Asymmetric Diels–Alder Reactions. Part 5.[1] Influence of Sugar Substituents upon the Diastereofacial Reactivity of (*E*)-3-(t-Butyldimethylsiloxy)-1-(D-glucopyranosyloxy)buta-1,3-dienes

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The 1-[3',4',6'-tri-*O*-acetyl-2'-*O*-(t-butyldimethylsilyl)-α-D-glucopyranosyloxy], 1-[2,',3',4'-tri-*O*-acetyl-6'-*O*-(t-butyldimethylsily)-α-D-glucopyranosyloxy], 1-(3',4',6'-tri-*O*-acetyl-2'-deoxy-α-D-glucopyranosyloxy), and 1-(2',3',4'-tri-*O*-acetyl-α-D-xylopyranosyloxy) derivatives of (*E*)-3-(t-butyldimethylsiloxy)buta-1,3-diene, *i.e.* (**6d–g**), and their β-anomers, *i.e.* (**11c–f**), have been prepared and their diastereofacial reactivities towards *N*-phenylmaleimide assessed. Whereas the 2'-*O*-(t-butyldimethylsilyl)-α-diene (**6d**) gave a 20:80 mixture of the cycloadducts (**9d**) and (**10d**), its β-anomer, *i.e.* (**11c**), afforded a 66:34 mixture of the cycloadducts (**12c**) and (**13c**) [the major cycloadducts having the (1*R*,2*R*,3*S*)-configuration]. The 6'-*O*-(t-butyldimethylsilyl)-α-diene (**6e**) gave a 71:29 mixture of the cycloadducts (**9e**) and (**10e**) [the major cycloadduct having the (1*S*,2*S*,3*R*)-geometry]; its β-anomer, *i.e.* (**11d**), afforded an 89:11 mixture of the cycloadducts (**12d**) and (**13d**) [the major product possessing the (1*R*,2*R*,3*S*)-stereochemistry]. Although no stereoselection was observed with the 2'-deoxy-α-diene (**6f**), an 80:20 mixture of the cycloadducts (**12e**) and (**13e**) [the major product having the (1*R*,2*R*,3*S*)-geometry] was formed in the case of its β-anomer, *i.e.* (**11e**). The diastereofacial reactivities of the α- and β-D-xylopyranosyldienes, *i.e.* (**6g**) and (**11f**), were found to be equal and opposite; thus, the α-diene (**6g**) yielded an 81:19 mixture of the cycloadducts (**9g**) and (**10g**) [the major product having the (1*S*,2*S*,3*R*)-configuration]. The stereostructure of the cycloadduct (**9g**) [(1*S*,2*S*,3*R*)-5-(t-butyldimethylsiloxy)-*N*-phenyl-3-(2',3',4'-tri-*O*-acetyl-α-D-xylopyranosyloxy)-cyclohex-4-ene-1,2-dicarboximide] was confirmed by an X-ray crystallographic analysis.

In earlier work,[2–4] we showed that the dienes (**1a–e**)† exhibited useful diastereofacial reactivities in cycloaddition reactions; for example, they reacted with *N*-phenylmaleimide (NPM) in benzene to give *ca.* 84:16 mixtures of the cycloadducts (**2a–e**) and (**3a–e**).‡ Significantly, the dienes (**1f–h**)—incorporating a methyl group at the 2-position—displayed better selectivities, affording only the cycloadducts (**2f–h**) with NPM.

To account for these results, it was suggested that the dienes (**1a–e**) underwent reaction by way of both the conformers (**4a–e**) (the major pathway) and (**5a–e**) whereas the dienes (**1f–h**) underwent reaction by way of only the conformers (**4f–h**). Thus, the cycloadducts (**2a–h**) were postulated to arise by *endo*-addition of the dienophile to the least-hindered 'top' faces of the conformers (**4a–h**); the cycloadducts (**3a–e**) were presumed to originate by *endo*-addition to the least-hindered 'top' faces of the conformers (**5a–e**) [although the possibility that they arose by *endo*-addition to the more-hindered 'bottom' faces of the conformers (**4a–e**) was not excluded].

On the basis of the aforecited model, it was predicted that the α-diene (**6a**) would undergo Diels–Alder reactions by way of the conformers (**7a**) and (**8a**) and that there would be a preference for dienophiles to add to the least-hindered 'top' face of the conformer (**7a**). Hence, the cycloadduct (**9a**) was expected to predominate over its diastereoisomer (**10a**) in the reaction with NPM. In the event,[1] the reaction led to a 55:45 mixture of the cycloadducts (**9a**) and (**10a**). Although the diene (**6a**) had displayed a diastereofacial reactivity which was opposite to that of its epimer (**1b**), the discrimination was much smaller than expected.

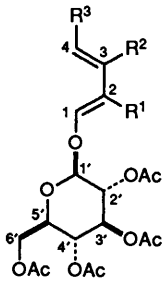
A study of the behaviour of the dienes (**6b** and **c**) and (**11a** and **b**) towards NPM in benzene revealed[1] that the diastereofacial reactivity was improved in the presence of a 6'-*O*-benzyl group and made worse in the presence of a 2'-*O*-benzyl group. Thus, the diene (**11a**) afforded only the cycloadduct (**12a**) whereas the diene (**11b**) gave rise to a 76:24 mixture of the cycloadducts (**12b**) and (**13b**). In the case of the diene (**6b**), a 69:31 mixture of the cycloadducts (**9b**) and (**10b**) was produced whereas, with the diene (**6c**), a 36:64 mixture of the cycloadducts (**9c**) and (**10c**) resulted.

It was suggested that the dienes (**11a** and **b**) underwent reaction mainly by way of the conformers (**14a** and **b**), and the dienes (**6b** and **c**) mainly by way of the conformers (**7b** and **c**). The benzyl group was considered to act as a more effective 'shield' than the acetyl group and, therefore, the 'bottom' face of the conformer (**14a**) and the 'top' face of the conformer (**14b**) were postulated to be less accessible than the corresponding faces of the conformer (**4b**). Similarly, the 'bottom' face of the conformer (**7b**) and the 'top' face of the conformer (**7c**) were envisaged to be more protected than the corresponding faces of the conformer (**7a**).

In this paper, we describe the synthesis of the dienes (**6d–g**) and (**11c–f**) and we assess their diastereofacial reactivities towards NPM.

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

‡ To facilitate comparisons, the cycloadducts are numbered in the manner shown in structure (**2**); derivatives of these compounds are numbered similarly. The α,β-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 stereochemistry is inverted).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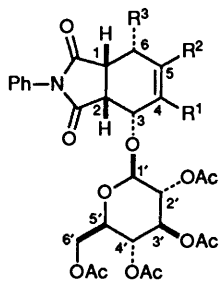
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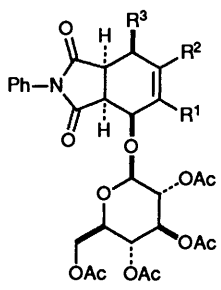
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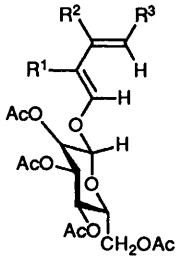
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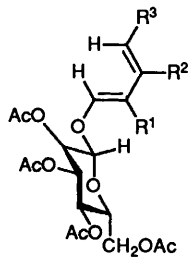
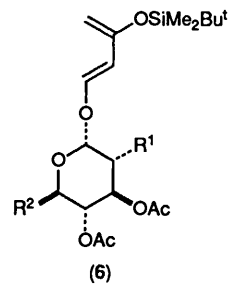

(5)

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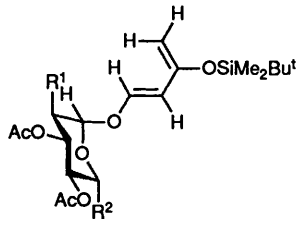
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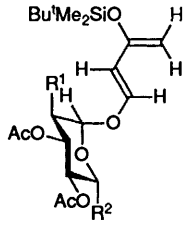
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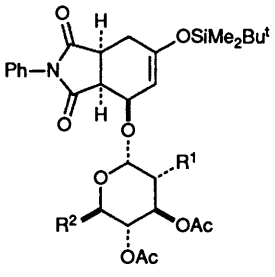
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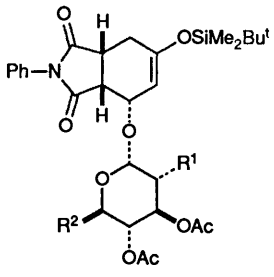

(10)

a; $R^1 = OAc$, $R^2 = CH_2OAc$
b; $R^1 = OAc$, $R^2 = CH_2OCH_2Ph$
c; $R^1 = OCH_2Ph$, $R^2 = CH_2OAc$
d; $R^1 = OSiMe_2Bu^t$, $R^2 = CH_2OAc$
e; $R^1 = OAc$, $R^2 = CH_2OSiMe_2Bu^t$
f; $R^1 = H$, $R^2 = CH_2OAc$
g; $R^1 = OAc$, $R^2 = H$

Results and Discussion

To determine whether the 'shielding' effect of the benzyl group was attributable to π-stacking or steric interactions, the dienes (**6d** and **e**) and (**11c** and **d**) were prepared.

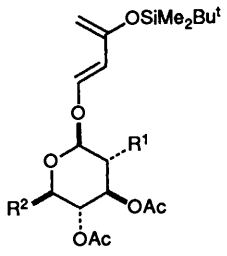
Compound (**15**)[5] [available from the reaction of the penta-acetate (**16**) with piperidine] was converted into the 2-*O*-(t-butyldimethylsilyl)-D-glucopyranose (**17a**) by treatment with t-butyldimethylsilyl triflate–triethylamine[6] in dichloromethane at 0 °C; the intermediate product was heated with acetic acid in aq. acetone. In the presence of *N*-methylmorpholine (NMM) and dichloromethane, butynone and compound (**17a**) underwent an addition reaction[1,7] to give a mixture of the glycosides (**18a**) and (**19a**), which was separated by chromatography. In the former product, obtained as an oil in 13% yield [based upon (**15**)], the anomeric hydrogen atom appeared as a doublet (*J* 4 Hz) at δ 5.17 in the 300 MHz ^1H NMR spectrum; in the latter product, which was isolated in a crystalline state in 11% yield [based upon (**15**)], it appeared as a doublet (*J* 8 Hz) at δ 4.71. In accord with Hudson's rule,[8] the optical rotation of the α-glucoside (**18a**) {$[\alpha]_D$ +129° (CH_2Cl_2)} was substantially more positive than that of its β-counterpart (**19a**) {$[\alpha]_D$ −5° ($CHCl_2$)}.

The butenones (**18a**) and (**19a**) were transformed into the dienes (**6d**) and (**11c**) in virtually quantitative yield by the action of t-butyldimethylsilyl triflate–triethylamine in dichloromethane at −20 °C. The dienes (**6d**) and (**11c**), isolated as slightly impure syrups after chromatography, were somewhat unstable and had to be processed rapidly. The anomeric hydrogen atom appeared as a doublet (*J* 4 Hz) at δ 5.05 in the case of the α-diene (**6d**) and as a doublet (*J* 8 Hz) at δ 4.57 in the case of the β-diene (**11c**).

The 6-*O*-benzyl-D-glucopyranose (**20a**)[1,9] served as the precursor of the dienes (**6e**) and (**11d**). Thus, it was converted *via* the alcohol (**20b**) (H_2, Pd/C, HOAc[10]), the silyl ether (**20c**) [Bu^tMe_2SiCl, imidazole, *N*,*N*-dimethylformamide (DMF)[11]], and the hemiacetal (**17b**) [NH_3, MeOH, tetrahydrofuran (THF)[12]], into the α-glucoside (**18b**) and its β-anomer (**19b**). After chromatography, the former product was isolated as a syrup in 41% overall yield, and the latter product as a crystalline solid in 8% overall yield. The anomeric hydrogen atom appeared as a doublet (*J* 3.5 Hz) at δ 5.50 in the α-glucoside (**18b**) and as a doublet (*J* 8 Hz) at δ 4.89 in the β-glucoside (**19b**). The optical rotation of compound (**18b**) {$[\alpha]_D$ +137° (CH_2Cl_2)} was substantially larger than that of its epimer (**19b**) {$[\alpha]_D$ +11° (CH_2Cl_2)}.

Under the usual enol silylation conditions, the butenones (**18b**) and (**19b**) were transformed into the dienes (**6e**) and (**11d**) in high yield. The anomeric hydrogen atom resonated as a doublet (*J* 4 Hz) at δ 5.34 in the former diene and as a doublet (*J* 8 Hz) at δ 4.74 in the latter diene.

The 2′-*O*-(t-butyldimethylsilyl)-α-diene (**6d**) reacted with NPM in benzene to give a 20:80 mixture of the cycloadducts (**9d**) and (**10d**); following chromatography, the minor cycloadduct (**9d**) was isolated as a slightly impure syrup in *ca.*



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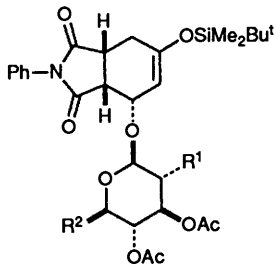

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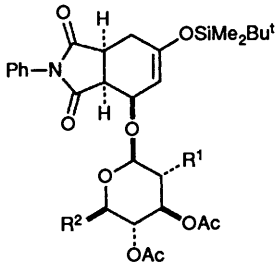

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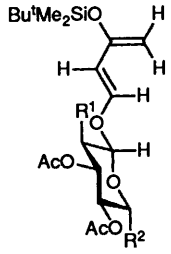
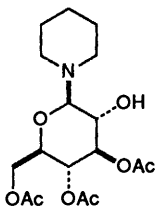


(14)

a; R^1 = OAc, R^2 = CH_2OCH_2Ph
b; R^1 = OCH_2Ph, R^2 = CH_2OAc
c; R^1 = $OSiMe_2Bu^t$, R^2 = CH_2OAc
d; R^1 = OAc, R^2 = $CH_2OSiMe_2Bu^t$
e; R^1 = H, R^2 = CH_2OAc
f; R^1 = OAc, R^2 = H



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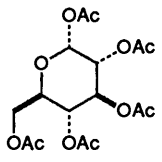

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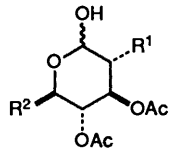

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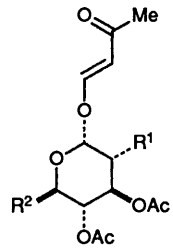

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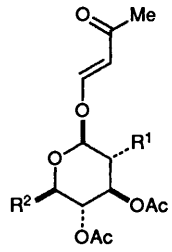
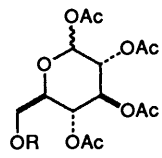


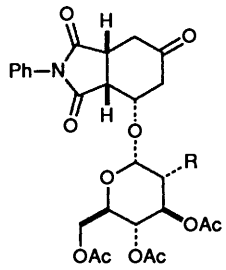
(19)

a; R^1 = $OSiMe_2Bu^t$, R^2 = CH_2OAc
b; R^1 = OAc, R^2 = $CH_2OSiMe_2Bu^t$
c; R^1 = H, R^2 = CH_2OAc
d; R^1 = OAc, R^2 = H



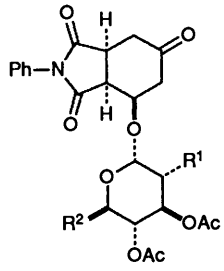
(20)

a; R = CH_2Ph
b; R = H
c; R = $SiMe_2Bu^t$



(21)

a; R = $OSiMe_2Bu^t$
b; R = OAc



(22)

a; R^1 = OAc, R^2 = CH_2OH
b; R^1 = OAc, R^2 = CH_2OAc
c; R^1 = OAc, R^2 = CH_2OCH_2Ph
d; R^1 = OAc, R^2 = H

13% yield, and the major cycloadduct (**10d**) as a pure foam in 64% yield. The stereostructures were assigned by CD spectroscopy; thus, the spectrum (MeCN) of compound (**9d**) featured a positive dichroism at 204 nm (Δε +6.0) and a negative one at 213 nm (Δε −13.0) whereas that of compound (**10d**) displayed a negative dichroism at 202 nm (Δε −8.1) and a positive one at 226 nm (Δε +10.6) [by comparison, compound (**9a**) exhibited dichroisms at 204sh (Δε −7.2), 214 (Δε −12.6), and 227sh nm (Δε −8.8), whereas compound (**10a**) possessed dichroisms at 202 (Δε −6.5) and 227 nm (Δε +10) [1]].

A 66:34 mixture of the cycloadducts (**12c**) and (**13c**) was produced in the reaction of the 2′-*O*-(t-butyldimethylsilyl)-β-diene (**11c**) with NPM. After chromatography, the major cycloadduct (**12c**) was isolated in a pure state in 33% yield, and the minor cycloadduct (**13c**) in an almost pure state in *ca.* 19% yield. The CD spectrum (MeCN) of the major cycloadduct (**12c**) displayed a negative dichroism at 199 nm (Δε −1.8) and a positive one at 222 nm (Δε +8.8) [by comparison, compound (**2a**) showed dichroisms at 212 (Δε −6.6), 238sh (Δε +6.8), and 247 nm (Δε +7.4), whereas compound (**3a**) showed dichroisms at 228 (Δε −3.8) and 248sh nm (Δε −2.8) [1]].

Acidic hydrolysis of the silyl enol ether (**10d**) afforded the ketone (**21a**) in 42% yield after recrystallisation. The hydrolysis of the cycloadduct (**12c**) was not examined.

The reaction of the 6′-*O*-(t-butyldimethylsilyl)-α-diene (**6e**) with NPM afforded a 71:29 mixture of the cycloadducts (**9e**) and (**10e**); following chromatography, the minor cycloadduct (**10e**) was isolated in 11% yield and the major cycloadduct (**9e**) in 42% yield. In the 300 MHz ^{1}H NMR spectra ($CDCl_3$), the acetyl methyl groups appeared at δ 1.95, 1.97, and 1.98 in the minor cycloadduct (**10e**) and at δ 1.32, 1.98, and 2.01 in the major cycloadduct (**9e**). The shielding of the 2′-acetyl methyl groups by the phenyl ring was noted earlier in the case of compounds (**9a** and **b**) [1] [but not for their counterparts (**10a** and **b**) [1]].

An 89:11 mixture of the cycloadducts (**12d**) and (**13d**) arose from the Diels–Alder reaction of the 6′-*O*-(t-butyldimethylsilyl)-β-diene (**11d**) with NPM. The major cycloadduct (**12d**) was isolated in 59% yield by crystallisation of the mixture; a small quantity of the minor cycloadduct (**13d**) was obtained in a slightly impure state by chromatographic fractionation of the mother liquor. In the 300 MHz ^{1}H NMR spectra ($CDCl_3$), the acetyl methyl groups resonated at δ 1.60, 1.95, and 1.99 in the major cycloadduct (**12d**) and at δ 1.89, 1.96, and 2.10 in the minor cycloadduct (**13d**). A similar shielding phenomenon of the 2′-acetyl methyl group was observed for compounds (**2a–h**) [2–4] and (**12a**) [1] [but not for compound (**3a**) [2]].

Acidic hydrolysis of the silyl enol ether (**9e**) afforded the ketone (**22a**) (57% yield after recrystallisation) in which the

2′-*O*-acetyl methyl group appeared at much higher field (δ 1.38) than the others (δ 2.01 and 2.07) [a similar shielding effect was noted for the ketones (**22b** and **c**) but not for their relative (**21b**)[1]]. Under comparable conditions, the silyl enol ether (**12d**) gave mainly the ketone (**23a**) in which the acetyl methyl groups resonated at δ 1.74, 1.97, and 2.02 [the acetyl methyl groups resonated at δ 1.56, 1.96, 2.01, and 2.12 in the ketone (**23b**) and at δ 1.97, 1.98, 2.01, and 2.04 in the ketone (**24**)[2]]; evidently, the 2′-*O*-acetyl methyl group was shielded to a lesser extent than in related compounds. When treated with acetic anhydride in pyridine, the alcohol (**22a**) was transformed into the acetate (**22b**)[1] in 69% yield and the alcohol (**23a**) was converted into the acetate (**23b**)[2] [68% yield based upon (**12d**)]. These results confirmed the stereochemical relationships between the cycloadducts (**10a** and **e**) and between the cycloadducts (**2b**) and (**12d**).

Clearly, in the case of α-dienes, the t-butyldimethylsilyl and benzyl groups exert a similar influence when located at the 6′-*O*-position of the sugar, both functions being more effective than the acetyl group in promoting the formation of the cycloadducts with the (1*S*,2*S*,3*R*)-configuration. When located at the 2′-*O*-position, the t-butyldimethylsilyl group promotes the formation of the cycloadduct with the (1*R*,2*R*,3*S*)-geometry to a greater extent than does the benzyl moiety; by contrast, the cycloadduct with the (1*S*,2*S*,3*R*)-configuration is marginally favoured when a 2′-*O*-acetyl group is present. In the case of β-dienes, the 6′-*O*-(t-butyldimethylsilyl) group is less effective than the 6′-*O*-benzyl group in inducing formation of the cycloadduct with the (1*R*,2*R*,3*S*)-configuration, both moieties being superior to the 6′-*O*-acetyl function for this purpose. When located at the 2′-*O*-position, the t-butyldimethylsilyl group promotes the formation of the cycloadduct with the (1*R*,2*R*,3*S*)-configuration to a lesser extent than does the benzyl group, both groups being inferior for this purpose to the acetyl function.

On the basis of the aforecited results, it appears unlikely that π-stacking interactions play a significant role in determining the diastereofacial reactivities of the dienes (**6b** and **c**) and (**11a** and **b**); steric factors are probably more relevant. To examine the consequences of removal of these steric effects, the dienes (**6f** and **g**) and (**11e** and **f**) were investigated.

3,4,6-Tri-*O*-acetyl-2-deoxy-D-glucopyranose (**17c**)[13] [obtained as a 4:1 mixture of the α- and the β-anomer from the reaction of the D-glucal (**25**)[14] with HBr in HOAc–CH_2Cl_2, followed by treatment with $AgNO_3$ in aq. Me_2CO] underwent an addition reaction with butynone in the presence of NMM to give a mixture of the glycosides (**18c**) and (**19c**). The α-anomer (**18c**), which was isolated in 17% yield after chromatography and crystallisation, displayed an optical rotation of +149° (CH_2Cl_2) whereas the β-anomer (**19c**), obtained as a slightly impure syrup in *ca.* 35% yield after chromatography, showed $[\alpha]_D$ −30° (CH_2Cl_2). A more efficient route to the β-anomer (**19c**) (69% yield after chromatography) involved treatment of compound (**17c**) in THF with the tosyl ester (**26a**) [generated *in situ* by addition of tosyl chloride to the salt (**26b**)[15]] followed by reaction with sodium hydride.[16]

Enol silylation of the butenones (**18c**) and (**19c**) gave the dienes (**6f**) and (**11e**), as slightly impure and somewhat unstable syrups, in yields of *ca.* 74 and 64%. The anomeric hydrogen atom appeared as a broad doublet (separation 3 Hz) at δ 5.27 in the α-diene (**6f**) and as a double doublet (*J* 8 and 1 Hz) at δ 4.87 in the β-diene (**11e**).

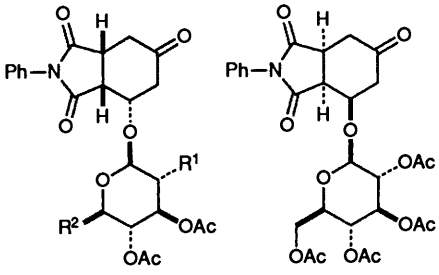
2,3,4-Tri-*O*-acetyl-D-xylose (**17d**)[17] [prepared from the reaction of the acetobromoxylose (**27a**)[18] with $AgNO_3$ in aq. Me_2CO] reacted with butynone in the presence of NMM to give a mixture of the glycosides (**18d**) and (**19d**), which was separated by chromatography. The α-xyloside (**18d**), isolated as a syrup in 32% yield after chromatography, displayed $[\alpha]_D$ +161° (CH_2Cl_2) whereas the β-xyloside (**19d**), obtained as a crystalline solid in 15% yield after chromatography, showed $[\alpha]_D$ −64° (CH_2Cl_2). A better route to the β-xyloside (**19d**) proceeded by way of the β-formyl derivative (**28**), prepared in 51% yield after recrystallisation, by treatment of the acetobromoxylose (**27a**) with silver(I) nitrate in formic acid. Compound (**28**) reacted with acetylmethylenetriphenylphosphorane in boiling ethyl acetate to give the β-xyloside (**19d**) in 65% yield after chromatography and crystallisation.

Enol silylation of the butenones (**18d**) and (**19d**) gave, after chromatography and crystallisation, the dienes (**6g**) and (**11f**) in yields of 49 and 52%. The anomeric hydrogen atom resonated as a doublet (*J* 3 Hz) at δ 5.28 in the α-diene (**6g**) and as a doublet (*J* 6 Hz) at δ 4.83 in the β-diene (**11f**). The optical rotation of the α-diene (**6g**) {$[\alpha]_D$ +129° (CH_2Cl_2)} was substantially more positive than that of its β-counterpart (**11f**) {$[\alpha]_D$ −40° (CH_2Cl_2)}.

The reaction of the 2′-deoxy-α-diene (**6f**) with NPM in benzene was non-selective, affording a 50:50 mixture of the cycloadducts (**9f**) and (**10f**). No attempt was made to separate the mixture.

An 80:20 mixture of the cycloadducts (**12e**) and (**13e**) was produced in the reaction of the 2′-deoxy-β-diene (**11e**) with NPM. Crystallisation of the mixture afforded the major cycloadduct (**12e**) in 49% yield. Its CD spectrum, which featured a positive dichroism at 226 nm (Δε +8.6), was similar to that of compound (**2a**), corroborating their common stereostructure. Acidic hydrolysis of the mixture of cycloadducts (**12e**) and (**13e**) gave, after crystallisation, the ketone (**23c**) in 48% yield.

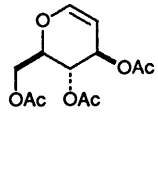
The Diels–Alder reaction of the α-xylose diene (**6g**) with NPM led to an 81:19 mixture of the cycloadducts (**9g**) and (**10g**). It was possible to isolate the major cycloadduct (**9g**) in a pure state by fractional crystallisation of the mixture; preparative HPLC gave pure samples of both the cycloadducts (**9g**) and (**10g**). The stereostructure of the cycloadducts was deduced on the basis of CD and NMR spectroscopy. Thus, the CD spectrum (MeCN) of the major cycloadduct (**9g**) was



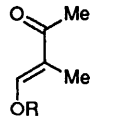
(**23**)

a; R^1 = OAc, R^2 = CH_2OH
b; R^1 = OAc, R^2 = CH_2OAc
c; R^1 = H, R^2 = CH_2OAc
d; R^1 = OAc, R^2 = H

(**24**)

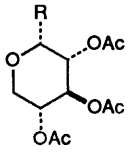


(**25**)



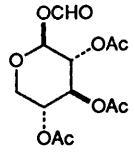
(**26**)

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



(**27**)

a; R = Br
b; R = OCHO



(**28**)

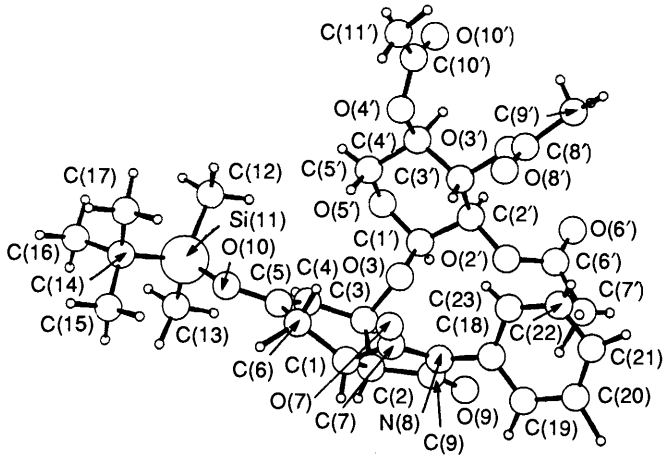


Figure. The molecular structure of compound (**9g**).

characterised by the presence of negative dichroisms at 218 ($\Delta\varepsilon$ −8.2) and 235 nm ($\Delta\varepsilon$ −7.5) [comparable with the spectrum observed for compound (**9a**) [1]], whereas that of the minor cycloadduct (**10g**) featured a negative dichroism at 202 nm ($\Delta\varepsilon$ −6.2) and a positive one at 227 nm ($\Delta\varepsilon$ +9.8) [very similar to the spectrum observed for compound (**10a**) [1]]. In the ^{1}H NMR spectrum of the major cycloadduct (**9g**), the acetyl methyl groups resonated at δ 1.32, 2.01, and 2.04; they resonated at δ 1.94, 198, and 2.01 in the major cycloadduct (**10g**).

Acidic hydrolysis of the mixture of the cycloadducts (**9g**) and (**10g**) gave the ketone (**22d**) in 51% yield after recrystallisation. Its CD spectrum (MeCN) incorporated dichroisms at 285 ($\Delta\varepsilon$ +3.4), 295 ($\Delta\varepsilon$ +3.7), 305 ($\Delta\varepsilon$ +3.0), and 315 nm ($\Delta\varepsilon$ +1.4) [by comparison, compound (**23b**) showed dichroisms at 295 ($\Delta\varepsilon$ −4.4), 303 ($\Delta\varepsilon$ −3.6), and 312sh nm ($\Delta\varepsilon$ −1.5) whereas compound (**24**) displayed dichroisms at 284 ($\Delta\varepsilon$ +2.9), 297 ($\Delta\varepsilon$ +3.2), 304 ($\Delta\varepsilon$ +2.5), and 312sh nm ($\Delta\varepsilon$ +1.2) [2]].

The β-xylose diene (**11f**) reacted with NPM to yield an 81:19 mixture of the cycloadducts (**12f**) and (**13f**) from which the major isomer was isolated in 48% yield after recrystallisation. On the basis of its CD spectrum [195 ($\Delta\varepsilon$ +2.4) and 225 nm ($\Delta\varepsilon$ +12.0)], the major cycloadduct was assigned the stereostructure (**12f**). In the ^{1}H NMR spectrum, the acetyl methyl groups resonated at δ 1.75, 1.95, and 2.04.

Acidic hydrolysis of the silyl enol ether (**12f**) gave the ketone (**23d**) (84% yield after recrystallisation), in which the acetyl methyl groups appeared at δ 1.59, 1.97, and 2.03.

Up until now, the stereostructures of the cycloadducts arising from the reactions of sugar-based dienes with NPM have not been rigorously established. The major cycloadduct arising from the reaction of the β-diene (**1a**) with the dienophile was assumed to possess the stereostructure (**2a**) by analogy with the result observed for *p*-benzoquinone (which was secured by X-ray evidence [2]). Other correlations, involving chemical and/or spectroscopic methods, hinged upon this assumption. To substantiate our inferences, an X-ray analysis was performed on the major cycloadduct obtained from the reaction of the α-xylose diene (**6g**) with NPM. The molecular structure (see Experimental section for crystal data and other information), together with its crystallographic numbering, is shown in the Figure. Refined fractional atomic co-ordinates are included in Table 1, selected bond lengths in Table 2, and selected bond angles in Table 3. Clearly, the cycloadduct possesses the stereostructure (**9g**) in accord with expectations. It is noteworthy that the 2′-*O*-acetyl methyl group lies within the shielding zone of the phenyl ring.

From the aforceited results, it is clear that the replacement of the 2′-acetoxy group by a hydrogen atom has only a very small effect on the diastereofacial reactivity of the corresponding dienes. Whereas the substitution of the 5′-acetoxymethyl group by hydrogen atom has only a small influence in the β-series, it has a marked effect in the α-series and promotes the formation of the cycloadduct with the (1*S*,2*S*,3*R*)-configuration.

The ratios of cycloadducts produced in the reactions of NPM with α- and β-dienes are collected in Tables 4 and 5. Clearly, the diastereofacial reactivity of α-dienes (Table 4) is very sensitive to substituent effects. In general, bulky 2′-substituents promote the formation of cycloadducts with the (1*R*,2*R*,3*S*)-configuration whereas bulky 6′-substituents favour the formation of cycloadducts with the (1*S*,2*R*,3*S*)-configuration. However, the latter cycloadducts are most favoured in the case of the α-xylose diene (**6g**), which lacks a 5′-oxymethyl group. The diastereofacial reactivity of β-dienes (Table 5) is less sensitive to substituent effects than is that of α-dienes. Cycloadducts with the (1*R*,2*R*,3*S*)-configuration always predominate but their formation is impeded by bulky 2′-substituents and promoted by bulky 6′-substituents. Again, however, the case of the β-xylose diene (**11f**), which lacks a 5′-oxymethyl group, is of note.

Evidently, a combination of steric, electronic, and conformational factors is implicated in determining the diastereofacial reactivity of sugar-based dienes.

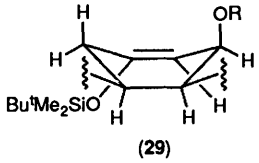
Conformational Considerations.—On the basis of vicinal spin–spin coupling constants, the cyclohexene ring of cycloadducts derived from D-glucose-derived dienes and NPM was previously considered to adopt a boat-like conformer in deuteriochloroform solution.[2,3] In the present study, we had the opportunity of comparing the cyclohexene ring geometry of the cycloadduct (**9g**) in solution and in the crystal state. The pertinent torsion angles, calculated from spin–spin coupling constants and obtained from X-ray analysis, are collected in Table 6. The results suggests that, in deuteriochloroform, the cyclohexene ring adopts the boat-like conformer (**29**) [a similar average conformational situation was postulated for the cyclohexene ring of the cycloadducts (**2a** and **f**) [2,3]]. In the crystal state, the cyclohexene ring possesses the flattened boat-like geometry (**30**).

The axial-like disposition of the xylopyranosyloxy substituent in compound (**9g**) is noteworthy; a similar phenomenon was observed earlier in related compounds.[2,3]. As before, we suggest that the axial-like orientation is stabilised by a through-space interaction between an electron pair on the oxygen atom and the π*-orbital of the 9-carbonyl group. Certainly, the O(3) • • • C(9)

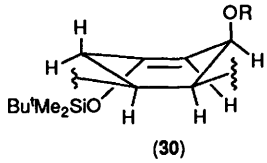
Table 1. Fractional atomic co-ordinates for compound (**9g**) with estimated standard deviations (esds) in parentheses.

Atom	*x*	*y*	*z*
C(1)	0.341 8(7)	0.344 2(2)	0.036 7(2)
C(2)	0.521 9(7)	0.304 3(2)	0.051 1(1)
C(3)	0.597 4(7)	0.335 5(2)	0.095 2(1)
O(3)	0.481 2(4)	0.300 6(1)	0.130 73(7)
C(4)	0.592 1(9)	0.429 5(3)	0.096 2(2)
C(5)	0.457 9(8)	0.470 7(3)	0.077 8(2)
C(6)	0.303 9(10)	0.433 1(3)	0.053 3(3)
C(7)	0.196 8(8)	0.282 5(2)	0.048 5(1)
O(7)	0.033 0(5)	0.293 1(2)	0.051 0(1)
N(8)	0.283 5(5)	0.204 6(2)	0.055 3(1)
C(9)	0.473 5(8)	0.211 0(3)	0.055 4(1)
O(9)	0.597 6(5)	0.154 7(2)	0.059 41(9)
O(10)	0.442 9(5)	0.556 4(2)	0.079 0(1)
Si(11)	0.569 3(3)	0.630 16(8)	0.101 08(5)
C(12)	0.570 5(12)	0.620 5(4)	0.162 7(2)
C(13)	0.803 0(9)	0.624 4(4)	0.078 4(3)
C(14)	0.459 6(10)	0.726 8(3)	0.082 0(2)
C(15)	0.425 8(15)	0.723 5(4)	0.031 1(3)
C(16)	0.567 2(13)	0.802 7(3)	0.093 3(3)
C(17)	0.279 9(14)	0.739 5(5)	0.105 1(3)
C(18)	0.189 0(7)	0.127 6(3)	0.062 6(2)
C(19)	0.226 0(9)	0.060 9(3)	0.035 3(2)
C(20)	0.128 7(15)	−0.015 0(4)	0.044 1(3)
C(21)	0.005 7(13)	−0.018 5(6)	0.079 3(3)
C(22)	−0.025 1(12)	0.049 2(6)	0.104 9(4)
C(23)	0.062 9(8)	0.123 0(4)	0.096 8(2)
C(1′)	0.571 3(7)	0.286 5(3)	0.171 6(1)
C(2′)	0.463 5(7)	0.221 2(3)	0.197 0(1)
O(2′)	0.441 2(4)	0.149 6(2)	0.168 35(8)
C(3′)	0.281 3(7)	0.253 1(3)	0.211 7(2)
O(3′)	0.197 8(5)	0.193 0(2)	0.241 1(1)
C(4′)	0.305 0(8)	0.334 2(3)	0.236 8(2)
O(4′)	0.129 4(5)	0.371 1(2)	0.244 6(1)
C(5′)	0.416 4(9)	0.394 6(3)	0.208 9(2)
O(5′)	0.590 4(5)	0.359 8(2)	0.197 35(9)
O(6′)	0.558 7(7)	0.063 6(2)	0.217 7(1)
C(6′)	0.501 5(7)	0.075 5(3)	0.181 9(2)
C(7′)	0.480 8(12)	0.013 9(4)	0.144 5(2)
O(8′)	−0.061 2(6)	0.189 5(3)	0.202 2(2)
C(8′)	0.024 0(9)	0.169 0(4)	0.233 9(2)
C(9′)	−0.048 1(13)	0.111 5(7)	0.270 5(3)
O(10′)	0.151 5(7)	0.352 1(4)	0.317 0(1)
C(10′)	0.061 7(10)	0.374 8(4)	0.286 7(2)
C(11′)	−0.126 1(17)	0.407 4(8)	0.288 8(4)

interatomic distance in compound (**9g**) (2.67 Å) is considerably less than the sum of the van der Waals radii of the atoms.



(29)



(30)

Experimental

Dry solvents, referred to in the ensuing experiments, were prepared as follows: dichloromethane was distilled from calcium chloride; DMF was stored over 4 Å molecular sieves; benzene was stored over sodium wire; THF was distilled from sodium–benzophenone. 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 siloxy compounds. Sodium hydride (80% dispersion in mineral oil) was washed (× 3) with light petroleum and dried *in vacuo* prior to use.

Table 2. Bond lengths for compound (**9g**) with esds in parentheses.

C(1)–C(2)	1.521(7)	C(1)–C(6)	1.532(7)
C(1)–C(7)	1.489(7)	C(2)–C(3)	1.511(6)
C(2)–C(9)	1.541(6)	C(3)–O(3)	1.464(5)
C(3)–C(4)	1.507(6)	O(3)–C(1′)	1.402(5)
C(4)–C(5)	1.300(8)	C(5)–C(6)	1.467(9)
C(5)–O(10)	1.379(5)	C(7)–O(7)	1.208(7)
C(7)–N(8)	1.413(5)	N(8)–C(9)	1.388(7)
N(8)–C(18)	1.429(5)	C(9)–O(9)	1.193(6)
O(10)–Si(11)	1.635(3)	Si(11)–C(12)	1.842(5)
Si(11)–C(13)	1.833(7)	Si(11)–C(14)	1.833(6)
C(14)–C(15)	1.53(1)	C(14)–C(16)	1.485(9)
C(14)–C(17)	1.49(1)	C(18)–C(19)	1.369(7)
C(18)–C(23)	1.374(8)	C(19)–C(20)	1.431(9)
C(20)–C(21)	1.38(1)	C(21)–C(22)	1.35(1)
C(22)–C(23)	1.37(1)	C(1′)–C(2′)	1.510(6)
C(1′)–O(5′)	1.409(5)	C(2′)–O(2′)	1.438(5)
C(2′)–C(3′)	1.489(7)	O(2′)–C(6′)	1.328(5)
C(3′)–O(3′)	1.436(6)	C(3′)–C(4′)	1.508(6)
O(3′)–C(8′)	1.340(8)	C(4′)–O(4′)	1.428(7)
C(4′)–C(5′)	1.511(8)	O(4′)–C(10′)	1.350(7)
C(5′)–O(5′)	1.427(7)	O(6′)–C(6′)	1.161(6)
C(6′)–C(7′)	1.495(8)	O(8′)–C(8′)	1.177(8)
C(8′)–C(9′)	1.52(1)	O(10′)–C(10′)	1.171(8)
C(10′)–C(11′)	1.47(2)		

Table 3. Bond angles (°) for compound (**9g**) with esds in parentheses.

C(6)–C(1)–C(2)	117.0(4)	C(7)–C(1)–C(2)	105.4(3)
C(7)–C(1)–C(6)	114.4(4)	C(3)–C(2)–C(1)	114.8(4)
C(9)–C(2)–C(1)	103.6(4)	C(9)–C(2)–C(3)	109.4(3)
O(3)–C(3)–C(2)	107.0(3)	C(4)–C(3)–C(2)	109.7(4)
C(4)–C(3)–O(3)	110.7(4)	C(1′)–O(3)–C(3)	114.7(3)
C(5)–C(4)–C(3)	121.2(5)	C(6)–C(5)–C(4)	125.1(4)
O(10)–C(5)–C(4)	123.6(5)	O(10)–C(5)–C(6)	111.2(4)
C(5)–C(6)–C(1)	113.9(5)	O(7)–C(7)–C(1)	128.4(4)
N(8)–C(7)–C(1)	107.7(4)	N(8)–C(7)–O(7)	123.8(4)
C(9)–N(8)–C(7)	112.4(4)	C(18)–N(8)–C(7)	124.7(4)
C(18)–N(8)–C(9)	122.9(3)	N(8)–C(9)–C(2)	107.4(4)
O(9)–C(9)–C(2)	126.4(5)	O(9)–C(9)–N(8)	126.1(4)
Si(11)–O(10)–C(5)	133.3(3)	C(12)–Si(11)–O(10)	110.0(3)
C(13)–Si(11)–O(10)	109.8(3)	C(13)–Si(11)–C(12)	111.0(4)
C(14)–Si(11)–O(10)	103.9(2)	C(14)–Si(11)–C(12)	112.5(3)
C(14)–Si(11)–C(13)	109.4(3)	C(15)–C(14)–Si(11)	110.3(4)
C(16)–C(14)–Si(11)	113.0(5)	C(16)–C(14)–C(15)	109.7(6)
C(17)–C(14)–Si(11)	110.7(5)	C(17)–C(14)–C(15)	108.6(7)
C(17)–C(14)–C(16)	104.3(6)	C(19)–C(18)–N(8)	119.3(4)
C(23)–C(18)–N(8)	118.7(4)	C(23)–C(18)–C(19)	122.0(5)
C(20)–C(19)–C(18)	117.2(6)	C(21)–C(20)–C(19)	119.6(7)
C(22)–C(21)–C(20)	120.4(8)	C(23)–C(22)–C(21)	121.3(9)
C(22)–C(23)–C(18)	119.4(6)	C(2′)–C(1′)–O(3)	107.6(4)
O(5′)–C(1′)–O(3)	112.6(3)	O(5′)–C(1′)–C(2′)	110.9(3)
O(2′)–C(2′)–C(1′)	108.4(3)	C(3′)–C(2′)–C(1′)	111.9(4)
C(3′)–C(2′)–O(2′)	110.4(4)	C(6′)–O(2′)–C(2′)	119.7(3)
O(3′)–C(3′)–C(2′)	109.1(4)	C(4′)–C(3′)–C(2′)	109.9(4)
C(4′)–C(3′)–C(3′)	109.0(4)	C(8′)–O(3′)–C(3′)	119.6(4)
O(4′)–C(4′)–C(3′)	109.6(4)	C(5′)–C(4′)–C(3′)	110.0(4)
C(5′)–C(4′)–O(4′)	107.8(4)	C(10′)–O(4′)–C(4′)	119.8(4)
O(5′)–C(5′)–C(4′)	111.0(4)	C(5′)–O(5′)–C(1′)	111.7(4)
O(6′)–C(6′)–O(2′)	123.0(4)	C(7′)–C(6′)–O(2′)	109.3(4)
C(7′)–C(6′)–O(6′)	127.7(4)	O(8′)–C(8′)–O(3′)	123.1(5)
C(9′)–C(8′)–O(3′)	112.7(6)	C(9′)–C(8′)–O(8′)	124.2(7)
O(10′)–C(10′)–O(4′)	119.9(6)	C(11′)–C(10′)–O(4′)	113.3(6)
C(11′)–C(10′)–O(10′)	126.8(7)		

Either a JASCO J40-CS or JASCO J600 spectropolarimeter was employed to measured CD spectra.[1]H NMR spectra were measured at 300 MHz with a Bruker AC 300. Mass spectra were recorded using a Kratos Concept 1S spectrometer. For other

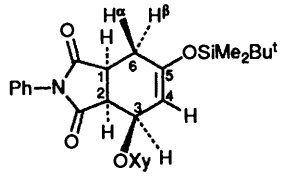
Table 4. Ratios of cycloadducts produced in the reactions of α-dienes with NPM.

Diene	Possible cycloadducts	Ratio
(**6a**)	(**9a**) and (**10a**)	55:45
(**6b**)	(**9b**) and (**10b**)	69:31
(**6c**)	(**9c**) and (**10c**)	36:64
(**6d**)	(**9d**) and (**10d**)	20:80
(**6e**)	(**9e**) and (**10b**)	71:29
(**6f**)	(**9f**) and (**10f**)	50:50
(**6g**)	(**9g**) and (**10g**)	81:19

Table 5. Ratios of cycloadducts produced in the reactions of β-dienes with NPM.

Diene	Possible cycloadducts	Ratio
(**1b**)	(**2b**) and (**3b**)	85:15
(**11a**)	(**12a**) and (**13a**)	76:24
(**11b**)	(**12b**) and (**13b**)	≥95:4
(**11c**)	(**12c**) and (**13c**)	66:44
(**11d**)	(**12d**) and (**13d**)	89:11
(**11e**)	(**12e**) and (**13e**)	80:20
(**11f**)	(**12f**) and (**13f**)	81:19

Table 6. Selected torsion angles (°) of compound (**9g**) determined from spin–spin coupling constants[a] (measured in $CDCl_3$) and X-ray analysis.



(**9g**; Xy = 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)

	Angle (from *J*)	Angle (from X-ray)
H^1,H^2	18	23
H^2,H^3	48	44
H^3,H^4		23
$H^1,H^{6\alpha}$	162	124
$H^1,H^{6\beta}$	31	9

[a] The spin–spin coupling constants (*J*) were converted into torsion angles (θ) by using the modified Karplus relationship: $J = 11 \cos^2 \theta$ (see L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, 1969, 2nd edn., p. 281).

instrumental and for chromatographic details, see earlier papers.[1–4]

Preparation of 3,4,6-*Tri*-O-*acetyl*-2-O-(*t-butyldimethylsilyl*)-D-*glucopyranose* (**17a**) *and its Reaction with Butynone.*—Butyldimethylsilyl triflate. (0.675 cm^3, 2.94 mmol) was added to a stirred, ice-cooled solution of compound (**15**)[5] (1.00 g, 2.68 mmol) and dry triethylamine (0.76 cm^3, 5.45 mmol) in dry dichloromethane (20 cm^3). After 30 min, the solvent was removed by evaporation and the residue was dissolved in 2:1 acetone–water (15 cm^3). Acetic acid (0.5 cm^3) was added and the solution was heated under reflux for 10 min. The cooled solution was partitioned between water and dichloromethane and the organic layer was washed successively with dil. hydrochloric acid, saturated aq. sodium hydrogen carbonate, and water. Evaporation of the dried ($MgSO_4$) organic phase left an oil (0.550 g) presumed to be the title silyl ether (**17a**). The material was dissolved in dry dichloromethane (5 cm^3) and the solution was treated with butynone (0.10 cm^3, 1.28 mmol) followed by NMM (1 drop). After 30 min, the solvent was removed by evaporation and the residue was subjected to silica gel chromatography [light petroleum–Et_2O (1:1) as eluant] to yield two fractions.

The first eluted material (0.167 g, 13%), isolated as a clear oil, was (E)-4-[3′,4′,6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*but*-3-*en*-2-*one* (**18a**); $[\alpha]_D$ +129° (0.34% in CH_2Cl_2); ν_{max}(film) 1 750 (ester C=O), 1 690 and 1 670 (vinylogous ester C=O), and 1 640 and 1 620 cm^{-1} (C=C); λ_{max}(EtOH) 240 nm (22 000); δ(300 MHz; $CDCl_3$) 0.06 and 0.08 (each 3 H, s, Me_2Si), 0.84 (9 H, s, Me_3C), 2.02, 2.04, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 2.20 (3 H, s, 1-H_3), 3.89 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.96 (1 H, ddd, *J* 10, 4, and 2 Hz, 5′-H), 4.03 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.29 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 5.03 (1 H, t, *J* 10 Hz, 4′-H), 5.17 (1 H, d, *J* 4 Hz, 1′-H), 5.37 (1 H, t, *J* 10 Hz, 3′-H), 5.94 (1 H, d, *J* 13 Hz, 3-H), and 7.47 (1 H, d, *J* 13 Hz, 4-H); *m/z* (CI) 506 ($M^+NH_4^+$, 45%), 489 (MH^+, 25), and 403 (100) (Found: C, 54.4; H, 7.4. $C_{22}H_{36}O_{10}Si$ requires C, 54.1; H, 7.45%).

The second eluted material (0.140 g, 11%), isolated as an oil which solidified with time, was (E)-4-[3′,4′,6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-β-D-*glucopyranosyloxy*]*but*-3-*en*-2-*one* (**19a**). After recrystallisation from diethyl ether–light petroleum, the sample showed m.p. 82–83 °C; $[\alpha]_D$ −5° (0.28% in CH_2Cl_2); ν_{max}(KBr) 1 755 (ester C=O), 1 675 (vinylogous ester C=O), and 1 640 cm^{-1} (C=C); λ_{max}(EtOH) 239 nm (18 300); δ(300 MHz; $CDCl_3$) 0.07 and 0.08 (each 3 H, s, Me_2Si), 0.83 (9 H, s, Me_3C), 2.03, 2.05, and 2.09 (each 3 H, s, 3 × $MeCO_2$), 2.21 (3 H, s, 1-H_3), 3.73–3.83 (2 H, m, 2′- and 5′-H), 4.10 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.30 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.71 (1 H, d, *J* 8 Hz, 1′-H), 5.00 (1 H, t, *J* 10 Hz, 4′-H), 5.14 (1 H, t, *J* 10 Hz, 3′-H), 5.83 (1 H, d, *J* 13 Hz, 3-H), and 7.45 (1 H, d, *J* 13 Hz, 4-H); *m/z* (CI) 393 (9%), 337 (71), and 320 (100) (Found: C, 53.8; H, 7.5%).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-[3′,4′,6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*buta*-1,3-*diene* (**6d**).—t-Butyldimethylsilyl triflate (0.170 cm^3, 0.74 mmol) was added to a stirred, cooled (CCl_4–solid CO_2) solution of the butenone (**18a**) (0.250 g, 0.51 mmol) and dry triethylamine (0.173 cm^3, 1.24 mmol) in dry dichloromethane (5 cm^3). After 15 min, the mixture was concentrated and the residue was subjected to low-temperature silica gel column chromatography [light petroleum–Et_2O (1:1) as eluant] to give the title diene (**6d**) (0.300 g, *ca.* 97%) as a slightly impure, somewhat unstable syrup; δ(300 MHz; $CDCl_3$) *inter alia* 0.05, 0.07, and 0.18 (3, 3, and 6 H, each s, 2 × Me_2Si), 0.85 and 0.96 (each 9 H, s, 2 × Me_3C), 2.02, 2.03, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 3.84 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.95–4.04 (2 H, m, 5′- and 6′-H), 4.15 and 4.16 (each 1 H, s, 4-H_2), 4.30 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 5.01 (1 H, t, *J* 10 Hz, 4′-H), 5.05 (1 H, d, *J* 4 Hz, 1′-H), 5.39 (1 H, t, *J* 10 Hz, 3′-H), 5.75 (1 H, d, *J* 12 Hz, 2-H), and 6.76 (1 H, d, *J* 12 Hz, 1-H).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-[3′,4′,6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-β-D-*glucopyranosyloxy*]*buta*-1,3-*diene* (**11c**)—The butenone (**19a**) (0.149 g, 0.30 mmol) was converted into the title diene (**11c**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After chromatography as before, the diene (**11c**) (0.184 g, *ca.* 100%) was isolated as a slightly impure, somewhat unstable syrup; δ(300 MHz; $CDCl_3$) *inter alia* 0.06, 0.08, and 0.18 (3, 3, and 6 H, each s, 2 × Me_2Si), 0.83 and 0.95 (each 9 H, s, 2 × Me_3C), 2.01, 2.04, and 2.07

(each 3 H, s, 3 × $MeCO_2$), 3.71 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 3.76 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.08 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.15 (2 H, s, 4-H_2), 4.27 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 4.57 (1 H, dd, *J* 8 Hz, 1′-H), 4.98 (1 H, t, *J* 10 Hz, 4′-H), 5.14 (1 H, t, *J* 10 Hz, 3′-H), 5.64 (1 H, d, *J* 12 Hz, 2-H), and 6.74 (1 H, d, *J* 12 Hz, 1-H).

Preparation of 2,3,4-*Tri*-O-*acetyl*-6-O-(*t-butyldimethylsilyl*)-D-*glucopyranose* (**17b**) *and its Reaction with Butynone.*—A mixture of 1,2,3,4-tetra-*O*-acetyl-6-*O*-benzyl-D-glucopyranose (**20a**)[1,9] (2.00 g, 4.56 mmol) (as a 50:50 mixture of α and β anomers) and 10% palladium–charcoal (0.20 g, 0.1 mass equiv.) was stirred in acetic acid (20 cm^3) under hydrogen for 6 h. The mixture was filtered through Celite and the filtrate was partioned between water and ethyl acetate. After having been washed successively with saturated aq. sodium hydrogen carbonate and by water, the organic phase was dried ($MgSO_4$) and concentrated to leave 1,2,3,4-tetra-*O*-acetyl-D-glucopyranose (**20b**) (1.20 g, 75%) as a 50:50 mixture of α and β anomers; δ(300 MHz, $CDCl_3$) 2.00, 2.01, 2.02, 2.03, 2.06, 2.07, 2.10, and 2.16 (each 1.5 H, s, 4 × $MeCO_2$), 2.35 (1 H, br s, OH), 3.53–3.79 (2.5 H, m, 0.5 × 5-H and 6-H_2), 3.92 (0.5 H, ddd, *J* 10, 4, and 2.5 Hz, 0.5 × 5-H), 5.03–5.13 (2 H, m, 2- and 4-H), 5.30 and 5.52 (each 0.5 H, t, *J* 10 Hz, 3-H), and 5.72 and 6.33 [each 0.5 H, d, (*J* 8 Hz) and d (*J* 3.5 Hz), 1-H].

A mixture of the alcohol (**20b**) (1.17 g, 3.36 mmol), t-butyldimethylsilyl chloride (0.610 g, 4.05 mmol), and imidazole (0.460 g, 6.76 mmol) in dry DMF (20 cm^3) was stirred overnight and then partitioned between water and diethyl ether. The organic phase was washed successively with dil. hydrochloric acid and water, dried ($MgSO_4$), and concentrated to leave a clear syrup which was predominantly the silyl ether (**20c**) as a 50:50 mixture of α and β anomers; δ(300 MHz; $CDCl_3$) *inter alia* 0.01, 0.02, 0.03, and 0.10 (each 3 H, s, 2 × Me_2Si), 0.871 and 0.874 (each 9 H, s, 2 × Me_3C), 2.008, 2.010, 2.018, 2.023, 2.028, 2.10, and 2.16 (1.5, 1.5, 1.5, 1.5, 3, 1.5, and 1.5 H, each s, 4 × $MeCO_2$), 3.60–3.80 (2.5 H, m, 0.5 × 5-H and 6-H_2), 3.87 (0.5 H, ddd, *J* 10, 4, and 2.5 Hz, 0.5 × 5-H), 5.02–5.25 (2.5 H, m, 2- and 4-H and 0.5 × 3-H), 5.46 (0.5 H, t, *J* 10 Hz, 0.5 × 3-H), and 5.69 and 6.33 [each 0.5 H, d (*J* 8 Hz) and d (*J* 3.5 Hz), 1-H].

The aforecited material was dissolved in a 7:3 mixture of THF–methanol (50 cm^3) and ammonia gas was bubbled through the solution, which was cooled in an ice-bath, for 10 min. After 35 min, the mixture was concentrated and the residue [presumed to be the title compound (**17b**)] was dissolved in dichloromethane (20 cm^3). Butynone (0.263 cm^3, 3.36 mmol) and NMM (1 drop) were added to the solution which was then stirred for 2 h and then concentrated. Purification of the residue by silica gel column chromatography [light petroleum–diethyl ether (1:1) as eluant] gave two fractions.

The first eluted material [0.667 g, 41% based on (**20a**)], isolated as a chromatographically homogeneous syrup, was (E)-4-[2′,3′,4′-*tri*-O-*acetyl*-6′-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*but*-3-*en*-2-*one* (**18b**); $[\alpha]_D$ +137° (0.15% in CH_2Cl_2); ν_{max}(film) 1 760 (ester C=O), 1 695 and 1 675 (vinylogous ester C=O), and 1 640 and 1 620 cm^{-1} (C=C); λ_{max}(EtOH) 239 nm (16 000); δ(300 MHz; $CDCl_3$) 0.03 (6 H, s, Me_2Si), 0.87 (9 H, s, Me_3C), 2.025, 2.031, and 2.07 (each 3 H, s, 3 × $MeCO_2$), 2.19 (3 H, s, 1-H_3), 3.62–3.72 (2 H, m, 6′-H_2), 3.80 (1 H, ddd, *J* 10, 4, and 3 Hz, 5′-H), 4.94 (1 H, dd, *J* 10 and 3.5 Hz, 2′-H), 5.14 (1 H, t, *J* 10 Hz, 4′-H), 5.50 (1 H, d, *J* 3.5 Hz, 1′-H), 5.52 (1 H, t, *J* 10 Hz, 3′-H), 5.93 (1 H, d, *J* 12.5 Hz, 3-H), and 7.43 (1 H, d, *J* 12.5 Hz, 4-H); *m/z* (FAB) 431 (2%), 403 (65), and 73 (100) (Found: C, 54.4; H, 7.7. $C_{22}H_{36}O_{10}Si$ requires C, 54.1; H, 7.45%).

The second eluted material was crystallised from diethyl ether–light petroleum to give (E)-4-[2′,3′,4′-*tri*-O-*acetyl*-6′-O-(*t-butyldimethylsilyl*)-β-D-*glucopyranosyloxy*]*but*-3-*en*-2-*one* (**19b**) [0.128 g, 8% based on (**20a**)]; m.p. 120–122 °C; $[\alpha]_D$ +11° (0.1% in CH_2Cl_2); ν_{max}(KBr) 1 760 and 1 750sh (ester C=O), 1 655 and 1 645 (vinylogous ester C=O), and 1 600 cm^{-1} (C=C); λ_{max}(EtOH) 238 nm (19 000); δ(300 MHz; $CDCl_3$) 0.02 and 0.03 (each 3 H, s, Me_2Si), 0.87 (9 H, s, Me_3C), 2.01, 2.03, and 2.05 (each 3 H, s, 3 × $MeCO_2$), 2.19 (3 H, s, 1-H_3), 3.60–3.78 (3 H, m, 5′-H and 6′-H_2), 4.89 (1 H, d, *J* 8 Hz, 1′-H), 5.09 (1 H, t, *J* 10 Hz, 4′-H), 5.11 (1 H, (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.23 (1 H, t, *J* 10 Hz, 3′-H), 5.83 (1 H, d, *J* 13 Hz, 3-H), and 7.43 (1 H, d, *J* 13 Hz, 4-H); *m/z* (FAB) 403 (65%), 241 (65), and 73 (100) (Found: C, 53.8; H, 7.5%).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-[2′,3′,4′-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*]*buta*-1,3-*diene* (**6e**).—The butenone (**18b**) (0.250 g, 0.51 mmol) was transformed into the title diene (**6e**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After chromatography as before, the *diene* (**6e**) (0.278 g, 90%) was isolated as a chromatographically homogeneous foam; $[\alpha]_D$ +104° (1.8% in CH_2Cl_2); ν_{max}(film) 1 755 (ester C=O) and 1 665 cm^{-1} (C=C); λ_{max}(EtOH) 239 nm (10 200); δ(300 MHz; $CDCl_3$) 0.02, 0.03, and 0.18 (3, 3, and 6 H, each s, 2 × Me_2Si), 0.88 and 0.95 (each 9 H, s, 2 × Me_3C), 2.01, 2.02, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 3.62–3.72 (2 H, m, 6′-H_2), 3.80 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.13 and 4.14 (each 1 H, s, 4-H_2), 4.91 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.16 (1 H, t, *J* 10 Hz, 4′-H), 5.34 (1 H, d, *J* 4 Hz, 1′-H), 5.52 (1 H, t, *J* 10 Hz, 3′-H), 5.72 (1 H, d, *J* 12 Hz, 2-H), and 6.72 (1 H, d, *J* 12 Hz, 1-H) (in an NOED spectroscopic study, irradiation of the signal at δ 5.34 enhanced those at δ 4.91, 5.72, and 6.72, by 18, 7.5, and 18%; irradiation of the signal at δ 5.72 caused a 2.5% enhancement of that at δ 5.34; when the signal at δ 6.72 was irradiated, a 5% enhancement of that at δ 5.34 resulted); *m/z* (FAB) 603 (MH^+, <1%), 403 (60), 336 (60), and 73 (100) (Found: C, 56.1; H, 8.6. $C_{28}H_{50}O_{10}Si$ requires C, 55.8; H, 8.35%).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*]-1-[2′,3′,4′-*tri*-O-*acetyl*-6′-O-(*t-butyldimethylsilyl*)-β-D-*glucopyranosyloxy*]*buta*-1,3-*diene* (**11d**).—The butenone (**19b**) (0.120 g, 0.24 mmol) was transformed into the title diene (**11d**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After chromatography as before, the title diene (**11d**) (0.138 g, 93%) was isolated as a white solid (although chromatographically homogeneous, the material failed to give an acceptable elemental analysis); m.p. 114–115 °C; $[\alpha]_D$ −12° (0.1% in CH_2Cl_2); ν_{max}(KBr) 1 750 and 1 735sh (ester C=O) and 1 640 cm^{-1} (C=C); λ_{max}(EtOH) 238 nm (18 300); δ(300 MHz; $CDCl_3$) 0.03, 0.04, and 0.18 (3, 3, and 6 H, each s, 2 × Me_2Si), 0.87 and 0.95 (each 9 H, s, 2 × Me_3C), 2.01, 2.02, and 2.04 (each 3 H, s, 3 × $MeCO_2$), 3.60 (1 H, br dt, *J* 10, 4, and 4 Hz, 5′-H), 3.67–3.77 (2 H, m, 6′-H_2), 4.13 (2 H, s, 4-H_2), 4.74 (1 H, d, *J* 8 Hz, 1′-H), 5.06 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.07 (1 H, t, *J* 10 Hz, 4′-H), 5.23 (1 H, t, *J* 10 Hz, 3′-H), 5.63 (1 H, d, *J* 12 Hz, 2-H), and 6.71 (1 H, d, *J* 12 Hz, 1-H) (in an NOED spectroscopic study, irradiation of the signal at δ 4.74 resulted in enhancements of 6, 5, and 11% of the signals at δ 5.23, 5.63, and 6.71; no enhancements were observed when the signal at δ 5.63 was irradiated; irradiation of the signal at δ 6.71 caused a 2.5% enhancement of that at δ 4.74); *m/z* (FAB) 402 (70%) and 240 (100).

Reaction of the 2′-O-(*t-Butyldimethylsilyl*)-α-*diene* (**6d**) *with NPM.*—A solution of the diene (**6d**) (0.142 g, 0.24 mmol) and NPM (0.043 g, 0.25 mmol) in dry benzene (1 cm^3) was left in the dark for 18 h. Evaporation of the solvent gave a white foam which comprised mainly a 20:80 mixture of the cycloadducts (**9d**) and (**10d**) by 300 MHz ^1H NMR spectroscopy [the ratio was estimated from the integrals of the singlets at δ 1.93 and 1.95, attributed to acetoxy groups of compounds (**10d**) and (**9d**),

and of the double doublets at δ 3.14 and 3.23, ascribed to the 2-hydrogen atoms of compounds (**9d**) and (**10d**)]. Subjection of the mixture to silica gel column chromatography [light petroleum–Et_2O (3:2) as eluant] gave two fractions.

The first eluted material (0.024 g, *ca.* 13%), isolated as a syrup, was mainly (1*S*,2*S*,3*R*)-5-(t-butyldimethylsiloxy)-*N*-phenyl-3-[3′,4′,6′-tri-*O*-acetyl-2′-*O*-(t-butyldimethylsilyl)-α-D-glucopyranosyloxy]cyclohex-4-ene-1,2-dicarboximide (**9d**); CD (MeCN) 204 (Δε +6.0) and 213 nm (Δε −13.0); δ(300 MHz; $CDCl_3$) *inter alia* 0.008, 0.015, 0.19, and 0.20 (each 3 H, s, 2 × Me_2Si), 0.81 and 0.94 (each 9 H, s, 2 × Me_3C), 1.95, 2.00, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 2.54 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.87 (1 H, ddd, *J* 17, 7, and 3 Hz, 6-H$^{\beta}$), 3.14 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.43 (1 H, dt, *J* 10, 10, and 7 Hz, 1-H), 3.73–3.82 (2 H, m, 2′- and 5′-H), 3.88 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.19 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.82 (1 H, dd, *J* 7 and 4 Hz, 3-H), 4.87–4.97 (2 H, m, 1′- and 4′-H), 5.16 (1 H, t, *J* 10 Hz, 3′-H), 5.23 (1 H, dd, *J* 7 and 3 Hz, 4-H), and 7.32–7.47 (5 H, m, Ph).

The second eluted material (0.117 g, 64%), isolated as a white foam, was (1R,2R,3S)-5-(*t-butyldimethylsiloxy*)-N-*phenyl*-3-[3′,4′,6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*cyclohex*-4-*ene*-1,2-*dicarboximide* (**10d**); $[\alpha]_D$ +64° (0.22% in CH_2Cl_2); CD (MeCN) 202 (Δε −8.1) and 226 nm (Δε +10.6); ν_{max}(KBr) 1 750 (ester C=O) and 1 715 cm^{-1} (imide C=O); λ_{max}(EtOH) 216sh nm (10 800); δ(300 MHz; $CDCl_3$) 0.00, 0.04, and 0.20 (3, 3, and 6 H, each s, 2 × Me_2Si), 0.82 and 0.93 (each 9 H, s, 2 × Me_3C), 1.93, 2.00, and 2.09 (each 3 H, s, 3 × $MeCO_2$), 2.53 (1 H, dd, *J* 16 and 10 Hz, 6-H$^{\alpha}$), 2.92 (1 H, ddd, *J* 16, 9, and 3 Hz, 6-H$^{\beta}$), 3.23 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.41 (1 H, q, separation 10 Hz, 1-H), 3.79 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.92–4.00 (1 H, m, 5′-H), 4.04 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.27 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.85–4.98 and 5.07–5.16 (3 and 2 H, each m, 1′-, 3-, 3′-, 4-, and 4′-H), and 7.38–7.52 (5 H, m, Ph); *m/z* (CI) 438 (81%) and 356 (100) (Found: C, 58.6; H, 7.4; N, 1.7. $C_{38}H_{57}NO_{12}Si_2$ requires C, 58.8; H, 7.4; N, 1.8%).

Preparation of (1R,2R,3S)-5-*Oxo*-N-*phenyl*-3-[3′-4′-6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*cyclohexane*-1,2-*dicarboximide* (**21a**).—0.1M-Hydrochloric acid (5 cm^3) was added to a stirred solution of the cycloadduct (**10d**) (0.100 g, 0.13 mmol) in THF (10 cm^3). After 2.5 days, the solution was poured onto water and the mixture was extracted with ethyl acetate. The organic layer was washed with water, dried ($MgSO_4$), and concentrated. Crystallisation of the residue from dichloromethane–diethyl ether gave the *title compound* (**21a**) (0.036 g, 42%); m.p. 233–224 °C; $[\alpha]_D$ +40° (0.6% in CH_2Cl_2); ν_{max}(KBr) 1 760 (ester C=O) and 1 720 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 210 nm (9 100); δ(300 MHz; $CDCl_3$) −0.01 and 0.07 (each 3 H, s, Me_2Si), 0.81 (9 H, s, Me_3C), 1.91, 2.01, and 2.06 (each 3 H, s, 3 × $MeCO_2$), 2.34 (1 H, dd, *J* 19 and 2 Hz, 4-H$^{\beta}$), 2.89 (1 H, dd, *J* 19 and 3 Hz, 4-H$^{\alpha}$), 2.95 (1 H, dd, *J* 16 and 8 Hz, 6-H$^{\alpha}$), 3.10 (1 H, dd, *J* 16 and 12 Hz, 6-H$^{\beta}$), 3.34 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.46 (1 H, ddd, *J* 12, 10, and 8 Hz, 1-H), 3.80 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 3.92 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.01 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.14 (1 H, dd, *J* 13 and 4 Hz, 6′-H), 4.86 (1 H, d, *J* 4 Hz, 1′-H), 4.88–4.98 (2 H, m, 3- and 4′-H), 5.16 (1 H, t, *J* 10 Hz, 3′-H), and 7.40–7.60 (5 H, m, Ph); *m/z* (FAB) 662 (MH^+, 5%), 403 (20), 316 (70), 283 (80), and 73 (100) (Found: C, 58.1; H, 6.4; N, 2.0. $C_{32}H_{43}NO_{12}Si$ requires C, 58.1; H, 6.55; N, 2.1%).

Reaction of the 2′-O-(*t-Butyldimethylsilyl*)-β-*diene* (**11c**) *with NPM*.—A solution of the diene (**11c**) (0.128 g, *ca.* 0.26 mmol) and NPM (0.035 g, 0.20 mmol) in dry benzene (1 cm^3) was left in the dark for 24 h. Evaporation of the solvent left a pale-yellow syrup which comprised mainly a 66:34 mixture of the cycloadducts (**12c**) and (**13c**) by 300 MHz ^1H NMR spectroscopy [the ratio was estimated from the heights of the singlets at δ 0.78 and 0.80, ascribed to methylsilyl groups of compounds (**13c**) and (**12c**), and from the integrals of the doublets at δ 4.43 and 4.51, attributed to the anomeric hydrogen atoms of compounds (**13c**) and (**12c**)]. Subjection of the mixture to silica gel column chromatography [light petroleum–Et_2O (1:1) as eluant] gave three fractions.

The first eluted material (0.055 g, 33%), isolated as a white foam, was (1R,2R,3S)-5-(*t-butyldimethylsiloxy*)-N-*phenyl*-3-[3′.4′.6′-*tri*-O-*acetyl*-2′-O-(*t-butyldimethylsilyl*)-β-D-*glucopyranosyloxy*]*cyclohex*-4-*ene*-1,2-*dicarboximide* (**12c**); $[\alpha]_D$ +106° (0.25% in CH_2Cl_2); CD (MeCN) 199 (Δε −1.8) and 222 nm (Δε +8.8); ν_{max}(KBr) 1 755 (ester C=O), 1 710 (imide C=O), and 1 650 cm^{-1} (C=C); λ_{max}(EtOH) 204 (21 200) and 215sh nm (16 000); δ(300 MHz; $CDCl_3$) −0.04, 0.00, and 0.25 (3, 3, and 6 H, each s, 2 × Me_2Si), 0.80 and 0.95 (each 9 H, s, 2 × Me_3C), 1.96, 1.99, and 2.01 (each 3 H, s, 3 × $MeCO_2$), 2.43 (1 H, dd, *J* 18 and 11 Hz, 6-H$^{\alpha}$), 2.97 (1 H, ddd, *J* 18, 6, and 2 Hz, 6-H$^{\beta}$), 3.17 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.37 (1 H, dt, *J* 11, 11, and 6 Hz, 1-H), 3.49 (1 H, dd, *J* 9 and 7 Hz, 2′-H), 3.56 (1 H, dt, *J* 10, 3, and 3 Hz, 5′-H), 4.02–4.12 (2 H, m, 6′-H_2), 4.51 (1 H, d, *J* 7 Hz, 1′-H), 4.92 (1 H, t, *J* 10 Hz, 4′-H), 4.98–5.11 (3 H, m, 3-, 3′-, and 4-H), and 7.29–7.50 (5 H, m, Ph); *m/z* (FAB) 890 [*M* $(C_6H_{15}Si)^+$, 5%], 356 (55), and 73 (100) (Found: C, 59.0; H, 7.6; N, 1.8. $C_{38}H_{57}NO_{12}Si$ requires C, 58.8; H, 7.4; N, 1.8%).

The second fraction (0.038 g, *ca.* 23%) was a 50:50 mixture of the cycloadducts (**12c**) and (**13c**).

The third fraction (0.032 g, *ca.* 19%), isolated as a clear syrup, was mainly (1*S*,2*S*,3*R*)-5-(t-butyldimethylsiloxy)-*N*-phenyl-3-[3′,4′,6′-tri-*O*-acetyl-2′-*O*-(t-butyldimethylsilyl)-β-D-glucopyranosyloxy]cyclohex-4-ene-1,2-dicarboximide (**13c**); δ(300 MHz; $CDCl_3$) *inter alia* −0.09 and −0.04 (each 3 H, s, Me_2Si), 0.19 and 0.20 (each 3 H, s, Me_2Si), 0.78 and 0.93 (each 9 H, s, 2 × Me_3C), 1.98, 2.00, and 2.07 (each 3 H, s, 3 × $MeCO_2$), 2.47 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.83 (1 H, ddd, *J* 17, 7, and 2 Hz, 6-H$^{\beta}$), 3.23 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.39 (1 H, dt, *J* 10, 10, and 7 Hz, 1-H), 3.54 (1 H, dd, *J* 8 and 7 Hz, 2′-H), 3.63–3.71 (1 H, m, 5′-H), 4.14–4.22 (2 H, m, 6′-H_2), 4.43 (1 H, d, *J* 7 Hz, 1′-H), 4.93–5.16 (4 H, m, 3-, 3′-, 4-, and 4′-H), and 7.34–7.51 (5 H, m, Ph).

Reaction of the 6′-O-(*t-Butyldimethylsilyl*)-α-*diene* (**6e**) *with NPM*.—A solution of the diene (**6e**) (0.274 g, 0.45 mmol) and NPM (0.079 g, 0.46 mmol) in dry benzene (2 cm^3) was left in the dark for 17 h. Evaporation of the solvent left a pale-yellow syrup which comprised a 71:29 mixture of the cycloadducts (**9e**) and (**10e**) by 300 MHz ^1H NMR spectroscopy [the ratio was estimated from the integrals of the singlets at δ 1.95 and 2.01, attributed to acetoxy groups of compounds (**10e**) and (**9e**)]. Subjection of the material to silica gel column chromatography [light petroleum–Et_2O (7:3 ⟶ 3:2); gradient elution] gave two fractions.

The first eluted material was crystallised from cold diethyl ether–light petroleum to give (1R,2R,3S)-5-(*t-butyldimethylsiloxy*)-N-*phenyl*-3-[2′,3′,4′-*tri*-O-*acetyl*-6′-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*cyclohex*-4-*ene*-1,2-*dicarboximide* (**10e**) (0.038 g, 11%); m.p. 109–111 °C; $[\alpha]_D$ +130° (0.3% in CH_2Cl_2); ν_{max}(KBr) 1 760 (ester C=O), 1 720 (imide C=O), and 1 650 cm^{-1} (C=C); λ_{max}(EtOH) 209 nm (15 200); δ(300 MHz; $CDCl_3$) 0.02, 0.03, 0.19, and 0.20 (each 3 H, s, 2 × Me_2Si), 0.88 and 0.93 (each 9 H, s, 2 × Me_3C), 1.95, 1.97, and 1.98 (each 3 H, s, 3 × $MeCO_2$), 2.54 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.66 (1 H, ddd, *J* 17, 8, and 2.5 Hz, 6-Hβ), 3.19 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.44 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.61 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 3.67 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 3.75 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.85 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 4.89 (1 H, dd, *J* 7 and 4 Hz, 3-H), 5.03 (1 H, t, *J* 10 Hz, 4′-H),

5.11 (1 H, dd, *J* 7 and 3 Hz, 4-H), 5.14 (1 H, d, *J* 4 Hz, 1'-H), 5.26 (1 H, t, *J* 10 Hz, 3'-H), and 7.35–7.60 (5 H, s, Ph); *m/z* (FAB) 725 (2%), 357 (70), and 74 (100) (Found: C, 58.7; H, 7.6; N, 1.8. $C_{38}H_{57}NO_{12}Si_2$ requires C, 58.8; H, 7.4; N, 1.8%).

The second eluted material was resubjected to chromatography to give (1S,2S,3R)-5-(*t-butyldimethylsiloxyl*)-N-*phenyl*-3-[2',3',4'-*tri*-O-*acetyl*-6'-O-(*t-butyldimethylsilyl*)-α-D-*glucopyranosyloxy*]*cyclohex*-4-*ene*-1,2-*dicarboximide* (**9e**) (0.147 g, 42%) as a chromatographically homogeneous glass; $[\alpha]_D$ −27° (0.16% in CH_2Cl_2); ν_{max}(KBr) 1 755 (ester C=O), 1 720 (imide C=O), and 1 655 cm^{-1} (C=C); λ_{max}(EtOH) 214sh nm (11 400); δ(300 MHz; $CDCl_3$) 0.016, 0.019, 0.19, and 0.20 (each 3 H, s, 2 × Me_2Si), 0.88 and 0.94 (each 9 H, s, 2 × Me_3C), 1.32, 1.98, and 2.01 (each 3 H, s, 3 × $MeCO_2$), 2.56 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.88 (1 H, ddd, *J* 17, 8, and 2.5 Hz, 6-H$^{\beta}$), 3.19 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.40 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.63 (2 H, d, separation 3 Hz, 6'-H_2), 3.71 (1 H, dt, *J* 10, 3, and 3 Hz, 5'-H), 4.60 (1 H, dd, *J* 7 and 5 Hz, 3-H), 4.68 (1 H, dd, *J* 10 and 4 Hz, 2'-H), 5.14 (1 H, d, *J* 4 Hz, 1'-H), 5.15 (1 H, t, *J* 10 Hz, 4'-H), 5.24 (1 H, dd, *J* 7 and 3 Hz, 4-H), 5.29 (1 H, t, *J* 10 Hz, 3'-H), and 7.30–7.50 (5 H, m, Ph); *m/z* (FAB) 727 (1%), 358 (60), and 74 (100) (Found: C, 59.2; H, 7.8; N, 1.8%).

Preparation of (1S,2S,3R)-5-*Oxo*-N-*phenyl*-3-(2',3',4'-*tri*-O-*acetyl*-α-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**22a**).—A solution of the cycloadduct (**9e**) (0.100 g, 0.13 mmol) in a mixture of THF (2 cm^3) and 0.1M-hydrochloric acid (2 cm^3) was left for 2.5 days and then partitioned between water and dichloromethane. After having been washed with water, the organic phase was dried ($MgSO_4$) and concentrated. Crystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave the *title compound* (**22a**) (0.040 g, 57%); m.p. 119–123 °C; $[\alpha]_D$ +170° (0.1% in CH_2Cl_2); ν_{max}(KBr) 3 500br (OH), 1 750 (ester C=O), and 1 715 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 203 (13 300) and 215 nm (10 100); δ(300 MHz; $CDCl_3$) 1.38, 2.01, and 2.07 (each 3 H, s, 3 × $MeCO_2$), 2.33 (1 H, br t, *J* 7 Hz, 6'-OH), 2.44 (1 H, dd, *J* 18 and 2 Hz, 4-H$^{\beta}$), 2.89 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 3.09 (1 H, dd, *J* 17 and 9 Hz, 6-H$^{\beta}$), 3.12 (1 H, dd, *J* 18 and 4 Hz, 4-H$^{\alpha}$), 3.35 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.42–3.58 (3 H, m, 1-, 5'-, and 6'-H), 3.67 (1 H, br ddd, *J* 13, 7, and 2 Hz, 6'-H), 4.65–4.73 (2 H, m, 2'- and 3-H), 4.95 (1 H, t, *J* 10 Hz, 4'-H), 5.25 (1 H, d, *J* 4 Hz, 1'-H), 5.31 (1 H, t, *J* 10 Hz, 3'-H), and 7.35–7.55 (5 H, m, Ph); *m/z* (FAB) 570 (*M*Na^+, 7%), 548 (*M*H^+, 4), and 109 (100) (Found: C, 56.7; H, 5.2; N, 2.3. $C_{26}H_{29}NO_{12}$ requires C, 57.05; H, 5.35; N, 2.55%).

Preparation of (1S,2S,3R)-5-*Oxo*-N-*phenyl*-3-(2',3',4',6'-*tetra*-O-*acetyl*-α-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**22b**).—The alcohol (**22a**) (0.015 g, 0.03 mmol) was treated with pyridine (0.5 cm^3) and acetic anhydride (0.5 cm^3) and, after 24 h, the mixture was partitioned between ethyl acetate and dil. hydrochloric acid. After having been washed successively with aq. sodium hydrogen carbonate and water, the organic phase was dried ($MgSO_4$) and concentrated. Crystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave the title compound (**22b**)[1] (0.011 g, 69%), identified by its 300 MHz ^{1}H NMR spectrum.

Reaction of the 6'-O-(*t-Butyldimethylsilyl*)-β-*diene* (**11d**) *with NPM*.—A solution of the diene (**11d**) (0.130 g, 0.22 mmol) and NPM (0.038 g, 0.22 mmol) in dry benzene (1 cm^3) was left in the dark for 17 h. Evaporation of the solvent left a residue which comprised an 89:11 mixture of the cycloadducts (**12d**) and (**13d**) by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the integrals of the singlets at δ 1.89 and 1.95, ascribed to acetoxy groups of compounds (**13d**) and (**12d**), and of the doublets at δ 4.57 and 4.61, attributed to the anomeric hydrogen atoms of compounds (**12d**) and (**13d**)]. Crystallisation of the material from cold diethyl ether–light petroleum gave (1R,2R,3S)-5-(*t-butyldimethylsiloxy*)-N-*phenyl*-3-[2',3',4'-*tri*-O-*acetyl*-6'-O-(*t-butyldimethylsilyl*)-β-D-*glucopyranosyloxy*]-*cyclohex*-4-*ene*-1,2-*dicarboximide* (**12d**) (0.099 g, 58%) as a hydrate; m.p. 170–171 °C; $[\alpha]_D$ +58° (0.4% in CH_2Cl_2); ν_{max}(KBr) 2 500br (OH), 1 760 (ester C=O), 1 715 (imide C=O), and 1 650 cm^{-1} (C=C); δ(300 MHz; $CDCl_3$) 0.03, 0.04, and 0.18 (3, 3, and 6 H, each 2 × Me_2Si), 0.88 and 0.94 (each 9 H, s, 2 × Me_3C), 1.60, 1.95, and 1.99 (each 3 H, s, 3 × $MeCO_2$), 2.49 (1 H, dd, *J* 16 and 10 Hz, 6-H$^{\alpha}$), 2.79 (1 H, ddd, *J* 16, 9, and 3 Hz, 6-H$^{\beta}$), 3.16 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.36 (1 H, dt, *J* 10, 10, and 9 Hz, 1-H), 3.47 (1 H, dt, *J* 10, 4, and 4 Hz, 5'-H), 3.63–3.73 (2 H, m, 6'-H_2), 4.61 (1 H, d, *J* 8 Hz, 1'-H), 4.77–4.84 (2 H, m, 2'-and 3-H), 5.04 (1 H, t, *J* 10 Hz, 4'-H), 5.13 (1 H, t, *J* 10 Hz, 3'-H), 5.19 (1 H, dd, *J* 7 and 3 Hz, 4-H), and 7.28–7.52 (5 H, m, Ph); *m/z* (FAB) 724 (1%), 357 (60), and 74 (100) (Found: C, 57.7; H, 7.2; N, 1.7. $C_{38}H_{57}NO_{12}Si_2 \cdot H_2O$ requires C, 57.5; H, 7.5; N, 1.75%).

The mother liquor from the aforecited crystallisation was subjected to silica gel column chromatography [light petroleum–Et_2O (2:1) as eluant] to give (1*S*,2*S*,3*R*)-5-(t-butyldimethylsiloxy)-*N*-phenyl-3-[2',3',4'-tri-*O*-acetyl-6'-*O*-(t-butyldimethylsilyl-β-D-glucopyranosyloxy]cyclohex-4-ene-1,2-dicarboximide (**13d**) (0.002 g, *ca.* 1%) containing a small amount of NPM; δ(300 MHz; $CDCl_3$) *inter alia* 0.06, 0.07, 0.23, and 0.25 (each 3 H, s, 2 × Me_2Si), 0.89 and 0.97 (each 9 H, s, 2 × Me_3C), 1.89, 1.96, and 2.10 (each 3 H, s, 3 × $MeCO_2$), 2.51 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.62 (1 H, ddd, *J* 17, 7, and 2 Hz, 6-H$^{\beta}$), 3.11 (1 H, dd, *J* 10 and 3 Hz, 2-H), 3.33–3.50 (2 H, m, 1- and 5'-H), 3.67 (2 H, d, separation 4 Hz, 6'-H_2), 4.57 (1 H, d, *J* 8 Hz, 1'-H), 4.89 (1 H, dd, *J* 10 and 8 Hz, 2'-H), 4.97 (1 H, t, *J* 10 Hz, 4'-H), 5.02–5.17 (3 H, m, 3-, 3'-, and 4-H), and 7.23–7.52 (m, Ph).

Hydrolysis of the Cycloadduct (**12d**) *and Reaction of the Product* (**23a**) *with Acetic Anhydride*.—A solution of the cycloadduct (**12d**) (0.055 g, 0.07 mmol) in THF (5 cm^3) containing 0.1M-hydrochloric acid (2 cm^3) was left for 17 h and then partitioned between water and dichloromethane. After having been washed with water, the organic phase was dried ($MgSO_4$) and concentrated to leave a white solid which was mainly (1*R*,2*R*,3*S*)-5-oxo-*N*-phenyl-3-(2',3',4'-tri-*O*-acetyl-β-D-glucopyranosyloxy)cyclohexane-1,2-dicarboximide (**23a**); δ(300 MHz; $CDCl_3$) *inter alia* 1.74, 1.97, and 2.02 (each 3 H, s, 3 × $MeCO_2$), 2.40 (1 H, dd, *J* 19 and 2 Hz, 4-H$^{\beta}$), 2.86 (1 H, dd, *J* 18 and 11 Hz, 6-H$^{\alpha}$), 2.94–3.12 (3 H, m, 4-H$^{\alpha}$, 6-H$^{\beta}$, and 6'-OH), 3.33 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.45 (1 H, ddd, *J* 11, 8, and 1 Hz, 1-H), 3.52–3.61 (3 H, m, 5'-H and 6'-H_2), 4.59 (1 H, d, *J* 8 Hz, 1'-H), 4.80–4.94 (3 H, m, 2'-, 3-, and 4'-H), 5.19 (1 H, t, *J* 10 Hz, 3'-H), and 7.30–7.53 (5 H, m, Ph).

The aforecited alcohol was treated with pyridine (1 cm^3) and acetic anhydride (1 cm^3) and, after 19 h, the mixture was partitioned between dichloromethane and dil. hydrochloric acid. After having been washed successively with aq. sodium hydrogen carbonate and water, the organic phase was dried ($MgSO_4$) and concentrated. Crystallisation of the residue 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] (0.028 g, 68%), identified by its 300 MHz ^{1}H NMR spectrum.

Preparation of 3,4,6-*Tri*-O-*acetyl*-2-*deoxy*-D-*glucopyranose* (**17c**) (*with M. M. L. Crilley*).—An ice-cooled solution of the glucal (**25**)[14] (5.00 g, 18.4 mmol) in dichloromethane (10 cm^3) was stirred with 45% hydrogen bromide in acetic acid (3.31 cm^3, 18.3 mol) for 1 h. The mixture was then poured onto water (100 cm^3), neutralised with saturated aq. sodium hydrogen

carbonate, and extracted with dichloromethane. After having been washed with water, the extract was dried ($MgSO_4$) and the solvent was removed by evaporation. The resultant syrup was dissolved in 3:1 acetone–water (30 cm^3), and silver(I) nitrate (3.11 g, 18.3 mol) was added to the stirred solution. After 1 h, the mixture was filtered and the filtrate was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and concentrated. Purification of the resultant oil by silica gel column chromatography [light petroleum–EtOAc (3:2) as eluant] and crystallisation of the product from diethyl ether–light petroleum gave the title compound (**17c**)[13] (1.08 g, 20%) which existed as a 4:1 mixture of α and β anomers in deuteriochloroform solution; m.p. 101–103 °C (lit.,[13] 93.5 °C); $[\alpha]_D$ +84° (1% in CH_2Cl_2) [lit.,[13] +86° (EtOH, after 10 min)]; ν_{max}(KBr) 3 400 (OH) and 1 730 cm^{-1} (ester C=O); δ(300 MHz; $CDCl_3$) 1.71 and 1.83 [0.2 and 0.8 H, br t (separation 12 Hz) and dt (separation 12 and 4 Hz), 2-H^{β}], 2.02, 2.04, 2.05, and 2.10 (2.4, 0.6, 3, and 3 H, each s, 3 × $MeCO_2$), 2.28 and 2.42 [0.8 and 0.2 H, dd (separation 12, 12, and 5 Hz) and dm (separation 12 Hz), 2-H^{α}], 2.90 and 3.40 [0.8 and 0.2 H, br s and br d (*J* 6 Hz), 1-OH], 3.65–3.70 (0.2 H, m, 0.2 × 5-H), 4.07–4.33 (2.8 H, m, 6-H_2 and 0.8 × 5-H), 4.93–5.10 (1.4 H, m, 0.2 × 1-H, 0.2 × 3-H, and 4-H), and 5.34–5.47 (1.6 H, m, 0.8 × 1-H and 0.8 × 3-H) [addition of D_2O caused the signals at δ 2.90 and 3.40 to disappear, the signal at δ 4.93–5.10 to appear as a dd (0.2 H, *J* 8 and 2 Hz) at δ 4.95, a t (1 H, *J* 10 Hz) at δ 5.03, and a m (0.2 H) centred at δ *ca.* 5.05, and the signal at δ 5.34–5.47 to appear as a ddd (*J* 12, 10, and 5 Hz) at δ 5.39 and a d (0.8 H, *J* 2 Hz) at δ 5.43]; *m/z* (CI) 273 (M^+ − OH, 20%) and 213 (100).

Reaction of 3,4,6-*Tri*-O-*acetyl*-2-*deoxy*-D-*glucopyranose* (**17c**) *with Butynone*.—Butynone (0.202 cm^3, 2.58 mmol) and NMM (1 drop) were added to a solution of the glucopyranose (**17c**) (0.750 g, 2.58 mmol) in dry dichloromethane (10 cm^3). After 30 min, the mixture was concentrated and the residue was subjected to silica gel column chromatography [light petroleum–Et_2O (1:4) as eluant] to yield two fractions.

The first eluted material was resubjected to column chromatography to give, after crystallisation from diethyl ether–light petroleum, (E)-4-(3′,4′,6′-*tri*-O-*acetyl*-2′-*deoxy*-α-D-*glucopyranosyloxy*)*but*-3-*en*-2-*one* (**18c**) (0.160 g, 17%); m.p. 99–100 °C; $[\alpha]_D$ +149° (0.25% in CH_2Cl_2); ν_{max}(KBr) 1 740 (ester C=O), 1 695 (vinylogous ester C=O), and 1 610 cm^{-1} (C=C); λ_{max}(EtOH) 241 nm (17 400); δ(300 MHz; $CDCl_3$) 1.94 (1 H, ddd, *J* 14, 12, and 4 Hz, 2′-H^{β}), 2.04, 2.05, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 2.20 (3 H, s, 1-H_3), 2.43 (1 H, ddd, *J* 14, 6, and 2 Hz, 2′-H^{α}), 3.92 (1 H, ddd, *J* 10, 5, and 2 Hz, 5′-H), 4.04 (1 H, dd, *J* 13 and 2 Hz, 6′-H), 4.30 (1 H, dd, *J* 13 and 5 Hz, 6′-H), 5.07 (1 H, t, *J* 10 Hz, 4′-H), 5.30 (1 H, ddd, *J* 12, 10, and 6 Hz, 3′-H), 5.42 (1 H, br d, separation 4 Hz, 1′-H), 5.89 (1 H, d, *J* 13 Hz, 3-H), and 7.48 (1 H, d, *J* 13 Hz, 4-H); *m/z* (FAB) 359 (MH^+, 20%) and 213 (100) (Found: C, 53.5; H, 6.1. $C_{16}H_{22}O_4$ requires C, 53.65; H, 6.20%).

The second eluted material was resubjected to column chromatography to give (*E*)-4-(3′,4′,6′-tri-*O*-acetyl-2′-deoxy-β-D-glucopyranosyloxy)but-3-en-2-one (**19c**) (0.325 g, *ca.* 35%) as a slightly impure syrup; $[\alpha]_D$ −30° (1.5% in CH_2Cl_2); ν_{max}(film) 1 750 (ester C=O), 1 690 and 1 670 (vinylogous ester C=O), and 1 640 and 1 620 cm^{-1} (C=C); λ_{max}(EtOH) 239 nm (11 200); δ(300 MHz; $CDCl_3$) *inter alia* 1.83–1.98 (1 H, m, 2′-H^{β}), 2.05, 2.06, and 2.09 (each 3 H, s, 3 × $MeCO_2$), 2.20 (3 H, s, 1-H_3), 2.49 (1 H, ddd, *J* 13, 5, and 2 Hz, 2′-H^{α}), 3.71–3.76 (1 H, m, 5′-H), 4.12 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.30 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 5.01–5.10 (3 H, m, 1′-, 3′-, and 4′-H), 5.82 (1 H, d, *J* 13 Hz, 3-H), and 7.48 (1 H, d, *J* 13 Hz, 4-H).

Reaction of 3,4,6-*Tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranose* (**17c**) *with* (E)-4-(p-*Tolylsulphonyloxy*)*but*-3-*en*-2-*one* (**26a**) (*with M. M. L. Crilley*).—Toluene-*p*-sulphonyl chloride (0.91 g, 4.77 mmol) was added to a stirred suspension of the sodium salt (**26b**)[15] (0.790 g, 7.31 mmol) in dry THF (15 cm^3) followed, after 20 min, by a solution of the pyranose (**17c**) (0.750 g, 2.59 mmol) in dry THF (5 cm^3) and then by sodium hydride (0.174 g, 7.25 mmol). After a further 1 h, the mixture was diluted with water and extracted with dichloromethane. The organic layer was washed with water, dried ($MgSO_4$), and concentrated. Purification of the residue by silica gel chromatography [light petroleum–EtOAc (3:2) as eluant] gave a syrup (0.640 g, 69%), which was identified as the butenone (**19c**) by 300 MHz ^1H NMR spectroscopy.

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-[3′,4′,6′-*tri*-O-*acetyl*-2′-*deoxy*-α-D-*glucopyranosyloxy*]*buta*-1,3-*diene* (**6f**).—The butenone (**18c**) (0.100 g, 0.28 mmol) was converted into the title diene (**6f**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After chromatography as before, the diene (**6f**) (0.098 g, *ca.* 74%) was isolated as slightly impure, somewhat unstable syrup; δ(300 MHz; $CDCl_3$) *inter alia* 0.18 (6 H, s, Me_2Si), 0.95 (9 H, s, Me_3C), 1.88 (1 H, ddd, *J* 13, 12, and 4 Hz, 2′-H^{β}), 2.03, 2.04, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 2.36 (1 H, ddd, *J* 13, 5, and 1 Hz, 2′-H^{α}), 3.90–4.03 (2 H, m, 5′- and 6′-H), 4.13 and 4.14 (each 1 H, s, 4-H_2), 4.34 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 5.06 (1 H, t, *J* 10 Hz, 4′-H), 5.27 (1 H, br d, separation 3 Hz, 1′-H), 5.35 (1 H, ddd, *J* 12, 10, and 5 Hz, 3′-H), 5.69 (1 H, d, *J* 12 Hz, 2-H), and 6.75 (1 H, d, *J* 12 Hz, 1-H).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-[3′,4′,6′-*tri*-O-*acetyl*-2′-*deoxy*-β-D-*glucopyranosyloxy*]*buta*-1,3-*diene* (**11e**).—The butenone (**19c**) (0.258 g, 0.72 mmol) was converted into the title diene (**11e**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After low-temperature silica gel column chromatography [light petroleum–Et_2O (7:3) as eluant], the diene (**11e**) (0.217 g, *ca.* 64%) was isolated as a slightly impure, somewhat unstable yellow oil; δ(300 MHz; $CDCl_3$) *inter alia* 0.20 (6 H, s, Me_2Si), 0.97 (9 H, s, Me_3C), 1.80–1.93 (1 H, m, 2′-H^{β}), 2.05 and 2.09 (6 and 3 H, each s, 3 × $MeCO_2$), 2.37–2.47 (1 H, m, 2′-H^{α}), 3.67–3.77 (1 H, m, 5′-H), 4.07–4.17 (3 H, m, 4-H_2 and 6′-H), 4.29 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.87 (1 H, dd, *J* 8 and 1 Hz, 1′-H), 4.96–5.13 (2 H, m, 3′- and 4′-H), 5.63 (1 H, d, *J* 12 Hz, 2-H), and 6.78 (1 H, d, *J* 12 Hz, 1-H).

Preparation of 2,3,4-*Tri*-O-*acetyl*-D-*xylopyranose* (**17d**).—Silver(I) nitrate (4.80 g, 28.3 mmol) was added to a stirred solution of the bromide (**27a**)[18] (8.00 g, 23.6 mmol) in 50% aq. acetone (100 cm^3). After 20 min, the mixture was filtered through Celite and the filtrate was partitioned between water and ethyl acetate. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from diethyl ether–light petroleum gave the α-anomer of the title compound (**17d**) (2.80 g, *ca.* 43%) as a slightly impure solid; m.p. 135–138 °C (lit.,[17] 138–141 °C); δ(300 MHz; $CDCl_3$) *inter alia* 2.028, 2.031, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 2.42 (1 H, br d, *J* 3.5 Hz, OH), 3.80 (1 H, dd, *J* 11 and 6 Hz, 5-H^{β}), 3.87 (1 H, t, *J* 11 Hz, 5-H^{α}), 4.83 (1 H, dd, *H* 10 and 3.5 Hz, 2-H), 4.95 (1 H, ddd, *J* 10, 9, and 6 Hz, 4-H), 5.37 (1 H, br t, *J* 3.5 Hz, 1-H), and 5.50 (1 H, t, *J* 9 Hz, 3-H).

Reaction of 2,3,4-*Tri*-O-*acetyl*-D-*xylopyranose* (**17d**) *with Butynone*.—A solution of the xylopyranose (**17d**)[17] (1.00 g, 3.6 mmol) (as mainly the α-anomer), butynone (0.312 cm^3, 4.0 mmol), and NMM (1 drop) in dry dichloromethane (10 cm^3) was stirred for 30 min. Evaporation and purification of the residue by silica gel column chromatography [light petroleum–Et_2O (7:3) as eluant] gave two fractions.

The first eluted material (0.393 g, 32%), isolated as a syrup,

was (E)-4-(2′,3′,4′-*tri*-O-*acetyl*-α-D-*xylopyranosyloxy*)*but*-3-*en*-2-*one* (**18d**); $[\alpha]_D$ +161° (1.4% in CH_2Cl_2); ν_{max}(film) 1 755 (ester C=O), 1 690 and 1 670 (vinylogous ester C=O), and 1 640 and 1 620 cm^{-1} (C=C); λ_{max}(EtOH) 239 nm (17 500); δ(300 MHz; $CDCl_3$) 2.04, 2.06, and 2.07 (each 3 H, s, 3 × $MeCO_2$), 2.20 (3 H, s, 1-H_3), 3.56 (1 H, t, *J* 11 Hz, 5′-H^{α}), 3.89 (1 H, dd, *J* 11 and 6 Hz, 5′-H^{β}), 4.92 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 5.02 (1 H, ddd, *J* 11, 10, and 5 Hz, 4′-H), 5.43 (1 H, d, *J* 4 Hz, 1′-H), 5.53 (1 H, t, *J* 10 Hz, 3′-H), 5.92 (1 H, d, *J* 13 Hz, 3-H), and 7.41 (1 H, d, *J* 13 Hz, 4-H); *m/z* (CI) 301 ($C_{13}H_{17}O_8^+$, 70%) and 112 (100) (Found: C, 52.0; H, 5.9. $C_{15}H_{20}O_9$ requires C, 52.35; H, 5.85%).

The second eluted material (0.192 g, 15%), isolated as a white solid, was (E)-4-(2′,3′,4′-*tri*-O-*acetyl*-β-D-*xylopyranosyloxy*)*but*-3-*en*-2-*one* (**19d**). After recrystallisation from dichloromethane–diethyl ether–light petroleum, the sample possessed m.p. 118–121 °C; $[\alpha]_D$ −64° (0.48% in CH_2Cl_2); ν_{max}(KBr) 1 760 and 1 745sh (ester C=O), 1 690 (vinylogous ester C=O), and 1 620 cm^{-1} (C=C); λ_{max}(EtOH) 239 nm (18 000); δ(300 MHz; $CDCl_3$) 2.07 and 2.08 (3 and 6 H, each s, 3 × $MeCO_2$), 2.20 (3 H, s, 1-H_3), 3.55 (1 H, dd, *J* 13 and 7 Hz, 5′-H^{α}), 4.16 (1 H, dd, *J* 13 and 5 Hz, 5′-H^{β}), 4.90–5.01 (3 H, m, 1′-, 2′-, and 4′-H), 5.17 (1 H, t, *J* 7 and 7 Hz, 3′-H), 5.83 (1 H, d, *J* 13 Hz, 3-H), and 7.43 (1 H, d, *J* 13 Hz, 4-H); *m/z* (CI) 362 (MNH_4^+, 11%) and 259 (100) (Found: C, 52.0; H, 5.6%).

Reaction of 2,3,4-*Tri*-O-*acetyl*-β-D-*xylopyranosyl Bromide* (**27a**) *with Formic Acid*.—Silver(I) nitrate (5.40 g, 31.8 mmol) was added to a stirred, ice-cooled solution of the bromide (**27a**)[18] (9.00 g, 26.5 mmol) in 98% formic acid (20 cm^3). After 30 min, the mixture was filtered through Celite and the filtrate was poured onto ice-cold water and shaken with dichloromethane. The organic phase was washed successively with water and aq. sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. Crystallisation of the product from cold dichloromethane–diethyl ether gave 2,3,4-*tri*-O-*acetyl*-1-O-*formyl*-β-D-*xylopyranose* (**28**) (4.13 g, 51%); m.p. 98–100 °C; $[\alpha]_D$ −7° (3.5% in CH_2Cl_2); ν_{max}(KBr) 1 740 cm^{-1} (ester C=O); λ_{max}(EtOH) 208 nm (800); δ(300 MHz; $CDCl_3$) 2.046, 2.051, and 2.054 (each 3 H, s, 3 × $MeCO_2$), 3.56 (1 H, dd, *J* 12 and 8 Hz, 5-H^{α}), 4.16 (1 H, dd, *J* 12 and 5 Hz, 5-H^{β}), 4.96 (1 H, dt, *J* 8, 8, and 5 Hz, 4-H), 5.04 (1 H, dd, *J* 8 and 6 Hz, 2-H), 5.19 (1 H, t, *J* 8 Hz, 2-H), 5.83 (1 H, d, *J* 6 Hz, 1-H), and 8.05 (1 H, s, OCHO); *m/z* (FAB) 259 (100%) (Found: C, 47.1; H, 5.3. $C_{12}H_{16}O_9$ requires C, 47.35; H, 5.30%).

Concentration of the filtrate gave a syrup (2.80 g, *ca.* 35%) which was very largely 2,3,4-tri-*O*-*acetyl*-1-*O*-*formyl*-α-D-*xylopyranose* (**27b**);[19] δ(300 MHz; $CDCl_3$) *inter alia* 2.02, 2.039, and 2.043 (each 3 H, s, 3 × $MeCO_2$), 3.73 (1 H, t, *J* 11 Hz, 5-H^{α}), 3.97 (1 H, dd, 11 and 6 Hz, 5-H^{β}), 4.98–5.09 (2 H, m, 2- and 4-H), 5.47 (1 H, t, *J* 10 Hz, 3-H), 6.37 (1 H, d, *J* 4 Hz, 1-H), and 8.14 (1 H, s, OCHO).

Reaction of the Formate (**28**) *with Acetylmethylenetriphenylphosphorane*.—A mixture of the formate (**28**) (3.00 g, 9.86 mmol) and acetylmethylenetriphenylphosphorane (4.71 g, 14.8 mmol) in ethyl acetate (50 cm^3) was heated under reflux for 18 h. Removal of the solvent, purification of the residue by silica gel column chromatography [light petroleum–Et_2O (3:7) as eluant], and crystallisation of the product from cold dichloromethane–diethyl ether gave the butenone (**19d**) (2.20 g, 65%), m.p. 116–118 °C, identified by its 300 MHz ^1H NMR spectrum.

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-(2′,3′,4′-*tri*-O-*acetyl*-α-D-*xylopyranosyloxy*)*buta*-1,3-*diene* (**6g**).—The butenone (**18d**) (0.557 g, 1.62 mmol) was converted into the title diene (**6g**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After chromatography as before and crystallisation of the product from diethyl ether–light petroleum, the *title diene* (**6g**) (0.437 g, 59%) showed m.p. 103–105 °C; $[\alpha]_D$ +129° (0.8% in CH_2Cl_2); ν_{max}(KBr) 1 760 (ester C=O) and 1 665 cm^{-1} (C=C); λ_{max}(EtOH) 238 nm (18 200); δ(300 MHz; $CDCl_3$) 0.18 (6 H, s, Me_2Si), 0.95 (9 H, s, Me_3Si), 0.95 (9 H, s, Me_3C), 2.03, 2.04, and 2.07 (each 3 H, s, 3 × $MeCO_2$), 3.58 (1 H, t, *J* 11 Hz, 5′-H^{α}), 3.82 (1 H, dd, *J* 11 and 6 Hz, 5′-H^{β}), 4.14 and 4.15 (each 1 H, s, 4-H_2), 4.88 (1 H, dd, *J* 10 and 3 Hz, 2′-H), 5.00 (1 H, ddd, *J* 11, 10, and 6 Hz, 4′-H), 5.28 (1 H, d, *J* 3 Hz, 1′-H), 5.54 (1 H, t, *J* 10 Hz, 3′-H), 5.75 (1 H, d, *J* 12 Hz, 2-H), and 6.71 (1 H, d, *J* 12 Hz, 1-H) (in an NOED spectroscopic study, irradiation of the signal at δ 5.28 caused enhancements of 23, 9, and 19% of the signals at δ 4.88, 5.75, and 6.71; irradiation of the signal at δ 5.75 enhanced that at δ 4.15 by 3% and that at δ 5.28 by 2%; irradiation of the signal at δ 6.71 resulted in a 5% enhancement of that at δ 5.28); *m/z* (CI) 459 (MH^+, 15%) and 259 (100) (Found: C, 54.7; H, 7.5. $C_{21}H_{34}O_9Si$ requires C, 55.0; H, 7.45%).

Preparation of (E)-3-(*t-Butyldimethylsiloxy*)-1-(2′.3′,4′-*tri*-O-*acetyl*-β-D-*xylopyranosyloxy*)*buta*-1,3-*diene* (**11f**).—The butenone (**19d**) (0.250 g, 0.73 mmol) was converted into the title diene (**11f**) by the method used to effect the (**18a**) ⟶ (**6d**) transformation. After chromatography as before and crystallisation of the product from light petroleum, the *title diene* (**11f**) (0.173 g, 52%) showed m.p. 54–55 °C; $[\alpha]_D$ −40° (0.8% in CH_2Cl_2); ν_{max}(KBr) 1 755 (C=O) and 1 670 cm^{-1} (C=C); λ_{max}(EtOH) 237 nm (17 400); δ(300 MHz; $CDCl_3$) 0.18 (6 H, s, Me_2Si), 0.95 (9 H, s, Me_3C), 2.067, 2.070, and 2.074 (each 3 H, s, 3 × $MeCO_2$), 3.51 (1 H, dd, *J* 12 and 7 Hz, 5′-H^{β}), 4.13 (2 H, s, 4-H_2), 4.16 (1 H, dd, *J* 12 and 4 Hz, 5′-H^{α}), 4.83 (1 H, d, *J* 6 Hz, 1′-H), 4.93 (1 H, dt, *J* 7, 7, and 4 Hz, 4′-H), 5.00 (1 H, dd, *J* 8 and 6 Hz, 2′-H), 5.16 (1 H, t, *J* 8 Hz, 3′-H), 5.64 (1 H, d, *J* 12 Hz, 2-H), and 6.72 (1 H, d, *J* 12 Hz, 1-H) (in an NOED spectroscopic study, irradiation of the signal at δ 4.83 enhanced those at δ 3.51, 5.16, 5.64, and 6.72 by 4, 8, 8, and 20%; irradiation of the signal at δ 5.64 resulted in a 3% enhancement of that at δ 4.83; when the signal at δ 6.72 was irradiated, that at δ 4.83 was enhanced by 7%); *m/z* (FAB) 459 (MH^+, 2%) and 259 (100) (Found: C, 54.7; H, 7.8. $C_{21}H_{34}O_9Si$ requires C, 55.0; H, 7.45%).

Reaction of the 2′-*Deoxy*-α-*diene* (**6f**) *with NPM*.—A solution of the diene (**6f**) (0.095 g, 0.20 mmol) and NPM (0.035 g, 0.20 mmol) in dry benzene (1 cm^3) was left for 15 h in the dark. Removal of the solvent afforded a syrup which comprised mainly a 50:50 mixture of the cycloadducts (**9f**) and (**10f**); δ(300 MHz; $CDCl_3$) *inter alia* 0.18, 0.19, and 0.20 (1.5, 3, and 1.5 H, each s, Me_2Si), 0.94 and 0.95 (each 4.5 H, s, Me_3C), 1.67 and 1.83 (each 0.5 H, ddd, *J* 14, 12, and 4 Hz, 2′-H^{β}), 1.96, 1.985, 1.993, 2.03, 2.088, and 2.094 (each 1.5 H, s, 3 × $MeCO_2$), 2.55 and 2.59 (each 0.5 H, dd, *J* 17 and 6 Hz, 6-H^{α}), 2.74 and 2.88 (each 0.5 H, dd, *J* 17, 8, and 3 Hz, 6-H^{β}), 3.21 and 3.24 (each 0.5 H, dd, *J* 11 and 5 Hz, 2-H), 3.38–3.49 (1 H, m, 1-H), 3.87–4.06 (2 H, m, 5′-and 6′-H), 4.30 (1 H, dd, *J* 12 and 4 Hz, 6′-H), 4.70 and 4.84 (each 0.5 H, dd, *J* 7 and 5 Hz, 3-H), 4.93–5.15 (3 H, m, 1′-, 3′-, and 4′-H), 5.18 and 5.21 (each 0.5 H, dd, *J* 7 and 3 Hz, 4-H), and 7.30–7.55 (5 H, m, Ph) (the signal for 2′-H^{α} was assumed to be obscured by the acetoxy signals).

Reaction of the 2′-*Deoxy*-β-*diene* (**11e**) *with NPM*.—A mixture of the diene (**11e**) (0.135 g, 0.29 mmol) and NPM (0.050 g, 0.29 mmol) in dry benzene (1 cm^3) was left in the dark for 16 h. Removal of the solvent left an off-white solid which comprised mainly an 80:20 mixture of the cycloadducts (**12e**) and (**13e**) by 300 MHz ^1H NMR spectroscopy [the ratio was estimated from the integrals of the dd's at δ 3.10 and 3.19, ascribed to the 2-hydrogen atoms of compounds (**13e**) and (**12e**), and of the dd's at δ 5.12 and 5.19, attributed to the 4-hydrogen atoms of compounds (**13e**) and (**12e**)]. Crystallisation of the mixture

from cold diethyl ether–light petroleum gave (1R,2R,3S)-5-(*t*-*butyldimethylsiloxy*)-N-*phenyl*-3-(3′,4′,6′-*tri*-O-*acetyl*-2′-*deoxy*-β-D-*glucopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**12e**) (0.091 g, 49%); m.p. 168–169 °C; $[\alpha]_D$ +85° (0.1% in CH_2Cl_2); CD (MeCN) 226 nm (Δε +8.6); ν_{max}(KBr) 1 755 (ester C=O), 1 715 (imide C=O), and 1 660 cm^{-1} (C=C); λ_{max}(EtOH) 214sh nm (10 900); δ(300 MHz; $CDCl_3$) 0.18 (6 H, s, Me_2Si), 0.93 (9 H, s, Me_3C), 1.99, 2.01, and 2.07 (each 3 H, s, 3 × $MeCO_2$), 2.11 (1 H, ddd, *J* 12, 5, and 2 Hz, 2-H$^{\alpha}$), 2.49 (1 H, dd, *J* 17 and 11 Hz, 6-H$^{\alpha}$), 2.80 (1 H, ddd, *J* 17, 7, and 3 Hz, 6-H$^{\beta}$), 3.19 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.41 (1 H, dt, *J* 10, 10, and 7 Hz, 1-H), 3.56 (1 H, ddd, *J* 10, 5, and 3 Hz, 5′-H), 4.07 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.21 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.63 (1 H, dd, *J* 9 and 2 Hz, 1′-H), 4.71 (1 H, dd, *J* 7 and 5 Hz, 3-H), 4.85–5.00 (2 H, m, 3′- and 4′-H), 5.19 (1 H, dd, *J* 7 and 3 Hz, 4-H), and 7.24–7.55 (5 H, m, Ph) (the signal for 2′-H$^{\beta}$ was partially obscured by the water signal at δ 1.58); *m*/*z* (FAB) 760 [*M* $(C_6H_{15}Si)^+$, 4%], 356 (70), and 73 (100) (Found: C, 59.2; H, 6.5; N, 2.1. $C_{32}H_{43}NO_{11}Si$ requires C, 59.5; H, 6.7; N, 2.15%).

Preparation of (1R,2R,3S)-5-*Oxo*-N-*phenyl*-3′,4′,6′-*tri*-O-*acetyl*-2′-*deoxy*-β-D-*glucopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**23c**).—A solution of the diene (**11e**) (0.166 g, 0.35 mmol) and NPM (0.061 g, 0.55 mmol) in dry benzene (1 cm^3) was left in the dark for 24 h. Evaporation of the solvent gave an oil, which was dissolved in THF (cm^3). 0.1M-Hydrochloric acid (1 cm^3) was added to the solution which, after 1 h, was partitioned between dichloromethane and water. The dried ($MgSO_4$) organic layer was concentrated and the residue was triturated with diethyl ether to give the *title compound* (**23c**) (0.089 g, 48%). After recrystallisation from dichloromethane–light petroleum, the sample displayed m.p. 197–198 °C; $[\alpha]_D$ −71° (0.5% in CH_2Cl_2); ν_{max}(KBr) 1 735 (ester C=O) and 1 710 cm^{-1} (ketone and imide C=O); λ_{max}(EtOH) 214sh nm (10 700); δ(300 MHz; $CDCl_3$) 1.60–1.75 (1 H, m, 2′-H$^{\beta}$), 2.03, 2.05, and 2.08 (each 3 H, s, 3 × $MeCO_2$), 2.23 (1 H, ddd, *J* 12, 5, and 2 Hz, 2′-H$^{\alpha}$), 2.39 (1 H, dd, *J* 18 and 2 Hz, 4-H$^{\beta}$), 2.85–3.00 (2 H, m, 6-H_2), 3.07 (1 H, dd, *J* 18 and 2 Hz, 4-H$^{\alpha}$), 3.26 (1 H, dd, *J* 9 and 3 Hz, 2-H), 3.39–3.49 (1 H, m, 1-H), 3.59 (1 H, ddd, *J* 9, 5, and 2 Hz, 5′-H), 4.13 (1 H, dd, *J* 12 and 2 Hz, 6′-H), 4.21 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.74 (1 H, dd, *J* 10 and 2 Hz, 1′-H), 4.82 (1 H, q, separation 3 Hz, 3-H), 4.88–5.04 (2 H, m, 3′-and 4′-H), and 7.24–7.26 and 7.42–7.58 (2 and 3 H, each m, Ph); *m*/*z* (FAB) 532 (*M*H^+, 7%) and 213 (100) (Found: C, 58.8; H, 5.4; N, 2.6. $C_{26}H_{29}NO_{11}$ requires C, 58.75; H, 5.5; N, 2.65%).

Reaction of the α-Xylose Diene (**6g**) *with NPM*.—(*a*) A mixture of the diene (**6g**) (0.250 g, 0.55 mmol) and NPM (0.095 g, 0.55 mmol) in dry benzene (2 cm^3) was left in the dark for 24 h. Removal of the solvent gave a syrupy residue which comprised an 81:19 mixture of the cycloadducts (**9g**) and (**10g**) by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the integrals of the singlets at δ 1.94 and 2.04, ascribed to acetoxy groups of compounds (**10g**) and (**9g**)]. The product was dissolved in diethyl ether and the solution was cooled; filtration gave white crystals (0.210 g, 61%) which comprised an 81:19 mixture of the cycloadducts (**9g**) and (**10g**). Two recrystallisations of this material from dichloromethane–diethyl ether afforded (1S,2S,3R)-5-(*t*-*butyldimethylsiloxy*)-N-*phenyl*-3-(2′,3′,4′-*tri*-O-*acetyl*-α-D-*xylopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**9g**); m.p. 185–187 °C; $[\alpha]_D$ −40° (0.2% in CH_2Cl_2); CD (MeCN) 218 (Δε −8.2) and 235 nm (Δε −7.5); ν_{max}(KBr) 1 760 (ester C=O), 1 705 (imide C=O), and 1 655 cm^{-1} (C=C); λ_{max}(EtOH) 214 nm (13 000); δ(300 MHz; $CDCl_3$) 0.18 and 0.19 (each 3 H, s, Me_2Si), 0.93 (9 H, s, Me_3C), 1.32, 2.01, and 2.04 (each 3 H, s, 3 × $MeCO_2$), 2.61 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.89 (1 H, ddd, *J* 17, 8, and 3 Hz, 6-H$^{\beta}$), 3.19 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.39–3.53 (2 H, m, 1-H and 5′-H$^{\alpha}$), 3.70 (1 H, dd, *J* 11 and 6 Hz, 5′-H$^{\beta}$), 4.57 (1 H, dd, *J* 7 and 5 Hz, 3-H), 4.62 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 4.90 (1 H, ddd, *J* 11, 10, and 6 Hz, 4′-H), 5.08 (1 H, d, *J* 4 Hz, 1′-H), 5.20 (1 H, dd, *J* 7 and 3 Hz, 4-H), 5.31 (1 H, t, *J* 10 Hz, 3′-H), and 7.34–7.48 (5 H, m, Ph); *m*/*z* (CI) 648 (*M*NH_3^+, 2%) and 294 (100) (Found: C, 58.7; H, 6.7; N, 2.2. $C_{31}H_{41}NO_{11}Si$ requires C, 58.95; H, 6.55; N, 2.2%).

(*b*) A mixture of the diene (**6g**) (0.200 g, 0.44 mmol) and NPM (0.076 g, 0.44 mmol) in dry benzene (2 cm^3) was left in the dark for 2.5 days. Removal of the solvent and subjection of the residue to preparative HPLC [hexane–EtOAc (4:1) as eluant] gave two fractions.

The first eluted material was crystallised from ethyl acetate–hexane to give the cycloadduct (**9g**) (0.158 g, 57%), m.p. 185–187 °C, identified by its 300 MHz ^{1}H NMR spectrum.

The second eluted material was crystallised from dichloromethane–diethyl ether–light petroleum to give (1R,2R,3S)-5-(*t*-*butyldimethylsiloxy*)-N-*phenyl*-3-(2′,3′,4′-*tri*-O-*acetyl*-α-D-*xylopyranoxyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**10g**) (0.016 g, 6%); m.p. 187–188 °C; $[\alpha]_D$ +153° (0.1% in CH_2Cl_2); CD (MeCN) 202 Δε −6.2) and 227 nm (Δε +9.8; ν_{max}(KBr) 1 760 (ester C=O), 1 720 (imide C=O), and 1 650 cm^{-1} (C=C); λ_{max}(EtOH) 214sh nm (11 200); δ(300 MHz; $CDCl_3$) 0.196 and 0.202 (each 3 H, s, Me_2Si), 0.93 (9 H, s, Me_3C), 0.93 (9 H, s, Me_3C), 1.94, 1.98, and 2.01 (each 3 H, s, 3 × $MeCO_2$), 2.56 (1 H, dd, *J* 17 and 10 Hz, 6-H$^{\alpha}$), 2.69 (1 H, ddd, *J* 17, 8, and 3 Hz, 6-H$^{\beta}$), 3.21 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.41 (1 H, dt, *J* 10, 10, and 8 Hz, 1-H), 3.51 (1 H, t, *J* 11 Hz, 5′-H$^{\alpha}$), 3.72 (1 H, dd, *J* 11 and 6 Hz, 5′-H$^{\beta}$), 4.81 (1 H, dd, *J* 10 and 4 Hz, 2′-H), 4.85–4.94 (2 H, m, 3-and 4′-H), 5.07–5.12 (2 H, m, 1′- and 4-H), 5.26 (1 H, t, *J* 10 Hz, 3′-H), and 7.40–7.60 (5 H, m, Ph); *m*/*z* (FAB) 574 (4%), 356 (80), and 73 (100) (Found: C, 58.7; H, 6.4; N, 2.3. $C_{31}H_{41}NO_{11}Si$ requires C, 58.95; H, 6.55; N, 2.2%).

Crystal Data for Compound (**9g**).—$C_{31}H_{41}N_{11}Si$, *M*, 631.74. Orthorhombic, *a* = 7.283(2), *b* = 16.021(2), *c* = 29.786(3) Å, *V* = 3 475.4 Å^3, space group $P2_12_12_1$, *Z* = 4, D_c = 1.21 g cm^{-3}, *F*(000) = 1 344.0. Crystal dimensions: 0.3 × 0.3 × 0.4 mm, μ = 0.086 mm^{-1}.

Data collection and processing. An Enraf-Nonius CAD4 diffractometer was employed using graphite-monochromated Mo–K_{α} radiation in ω–2θ scan mode with ω scan width = 0.50 + 0.35 tan θ, and ω scan speed in the range 0.5–5.0° min^{-1} depending on the intensity gathered in a pre-scan; 4 911 reflections were measured ($-3 \leq h \leq 8$, $0 \leq k \leq 19$, $0 \leq l \leq 35$, $0 \leq \theta \leq 25°$), yielding 3 809 unique structure factors (R_{int} 0.012) of which 3 093 were observed [$F \geq 3\sigma F$]. The intensity standards (1 −6 −8, 2 −5 −7, 4 0 0), measured every 2.5 h, showed 11% decomposition. Lorentz and polarisation corrections were applied but absorption effects were ignored.

Structure analysis and refinement. Direct methods (MULTAN-80[20]) were used to solve the phase problem and to locate non-hydrogen atoms. Difference Fourier maps, produced during the course of full-matrix least-squares refinement (SHELX-76[21]), were employed to locate the hydrogen atoms except for those associated with the silyl group, which were constrained to chemically reasonable positions. A final *R*-value of 0.052 was obtained {R_w 0.051, w = 1.937 30/[$\sigma^2(|F_o|)$ + 0.000 20 F_o^2], $\sigma|F_o|$ from counting statistics} with non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The maximum shift/esd on the final cycle was 0.09. Fluctuations in the final difference Fourier map were in the range −0.3 to 0.2 e Å^{-3}. Neutral atom-scattering factors were obtained from 'International Tables for X-Ray Crystallography;'[22] computations were carried out on the Amdahl 5890 computer of the University of Manchester Regional Computing Centre. Fractional atomic co-ordinates are presented in Table 1, bond

lengths in Table 2, and bond angles in Table 3.* The molecule and its atomic labelling, drawn using PLUTO,[23] is displayed in the Figure.

Preparation of (1S,2S,3R)-5-*Oxo*-N-*phenyl*-3-(2′,3′,4′-*tri*-O-*acetyl*-α-D-*xylopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**22d**).—A solution of the diene (**6g**) (0.200 g, 0.44 mol) and NPM (0.076 g, 0.44 mmol) in dry benzene (2 cm^3) was left in the dark for 2.5 h. Evaporation of the solvent left a residue, which was dissolved in THF (5 cm^3). 0.1M-Hydrochloric acid (2 cm^3) was added to the solution which, after 22 h, was partitioned between water and dichloromethane. The organic phase was washed with water, dried ($MgSO_4$), and concentrated. Crystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave the *title compound* (**22d**) (0.118 g, 51%); m.p. 227–229 °C; $[\alpha]_D$ +64° (0.1% in CH_2Cl_2); CD (MeCN) 210 (Δε −5.2), 238 (Δε −2.4), 285 (Δε +3.4), 295 (Δε + 3.7), 305 (Δε +3.0), and 315 nm (Δε +1.4); ν_{max}(KBr) 1 760 (ester C=O) and 1 710 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 214sh nm (10 000); δ(300 MHz; $CDCl_3$) 1.37, 2.02, and 2.04 (each 3 H, s, 3 × $MeCO_2$), 2.42 (1 H, dd, *J* 18 and 2 Hz, 4-H$^{\beta}$), 2.91 (1 H, dd, *J* 17 and 11 Hz, 6-H$^{\alpha}$), 3.03 (1 H, dd, *J* 18 and 3 Hz, 4-H$^{\alpha}$), 3.11 (1 H, dd, *J* 17 and 8 Hz, 6-H$^{\beta}$), 3.25–3.35 (2 H, m, 2- and 5′-H$^{\alpha}$), 3.42–3.53 (1 H, m, 1-H), 3.83 (1 H, dd, *J* 12 and 6 Hz, 5′-H$^{\beta}$), 4.63–4.74 (2 H, m, 2′-and 3-H), 4.91 (1 H, ddd, *J* 11, 10, and 6 Hz, 4′-H), 5.15 (1 H, d, *J* 4 Hz, 1′-H), 5.26 (1 H, t, *J* 10 Hz, 3′-H), and 7.35–7.52 (5 H, m, Ph); *m/z* (FAB) 518 (*M*H$^+$, 10%) and 97 (100) (Found: C, 57.7; H, 5.1; N, 2.8. $C_{25}H_{27}NO_{11}$ requires C, 58.0; H, 5.25; N, 2.7%).

Reaction of the β-*Xylose Diene* (**11f**) *with NPM*.—A mixture of the diene (**11f**) (0.150 g, 0.33 mmol) and NPM (0.057 g, 0.33 mmol) in dry benzene (1 cm^3) was stirred for 24 h. Removal of the solvent left a pale-yellow syrup which comprised an 81:19 mixture of the cycloadducts (**12f**) and (**13f**) by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the integrals of the singlets at δ 0.94 and 0.96, attributed to the t-butyl groups of compounds (**12f**) and (**13f**), and the heights of the singlets at δ 1.75 and 1.94, ascribed to the acetoxy groups of compounds (**12f**) and (**13f**)]. Addition of diethyl ether to the syrup induced the crystallisation of (1R,2R,3S)-5-(*t-butyldimethylsiloxy*)-N-*phenyl*-3-(2′,3′,4′-*tri*-O-*acetyl*-β-D-*xylopyranosyloxy*)*cyclohex*-4-*ene*-1,2-*dicarboximide* (**12f**) (0.100 g, 48%); m.p. 158–160 °C; $[\alpha]_D$ +34° (0.22% in CH_2Cl_2); CD (MeCN) 197 (Δε +2.4) and 225 nm (Δε +12.0); ν_{max}(KBr) 1 760 and 1 740 (ester C=O), 1 710 (imide C=O), and 1 650 cm^{-1} (C=C); λ_{max}(EtOH) 216sh nm (17 100); δ(300 MHz; $CDCl_3$) 0.186 and 0.191 (each 3 H, s, Me_2Si), 0.94 (9 H, s, Me_3C), 1.75, 1.95, and 2.04 (each 3 H, s, 3 × $MeCO_2$), 2.53 (1 H, dd, *J* 16 and 10 Hz, 6-H$^{\alpha}$), 2.79 (1 H, ddd, *J* 16, 8, and 3 Hz, 6-H$^{\beta}$), 3.15 (1 H, dd, *J* 10 and 5 Hz, 2-H), 3.28–3.43 (2 H, m, 1-H and 5′-H$^{\alpha}$), 4.02 (1 H, dd, *J* 12 and 5 Hz, 5′-H$^{\beta}$), 4.62 (1 H, d, *J* 6 Hz, 1′-H), 4.68–4.78 (2 H, m, 2′- and 3-H), 4.86 (1 H, dt, *J* 8, 8, and 5 Hz, 4′-H), 5.06 (1 H, t, *J* 8 Hz, 3′-H), 5.18 (1 H, dd, *J* 6 and 3 Hz, 4-H), and 7.28–7.50 (5 H, m, Ph); *m/z* (FAB) 574 (40%), 356 (70), and 73 (100) (Found: C, 58.6; H, 6.3; N, 2.0. $C_{31}H_{41}NO_{11}Si$ requires C, 58.95; H, 6.55; N, 2.2%)

Preparation of (1R,2R,3S)-5-*Oxo*-N-*phenyl*-3-(2′,3′,4′-*tri*-O-*acetyl*-β-D-*xylopyranosyloxy*)*cyclohexane*-1,2-*dicarboximide* (**23d**).—A solution of the cycloadduct (**12f**) (0.082 g, 0.13 mmol) in THF (4 cm^3) was treated with 0.1M-hydrochloric acid (1 cm^3) and, after 20 h, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from dichloromethane–diethyl ether gave the *title compound* (**23d**) (0.058 g, 84%); m.p. 207–208 °C; $[\alpha]_D$ −107° (0.15% in CH_2Cl_2); ν_{max}(KBr) 1 750 (ester C=O) and 1 710 cm^{-1} (imide and ketone C=O); λ_{max}(EtOH) 217 nm (10 200); δ(300 MHz; $CDCl_3$) 1.59, 1.97, and 2.03 (each 3 H, s, 3 × $MeCO_2$), 2.35 (1 H, dd, *J* 19 and 2 Hz, 4-H$^{\beta}$), 2.86 (1 H, dd, *J* 17 and 12 Hz, 6-H$^{\alpha}$), 2.96 (1 H, dd, *J* 17 and 8 Hz, 6-H$^{\beta}$), 3.01 (1 H, dd, *J* 19 and 3 Hz, 4-H$^{\alpha}$), 3.27 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.32–3.44 (2 H, m, 1-H and 5′-H$^{\alpha}$), 4.05 (1 H, dd, *J* 12 and 5 Hz, 5′-H$^{\beta}$), 4.65 (1 H, d, *J* 7 Hz, 1′-H), 4.76–4.83 (2 H, m, 2′- and 3-H), 4.89 (1 H, dt, *J* 9, 9, and 5 Hz, 4′-H), 5.12 (1 H, t, *J* 9 Hz, 3′-H), and 7.32–7.53 (5 H, m, Ph); *m/z* (FAB) 518 (*M*H$^+$, 4%), 259 (80), and 97 (100) (Found: C, 57.8; H, 5.1; N, 2.7. $C_{25}H_{27}NO_{11}$ requires C, 58.0; H, 5.2; N, 2.7%).

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* *Supplementary data* (see Section 5.6.3 of Instruction for Authors in the January issue). Vibrational parameters for non-hydrogen atoms, fractional atomic co-ordinates and vibrational parameters for hydrogen atoms, and bond lengths and bond angles involving hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

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