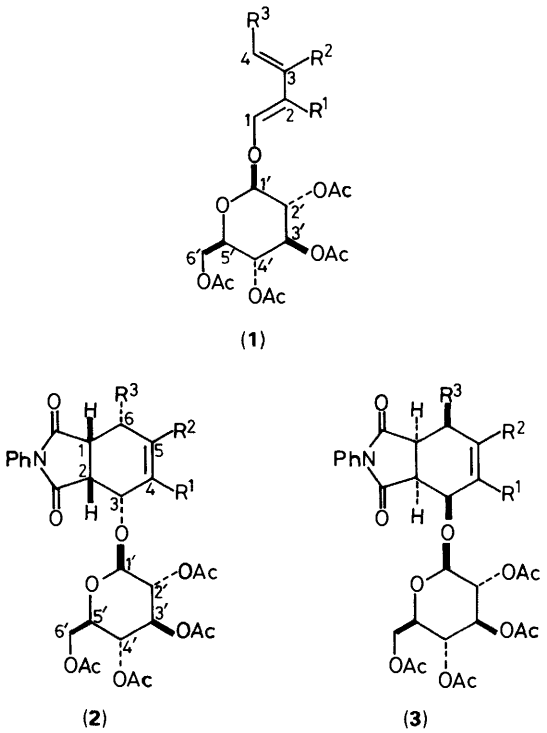
(**1**) (**6**) (**7**)

R^1	R^2	R^3	Diene	Possible cycloadducts	Ratio
H	$OSiMe_3$	H	(**1a**)	(**6a**) and (**7a**)	67:33
Me	$OSiMe_3$	H	(**1b**)	(**6b**) and (**7b**)	80:20
H	H	H	(**1c**)	(**6c**) and (**7c**)	69:31
H	Me	H	(**1d**)	(**6d**) and (**7d**)	76:24
Me	Me	H	(**1e**)	(**6e**) and (**7e**)	78:22
H	$OSiMe_2Bu^t$	OAc	(**1f**)	(**6f**) and (**7f**)	71:29
H	$OSiMe_2Bu^t$	H	(**1g**)	(**6g**) and (**7g**)	70:30
Me	$OSiMe_2Bu^t$	Me	(**1h**)	(**6h**) and (**7h**)	89:11

Gl = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl

though the reduction was readily accomplished in methanol by using sodium borohydride in the presence of a cerium(III) salt,[8] the derived butenol (**15a**) (isolated as a 50:50 mixture of diastereoisomers in *ca.* 74% yield in the form of a slightly impure, unstable syrup) was converted into mixtures of products by a range of dehydrating agents; there was no evidence to suggest that the desired diene (**1c**) was a component of these mixtures. Attempts to transform the alcohol (**15a**) into the corresponding chloride, mesylate, and tosylate—compounds which, it was hoped, would be more amenable to elimination—were similarly unrewarding; mixtures of products, which lacked the diene (**1c**), again resulted. The butenol (**15a**) could be converted into the stable, crystalline t-butyldimethylsilyl ether (**15b**) (isolated as a 50:50 mixture of diastereoisomers in 75% yield after recrystallisation) by the action of t-butyldimethylsilyl chloride and imidazole in *N*,*N*-dimethylformamide (DMF).[9]

Formyl esters are known to undergo Wittig condensations with stabilised phosphoranes[10] and, for example, the diene (**16a**) has been prepared by such a process.[11] When treated with formic acid and silver(I) nitrate, the acetobromoglucose (**17**)[12] was transformed into the crystalline formyl derivative (**18**)[13] in 48% yield. Disappointingly, there was no evidence for the production of the diene (**1c**) when compound (**18**) was treated in tetrahydrofuran (THF) with vinylmethylenetriphenylphosphorane.[14]

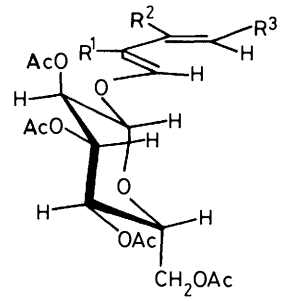


(**1**) (**2**) (**3**)

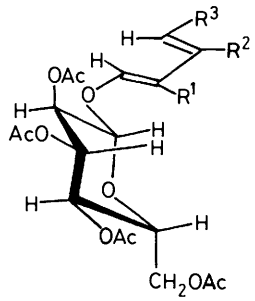
a; R^1 = H, R^2 = $OSiMe_3$, R^3 = H
b; R^1 = Me, R^2 = $OSiMe_3$, R^3 = H
c; R^1 = H, R^2 = H, R^3 = H
d; R^1 = H, R^2 = Me, R^3 = H
e; R^1 = Me, R^2 = Me, R^3 = H
f; R^1 = H, R^2 = $OSiMe_2Bu^t$, R^3 = OAc
g; R^1 = H, R^2 = $OSiMe_2Bu^t$, R^3 = H
h; R^1 = Me, R^2 = $OSiMe_2Bu^t$, R^3 = Me

A variety of methods are available for the methylenation of carbonyl compounds and, therefore, it was decided to examine such a tactic using the propenone (**14b**). The last-cited compound was prepared in a manner analogous to that used for the synthesis of the butenones (**14a**, **c**). Thus, treatment of the acetobromoglucose (**17**) in dimethyl sulphoxide with the potassium salt (**19a**)[15] gave the crystalline propenone (**14b**) in 47% yield. Using the Lombardo modification[16] (the reagent was preformed in dry THF at −40 °C and stored at *ca.* 5 °C) of the Oshima methylenation procedure[17] ($CH_2Br_2/Zn/TiCl_4$), the propenone (**14b**) was transformed into the crystalline diene (**1c**), isolated in 33% yield after purification by silica-gel chromatography.

The diene (**1c**) reacted with *N*-phenylmaleimide in benzene at ambient temperature to give an 86:14 mixture of the cycloadducts (**2c**) and (**3c**). The major cycloadduct, isolated in 59% yield after crystallisation of the mixture, was assigned the stereostructure (**2c**) by analogy with the result observed for the diene (**1a**).[2] Support for this assignment was provided by n.m.r. spectroscopy. Thus, previously, it was reported[2] that the acetyl methyl groups of the cycloadduct (**2a**) absorbed ($CDCl_3$) at δ 1.58, 1.95, 2.00, and 2.08 in the 300 MHz ^1H n.m.r. spectrum; those of the cycloadduct (**3a**) appeared at δ 1.93, 1.99, 2.04, and 2.12. Clearly, one of the acetyl methyl groups of the cycloadduct (**2a**) (probably that at the 2′-position) lay in the shielding zone of the phenyl ring [a similar phenomenon was noted[1] for the cycloadduct (**2b**) in which the acetyl methyl groups resonated

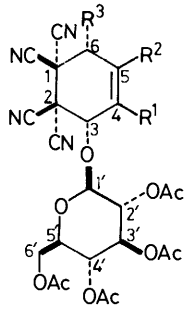


(4)

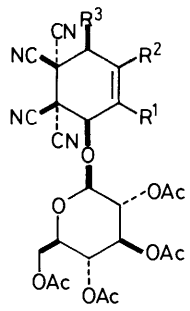


(5)

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



(6)

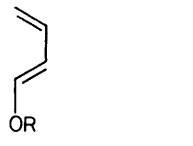


(7)

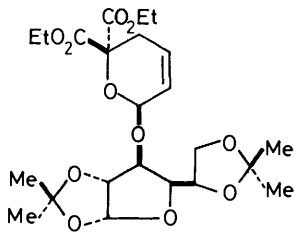
a; R^1 = H, R^2 = $OSiMe_3$, R^3 = H
b; R^1 = Me, R^2 = $OSiMe_3$, R^3 = H
c; R^1 = H, R^2 = H, R^3 = H
d; R^1 = H, R^2 = Me, R^3 = H
e; R^1 = Me, R^2 = Me, R^3 = H
f; R^1 = H, R^2 = $OSiMe_2Bu^t$, R^3 = OAc
g; R^1 = H, R^2 = $OSiMe_2Bu^t$, R^3 = H
h; R^1 = Me, R^2 = $OSiMe_2Bu^t$, R^3 = Me

(CDCl$_3$) at δ 1.47, 1.96, 2.02, and 2.09]. The acetyl methyl groups of the cycloadduct (**2c**) absorbed ($CDCl_3$) at δ 1.64, 1.98, 2.03, and 2.12, strongly implying that the stereochemistry of the compound matched that of the cycloadduct (**2a**).

The diene (**1c**) reacted with tetracyanoethylene in benzene to give a 69 31 mixture of the cycloadducts (**6c**) and (**7c**), from which the major product was isolated in 33% yield after two recrystallisations. As in the case of compound (**6a**), the stereochemistry of the major cycloadduct was not rigorously established; the stereostructure (**6c**) was presumed by analogy with the result observed for *N*-phenylmaleimide.



(8)



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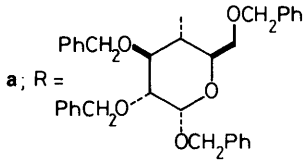
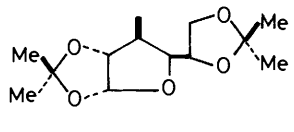
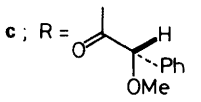
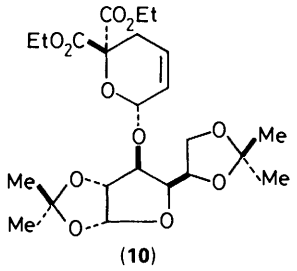








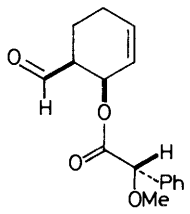
(10)

During the course of our studies, the diene (**1c**) was described by Lubineau and Queneau.[18] It was prepared from the propenone (**14b**), obtained in a manner identical to that reported herein, by the action of methylenetriphenylphosphorane under salt-free conditions. Although our sample displayed a ^{1}H n.m.r. spectrum which matched that reported, its m.p. was substantially lower than the literature value (m.p. 106—107 °C *vs.* 152—153 °C). The properties of our sample of the propenone (**14b**) were in accord with those published.

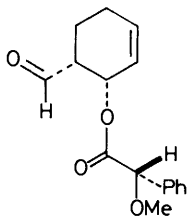
The synthesis of the dienes (**1d**, **e**) was next examined. Whereas oxygenated dienes of type (**16**; R = achiral ligand) have been extensively studied[3] and used in natural product synthesis, *e.g.* bostrycin,[19] there are few examples of dienes of type (**20**; R = achiral ligand).[20] To our knowledge, homochiral versions of the forecited dienes are unknown.

The Lombardo conditions were effective in transforming the butenones (**14a**)[7] and (**14c**)[1] into the corresponding dienes (**1d**, **e**), which were isolated in a crystalline state in respective yields of 44 and 34% after silica-gel purification.

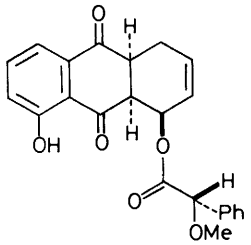
With *N*-phenylmaleimide in benzene, the diene (**1d**) reacted to give an 88:12 mixture of the cycloadducts (**2d**) and (**3d**) whereas the diene (**1e**) afforded only the cycloadduct (**2e**). Compounds (**2d**, **e**) were isolated in respective yields of 60 and 68% after crystallisation. In their ^{1}H n.m.r. spectra, the acetyl methyl groups [which absorbed at δ 1.67, 1.97, 2.03 and 2.12 in compound (**2d**) and at δ 1.57, 1.97, 2.03, and 2.12 in compound (**2e**)] showed chemical shifts comparable with those of the cycloadduct (**2a**). Further evidence that compounds (**2c**—**e**) shared a common stereostructure was provided by the simi-



(11)



(12)



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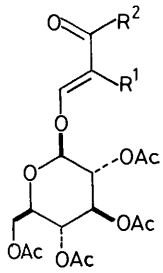
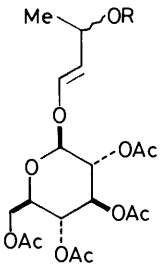
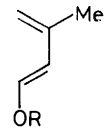


(14)

a; R^1 = H, R^2 = Me
b; R^1 = H, R^2 = H
c; R^1 = Me, R^2 = Me
d; R^1 = H, R^2 = CH_2OAc
e; R^1 = Me, R^2 = Et



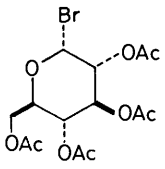
(15)



(16)

a, R = H
b, R = $SiMe_2Bu^t$

a, R = CH_2CH_2OMe



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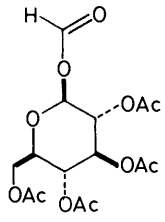

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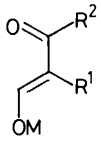


(19)

a; R^1 = H, R^2 = H, M = K
b; R^1 = Me, R^2 = Et, M = Na

larity of their c.d. spectra. Thus the compounds showed weak negative dichroisms at *ca.* 270 nm [267 nm ($\Delta\varepsilon$ − 0.2) for (**2c**); 264 ($\Delta\varepsilon$ − 0.07) and 271 nm ($\Delta\varepsilon$ − 0.05) for (**2d**); 273 nm ($\Delta\varepsilon$ − 0.03) for (**2e**)] and strong positive dichroisms at *ca.* 200 nm [200 nm ($\Delta\varepsilon$ + 14.4) for (**2c**); 200 nm ($\Delta\varepsilon$ + 12.6) for (**2d**); 202 nm ($\Delta\varepsilon$ +16.2) for (**2e**)].

The dienes (**1d, e**) underwent reaction with tetracyanoethylene in benzene. In the former case, a 76:24 mixture of the cycloadducts (**6d**) and (**7d**) was produced, from which the major cycloadduct was isolated in 61% yield after recrystallisation. In the latter instance, a 78:22 mixture of the cycloadducts (**6e**) and (**7e**) resulted, from which it was possible to isolate the major cycloadduct in a crystalline state in 35% yield. As before, the stereostructures of the major cycloadducts were not rigorously defined.

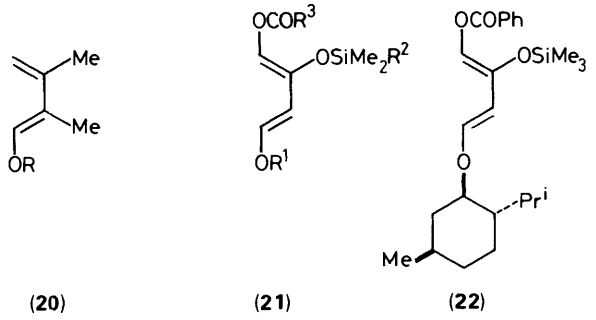
Three new stereocentres are generated in the reaction of the dienes (**1a**—**e**) with *N*-phenylmaleimide. It was of interest, therefore, to extend the study to dienes with a substituent at position 4 since their corresponding cycloadditions should afford cyclohexenes containing four contiguous asymmetric centres.

The dienes of type (**21**; R^1 = achiral ligand), which have been extensively studied by Danishefsky's group, are versatile intermediates in natural product synthesis undergoing cyclocondensations with aldehydes.[21] Moreover, homochiral versions of the dienes, *e.g.* (**22**),[22] have been developed although they show poor diastereofacial selectivity towards aldehydes. The reactivity of the aforecited dienes towards activated alkenes has not been reported. We decided, therefore, to prepare the diene (**1f**) and to examine its behaviour towards *N*-phenylmaleimide and tetracyanoethylene.

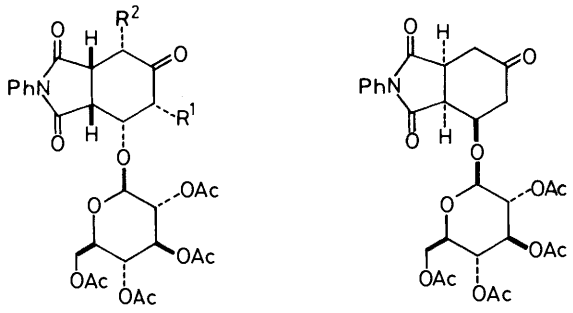
The strategy developed by Danishefsky was employed to effect the synthesis of compound (**1f**). Thus sequential treatment of the diene (**1a**) with *m*-chloroperoxybenzoic acid in dichloromethane, with methanol, and with acetic anhydride–pyridine gave the acetoxybutenone (**14d**) (39% yield after chromatography and recrystallisation). In the presence of t-butyldimethylsilyl triflate and triethylamine in dichloromethane,[23] compound (**14d**) was transformed into the diene (**1f**), isolated in 41% yield after chromatographic purification and recrystallisation.

The reaction of the diene (**1f**) with *N*-phenylmaleimide in benzene led to an 89:11 mixture of the cycloadducts (**2f**) and (**3f**), from which compound (**2f**) was isolated in 59% yield. The major cycloadduct was assigned the stereostructure (**2f**) on the basis of 300 MHz ^{1}H n.m.r. spectroscopy. Thus, one of the acetyl methyl groups appeared ($CDCl_3$) at much higher field (δ 1.40) than the others (δ 1.97, 2.08, 2.12, and 2.16). Furthermore, the 6-hydrogen atom, which resonated at δ 5.83, appeared as a double doublet (*J* 7 and 1 Hz) due to geminal coupling with the 1-hydrogen atom and long-range coupling (W-pathway)[24] with the 4-hydrogen atom [in the case of (**2a**),[2] the 6 β-hydrogen atom, which absorbed at δ 2.79, was present as a doublet of double doublets (*J* 16, 8.5, and 2.5 Hz) whereas the 6 α-hydrogen atom, which resonated at δ 2.51, appeared as a double doublet (*J* 16 and 10 Hz)]. Evidently, the 6-acetoxy group was α-orientated in compound (**2f**), corroborating that the 3,4-double bond of the diene (**1f**) did indeed possess the *Z*-configuration at position 3.

When subjected to the action of dilute hydrochloric acid in THF, compound (**2f**) was transformed into the crystalline ketone (**23a**) in 61% yield. In its 300 MHz ^{1}H n.m.r. spectrum, one of the acetyl methyl groups resonated ($CDCl_3$) at significantly higher field (δ 1.58) than the others (δ 1.97, 2.03, 2.11, and 2.23); a similar effect was observed[2] with the ketone (**23b**) (in which the signals appeared at δ 1.56, 1.96, 2.01, and 2.12) but not with its diastereoisomer (**24**) (in which the signals absorbed at δ 1.97, 1.98, 2.01, and 2.04). Moreover, the 6-hydrogen atom, which resonated at δ 5.58, appeared as a doublet (*J* 7 Hz) due to

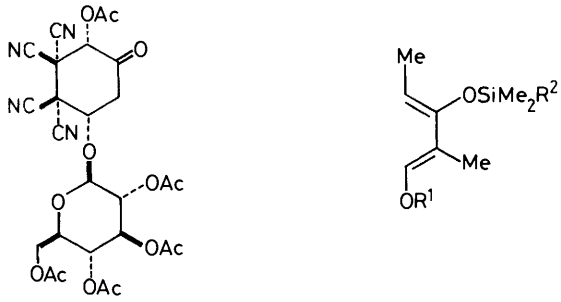


(20) (21) (22)

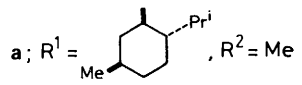


(23) (24)

a; R^1 = H, R^2 = OAc
b; R^1 = H, R^2 = H
c; R^1 = Me, R^2 = Me



(25) (26)



a; R^1 = , R^2 = Me

coupling with the 1-hydrogen [in the case of (**23b**), the 6β-hydrogen atom was present as a double doublet (*J* 16 and 9 Hz) at δ 2.94 whereas the 6α-hydrogen atom resonated as a double doublet (*J* 16 and 11 Hz) at δ 2.91]. These observations suggested that the ketone possessed the stereostructure (**23a**) and that no epimerisation of the 6-acetoxy group had occurred during the hydrolysis of compound (**2f**).

That compounds (**23a**, **b**) possessed the same absolute configuration at positions 1, 2, and 3 was unequivocally established by chemical means. Thus, chromium(II) chloride in aqueous acetone[25] effected the reductive deacetoxylation of the acetoxy ketone (**23a**) to give the ketone (**23b**) in 66% yield.

A 71 29 mixture of the cycloadducts (**6f**) and (**7f**) arose in the reaction of the diene (**1f**) with tetracyanoethylene in benzene; crystallisation of the mixture gave the major adduct in 54% yield. Attempts to transform the cycloadduct (**6f**) into the ketone (**25a**) under acidic conditions led to a mixture of products [there was no evidence for the presence of (**25**) by 300 MHz ^{1}H n.m.r. spectroscopy] which was not further investigated.

The similar ratios of cycloadducts produced in the reactions of the dienes (**1a**, **f**) with *N*-phenylmaleimide and tetracyanoethylene implied that the nature of the silyloxy group had little bearing on the diastereoselection process. To verify this notion, the diene (**1g**) was prepared [by treatment of (**14a**) with $Bu^tMe_2SiOSO_2CF_3$–Et_3N in CH_2Cl_2];[23] following low-temperature chromatographic purification, it was obtained as a crystalline solid in 89% yield. The diene (**1g**) reacted with *N*-phenylmaleimide in benzene to give an 85:15 mixture of the cycloadducts (**2g**) and (**3g**) and with tetracyanoethylene in benzene to give a 70:30 mixture of the cycloadducts (**6g**) and (**7g**). The major cycloadducts (**2g**) and (**6g**) were isolated in a crystalline state in respective yields of 70 and 58%. Acidic hydrolysis of compound (**2g**) gave the ketone (**23b**) in 70% yield. However, under similar conditions, the cycloadduct (**6g**) afforded a mixture of products which was not further investigated.

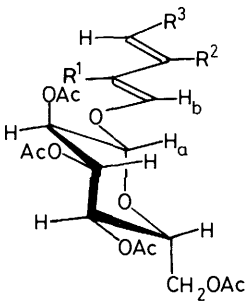
Dienes of type (**26**; R^1 = achiral ligand) have found application in Diels–Alder[26] and hetero-Diels–Alder[27] reactions. Compound (**26a**) (and its enantiomer), prepared by Danishefsky,[22,28] appears to be the sole homochiral representative but it showed virtually no diastereofacial discrimination towards benzaldehyde. It was of interest, therefore, to assess the behaviour of the diene (**1h**).

Treatment of the acetobromoglucose (**17**)[12] with the salt (**19b**)[29] in dimethyl sulphoxide afforded the pentenone (**14e**) in 6% yield after chromatographic purification and recrystallisation. Under the usual enol silylating conditions, compound (**14e**) was transformed into the syrupy diene (**1h**) (62% yield after low-temperature chromatographic purification).

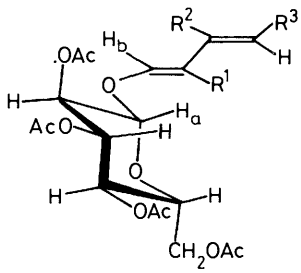
The diene (**1h**) reacted with *N*-phenylmaleimide in benzene to give only the cycloadduct (**2h**). In the 300 ^{1}H n.m.r. spectrum, one of the acetyl methyl groups appeared ($CDCl_3$) at much higher field (δ 1.43) than the others (δ 1.93, 2.01, and 2.07), as observed in the case of the stereochemically related cycloadducts (**2a**—**g**). Acidic hydrolysis of compound (**2h**) led to the isolation of the crystalline ketone (**23c**) in 68% yield. The stereostructure of the product was deduced by n.m.r. spectroscopy. Thus, one of the acetyl methyl groups was substantially shielded (δ 1.58) compared with the others (δ 1.94, 2.01, and 2.09). Moreover, in a nuclear Overhauser effect difference (n.O.e.d.) experiment, irradiation of the signal for the 1- and 2-hydrogen atoms (a multiplet at δ 3.57—3.67) enhanced that of the 3-hydrogen atom (a multiplet at δ 4.77—4.80) by 10%, that of the 4-hydrogen atom (a double quartet at δ 2.48) by 3%, and that of the 6-hydrogen atom (a multiplet at δ 3.00—3.05) by 18%. Irradiation of the signal for the 3-hydrogen atom caused a 5% enhancement of that for the 1- and 2-hydrogen atoms and a 6% enhancement of that for the 4-hydrogen atom. The signals for the 3- and 6-hydrogen atoms were enhanced by 5 and 4%, respectively, when the signal for the 4-hydrogen atom was irradiated. Finally, irradiation of the signal for the 6-hydrogen atom resulted in a 5% enhancement of that for the 1-and 2-hydrogen atoms.

An 89:11 mixture of the cycloadducts (**6h**) and (**7h**) was produced when the diene (**1h**) was treated with tetracyanoethylene in benzene. Crystallisation of the mixture gave the major cycloadduct in 73% yield. As before, its stereostructure was not rigorously established but was assumed by analogy.

The ratios of the cycloadducts produced in the reactions of the dienes (**1a**—**h**) with *N*-phenylmaleimide and tetracyanomethylene are summarised in Tables 1 and 2. From the result, it is clear that better selectivities are always observed with the former dienophile than with the latter. Furthermore, butadienes incorporating a methyl group at position 2, *i.e.* (**1b**, **e**, **h**) show a higher diastereofacial reactivity than those with a hydrogen



(27)



(28)

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

atom at that position, *i.e.* (**1a**, **c**, **d**, **f**, **g**). Finally, the diastereofacial reactivities of butadienes that are unsubstituted at positions 2 and 4, *i.e.* (**1a**, **c**, **d**, **g**), is at a maximum when a methyl group is present at position 3.

In accord with previous findings with compound (**1b**),[1] the dienes (**1e**, **h**) were shown to adopt the conformers (**27e**, **h**) by n.O.e.d. spectroscopy. Thus, in the case of the diene (**1e**), irradiation of the signal for the anomeric hydrogen atom* enhanced that for the hydrogen atom at position 1 of the butadiene entity by 13% without effect upon the 2-methyl group; conversely, irradiation of the signal for the butadiene 1-hydrogen atom resulted in a 14% enhancement of that for the anomeric hydrogen atom. For the diene (**1h**), the signal for the pentadiene 1-hydrogen atom was enhanced by 16% when that for the anomeric hydrogen atom was irradiated whereas the signal for the anomeric hydrogen atom was enhanced by 13% upon irradiation of that for the 1-hydrogen atom.

We assume that the dienes (**1e**, **h**) undergo cycloaddition only by way of the conformers (**4e**, **h**). In the case of *N*-phenylmaleimide, the cycloadducts (**2e**, **h**) arise by *endo*-addition to the least-hindered 'top' face of these conformers; with tetracyanoethylene, addition occurs to the 'top' face to give the cycloadducts (**6e**, **h**) (the major pathway) and from the 'bottom' face to give the cycloadducts (**7e**, **h**).

The conformational behaviour of the dienes (**1c**, **d**, **f**, **g**) matched that of their relative (**1a**). Thus according to n.O.e.d. spectroscopy, the dienes (**1c**, **d**, **f**, **g**) were present as a mixture of the conformers (**27c**, **d**, **f**, **g**) and (**28c**, **d**, **f**, **g**), with the former conformers being preferred. Irradiation of the signal for the anomeric hydrogen atom enhanced those for the butadiene 1- and 2-hydrogen atoms by 11 and 5% respectively in the case of compounds (**1c**, **f**) (in $CDCl_3$), by 9 and 4% respectively in the case of compound (**1d**) (in CD_3COCD_3), and by 18 and 8% respectively in the case of compound (**1g**) (in $CDCl_3$).

The demonstration that the diene (**1a**) was present in solution as a mixture of the conformers (**27a**) and (**28a**) led us to propose[1] that it reacted by way of both the conformers (**4a**) and (**5a**). Thus, with *N*-phenylmaleimide, the major and minor cycloadducts (**2a**) and (**3a**) were considered to arise by *endo*-addition to the least-hindered 'top' face of the conformers (**4a**) and (**5a**), respectively. This notion was seemingly supported by the finding that only the cycloadduct (**2b**) was produced in the reaction of the diene (**1b**) [which is likely to react only by way of the conformer (**4b**)] with *N*-phenylmaleimide. In the case of tetracyanoethylene, we postulated that the major cycloadduct (**6a**) arose by addition to the 'top' face of the conformer (**4a**) whereas the minor cycloadduct (**5a**) was formed by addition to both the 'bottom' face of the conformer (**4a**) and the 'top' face of the conformer (**5a**). We presume that the dienes (**1c**, **d**, **f**, **g**) react in an analogous manner by way of the conformers (**4c**, **d**, **f**, **g**) and (**5c**, **d**, **f**, **g**), although the possibility that the cycloadducts (**6c**, **d**, **f**, **g**) and (**7c**, **d**, **f**, **g**) originate only from the conformers (**4c**, **d**, **f**, **g**) cannot be excluded.

Experimental

Dry solvents, referred to in the ensuing experiments, were prepared as follows: DMF was stored over 4 Å molecular sieves; dimethyl sulphoxide was distilled under reduced pressure from calcium hydride and stored over 4 Å molecular sieves; THF was distilled from sodium–benzophenone immediately prior to use; dichloromethane was distilled from calcium chloride; benzene was stored over sodium wire. Light petroleum refers to that fraction boiling in the range 40—60 °C. Deuteriochloroform, used as a solvent for the determination of n.m.r. spectra of silyloxy compounds, was stored over tin granules.

Low temperature silica-gel chromatography was carried out using cooled (Me_2CO–solid CO_2) solvents. Thus the material to be purified was loaded onto the column (which had been pre-washed with the cooled eluant) in cooled dichloromethane; the column was then eluted with the cooled mobile phase. Fast atom bombardment (f.a.b.) positive ion mass spectra were recorded with a Kratos MS45 spectrometer using *m*-nitrobenzyl alcohol as the sample matrix. For other instrumental and chromatographic details, see Parts 1[2] and 2.[1]

Preparation of (E)-1-(2′,3′,4′,6′-*Tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-1-*en*-3-*ol* (**15a**) (*with M. M. L. Crilley*).—Sodium borohydride (0.543 g, 14.4 mmol) was added to a stirred solution of the butenone (**14a**)[7] (5.00 g, 12.0 mmol) and cerium(III) nitrate hexahydrate (4.34 g, 10 mmol) in methanol (25 cm^3). After 1 h, the mixture was partitioned between water and ethyl acetate. Evaporation of the dried ($MgSO_4$) organic layer gave the title compound (**15a**) (3.70 g, *ca.* 74%) as a 1:1 mixture of diastereoisomers, in the form of a slightly impure, unstable syrup; $\nu_{max.}$(film) 3 480 (OH), 1 750 (ester CO), and 1 675 cm^{-1} (C=C); δ(300 MHz; $CDCl_3$) *inter alia* 1.28 (3 H, d, *J* 6 Hz, 4-H_3), 1.84 (1 H, s br, OH), 2.02, 2.04, 2.06, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.75—3.81 (1 H, m, 5′-H), 4.15 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.20—4.33 (2 H, m, 6′- and 3-H), 4.77 and 4.78 (each 0.5 H, d, *J* 8 Hz, 1′-H), 5.08—5.32 (4 H, m, 2′-, 3′-, 4′-, and 2-H), and 6.44 (1 H, d, *J* 12 Hz, 1-H); *m/z* (c.i.) 436 (MNH_4^+) and 418 (M^+).

Preparation of (E)-3-(*t-Butyldimethylsilyloxy*)-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-1-*ene* (**15b**) (*with M. M. L. Crilley*).—Imidazole (1.07 g, 15.7 mmol) and 97% t-butyldimethylsilyl chloride (1.71 g, 11.0 mmol) were added to a stirred solution of the butenol (**15a**) (2.73 g, 6.53 mmol) in dry DMF (20 cm^3). After 24 h, the mixture was diluted with ethyl acetate and washed with brine (× 3). Evaporation of the dried ($MgSO_4$) organic layer and recrystallisation of the resultant solid from light petroleum gave the *title compound* (**15b**) (2.59 g, 75%) showing m.p. 88—90 °C; $[\alpha]_D$ −5° (*c* 1% in $CHCl_3$);

* In deuteriobenzene, this signal did not appear as the customary doublet (*J* 8 Hz) but as a symmetrical multiplet [comprising 2 large lines (separation 8 Hz) encompassing 2 medium lines (separation 2 Hz) and surrounded by 2 small lines (separation 12 Hz)] due to 'virtual' coupling (see ref. 24, p. 147).

$\nu_{max.}$(KBr) 1 750 and 1 740sh cm^{-1} (ester CO); $\lambda_{max.}$(EtOH) 213 nm (ε 530); δ(300 MHz; $CDCl_3$) 0.05 and 0.06 (each 3 H, s, Me_2Si), 0.89 (9 H, s, Me_3CSi), 1.22 and 1.23 (each 1.5 H, d, *J* 6 Hz, 4-H_3), 2.01, 2.03, 2.05, and 2.09 (each 3 H, s, 4 × $MeCO_2$), 3.75—3.79 (1 H, m, 5′-H), 4.13 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.23—4.33 (2 H, m, 6′- and 3-H), 4.73 and 4.74 (each 0.5 H, d, *J* 8 Hz, 1′-H), 5.06—5.27 (4 H, m, 2′-, 3′-, 4′-, and 2-H), and 6.33 and 6.34 (each 0.5 H, d, *J* 12 Hz, 1-H); *m/z* (e.i.) 475 ($M^+ - C_4H_9$), 405, and 331 ($C_{14}H_{19}O_9^+$) (Found: C, 54.1; H, 7.4. $C_{23}H_{40}O_{11}Si$ requires C, 54.1; H, 7.55%).

Preparation of 1-O-*Formyl*-2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranose* (**18**) (*with M. M. L. Crilley*).—Silver(I) nitrate (0.093 g, 0.55 mmol) was added to a stirred solution of the acetobromoglucose (**17**)[12] (0.206 g, 0.50 mmol) in formic acid (5 cm^3). After 45 min, the mixture was filtered and the filtrate was diluted with chloroform and washed with aqueous sodium hydrogen carbonate. Evaporation of the dried ($MgSO_4$) organic layer and recrystallisation of the product from ethyl acetate–light petroleum gave the title compound (**18**) (0.090 g, 48%) with m.p. 122—123 °C (lit.,[13] 121 °C); $[\alpha]_D$ +5° (*c* 1.1% in $CHCl_3$) [lit.,[13] +6° ($CHCl_3$)]; $\nu_{max.}$(KBr) 1 755sh and 1 740 cm^{-1} (ester CO); $\lambda_{max.}$(EtOH) 217 nm (ε 460); δ(300 MHz; $CDCl_3$) 2.02, 2.04, 2.05, and 2.09 (each 3 H, s, 4 × $MeCO_2$), 3.85—3.91 (1 H, m, 5-H), 4.13 (1 H, dd, *J* 13 and 2 Hz, 6-H), 4.30 (1 H, dd, *J* 13 and 4 Hz, 6-H), 5.12—5.31 (3 H, m, 2-, 3-, and 4-H), 5.83 (1 H, d, *J* 8 Hz, 1-H), and 8.07 (1 H, s, OCHO); *m/z* (e.i.) 347 ($C_{14}H_{19}O_{10}^+$) and 331 ($C_{14}H_{19}O_9^+$) (Found: C, 47.8; H, 5.2. Calc. for $C_{15}H_{20}O_{11}$: C, 47.85; H, 5.35%).

Preparation of (E)-3-(2′,3′,4′,6′-*Tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*propenal* (**14b**) (*with R. C. Gupta*).—The salt (**19a**)[15] (56.0 g, 0.51 mmol) was added to a stirred suspension of the acetobromoglucose (**17**)[12] (139 g, 0.338 mol) in dry dimethyl sulphoxide (700 cm^3). After 12 h, the mixture was poured over ice–water and extracted with dichloromethane (×4). After being washed with water (×4), the organic extracts were combined, dried ($MgSO_4$), and concentrated. Two recrystallisations of the product from dichloromethane–diethyl ether–light petroleum gave the title compound (**14b**) (64.0 g, 47%) which showed m.p. 132—133 °C (lit.,[18] 134.5—135 °C); $[\alpha]_D$ −19° (*c* 5% in CH_2Cl_2) [lit.,[18] −22° (CH_2Cl_2)]; $\nu_{max.}$(KBr) 1 745 (ester CO), 1 675 (vinylogous ester CO), and 1 620 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 230 nm (ε 19 800); δ(300 MHz; $CDCl_3$) 2.03, 2.05, 2.07, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.82—3.88 (1 H, m, 5′-H), 4.16 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.29 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 5.00 (1 H, d, *J* 7 Hz, 1′-H), 5.12—5.30 (3 H, m, 2′-, 3′-, and 4′-H), 5.80 (1 H, dd, *J* 13 and 8 Hz, 2-H), 7.31 (1 H, d, *J* 13 Hz, 3-H), and 9.43 (1 H, d, *J* 8 Hz, 1-H); *m/z* (e.i.) 331 ($C_{14}H_{19}O_9^+$) (Found: C, 50.5; H, 5.3. Calc. for $C_{17}H_{22}O_{11}$: C, 50.55; H, 5.5%).

Preparation of the Methylenation Reagent.[16]—Titanium(IV) chloride (2.3 cm^3, 21 mmol) was added in drops over 10 min to a stirred, cooled (cyclohexanone–solid CO_2) mixture of zinc dust (5.75 g, 88 mmol), dibromomethane (2.02 cm^3, 29 mmol), and dry THF (50 cm^3) under argon. The mixture was stirred in an ice-bath for 5 h and then stored in a refrigerator for 12 h prior to use.

Preparation of (E)-1-(2′,3′,4′,6′-*Tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*buta*-1,3-*diene* (**1c**).—A slurry of the methylenation reagent was added in portions (*ca.* 2 cm^3) to a stirred solution of the propenal (**14b**) (2.00 g, 4.97 mmol) in dry dichloromethane (20 cm^3). The reaction was monitored by t.l.c. and, when no starting material remained, the mixture was poured onto sodium hydrogen carbonate (1.0 g). Water (50 cm^3) was then added and the mixture was stirred for 5 min. Hyflo (5 g) was added to the mixture which was filtered. The organic phase of the filtrate was separated, washed with water, and dried ($MgSO_4$). Evaporation of the combined organic phases left a pale-yellow oil which was subjected to silica-gel chromatography [light petroleum–Et_2O (1:1) as eluant]. After recrystallisation of the purified material from diethyl ether–light petroleum, the title compound (**1c**) (0.655 g, 33%) was isolated as white crystals with m.p. 106—107 °C (lit.,[18] 152—153 °C); $[\alpha]_D$ −10° (*c* 0.5% in CH_2Cl_2) [lit.,[18] − 13° (CH_2Cl_2)]; $\nu_{max.}$(KBr) 1 760 and 1 730 (ester CO) and 1 655 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 229 nm (ε 27 000); δ(300 MHz; $CDCl_3$) 2.03, 2.05, 2.07, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.80 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.16 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.29 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.80 (1 H, d, *J* 8 Hz, 1′-H), 4.96 (1 H, d br, *J* 11 Hz, 4-H), 5.06—5.17 (3 H, m, 4-, 2′-, and 4′-H), 5.25 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.83 (1 H, t, separation 12 Hz, 2-H), 6.20 (1 H, dt, *J* 17, 11, and 11 Hz, 3-H), and 6.53 (1 H, d, *J* 12 Hz, 1-H) [in an n.O.e.d. experiment, irradiation of the signal at δ 4.80 enhanced the signal at δ 3.80 by 10%, that at δ 5.25 by 9%, that at δ 5.83 by 5%, and that at δ 6.53 by 11%; irradiation of the signal at δ 5.83 caused a 3% enhancement of the signal at δ 4.80, a 10% enhancement of part of the signal at 5.06—5.17 (the doublet at δ 5.09), and a 3.5% enhancement of the signal at δ 6.53; irradiation of the signal at δ 6.53 brought about a 4% enhancement of the signal at δ 4.80 and an 8% enhancement of the signal at δ 6.20]; *m/z* (c.i.) 332 ($C_{14}H_{20}O_9^+$, 14%), 331 ($C_{14}H_{19}O_9^+$, 88), 169 (88), and 43 ($C_2H_3O^+$, 100) (Found: C, 53.8; H, 5.9. Calc. for $C_{18}H_{24}O_{10}$: C, 54.0; H, 6.05%).

Reaction of the Butadiene (**1c**) *with* N-*Phenylmaleimide.*—A solution of the butadiene (**1c**) (0.100 g, 0.25 mmol) and *N*-phenylmaleimide (0.065 g, 0.375 mmol) in dry benzene (2 cm^3) was left at ambient temperature for 3 days. Evaporation gave a white foam which was considered to be an 86:14 mixture of the cycloadducts (**2c**) and (**3c**) on the basis of 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at δ 1.63 and 1.92, ascribed to acetoxy groups of compounds (**2c**) and (**3c**), respectively]. Crystallisation of the material from dichloromethane–diethyl ether gave (1R,2R,3S)-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-*cyclohex*-4-*ene*-1,2-*dicarboximide* (**2c**) (0.085 g, 59%), m.p. 142—144 °C; $[\alpha]_D$ +63° (*c* 0.6% in CH_2Cl_2); c.d. (MeCN) 200 (Δε + 14.4) and 267 nm (Δε −0.2); $\nu_{max.}$(KBr) 1 755 and 1 745sh (ester CO) and 1 705 cm^{-1} (imide CO); $\lambda_{max.}$(EtOH) 216 nm (ε 10 000); δ(300 MHz; $CDCl_3$) 1.64, 1.98, 2.03, and 2.12 (each 3 H, s, 4 × $MeCO_2$), 2.63—2.72 (2 H, m, 6-H_2), 3.16—3.33 (2 H, m, 1- and 2-H), 3.70 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.14 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.23 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.68—4.73 (1 H, m, 3-H), 4.71 (1 H, d, *J* 8 Hz, 1′-H), 4.89 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.06 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.18 (1 H, t, *J* 10 and 10 Hz, 3′-H), 6.10—6.27 (2 H, m, 4- and 5-H), and 7.26—7.53 (5 H, m, Ph); *m/z* (f.a.b.) 574 (MH^+, 30%) and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 58.9; H, 5.2; N, 2.4. $C_{28}H_{31}NO_{12}$ requires C, 58.65; H, 5.45; N, 2.45%).

Reaction of the Butadiene (**1c**) *with Tetracyanoethylene.*—A solution of the butadiene (**1c**) (0.200 g, 0.50 mmol) and tetracyanoethylene (0.064 g, 0.5 mmol) in dry benzene (2 cm^3) was left at ambient temperature for 3 h. Evaporation gave an off-white solid which was considered to be a 69:31 mixture of the cycloadducts (**6c**) and (**7c**) on the basis of 300 MHz ^1H n.m.r. spectroscopy; the ratio was estimated from the heights of the singlets at δ 2.02 and 2.06, attributed to acetoxy groups of compounds (**6c**) and (**7c**), respectively. Recrystallisation of the material from dichloromethane–diethyl ether followed by ethyl acetate–light petroleum gave (3S)-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1,1,2,2-*tetracyanocyclohex*-4-*ene* (**1c**) (0.088 g, 33%), m.p. 197—198 °C; $[\alpha]_D$ +23° (*c* 0.1% in

CH_2Cl_2); $\nu_{max.}$(KBr) 1 760 and 1 745sh cm^{-1} (ester CO); δ(300 MHz; $CDCl_3$) 2.02, 2.05, 2.10, and 2.12 (each 3 H, s, 4 × $MeCO_2$), 3.07—3.25 (2 H, m, 6-H_2), 3.81 (1 H, dt, *J* 10, 7, and 7 Hz, 5′-H), 4.25 (2 H, apparent d, separation 3.5 Hz, 6′-H_2), 4.85—4.91 (1 H, m, 3-H), 4.96 (1 H, d, *J* 8 Hz, 1′-H), 5.07—5.17 (2 H, m, 2′- and 4′-H), 5.25 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 5.90—6.05 (2 H, m, 4- and 5-H); *m/z* (f.a.b.) 551 (MNa^+, 6%), 529 (MH^+, 6), 469 (20), and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 54.5; H, 4.6; N, 10.3. $C_{24}H_{24}N_4O_{10}$ requires C, 54.55; H, 4.6; N, 10.6%).

Preparation of (E)-3-*Methyl*-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*buta*-1,3-*diene* (**1d**).—A solution of the butenone (**14a**)[7] (2.00 g, 4.80 mmol) in dry dichloromethane (20 cm^3) was treated with a slurry of the methylenation reagent, as described for compound (**14b**). Work-up and purification of the product as before yielded, after recrystallisation from diethyl ether–light petroleum, the *title compound* (**1d**) (0.880 g, 44%), m.p. 108—109 °C; $[\alpha]_D$ −14° (*c* 0.6% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester CO), 1 660, and 1 640 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 233 nm (ε 26 400); δ(300 MHz; $CDCl_3$) 1.82 (3 H, s br, 3-Me), 2.04, 2.06, 2.07, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.81 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′-H), 4.18 (1 H, dd, *J* 13 and 3 Hz, 6′-H), 4.30 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.82 and 4.85 (each 1 H, s br, 4-H_2), 4.83 (1 H, d, *J* 8 Hz, 1′-H), 5.08—5.20 (2 H, m, 2′- and 4′-H), 5.26 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.93 (1 H, d, *J* 13 Hz, 2-H), and 6.47 (1 H, d, *J* 13 Hz, 1-H); δ(300 MHz; CD_3COCD_3) 1.92 (3 H, s br, 3-Me), 2.11, 2.15, 2.16, and 2.17 (each 3 H, s, 4 × $MeCO_2$), 4.22 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′-H), 4.27 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.39 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.89—4.91 and 4.95—4.98 (each 1 H, m, 4-H_2), 5.19 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.22 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.31 (1 H, d, *J* 8 Hz, 1′-H), 5.46 (1 H, t, *J* 10 and 10 Hz, 3′-H), 6.03 (1 H, d, *J* 12 Hz, 2-H), and 6.84 (1 H, d, *J* 12 Hz, 1-H) (in an n.O.e.d. experiment, irradiation of the signal at δ 5.31 enhanced the signal at δ 6.03 by 4% and that at δ 6.84 by 9%; irradiation of the signal at δ 6.03 caused a 4% enhancement of the signal at δ 4.89—4.91 and a 1% enhancement of that at δ 5.31; irradiation of the signal at δ 6.84 resulted in a 3% enhancement of that at δ 5.31); *m/z* (c.i.) 332 ($C_{14}H_{20}O_9^+$, 22%), 331 ($C_{14}H_{19}O_9^+$, 75), 169 (77), and 43 ($C_2H_3O^+$, 100) (Found: C, 54.8; H, 6.2. $C_{19}H_{26}O_{10}$ requires C, 55.05; H, 6.3%).

Reaction of the Methylbutadiene (**1d**) *with* N-*Phenylmaleimide*.—A solution of the methylbutadiene (**1d**) (0.100 g, 0.24 mmol) and *N*-phenylmaleimide (0.042 g, 0.24 mmol) in dry benzene (2 cm^3) was left at ambient temperature for 18 h. Evaporation gave a white solid which was considered to be mainly an 88:12 mixture of the cycloadducts (**2d**) and (**3d**) on the basis of 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at δ 1.67 and 1.92, ascribed to acetoxy groups of compounds (**2d**) and (**3d**), respectively]. Crystallisation of the material from dichloromethane–diethyl ether gave (1R,2R,3S)-5-*methyl*-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**2d**) (0.085 g, 60%), m.p. 195—196 °C; $[\alpha]_D$ +86° (*c* 0.5% in CH_2Cl_2); c.d. (MeCN) 200 (Δε +12.6), 264 (Δε −0.07), and 271 nm (Δε −0.05); $\nu_{max.}$(KBr) 1 755 (ester CO) and 1 710 cm^{-1} (imide CO); $\lambda_{max.}$(EtOH) 216sh nm (ε 9 900); δ(300 MHz; $CDCl_3$) 1.67, 1.97, 2.03, and 2.12 (each 3 H, s, 4 × $MeCO_2$), 1.87 (3 H, s br, 5-Me), 2.49 (1 H, dd, *J* 16 and 8 Hz, 6-Hα), 2.69 (1 H, dd br, *J* 16 and 7 Hz, 6-Hβ), 3.12—3.29 (2 H, m, 1- and 2-H), 3.64—3.72 (1 H, m, 5′-H), 4.13—4.22 (2 H, m, 6′-H_2), 4.68 (1 H, d, *J* 8 Hz, 1′-H), 4.69 (1 H, t, *J* 5 and 5 Hz, 3-H), 4.87 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 5.08 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.17 (1 H, t, *J* 9 and 9 Hz, 3′-H), 5.82—5.86 (1 H, m, 4-H), and 7.33—7.53 (5 H, m, Ph); *m/z* (f.a.b.) 588 (MH^+, 10%), 331 ($C_{14}H_{19}O_9^+$, 80), and 307 (100) (Found: C, 59.1; H, 5.6; N, 2.5. $C_{29}H_{33}NO_{12}$ requires C, 59.25; H, 5.65; N, 2.4%).

Reaction of the Methylbutadiene (**1d**) *with Tetracyanoethylene*.—A solution of the methylbutadiene (**1d**) (0.200 g, 0.48 mmol) and tetracyanoethylene (0.062 g, 0.48 mmol) in dry benzene (2 cm^3) was left at ambient temperature overnight. Evaporation of the solvent gave a white solid which was considered to be mainly a 76:24 mixture of the cycloadducts (**6d**) and (**7d**) by 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the broad singlets at δ 5.55 and 5.74, attributed to the 4-hydrogen atoms of compounds (**7d**) and (**6d**), respectively]. Recrystallisation of the material from dichloromethane–diethyl ether gave (3S)-5-*methyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1,1,2,2-*tetracyanocyclohex*-4-*ene* (**6d**) (0.160 g, 61%), m.p. 177—178 °C; $[\alpha]_D$ +27° (*c* 0.3% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755 cm^{-1} (ester CO); $\lambda_{max.}$(EtOH) 205 nm (ε 2 900); δ(300 MHz; $CDCl_3$) 1.93 (3 H, s br, 5-Me), 2.06, 2.08, 2.14, and 2.15 (each 3 H, s, 4 × $MeCO_2$), 2.97 and 3.14 (each 1 H, d br, *J* 18 Hz, 6-H_2), 3.83 (1 H, dt, *J* 10, 4, and 4 Hz, 5′-H), 4.27 (2 H, apparent d, separation 3 Hz, 6′-H_2), 4.85—4.92 (1 H, m, 3-H), 4.97 (1 H, d, *J* 8 Hz, 1′-H), 5.10—5.20 (2 H, m, 2′- and 4′-H), 5.29 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 5.37 (1 H, s br, 4-H); *m/z* (f.a.b.) 565 (MNa^+, 3%) 543 (MH^+, 8), and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 55.5; H, 4.8; N, 10.1. $C_{29}H_{33}NO_{12}$ requires C, 55.35; H, 4.85; N, 10.3%).

Processing of the mother liquor led to a further crystalline fraction which comprised a 23:77 mixture of compounds (**6d**) and (**7d**); δ(300 MHz; $CDCl_3$) [for (**7d**)] 1.95 (3 H, s br, 5-Me), 2.04, 2.06, 2.08, and 2.12 (each 3 H, s, 4 × $MeCO_2$), 2.97 and 3.17 (each 1 H, d br, *J* 18 Hz, 6-H_2), 3.82—3.90 (1 H, m, 5′-H), 4.23—4.33 (2 H, m, 6′-H_2), 4.87 (1 H, d, *J* 8 Hz, 1′-H), 4.90—4.93 (1 H, m, 3-H), 5.10—5.30 (3 H, m, 2′-, 3′-, and 4′-H), and 5.55 (1 H, s br, 4-H).

Preparation of (E)-2,3-*Dimethyl*-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*buta*-1,3-*diene* (**1e**).—A solution of the butenone (**14c**)[1] (2.00 g, 4.65 mmol) in dry dichloromethane (20 cm^3) was treated with a slurry of the methylenation reagent, as described for compound (**14b**). Work-up and purification of the product as before gave, after recrystallisation from diethyl ether–light petroleum, the *title compound* (**1e**) (0.710 g, 34%), m.p. 126—128 °C; $[\alpha]_D$ −24° (*c* 0.9% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755 and 1 745 (ester CO) and 1 650 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 237 nm (ε 23 400); δ(300 MHz; $CDCl_3$) 1.75 and 1.88 (each 3 H, s br, 2- and 3-Me), 2.04, 2.06, 2.07, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.81 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.17 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.31 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.77 (1 H, d, *J* 8 Hz, 1′-H), 4.84 and 4.95 (each 1 H, s br, 4-H_2), 5.12—5.22 (2 H, m, 2′- and 4′-H), 5.27 (1 H, t, *J* 9 and 9 Hz, 3′-H), and 6.45 (1 H, s br, 1-H); δ (300 MHz; C_6D_6) 1.90, 1.91, 1.93, and 1.94 (each 3 H, s, 4 × $MeCO_2$), 2.03 (3 H, s br, 3-Me), 2.11 (3 H, d, *J* 1 Hz, 2-Me), 3.48 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′-H), 4.20 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.49 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.63—4.66 (1 H, m, 1′-H), 5.07 and 5.22 (each 1 H, s br, 4-H_2), 5.49—5.57 and 5.61—5.71 (1 and 2 H, each m, 2′-, 3′-, and 4′-H), 6.71 (1 H, d, *J* 1 Hz, 1-H) (in an n.O.e.d. experiment, irradiation of the signal at δ 2.03 enhanced the signals at δ 5.07 and 6.71 by 8% and 20%, respectively; irradiation of the signal at δ 2.11 caused a 13% enhancement of that at δ 5.22; irradiation of the signal at δ 4.65 resulted in a 10% enhancement of that at δ 3.48, a 7% enhancement of that at δ 5.61—5.71, and a 13% enhancement of that at δ 6.71; irradiation of the signal at δ 6.71 enhanced the signal at δ 2.03 by 4% and that at δ 4.65 by 14%); *m/z* (c.i.) 332 ($C_{14}H_{20}O_9^+$, 17%), 331 ($C_{14}H_{19}O_9^+$, 85), 169 (84), and 43 ($C_2H_3O^+$, 100) (Found: C, 56.0; H, 6.6. $C_{20}H_{28}O_{10}$ requires C, 56.05; H, 6.6%).

Reaction of the Dimethylbutadiene (**1e**) *with* N-*Phenylmaleimide*.—A solution of the dimethylbutadiene (**1e**) (0.100 g, 0.23 mmol) and *N*-phenylmaleimide (0.040 g, 0.23 mmol) in dry benzene (2 cm^3) was left at ambient temperature for 18 h. Evaporation of the solvent gave a white solid which comprised predominantly the cycloadduct (**2e**) by 300 MHz ^1H n.m.r. spectroscopy [there was no evidence for the presence of (**3e**)]. Crystallisation of the product from dichloromethane–diethyl ether gave (1R,2R,3S)-4,5-*dimethyl*-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**2e**) (0.095 g, 68%), m.p. 224—225 °C; $[\alpha]_D$ +65° (*c* 0.3% in CH_2Cl_2); c.d. (MeCN) 202 ($\Delta\varepsilon$ +16.2) and 273 nm ($\Delta\varepsilon$ −0.03); $\nu_{max.}$ 1 750 (ester CO) and 1 705 cm^{-1} (imide CO); $\lambda_{max.}$(EtOH) 216sh nm (ε 11 500); δ(300 MHz; $CDCl_3$) 1.57, 1.97, 2.03, and 2.11 (each 3 H, s, 4 × $MeCO_2$), 1.83 and 1.85 (each 3 H, s br, 4- and 5-Me), 2.49 (1 H, dd br, separation 18 and 8 Hz, 6-Hα), 2.72 (1 H, d br, *J* 18 Hz, 6-Hβ), 3.11—3.32 (2 H, m, 1- and 2-H), 3.67—3.74 (1 H, m, 5′-H), 4.11—4.22 (2 H, m, 6′-H_2), 4.53—4.56 (1 H, m, 3-H), 4.68 (1 H, d, *J* 8 Hz, 1′-H), 4.86 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.03 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.18 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.33—7.53 (5 H, m, Ph); *m/z* (f.a.b.) 602 (MH^+, 15%), 331 ($C_{14}H_{19}O_9^+$, 55), and 307 (70) (Found: 60.1; H, 5.9; N, 2.4. $C_{30}H_{35}NO_{12}$ requires C, 59.9; H, 5.85; N, 2.35%).

Reaction of the Dimethylbutadiene (**1e**) *with Tetracyanoethylene*.—A solution of the dimethylbutadiene (**1e**) (0.200 g, 0.47 mmol) and tetracyanoethylene (0.060 g, 0.47 mmol) in dry benzene (2 cm^3) was left overnight at ambient temperature. Evaporation of the solvent gave a syrup which comprised a 78:22 mixture of the cycloadducts (**6e**) and (**7e**) according to 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the broad singlets at δ 4.70 and 4.78, ascribed to the 3-hydrogen atoms of compounds (**7e**) and (**6e**), respectively]. Crystallisation of the material from dichloromethane–diethyl ether–light petroleum gave a white solid (0.211 g, 81%) which was then recrystallised from dichloromethane–diethyl ether; the resultant solid (0.057 g, 22%) was a 50:50 mixture of the cycloadducts (**6e**) and (**7e**). Trituration of the mother liquor with diethyl ether gave (3S)-4,5-*dimethyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1,1,2,2-*tetracyanocyclohex*-4-*ene* (**6e**) (0.092 g, 35%) as a white solid, m.p. 187—190 °C; $[\alpha]_D$ −2° (*c* 0.6% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755 cm^{-1} (ester CO); $\lambda_{max.}$(EtOH) 202 nm (ε 6 500); δ(300 MHz; $CDCl_3$) 1.79 and 1.81 (each 3 H, s br, 4- and 5-Me), 2.01, 2.05, 2.09, and 2.11 (each 3 H, s, 4 × $MeCO_2$), 2.94 and 3.14 (each 1 H, d br, *J* 18 Hz, 6-H_2), 3.83 (1 H, ddd, *J* 10, 5, and 2.5 Hz, 5′-H), 4.22 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.30 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.77 (1 H, s br, 3-H), and 5.07—5.29 (4 H, m, 1′-, 2′-, 3′-, and 4′-H); *m/z* (f.a.b.) 579 (MNa^+, 1%), 497 (10), 331 ($C_{14}H_{19}O_9^+$, 60), and 169 (100) (Found: C, 56.4; H, 5.3; N, 10.1. $C_{26}H_{28}N_4O_{10}$ requires C, 56.1; H, 5.05; N, 10.05%).

Preparation of (E)-1-*Acetoxy*-4-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**14d**).—85% *m*-Chloroperoxybenzoic acid (0.660 g, 3.25 mmol) was added to a stirred, cooled (Me_2CO–solid CO_2) solution of the butadiene (**1a**)[1,7] (1.00 g, 2.06 mmol) in dry dichloromethane (10 cm^3). After 1 h, the mixture was allowed to warm up to room temperature and stirred for a further 2 days. The mixture was then diluted with dichloromethane and washed with aqueous sodium hydrogen carbonate. Evaporation of the dried ($MgSO_4$) organic layer gave an oil which was dissolved in methanol (5 cm^3). After 1 h, the solvent was removed by evaporation. The residue was dissolved in pyridine (5 cm^3) and to the stirred, ice-cooled solution was added acetic anhydride (5 cm^3). After 1 h at 0 °C and then 1 h at room temperature, the mixture was diluted with dichloromethane and washed with dilute hydrochloric acid. Evaporation of the dried ($MgSO_4$) organic layer and purification of the oil by silica-gel chromatography [light petroleum–Et_2O (4:1) as eluant] gave a white solid (0.540 g) which was recrystallised from dichloromethane–light petroleum. The resultant *title compound* (**14d**) (0.378 g, 39%) was isolated as white needles, m.p. 108—110 °C; $[\alpha]_D$ −16° (*c* 0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester CO), 1 675 (vinylogous ester CO), and 1 620 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 240 nm (ε 18 300); δ(300 MHz; $CDCl_3$) 2.02, 2.04, 2.07, 2.10, and 2.19 (each 3 H, s, 5 × $MeCO_2$), 3.83 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′-H), 4.15 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.29 (1 H, d, *J* 12 and 5 Hz, 6′-H), 4.70 (2 H, s, 1-H_2), 4.94 (1 H, d, *J* 8 Hz, 1′-H), 5.11—5.19 (2 H, m, 2′- and 4′-H), 5.26 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.93 (1 H, d, *J* 12 Hz, 3-H), and 7.58 (1 H, d, *J* 12 Hz, 4-H); *m/z* (c.i.) 331 ($C_{14}H_{19}O_9^+$, 53%) and 169 (100) (Found: C, 50.8; H, 5.7. $C_{20}H_{26}O_{13}$ requires C, 50.65; H, 5.5%).

Preparation of (1E,3Z)-4-*Acetoxy*-3-(*t-butyldimethylsilyloxy*)-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*buta*-1,3-*diene* (**1f**).—t-Butyldimethylsilyl triflate (0.11 cm^3, 0.48 mmol) was added to a stirred, cooled (CCl_4–solid CO_2) solution of the butenone (**14d**) (0.200 g, 0.42 mmol) and dry triethylamine (0.12 cm^3, 0.86 mmol) in dry dichloromethane (5 cm^3). After 10 min, the mixture was treated with triethylamine (0.5 cm^3) and concentrated. Purification of the resultant orange oil by low-temperature chromatography on silica gel [light petroleum–Et_2O (7:3) as eluant] gave the *title compound* (**1f**) (0.103 g, 41%). After recrystallisation from diethyl ether–light petroleum, the sample showed m.p. 103—105 °C; $[\alpha]_D$ −16° (*c* 0.2% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755 and 1 730 (ester CO) and 1 670 and 1 635 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 250 nm (ε 25 000); δ(300 MHz; $CDCl_3$) 0.20 (6 H, s, Me_2Si), 1.01 (9 H, s, Me_3CSi), 2.04, 2.06, 2.07, 2.11, and 2.17 (each 3 H, s, 5 × $MeCO_2$), 3.79 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.14 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.28 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.78 (1 H, d, *J* 8 Hz, 1′-H), 5.09—5.17 (2 H, m, 2′- and 4′-H), 5.27 (1 H, t, *J* 9 and 9 Hz, 3′-H), 5.57 (1 H, d, *J* 12 Hz, 2-H), 6.70 (1 H, d, *J* 12 Hz, 1-H), and 6.78 (1 H, s, 4-H) (in an n.O.e.d. experiment, irradiation of the signal at δ 4.78 caused a 10% enhancement of the signal at δ 3.80, a 6% enhancement of that at δ 5.27, a 5% enhancement of that at δ 5.57, and an 11% enhancement of that at δ 6.70; irradiation of the signal at δ 5.57 enhanced the signal at δ 4.78 by 2% and that at δ 6.78 by 13%; irradiation of the signal at δ 6.70 enhanced that at δ 4.78 by 4% and that at δ 5.57 by 3%); *m/z* (c.i.) 331 ($C_{14}H_{19}O_9^+$, 24%) and 169 (100) (Found: C, 53.1; H, 7.0. $C_{26}H_{40}O_{13}Si$ requires C, 53.05; H, 6.85%).

Reaction of the Acetoxybutadiene (**1f**) *with* N-*Phenylmaleimide and Hydrolysis of the Major Cycloadduct* (**2f**).—A solution of the acetoxybutadiene (**1f**) (0.172 g, 0.29 mmol) and *N*-phenylmaleimide (0.051 g, 0.29 mmol) in dry benzene (1 cm^3) was left overnight at ambient temperature. Evaporation of the solvent gave a syrup which comprised mainly an 89:11 mixture of the cycloadducts (**2f**) and (**3f**) by 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the heights of the singlets at δ 0.17 and 0.19, ascribed to the dimethylsilyl group of compound (**2f**), with respect to those at δ 0.23 and 0.26, attributed to the dimethylsilyl group of compound (**3f**)]. Addition of diethyl ether to the product and filtration gave (1R,2R,3S,6S)-6-*acetoxy*-N-*phenyl*-5-(*t-butyldimethylsilyloxy*)-3-(1′,2′,3′,4′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**2f**) (0.132 g, 59%) as a white solid. After recrystallisation from dichloromethane–light petroleum, the sample displayed m.p. 197—200 °C (decomp.); $[\alpha]_D$ +9° (*c* 0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester CO), 1 710 (imide CO), and 1 665 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 210sh nm (ε 22 200); δ(300 MHz; $CDCl_3$) 0.18 and 0.21 (each 3 H, s, Me_2Si), 0.97 (9 H, s, Me_3CSi), 1.40, 1.97, 2.08, 2.12, and 2.16 (each 3 H, s, 5 ×

$MeCO_2$), 3.43 (1 H, dd, *J* 11 and 7 Hz, 2-H), 3.58 (1 H, dd, *J* 11 and 7 Hz, 1-H), 3.69—3.77 (1 H, m, 5′-H), 4.15 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.24 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.72 (1 H, d, *J* 8 Hz, 1′-H), 4.77 (1 H, t, *J* 7 and 7 Hz, 3-H), 4.91 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.05 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.17 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.42 (1 H, dd, *J* 7 and 1 Hz, 4-H), 5.83 (1 H, dd, *J* 7 and 1 Hz, 6-H), and 7.30—7.55 (5 H, m, Ph); *m/z* (f.a.b.) 784 (MNa$^+$, 3%) and 414 (40) (Found: C, 56.6; H, 6.4; N, 1.9. $C_{34}H_{45}NO_{13}Si$ requires C, 56.75; H, 6.2; N, 1.85%).

A solution of the cycloadduct (**2f**) (0.100 g, 0.13 mmol) in THF (10 cm^3) was treated with 0.1M hydrochloric acid (5 cm^3). After 3 h, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and recrystallisation of the product from dichloromethane–light petroleum gave (1R,2R,3S,6 S)-6-*acetoxy*-5-*oxo*-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**23a**) (0.052 g, 61%) as a white solid, m.p. 195—198 °C; $[\alpha]_D$ +10° (*c* 0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester CO) and 1 720 cm^{-1} (imide and ketone CO); $\lambda_{max.}$(EtOH) 218sh nm (ε 11 000); δ(300 MHz; $CDCl_3$) 1.58, 1.97, 2.03, 2.11, and 2.23 (each 3 H, s, 5 × $MeCO_2$), 2.70 (1 H, dd, *J* 18 and 4 Hz, 4-Hβ), 3.15 (1 H, dd, *J* 18 and 4 Hz, 4-Hα), 3.55 (1 H, dd, *J* 11 and 6 Hz, 2-H), 3.67—3.77 (2 H, m, 1- and 5′-H), 4.19 (2 H, d, *J* 4 Hz, 6′-H_2), 4.74 (1 H, d, *J* 8 Hz, 1′-H), 4.81 (1 H, apparent q, separation 6 Hz, 3-H), 4.91 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.03 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.17 (1 H, t, *J* 10 and 10 Hz, 3′-H), 5.58 (1 H, d, *J* 7 Hz, 6-H), and 7.28—7.55 (5 H, m, Ph); *m/z* (f.a.b.) 670 (MNa$^+$, 1%), 648 (MH$^+$, 1), 331 ($C_{14}H_{19}O_9^+$, 60), and 169 (100) (Found: C, 55.7; H, 5.5; N, 1.8. $C_{30}H_{33}NO_{15}$ requires C, 55.65; H, 5.15; N, 2.15%).

Reaction of the Acetoxy Ketone (**23a**) *with Chromium*(II) *Chloride.*—An aqueous solution of chromium(II) chloride [generated by adding $CrCl_3$ (1.5 g) in portions over 0.5 h to a vigorously stirred suspension of Zn.Hg (5.4 g) in water (10 cm^3) and conc. HCl (1 cm^3) under an atmosphere of argon; the mixture was stirred for 1 h before use][25] was added to a solution of the acetoxy ketone (**23a**) (0.040 g, 0.06 mmol) in acetone (40 cm^3) under argon. After 24 h, the mixture was concentrated (to *ca.* 20 cm^3) and poured onto water (100 cm^3). The mixture was extracted with dichloromethane and the organic layer was washed with water, dried ($MgSO_4$), and evaporated. Recrystallisation of the product from dichloromethane–diethyl ether gave (1*R*,2*R*,3*S*)-5-oxo-*N*-phenyl-3-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)cyclohexane-1,2-dicarboximide (**23b**)[2] (0.024 g, 66%), identified by its ^{1}H n.m.r. spectrum; δ(300 MHz; $CDCl_3$) 1.57, 1.97, 2.02, and 2.13 (each 3 H, s, 4 × $MeCO_2$), 2.35 (1 H, dd, *J* 19 and 2 Hz, 4-Hβ), 2.87 (1 H, d, *J* 18 and 10 Hz, 6-Hα), 2.96 (1 H, dd, *J* 18 and 5 Hz, 6-Hβ), 3.03 (1 H, dd, *J* 19 and 3 Hα, 4-Hα), 3.27 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.33—3.43 (1 H, m, 1-H), 3.70 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′-H), 4.08—4.09 (2 H, m, 6′-H_2), 4.66 (1 H, d, *J* 8 Hz, 1′-H), 4.81—4.84 (1 H, m, 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 7.34—7.53 (5 H, m, Ph).

Reaction of the Acetoxybutadiene (**1f**) *with Tetracyanoethylene.*—A solution of the acetoxybutadiene (**1f**) (0.100 g, 0.17 mmol) and tetracyanoethylene (0.022 g, 0.17 mmol) in dry benzene (1 cm^3) was left overnight at ambient temperature. Evaporation of the solvent gave a solid considered to be a 71:29 mixture of the cycloadducts (**6f**) and (**7f**) by 300 MHz ^{1}H n.m.r. spectroscopy [the ratio was estimated from the heights of the broad singlets at δ 5.92 and 5.96, ascribed to the 4-hydrogen atoms of compounds (**6f**) and (**7f**), respectively]. Crystallisation of the material from dichloromethane–diethyl ether gave (3S,6S)-6-*acetoxy*-5-(*t-butyldimethylsilyloxy*)-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1,1,2,2-*tetracyanocyclohex*-4-*ene* (**6f**) (0.066 g, 54%) as a white solid, m.p. 174—176 °C; $[\alpha]_D$ +12° (*c* 0.1% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755 (ester CO) and 1 675 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 206 nm (ε 9 500); δ(300 MHz; $CDCl_3$) 0.22 and 0.24 (each 3 H, s, Me_2Si), 0.89 (9 H, s, Me_3CSi), 2.02, 2.05, 2.09, 2.12, and 2.25 (each 3 H, s, 5 × $MeCO_2$), 3.81 (1 H, ddd, *J* 10, 4, and 3 Hz, 5′-H), 4.18—4.28 (2 H, m, 6′-H_2), 4.91 (1 H, dd, *J* 2.5 and 1 Hz, 3-H), 4.96 (1 H, d, *J* 8 Hz, 1′-H), 5.10—5.18 (2 H, m, 2′- and 4′-H), 5.23 (1 H, dd, *J* 2.5 and 0.5 Hz, 4-H), 5.26 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 5.92 (1 H, s br, 6-H); *m/z* (f.a.b.) 659 ($M^+ - C_4H_8$, 30%), 463 (32), 369 (80), and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 53.4; H, 5.5; N, 7.8. $C_{32}H_{40}N_4O_{13}Si$ requires C, 53.6; H, 5.6; N, 7.8%).

Trituration of the mother liquor from the foregoing crystallisation with light petroleum gave a white solid (0.035 g, 29%), considered to comprise a 26:74 mixture of the cycloadducts (**6f**) and (**7f**); δ(300 MHz; $CDCl_3$) [for (**7f**)] 0.21 and 0.25 (each 3 H, s, Me_2Si), 0.91 (9 H, s, Me_3CSi), 2.03, 2.04, 2.05, 2.10, and 2.26 (each 3 H, s, 5 × $MeCO_2$), 3.76—3.86 (1 H, m, 5′-H), 4.20—4.28 (2 H, m, 6′-H_2), 4.87 (1 H, d, *J* 8 Hz, 1′-H), 5.01 (1 H, dd, *J* 2.5 and 1 Hz, 3-H), 5.05 (1 H, dd, *J* 2.5 and 0.5 Hz, 4-H), 5.11 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 5.17 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.27 (1 H, t, *J* 9 and 9 Hz, 3′-H), and 5.96 (1 H, s br, 6-H).

Preparation of (E)-3-(*t-Butyldimethylsilyloxy*)-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*buta*-1,3-*diene* (**1g**).—t-Butyldimethylsilyl triflate (0.55 cm^3, 2.4 mmol) was added in drops to a stirred solution of the butenone (**14a**)[7] (0.500 g, 1.2 mmol) and dry triethylamine (0.34 cm^3, 2.4 mmol) in dry dichloromethane (10 cm^3). After 1 h, the mixture was treated with triethylamine (1 cm^3), diluted with dichloromethane, and washed with aqueous sodium hydrogen carbonate. Evaporation of the dried ($MgSO_4$) organic layer and purification of the resultant orange oil by low-temperature chromatography on silica gel [light petroleum–Et_2O (3:2) as eluant] gave the *title compound* (**1g**) (0.570 g, 89%) as a white solid. After recrystallisation from diethyl ether–light petroleum, the sample was obtained as white needles, m.p. 112—114 °C; $[\alpha]_D$ −12° (*c* 0.9% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester CO) and 1 645 and 1 620 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 235 nm (ε 12 400); δ(300 MHz; $CDCl_3$) 0.20 (6 H, s, Me_2Si), 0.98 (9 H, s, Me_3CSi), 2.03, 2.05, 2.07, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.82 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.11—4.18 (3 H, m, 6′-H and 4′-H_2), 4.27 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.80 (1 H, d, *J* 8 Hz, 1′-H), 5.11 and 5.12 (each 1 H, t, *J* 9 and 9 Hz, 2′- and 4′-H), 5.26 (1 H, t, *J* 9 and 9 Hz, 3′-H), 5.65 (1 H, d, *J* 12 Hz, 2-H), and 6.75 (1 H, d, *J* 12 Hz, 1-H) [in an n.O.e.d. experiment, irradiation of the signal at δ 4.80 enhanced that at δ 3.82 by 12%, that at δ 5.26 by 8%, that at δ 5.65 by 8%, and that at δ 6.75 by 18%; irradiation of the signal at δ 5.65 caused a 3% enhancement of a part of that at δ 4.11—4.18 (the singlet at δ 4.17) and a 3% enhancement of that at δ 4.80; irradiation of the signal at δ 6.75 enhanced that at δ 4.80 by 8%]; *m/z* (c.i.) 331 ($C_{14}H_{19}O_9^+$, 79%) and 169 (100) (Found: C, 54.1; H, 7.3. $C_{24}H_{38}O_{11}Si$ requires C, 54.3; H, 7.2%).

Reaction of the Butadiene (**1g**) *with* N-*Phenylmaleimide and Hydrolysis of the Major Cycloadduct* (**2g**).—A mixture of the butadiene (**1g**) (0.200 g, 0.38 mmol) and *N*-phenylmaleimide (0.065 g, 0.38 mmol) in dry benzene (2 cm^3) was left for 48 h at ambient temperature. Evaporation of the solvent gave a residue which comprised mainly an 85:15 mixture of the cycloadducts (**2g**) and (**3g**) according to 300 MHz ^{1}H n.m.r. spectroscopy [the ratio was estimated from the heights of the singlets at δ 1.93 and 1.96, ascribed to acetoxy groups of compounds (**3g**) and (**2g**), respectively]. Addition of diethyl ether to the product and filtration gave (1R,2R,3S)-5-(*t-butyldimethylsilyloxy*)-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**2g**) (0.187 g, 70%) as a white solid. The sample, after recrystallisation from dichloromethane–light pet-

roleum, was obtained as needles, m.p. 168—170 °C; $[\alpha]_D$ +70° (*c* 0.9% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester CO), 1 710 (imide CO), and 1 645 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 210sh nm (ε 16 600); δ(300 MHz; $CDCl_3$) 0.20 (6 H, s, Me_2Si), 0.94 (9 H, s, Me_3CSi), 1.53, 1.95, 2.00, and 2.08 (each 3 H, s, 4 × $MeCO_2$), 2.54 (1 H, dd, *J* 16 and 9 Hz, 6-Hα), 2.79 (1 H, dd, *J* 16 and 8 Hz, 6-Hβ), 3.18 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.39 (1 H, apparent q, separation 9 Hz, 1-H), 3.64 (1 H, ddd, *J* 10, 4, and 2 Hz, 5′-H), 4.06 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.21 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.63 (1 H, d, *J* 8 Hz, 1′-H), 4.76 (1 H, dd, *J* 7 and 4 Hz, 3-H), 4.81 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 5.04 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.12 (1 H, t, *J* 9 and 9 Hz, 3′-H), 5.18 (1 H, dd, *J* 7 and 3 Hz, 4-H), and 7.30—7.50 (5 H, s, Ph); *m/z* (f.a.b.) 646 ($M^+ - C_4H_8$, 1%), 356 (72), and 73 (100) (Found: C, 58.1; H, 6.3; N, 2.0; Si, 4.3. $C_{34}H_{45}NO_{13}Si$ requires C, 58.0; H, 6.45; N, 2.0; Si, 4.0%).

A mixture of the cycloadduct (**2g**) (0.084 g, 0.12 mmol) and 0.1M hydrochloric acid (1 cm^3) in THF (5 cm^3) was left for 1 h at ambient temperature. The solution was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer gave material (0.049 g, 70%) which was identified as compound (**23b**) on the basis of its m.p. of 198—202 °C (lit.,[2] 205—207 °C) and 300 MHz ^{1}H n.m.r. spectrum.

Reaction of the Butadiene (**1g**) *with Tetracyanoethylene.*—A mixture of the diene (**1g**) (0.200 g, 0.377 mmol) and tetracyanoethylene (0.048 g, 0.377 mmol) in dry benzene (2 cm^3) was left for 2 h. Evaporation of the solvent gave a white solid, which comprised mainly a 70:30 mixture of the cycloadducts (**6g**) and (**7g**) on the basis of 300 MHz ^{1}H n.m.r. spectroscopy [the ratio was estimated from the heights of the singlets at δ 0.92 and 0.94 ascribed to the t-butyl groups of compounds (**6g**) and (**7g**), respectively]. Crystallisation of the product from ethyl acetate–light petroleum gave (3S)-1,1,2,2-*tetracyano*-5-(*t-butyldimethylsilyloxy*)-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-*cyclohex*-4-*ene* (**6g**) (0.148 g, 58%) as white needles, m.p. 173—174 °C; $[\alpha]_D$ +19° (*c* 1% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 760 (ester CO) and 1 670 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 204 nm (ε 10 400); δ(300 MHz; $CDCl_3$) 0.25 (6 H, s, Me_2Si), 0.95 (9 H, s, Me_3CSi), 2.04, 2.07, 2.12, and 2.14 (each 3 H, s, 4 × $MeCO_2$), 2.98 (1 H, d, *J* 18 Hz, 6-Hβ), 3.15 (1 H, dt, *J* 18, 2, and 2 Hz, 6-Hα), 3.81 (1 H, ddd, *J* 10, 4, and 3 Hz, 5′-H), 4.22 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.29 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.94 (1 H, s br, 3-H), 4.96 (1 H, d, *J* 8 Hz, 1′-H), 5.12 (1 H, s br, 4-H), 5.14 (2 H, t, separation 9 Hz, 2′- and 4′-H), and 5.28 (1 H, t, *J* 9 and 9 Hz, 3′-H); *m/z* (f.a.b.) 601 ($M^+ - C_4H_9$, 12%), 463 (20), and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 54.9; H, 5.8; N, 8.5; Si, 4.1. $C_{30}H_{38}N_4O_{11}Si$ requires C, 54.7; H, 5.8; N, 8.5; Si, 4.25%).

Preparation of (E)-2-*Methyl*-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*pent*-1-*en*-3-*one* (**14e**) (*with E. Hart*).—The salt (**19b**)[29] (2.50 g, 18.4 mmol) was added to a stirred solution of the acetobromoglucose (**17**)[12] (5.00 g, 12.2 mmol) in dry dimethyl sulphoxide (50 cm^3). After 30 min, the mixture was poured onto ice–water and extracted (×4) with dichloromethane. After being washed with water (×3), the organic extracts were combined, dried ($MgSO_4$), and concentrated. Fractionation of the product by silica-gel chromatography [light petroleum–Et_2O (3:2) to remove impurities; Et_2O to elute the required material] gave the *title compound* (**14e**). After recrystallisation from diethyl ether–light petroleum, the material (0.303 g, 6%) was isolated as a white solid, m.p. 97—99 °C; $[\alpha]_D$ −10° (*c* 1% in $CHCl_3$); $\nu_{max.}$(KBr) 1 755 and 1 735 (ester CO) and 1 650 cm^{-1} (vinylogous ester CO); $\lambda_{max.}$(EtOH) 242 nm (ε 15 300); δ(300 MHz; $CDCl_3$) 1.09 (3 H, t, *J* 7 Hz, 5-H_3), 1.71 (3 H, d, *J* 1 Hz, 3-Me), 2.02, 2.03, 2.04, and 2.08 (each 3 H, s, 4 × $MeCO_2$), 2.55 (2 H, q, *J* 7 Hz, 4-H_2), 3.82 (1 H, ddd, *J* 10, 5, and 2.5 Hz, 5′-H), 4.15 (1 H, dd, *J* 12.5 and 2.5 Hz, 6′-H), 4.29 (1 H, dd, *J* 12.5 and 5 Hz, 6′-H), 4.89 (1 H, d, *J* 7 Hz, 1′-H), 5.10—5.30 (3 H, m, 2′-, 3′-, and 4′-H), and 7.35 (1 H, apparent d, separation 1 Hz, 1-H); *m/z* (f.a.b.) 445 (MH^+, 20%) and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 54.3; H, 6.4. $C_{20}H_{28}O_{11}$ requires C, 54.05; H, 6.35%).

Preparation of (1E,3Z)-3-(*t-Butyldimethylsilyloxy*)-2-*methyl*-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*penta*-1,3-*diene* (**1h**).—t-Butyldimethylsilyl triflate (0.124 cm^3, 0.54 mmol) was added to a stirred, cooled (CCl_4–solid CO_2) solution of the pentenone (**14e**) (0.200 g, 0.45 mmol) and dry triethylamine (0.127 cm^3, 0.91 mmol) in dry dichloromethane (5 cm^3). After 15 min, the mixture was concentrated and the residue was then subjected to low-temperature chromatography on silica-gel [light petroleum–Et_2O (1:1) as eluant] to give the *title diene* (**1h**) (0.157 g, 62%) as a syrup which showed $[\alpha]_D$ −25° (*c* 0.2% in CH_2Cl_2); $\nu_{max.}$(film) 1 760 (ester CO) and 1 660 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 238 nm (ε 16 200); δ(300 MHz; $CDCl_3$) 0.09 and 0.10 (each 3 H, s, Me_2Si), 0.99 (9 H, s, Me_3CSi), 1.61 (3 H, d, *J* 7 Hz, 5-H_3), 1.65 (3 H, d, *J* 1 Hz, 3-Me), 2.02, 2.03, 2.04, and 2.08 (each 3 H, s, 4 × $MeCO_2$), 3.75 (1 H, ddd, *J* 10, 5, and 2.5 Hz, 5′-H), 4.12 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.26 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.68 (1 H, d, *J* 8 Hz, 1′-H), 4.81 (1 H, q, *J* 7 Hz, 4-H), 5.07—5.18 (2 H, m, 2′- and 4′-H), 5.25 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 6.54 (1 H, s br, 1-H) (in an n.O.e.d. experiment, irradiation of the signal at δ 1.65 caused a 24% enhancement of that at δ 4.81; irradiation of the signal at δ 4.68 caused a 9% enhancement of that at δ 3.75 and a 16% enhancement of that at δ 6.54; irradiation of the signal at δ 6.54 enhanced that at δ 4.68 by 13%); *m/z* (f.a.b.) 559 (MH^+, 10%), 331 ($C_{14}H_{19}O_9^+$, 100), and 169 (100) (Found: C, 56.0; H, 7.9. $C_{26}H_{42}O_{11}Si$ requires C, 55.9; H, 7.6%).

Reaction of the Pentadiene (**1h**) *with* N-*Phenylmaleimide and Hydrolysis of the Cycloadduct* (**2h**).—A solution of the pentadiene (**1h**) (0.140 g, 0.25 mmol) and *N*-phenylmaleimide (0.043 g, 0.25 mmol) in dry benzene (1 cm^3) was left overnight. Evaporation of the solvent gave an off-white solid which was mainly the cycloadduct (**2h**) by 300 MHz ^{1}H n.m.r. spectroscopy [signals attributable to the cycloadduct (**3h**) were not detected]. Crystallisation of the material from dichloromethane–diethyl ether gave (1R,2R,3R,6S)-5-(*t-butyldimethylsilyloxy*)-4,6-*dimethyl*-N-*phenyl*-3-(1′,2′,3′,4′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**2h**) (0.143 g, 78%) as white crystals, m.p. 190—192 °C; $[\alpha]_D$ +21° (*c* 0.2% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 760, 1 750, and 1 740 (ester CO), 1 715 (imide CO), and 1 670 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 215sh nm (ε 14 000); δ(300 MHz; $CDCl_3$) 0.17 and 0.18 (each 3 H, s, Me_2Si), 0.96 (9 H, s, Me_3Si), 1.34 (3 H, d, *J* 7 Hz, 6-Me), 1.43, 1.93, 2.01, and 2.07 (each 3 H, s, 4 × $MeCO_2$), 1.75 (3 H, s, 4-Me), 2.83 (1 H, quintet, separation 7 Hz, 6-H), 3.34 (1 H, dd, *J* 11 and 5.5 Hz, 2-H), 3.42 (1 H, dd, *J* 11 and 8 Hz, 1-H), 3.70 (1 H, dt, *J* 10, 4, and 4 Hz, 5′-H), 4.15 (2 H, d, separation 4 Hz, 6′-H_2), 4.59 (1 H, d, *J* 5.5 Hz, 3-H), 4.72 (1 H, d, *J* 8 Hz, 1′-H), 4.85 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 4.99 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.15 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.30—7.50 (5 H, s, Ph); *m/z* (f.a.b.) 674 ($M^+ - C_4H_9$, 20%), 384 (100), and 73 (100) (Found: C, 58.8; H, 6.7; N, 1.8. $C_{36}H_{49}NO_{13}Si$ requires C, 59.1; H, 6.75; N, 1.9%).

A solution of the cycloadduct (**2h**) (0.100 g, 0.14 mmol) in THF (10 cm^3) was treated with 0.5M hydrochloric acid (5 cm^3). After 18 h, the mixture was poured onto water and extracted with dichloromethane. Evaporation of the dried ($MgSO_4$) organic layer and recrystallisation of the product from dichloromethane–diethyl ether gave (1R,2R,3S,4R,6S)-4,6-*dimethyl*-5-*oxo*-N-*phenyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**23c**) (0.054 g, 68%) as a white solid, m.p. 223—227 °C (decomp.); $[\alpha]_D$ −64° (*c* 0.1% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755 (ester CO) and 1 710 cm^{-1} imide CO; $\lambda_{max.}$(EtOH) 219 nm (ε 10 200); δ(300 MHz; $CDCl_3$) 1.22 (3

H, d, *J* 7 Hz, 4-Me), 1.27 (3 H, d, *J* 8 Hz, 6-Me), 1.58, 1.94, 2.01, and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.48 (1 H, dq, *J* 7 and 2 Hz, 4-H), 3.00—3.05 (1 H, m, 6-H), 3.57—3.67 (2 H, m, 1- and 2-H), 3.71 (1 H, ddd, *J* 10, 5, and 2.5 Hz, 5′-H), 4.13 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.25 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.77—4.80 (1 H, m, 3-H), 4.86 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 4.95 (1 H, d, *J* 8 Hz, 1′-H), 5.05 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.15 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 7.34—7.53 (5 H, s, Ph) (in an n.O.e.d. experiment, irradiation of the signal at δ 2.48 enhanced that at δ 1.22 by 2%, that at δ 3.00—3.05 by 4%, and that at δ 4.77—4.80 by 5%; irradiation of the signal at δ 3.03 caused a 3% enhancement of that at δ 1.27 and a 5% enhancement of that at δ 3.57—3.67; irradiation of the signal at δ 3.62 enhanced the signal at δ 2.48 by 3%, that at δ 3.00—3.05 by 18%, and that at δ 4.77—4.80 by 10%; when the signal at δ 4.78 was irradiated, that at δ 1.22 was enhanced by 1%, that at δ 2.48 by 6%, that at δ 3.57—3.67 by 5%, and that at δ 4.95 by 8%); *m/z* (f.a.b.) 640 (MNa$^+$, 1%) and 169 (100) (Found: C, 58.0; H, 5.7; N, 2.3. $C_{30}H_{35}NO_{13}$ requires C, 58.35; H, 5.7; N, 2.25%).

Reaction of the Pentadiene (**1h**) *with Tetracyanoethylene.*—A solution of the pentadiene (**1h**) (0.105 g, 0.19 mmol) and tetracyanoethylene (0.024 g, 0.19 mmol) in dry benzene (1 cm^3) was left overnight. Evaporation of the solvent gave a pale-yellow syrup which was considered to be an 89:11 mixture of the cycloadducts (**6h**) and (**7h**) by 300 MHz ^{1}H n.m.r. spectroscopy [the ratio was estimated from the integrals of the broad singlets at δ 4.74 and 4.79, ascribed to the 3-hydrogen atoms of compounds (**6h**) and (**7h**), respectively]. Trituration of the syrup with diethyl ether gave (3R,6S)-5-(*t-butyldimethylsilyloxy*)-1,1,-2,2-*tetracyano*-4,6-*dimethyl*-3-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene* (**6h**) (0.094 g, 73%) as a white solid, m.p. 211—213 °C; $[\alpha]_D$ −13° (*c* 0.1% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 770sh, 1 765, 1 745, and 1 735 (ester C=O) and 1 675 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 204 nm (ε 11 300); δ(300 MHz; $CDCl_3$) 0.14 and 0.18 (each 3 H, s, Me_2Si), 0.99 (9 H, s, Me_3Si), 1.60 (3 H, d, *J* 7 Hz, 6-Me), 1.71 (3 H, d, *J* 2 Hz, 4-Me), 1.99, 2.05, 2.07, and 2.10 (each 3 H, s, 4 × $MeCO_2$), 2.98 (1 H, q br, *J* 7 Hz, 6-H), 3.81 (1 H, ddd, *J* 10, 4.5, and 2.5 Hz, 5′-H), 4.21 (1 H, dd, *J* 12.5 and 4.5 Hz, 6′-H), 4.29 (1 H, dd, *J* 12.5 and 2.5 Hz, 6′-H), 4.73 (1 H, s br, 3-H), and 5.05—5.28 (4 H, m, 1′-, 2′-, 3′-, and 4′-H); *m/z* (f.a.b.) 629 ($M^+ - C_4H_9$, 4%), 463 (8), 331 ($C_{14}H_{19}O_9^+$, 31), and 73 (100) (Found: C, 55.7; H, 6.1; N, 8.1. $C_{32}H_{42}N_4O_{11}Si$ requires C, 55.95; H, 6.15; N, 8.2%).

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