

**Asymmetric Diels–Alder Reactions. Part 2.<sup>1</sup> A Model to Account for the Diastereofacial Reactivity of (*E*)-1-(2',3',4',6'-Tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)-3-trimethylsiloxybuta-1,3-diene and its 2-Methyl Derivative. X-Ray Molecular Structure of (*E*)-1-(2',3',4',6'-Tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)-3-trimethylsiloxybuta-1,3-diene and of (1*R*,6*R*,9*R*,10*S*)-9-Methyl-10-(2',3',4',6'-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)bicyclo[4.4.0]dec-3-ene-2,5,8-trione<sup>2,†</sup>**

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The geometry of the title diene (**1a**) has been probed by X-ray crystallography and nuclear Overhauser difference (n.O.e.d.) spectroscopy. In the crystal state, the sugar adopts the expected chair conformation and the equatorially disposed anomeric substituent is planar, with the *s-trans*-diene entity and the anomeric C–O bond bearing an *anti*-relationship, *i.e.* (**13a**). Although the aforesaid conformer is the main rotamer in deuteriochloroform, there is also evidence for a conformer in which the *s-trans*-diene moiety and the anomeric C–O bond possess a *syn*-disposition, *i.e.* (**14a**). On the basis of n.O.e.d. spectroscopy, the 2-methyl derivative of the title diene, *i.e.* (**1b**), is present in deuteriochloroform as a single conformer in which the *s-trans*-diene entity and the anomeric C–O bond bear an *anti*-disposition, *i.e.* (**13b**). The geometries (**13a** and **b**) and (**14a**) are considered to be stabilised by the *exo*-anomeric effect.

Essentially single cycloadducts were produced in the reactions of the diene (**1b**) with *p*-benzoquinone, methoxycarbonyl-*p*-benzoquinone, acetyl-*p*-benzoquinone, and *N*-phenylmaleimide. The cycloadduct obtained from *p*-benzoquinone was shown to possess the stereostructure (**6d**) on the basis of an X-ray crystallographic study of its hydrolysis product (**9d**). An 80:20 mixture of cycloadducts, with the presumed stereostructures (**24b**) and (**25b**), arose in the reaction of the diene (**1b**) with tetracyanoethylene [the corresponding reaction of the diene (**1a**) led to a 65:35 mixture of the presumed cycloadducts (**24a**) and (**25a**)].

The improved diastereofacial reactivity of the methylated diene (**1b**) over its counterpart (**1a**) is attributed to it reacting only by way of a conformer in which the *s-cis*-diene entity and the anomeric C–O bond bear an *anti*-relationship, *i.e.* (**19b**). Dienophiles then undergo *endo*-additions preferentially to the least-hindered 'top' face of this conformer. In the case of the diene (**1a**), two reacting conformers are postulated. The major and minor cycloadducts of cyclic dienophiles are considered to arise by *endo*-additions to the last-hindered 'top' faces of the conformers (**19a**) and (**20**), in which the *s-cis*-diene moiety and the anomeric C–O bond bear respective *anti*- and *syn*-orientations.

Recently, we reported that the diene (**1a**) showed a notable diastereofacial reactivity towards a range of cyclic dienophiles.<sup>1</sup> Thus in benzene at ambient temperature, it reacted with the epoxytetraone (**2**) to give a 75:25 mixture of the cycloadducts (**3**) and (**4**). By virtue of its transformation into (+)-4-demethoxydaunomycinone (**5**), the major cycloadduct was assigned the stereostructure (**3**).

Under corresponding conditions, the diene (**1a**) reacted with *p*-benzoquinone to give an 89:11 mixture of the cycloadducts (**6a**) and (**7a**),<sup>‡</sup> with methoxycarbonyl-*p*-benzoquinone to give an 88:12 mixture of the cycloadducts (**6b**) and (**7b**), and with acetyl-*p*-benzoquinone to give a 75:25 mixture of the cycloadducts (**6c**) and (**7c**). The geometry of the cycloadduct

(**6a**) was established by its conversion into the trione (**8**), the structure of which was determined by X-ray crystallography. On the basis of c.d. spectroscopy, the enetrones (**9a–c**)—obtained from the major cycloadducts (**6a–c**) by acidic hydrolysis—possessed similar stereostructures.

The diene (**1a**) also reacted in benzene with *N*-phenylmaleimide to give an 86:14 mixture of the cycloadducts (**10a**) and (**11a**),<sup>§</sup> with maleimide to give an 85:15 mixture of the cycloadducts (**10b**) and (**11b**), and with maleic anhydride to give predominantly the cycloadduct (**10c**). The stereostructures of the major cycloadducts were not rigorously established but were assumed by analogy with the earlier results. Certainly, on the basis of c.d. spectroscopy and a chemical correlation, the ketones (**12a–c**)—obtained from the major cycloadducts (**10a–c**) by acidic hydrolysis—were stereochemically identical.

<sup>†</sup> Part of this work was carried out in the Department of Organic Chemistry, University of Newcastle upon Tyne.

<sup>‡</sup> To facilitate comparisons, the numbering and lettering shown in structure (**6**) is used in this paper to describe the cycloadducts of the dienes (**1a** and **b**) and *p*-benzoquinone, methoxycarbonyl-*p*-benzoquinone, and acetyl-*p*-benzoquinone; derivatives of the aforesaid compounds are numbered in an analogous manner.

<sup>§</sup> To facilitate comparisons, the numbering and lettering shown in structure (**10**) is used to describe the cycloadducts of the dienes (**1a** and **b**) and *N*-phenylmaleimide, maleimide, and maleic anhydride; derivatives of the aforesaid compounds are numbered in an analogous manner.

In this paper, we propose a model to account for the diastereoselective Diels-Alder reactions and we examine some of its consequences.

### Results and Discussion

The *X*-ray structure of compound (**1a**) (see Experimental section for crystal data and other information) is shown in Figure 1 together with its crystallographic numbering. Refined atomic co-ordinates are given in Table 1, and bond lengths and bond angles in Table 2.

Clearly, in the crystal state, the diene moiety of compound (**1a**) is planar and adopts the *s-trans*-geometry. Of special interest is the orientation of the equatorial butadienyloxy moiety with respect of the sugar. Thus the C(1)–O(1)–C(1') bond angle of 117.2(6)° together with the O(1')–C(1')–O(1)–C(1) torsion angle of –87.0(7)° suggest that O(1) is *sp*<sup>2</sup>-hybridised

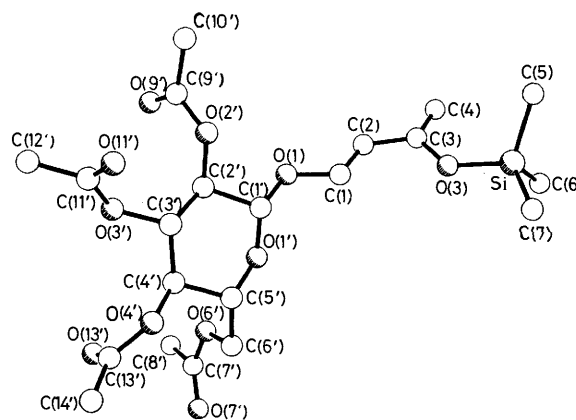
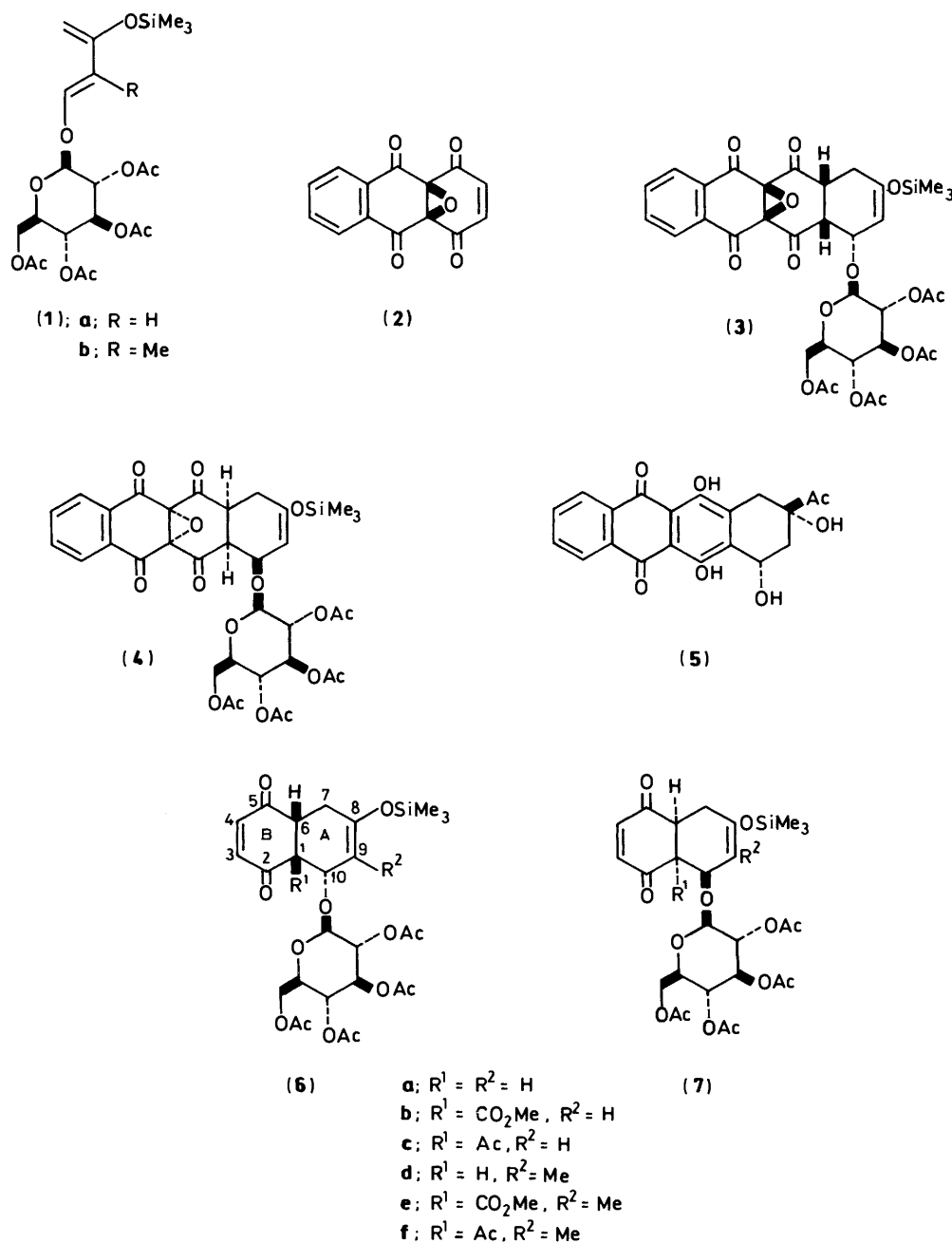
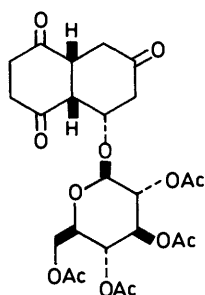
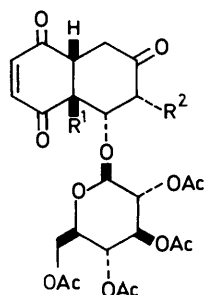


Figure 1. The molecular structure of compound (**1a**)

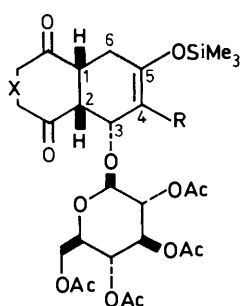




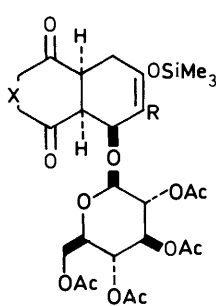
(8)



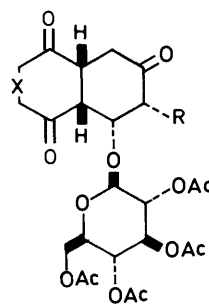
(9) a;  $R^1 = R^2 = H$   
 b;  $R^1 = CO_2Me, R^2 = H$   
 c;  $R^1 = Ac, R^2 = H$   
 d;  $R^1 = H, R^2 = Me$   
 e;  $R^1 = CO_2Me, R^2 = Me$   
 f;  $R^1 = Ac, R^2 = Me$



(10) a; X = NPh, R = H  
 b; X = NH, R = H  
 c; X = O, R = H  
 d; X = NPh, R = Me



(11) a; X = NPh, R = H  
 b; X = NH, R = H  
 c; X = NPh, R = Me



(12) a; X = NPh, R = H  
 b; X = NH, R = H  
 c; X = O, R = H  
 d; X = NPh, R = Me

and that its  $p$ -orbital non-bonded electron pair is available for overlap with both a  $\pi^*$ -orbital of the diene function and the  $\sigma^*$ -orbital of the  $C(1')-O(1')$  bond.

The geometry of compound (1a) in deuteriochloroform solution was probed by nuclear Overhauser effect difference (n.O.e.d.) spectroscopy. Thus irradiation of  $1'-H$  [a doublet ( $J$  8 Hz) at  $\delta$  4.77] caused a 13% enhancement of  $1-H$  [a doublet ( $J$  12 Hz) at  $\delta$  6.66] and a 4% enhancement of  $2-H$  [a doublet ( $J$  12 Hz) at  $\delta$  5.63]. When  $1-H$  and  $2-H$  were irradiated,  $1'-H$  showed respective enhancements of 6% and 3%. On the basis of these results, it is inferred that compound (1a) is present in deuteriochloroform as a mixture of conformers. The major conformer, *i.e.* (13a), is believed to be comparable to that present in the crystal state; the minor conformer is considered to possess the structure (14a).

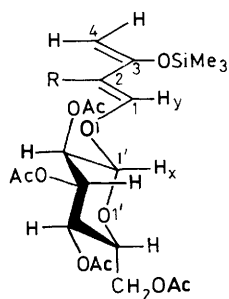
The adoption of the conformers (13a) and (14a) is in accord with expectations based upon the *exo*-anomeric effect.<sup>3</sup> Thus in glycopyranosides, *e.g.* (15), in which the glycone is linked by an  $sp^3$ -hybridised C, the aglycone O-C bond prefers to be *syn*-clinal to the ring O and the anomeric H, *i.e.* the torsion angle is *ca.*  $-60^\circ$  [see structure (16)]; nevertheless, the glycosidic O still possesses a significant amount of trigonal character.<sup>3</sup> As the  $sp^2$ -character of the glycosidic O increases, the torsion angle is expected to approach  $-90^\circ$  [*e.g.* structure (17) in the case of compound (1a)]. Presumably, the geometric change from (16) to (17) would result in a weakening of the stabilisation associated with the *exo*-anomeric effect. The preference for the

conformer (13a) over its counterpart (14a) is of interest since, in the case of methyl vinyl ether, the *syn*-conformer (18) is favoured over its *anti*-counterpart.<sup>4</sup> Presumably, the steric interaction between  $H_x$  and  $H_z$  in the conformer (14a) outweighs that between  $H_x$  and  $H_y$  in the conformer (13a) and tips the balance in favour of the latter geometry.

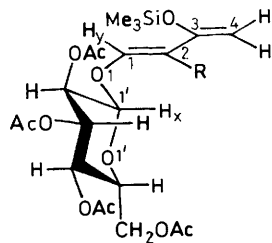
To participate in a Diels-Alder reaction, a diene must adopt an *s-cis*-geometry. In principle therefore, compound (1a) may react by way of the conformers (19a) and/or (20). The former conformer is expected to be of lower energy than the latter because of the steric effect alluded to earlier. To account for the formation of the observed major cycloadducts, *i.e.* (3), (6a-c), and (10a-c), it is necessary to invoke *endo*-addition of the dienophiles to the 'top' face of the preferred conformer (19a) or to the 'bottom' face of the unpreferred conformer (20). The former approach is sterically less demanding than the latter, since the generation of a *syn*-1,3-interaction between the dienophile and the  $C(1')-O(1')$  bond is avoided. We therefore infer that the major cycloadducts are formed by *endo*-addition of the dienophile to the least hindered 'top' face of the conformer (19a).\*

Two pathways must also be considered in the formation of the observed minor cycloadducts, *i.e.* (4), (7a-c), and (11a and

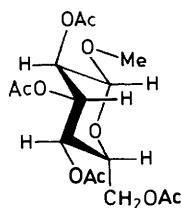
\* It seems likely that the stabilisation associated with the *exo*-anomeric effect will increase as the transition state of the cycloaddition reaction is developed.



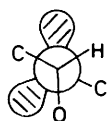
(13) a; R = H<sub>z</sub>  
b; R = Me



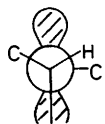
(14) a; R = H<sub>z</sub>  
b; R = Me



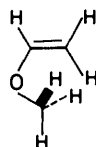
(15)



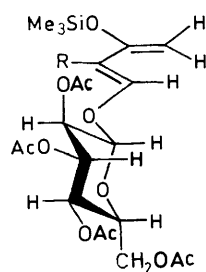
(16)



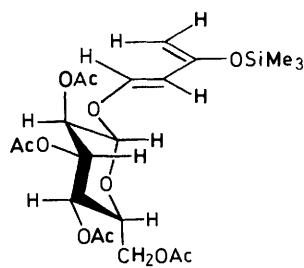
(17)



(18)



(19) a; R = H  
b; R = Me



(20)

b). Thus the dienophiles may undergo *endo*-addition to the 'bottom' face of the preferred conformer (19a) or to the 'top' face of the unpreferred conformer (20a). The former approach is sterically more demanding than the latter, since it requires the generation of a *syn*-1,3-interaction between the dienophile and the C(1')-O(1') bond of the diene.

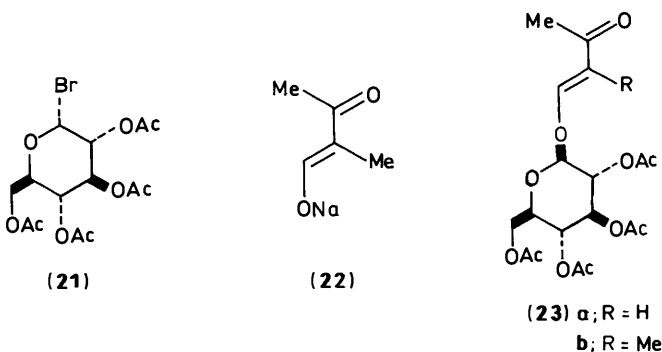
In order to probe the availability of one or both of these pathways, it was decided to examine the diastereofacial reactivity of the methylated diene (1b). It was envisaged that in this compound the conformer (13b) would be overwhelmingly preferred to its counterpart (14b) (which possesses a severe interaction between the 2-methyl group and the anomeric hydrogen atom). Consequently, the Diels-Alder reactions would be expected to occur only by way of the *s-cis*-conformer (19b) [assuming that the *exo*-anomeric effect operates in the ground state of compound (1b) and that it is augmented in the transition state of the cycloaddition reaction]. If the diastereofacial reactivity of the methylated diene (1b) were to parallel that of its counterpart (1a), then it may be inferred that

Table 1. Atomic co-ordinates ( $\times 10^4$ ) for compound (1a) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
O(1)	121(7)	3 133(4)	-1 591(1)
C(1)	-1 075(10)	2 465(6)	-1 814(2)
C(2)	-734(12)	2 049(7)	-2 206(3)
C(3)	-1 780(14)	1 295(8)	-2 479(3)
C(4)	-1 351(17)	944(10)	-2 891(3)
O(3)	-3 297(9)	996(5)	-2 295(2)
Si	-4 751(4)	3(3)	-2 474(1)
C(5)	-3 726(20)	-1 456(9)	-2 579(4)
C(6)	-5 683(18)	520(12)	-2 989(4)
C(7)	-6 365(15)	-66(12)	-2 036(4)
C(1')	-291(10)	3 528(6)	-1 168(2)
O(1')	-1 149(6)	4 655(4)	-1 217(1)
C(2')	1 327(9)	3 785(6)	-916(2)
O(2')	2 226(7)	2 638(4)	-883(2)
C(3')	920(9)	4 231(5)	-456(2)
O(3')	2 434(6)	4 644(3)	-241(1)
C(4')	-238(10)	5 344(5)	-487(2)
O(4')	-909(6)	5 594(4)	-55(1)
C(5')	-1 693(10)	5 139(6)	-805(2)
C(6')	-2 586(10)	6 307(7)	-909(2)
O(6')	-1 416(7)	7 089(4)	-1 144(2)
C(7')	-1 775(14)	8 242(8)	-1 194(3)
O(7')	-2 992(12)	8 693(7)	-1 037(4)
C(8')	-467(14)	8 918(8)	-1 448(3)
C(9')	3 901(14)	2 624(8)	-967(3)
O(9')	4 656(9)	3 506(6)	-1 079(3)
C(10')	4 600(13)	1 381(7)	-924(3)
C(11')	3 162(9)	3 891(5)	62(2)
O(11')	2 603(7)	2 926(4)	165(2)
C(12')	4 806(11)	4 408(6)	224(3)
C(13')	-689(10)	6 742(6)	121(3)
O(13')	32(9)	7 501(6)	-64(2)
C(14')	-1 511(12)	6 827(7)	558(3)

the minor cycloadducts arise by addition of the dienophile to the 'bottom' face of the conformer (19a). Were the minor cycloadducts to originate by addition of the dienophiles to the 'top' face of the conformer (20), then it may be expected that the methylated diene (1b) would show a much enhanced diastereofacial discrimination over its counterpart (1a).

The methylated diene (1b) was prepared by a route similar to that used for the synthesis of compound (1a).<sup>5</sup> Thus treatment of the bromide (21)<sup>6</sup> with the salt (22)<sup>7</sup> in dimethyl sulphoxide (DMSO) gave the crystalline butenone (23b) in 17% yield.



(23) a; R = H  
b; R = Me

When heated in benzene with trimethylsilyl chloride in the presence of zinc chloride and trimethylamine, the butenone (23b) was transformed into the methylated diene (1b) (76% yield after recrystallisation). The last cited compound was also prepared (77% yield) from the butenone (23b) in dichloro-

**Table 2.** Bond lengths (Å) and bond angles (°) for compound (**1a**) with e.s.d.s in parentheses

(a) Bond lengths			
O(1)-C(1)	1.371(9)	O(1)-C(1')	1.380(8)
C(1)-C(2)	1.291(10)	C(2)-C(3)	1.429(13)
C(3)-C(4)	1.339(13)	C(3)-O(3)	1.359(13)
O(3)-Si	1.672(7)	Si-C(5)	1.823(12)
Si-C(6)	1.805(12)	Si-C(7)	1.832(12)
C(1')-O(1')	1.419(8)	C(1')-C(2')	1.511(10)
O(1')-C(5')	1.413(8)	C(2')-O(2')	1.449(9)
C(2')-C(3')	1.502(9)	O(2')-C(9')	1.345(12)
C(3')-O(3')	1.431(8)	C(3')-C(4')	1.530(9)
O(3')-C(11')	1.358(8)	C(4')-O(4')	1.426(7)
C(4')-C(5')	1.510(10)	O(4')-C(13')	1.380(8)
C(5')-C(6')	1.497(10)	C(6')-O(6')	1.445(9)
O(6')-C(7')	1.306(10)	C(7')-O(7')	1.179(14)
C(7')-C(8')	1.482(14)	C(9')-O(9')	1.186(12)
C(9')-C(10')	1.479(12)	C(11')-O(11')	1.189(8)
C(11')-C(12')	1.496(11)	C(13')-O(13')	1.154(10)
C(13')-C(14')	1.466(11)		
(b) Bond angles			
C(1)-O(1)-C(1')	117.2(6)	O(1)-C(1)-C(2)	119.6(7)
C(1)-C(2)-C(3)	127.6(9)	C(2)-C(3)-C(4)	123.6(10)
C(2)-C(3)-O(3)	114.4(8)	C(4)-C(3)-O(3)	122.0(10)
C(3)-O(3)-Si	129.0(6)	O(3)-Si-C(5)	109.0(5)
O(3)-Si-C(6)	110.5(5)	C(5)-Si-C(6)	108.0(6)
O(3)-Si-C(7)	105.8(5)	C(5)-Si-C(7)	113.3(6)
C(6)-Si-C(7)	110.3(6)	O(1)-C(1')-O(1')	107.0(5)
O(1)-C(1')-C(2')	108.8(6)	O(1')-C(1')-C(2')	106.9(5)
C(1')-O(1')-C(5')	112.5(5)	C(1')-C(2')-O(2')	106.5(5)
C(1')-C(2')-C(3')	110.1(6)	O(2')-C(2')-C(3')	108.9(5)
C(2')-O(2')-C(9')	118.5(6)	C(2')-C(3')-O(3')	109.9(6)
C(2')-C(3')-C(4')	109.4(5)	O(3')-C(3')-C(4')	105.7(5)
C(3')-O(3')-C(11')	117.5(5)	C(3')-C(4')-O(4')	108.7(5)
C(3')-C(4')-C(5')	111.9(5)	O(4')-C(4')-C(5')	108.8(6)
C(4')-O(4')-C(13')	118.6(5)	O(1')-C(5')-C(6')	112.3(6)
O(1')-C(5')-C(6')	106.3(5)	C(4')-C(5')-C(6')	111.2(6)
C(5')-C(6')-O(6')	108.2(6)	C(6')-O(6')-C(7')	119.7(7)
O(6')-C(7')-O(7')	122.6(9)	O(6')-C(7')-C(8')	113.2(8)
O(7')-C(7')-C(8')	124.1(9)	O(2')-C(9')-O(9')	122.5(8)
O(2')-C(9')-C(10')	111.1(8)	O(9')-C(9')-C(10')	126.4(10)
O(3')-C(11')-O(11')	124.2(6)	O(3')-C(11')-C(12')	110.7(5)
O(11')-C(11')-C(12')	125.1(6)	O(4')-C(13')-O(13')	122.5(7)
O(4')-C(13')-C(14')	110.3(6)	O(13')-C(13')-C(14')	127.2(7)

methane at *ca.* -20 °C by the action of trimethylsilyl trifluoromethanesulphonate and triethylamine.<sup>8</sup>

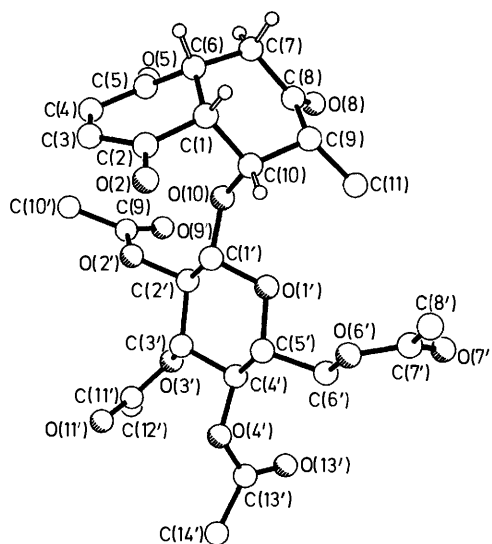
The conformation of the methylated diene (**1b**) in deuteriochloroform solution was probed by n.O.e.d. spectroscopy. Thus irradiation of 1'-H [a doublet (*J* 8 Hz) at  $\delta$  4.75] caused a 32% enhancement of 1-H (a broad singlet at  $\delta$  6.70). When 1-H was irradiated, a 13% enhancement of 1'-H was noted. Irradiation of the 2-methyl group [a doublet (*J* 1 Hz) at  $\delta$  1.68] caused a 10% enhancement of one of the 4-Hs [a doublet (*J* 1 Hz) at  $\delta$  4.32]. Besides establishing that the methylated diene (**1b**) possessed an *anti*-arrangement of its 1-hydrogen atom and 2-methyl group, the results left little doubt that compound (**1b**) was present in deuteriochloroform as the conformer (**13b**).

Under conditions in which the diene (**1a**) reacted with *p*-benzoquinone to give mainly an 89:11 mixture of the cycloadducts (**6a**) and (**7a**), the methylated diene (**1b**) afforded largely the cycloadduct (**6d**) (isolated in 69% yield). According to 300 MHz <sup>1</sup>H n.m.r. spectroscopic analysis, there was no evidence for the presence of the cycloadduct (**7d**) in the crude product.

Under mildly acidic conditions, the cycloadduct (**6d**) was

**Table 3.** Atomic co-ordinates ( $\times 10^4$ ) for compound (**9d**) with estimated e.s.d.s in parentheses

Atom	x	y	z
C(1)	10 565(4)	4 477(3)	237(2)
C(2)	10 503(5)	5 623(3)	108(2)
O(2)	11 236(4)	6 220(2)	398(1)
C(3)	9 531(6)	6 000(4)	-344(2)
C(4)	8 538(5)	5 401(4)	-608(2)
C(5)	8 434(5)	4 302(3)	-472(2)
O(5)	7 316(3)	3 827(3)	-591(2)
C(6)	9 815(4)	3 814(3)	-243(2)
C(7)	9 606(5)	2 678(3)	-60(2)
C(8)	9 147(4)	2 527(3)	555(2)
O(8)	8 172(4)	1 940(2)	687(2)
C(9)	10 037(4)	3 124(3)	1 001(2)
C(10)	9 967(4)	4 268(3)	841(1)
O(10)	8 435(2)	4 583(2)	861(1)
C(11)	9 590(7)	2 879(3)	1 618(2)
C(1')	8 103(4)	5 389(3)	1 240(1)
O(1')	8 477(3)	5 067(2)	1 813(1)
C(2')	6 464(4)	5 569(3)	1 221(1)
O(2')	6 044(3)	5 955(2)	658(1)
C(3')	5 999(4)	6 347(3)	1 679(1)
O(3')	4 410(3)	6 312(2)	1 715(1)
C(4')	6 620(4)	6 098(3)	2 274(2)
O(4')	6 444(3)	7 019(2)	2 622(1)
C(5')	8 256(4)	5 831(3)	2 251(1)
C(6')	8 756(4)	5 357(3)	2 813(2)
O(6')	10 338(3)	5 294(2)	2 800(1)
C(7')	10 976(5)	4 535(4)	3 098(2)
O(7')	10 308(5)	3 902(3)	3 356(2)
C(8')	12 612(5)	4 581(5)	3 056(3)
C(9')	4 959(5)	5 433(3)	370(2)
O(9')	4 359(4)	4 701(2)	564(1)
C(10')	4 650(6)	5 913(5)	-209(2)
C(11')	3 629(5)	7 191(3)	1 735(2)
O(11')	4 194(4)	8 031(2)	1 727(2)
C(12')	2 035(4)	6 982(4)	1 783(2)
C(13')	5 601(5)	6 960(3)	3 105(2)
O(13')	5 221(5)	6 163(3)	3 308(2)
C(14')	5 342(8)	8 004(4)	3 356(2)

**Figure 2.** The molecular structure of compound (**9d**)

transformed into compound (**9d**), isolated as a single diastereoisomer in 74% yield. The X-ray structure of compound (**9d**) (see Experimental section for crystal data and other information) is shown in Figure 2, together with its

crystallographic numbering. Refined atomic co-ordinates are included in Table 3, while bond lengths and bond angles are available as a separate publication.

Clearly, the *X*-ray structure confirmed that the cycloadduct arising from the reaction of the methylated diene (**1b**) with *p*-benzoquinone possessed the expected stereostructure (**6d**). It also established that the new stereocentre at position 9 of the hydrolysis product (**9d**) had been generated in a selective manner.

Only a single cycloadduct, isolated in 72% yield and assigned the stereostructure (**6e**), was detected in the reaction of the methylated diene (**1b**) with methoxycarbonyl-*p*-benzoquinone in benzene. Previously, the corresponding reaction of the diene (**1a**) had led to an 88:12 mixture of the cycloadducts (**6b**) and (**7b**). Under the usual hydrolysis conditions [0.1M-HCl-tetrahydrofuran (THF) (1:4)], compound (**6e**) was transformed into a mixture of products. However, it was converted into the ketone (**9e**) in 43% yield by the action of a few drops of conc. hydrochloric acid in chloroform.

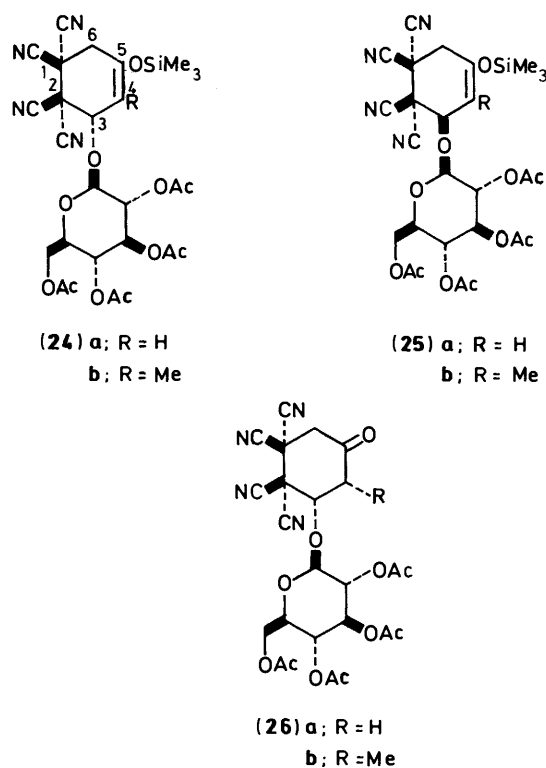
As stated earlier, a 75:25 mixture of the cycloadducts (**6c**) and (**7c**) was produced in the reaction of the diene (**1a**) with acetyl-*p*-benzoquinone in benzene. In the case of the methylated diene (**1b**), only one cycloadduct was detected; it was obtained in 65% yield and was assigned the stereostructure (**6f**). Again a mixture of products resulted when the cycloadduct (**6f**) was subjected to the standard hydrolysis conditions. The use of a few drops of conc. hydrochloric acid in dichloromethane was effective, however, in transforming the cycloadduct (**6f**) into the ketone (**9f**) in 61% yield.

The reaction of the methylated diene (**1b**) with *N*-phenylmaleimide in benzene also led to only one cycloadduct according to 300 MHz <sup>1</sup>H n.m.r. spectroscopic analysis. The product, assigned the stereostructure (**10d**), was obtained in 87% yield. As previously stated, an 86:14 mixture of the cycloadducts (**10a**) and (**11a**) was formed in the corresponding Diels-Alder reaction involving the diene (**1a**). Under the usual acidic conditions, the cycloadduct (**10d**) was transformed into the ketone (**12d**) in 77% yield.

On the basis of the aforementioned results, it is evident that the methylated diene (**1b**) shows a higher diastereofacial discrimination towards cyclic dienophiles than does its relative (**1a**). In the case of the former compound, we infer that the cycloadducts arise by addition of the dienophiles to the 'top' face of the conformer (**19b**). With compound (**1a**), we suggest that the major and the minor cycloadducts are formed by addition of the dienophiles to the 'top' faces of the conformers (**19a**) and (**20**), respectively.

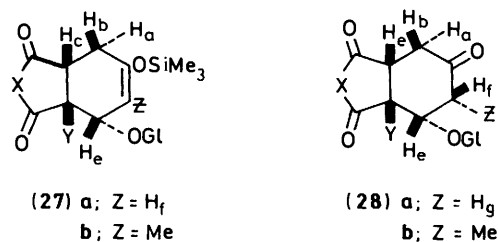
It was of interest to extend our study to acyclic dienophiles. Unfortunately, the majority of these proved to be unreactive under thermal conditions that were compatible with the survival of the dienes (**1a**) and (**1b**). Tetracyanoethylene, however, did undergo the desired cycloadditions. In benzene, it reacted with the former diene to give a 67:33 mixture of cycloadducts. The major cycloadduct, isolated by virtue of its insolubility in diethyl ether and obtained in 42% yield after recrystallisation, was assigned the stereostructure (**24a**)\* by analogy with the earlier results; the minor cycloadduct, which was not obtained in a pure state, was considered to possess the stereostructure (**25a**). An 80:20 mixture of the cycloadducts (**24b**) and (**25b**) was produced in the reaction of the diene (**1b**) with tetracyanoethylene in benzene. Again, only the major cycloadduct (**24b**) was obtained (69% yield) in a pure state.

Attempts to transform the major cycloadducts (**24a** and **b**) into the ketones (**26a** and **b**), under the usual and modified



acidic conditions, led to mixtures of products which were not further investigated.

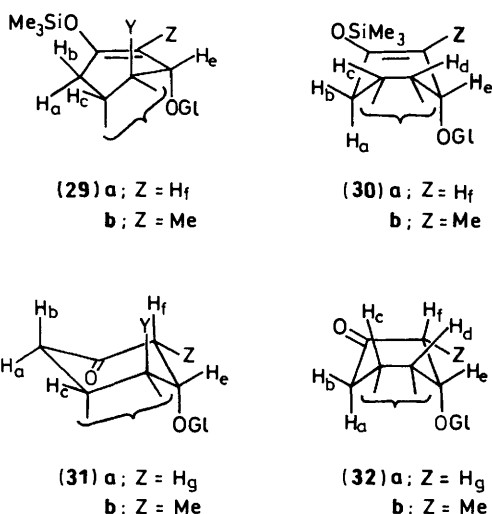
Clearly, the diastereofacial reactivity of the diene (**1a**) towards tetracyanoethylene is poorer than towards any of the cyclic dienophiles hitherto studied. Moreover, although the methylated diene (**1b**) shows a better discrimination than the diene (**1a**), it does give rise to *ca.* 20% of the minor cycloadduct (**25b**). We therefore infer that tetracyanoethylene adds to the 'top' and 'bottom' faces of the conformer (**19b**) with a selectivity of *ca.* 4:1. The unencumbered nature of the dienophile may be responsible for this behaviour.



*Conformational Considerations.*—The conformational behaviour of the A-rings of the cycloadducts (**6a–c**) and (**10a**) [denoted by the generalised formula (**27a**)] and of compounds (**9a–c**) and (**12a**) [depicted by the generalised formula (**28a**)] was previously assessed by 300 MHz <sup>1</sup>H n.m.r. spectroscopy.<sup>1</sup> In the case of the cycloadducts (**6a–c**), a sofa-like geometry [represented by the generalised structure (**29a**)] was inferred. For the cycloadduct (**10a**), a boat-like conformation of type (**30a**) was favoured. Compounds (**9a–c**) were considered to adopt a partially flattened chair-like conformation of type (**31a**). A boat-like geometry of type (**32a**) was postulated for compound (**12a**).

The coupling constants of the A-ring-associated protons of the cycloadducts (**6d–f**) and (**10d**) [denoted by the generalised formula (**27b**)] and of compounds (**9d–f**) and (**12d**) [represented by the generalised structure (**28b**)] are summarised

\* To facilitate comparisons, the numbering shown in structure (**24**) is used to describe the cycloadducts of the dienes (**1a**) and (**1b**) and tetracyanoethylene.



in Tables 4 and 5, respectively. The values are very similar to those of their relatives, implying that the cycloadducts (6d–f) adopt a sofa-like geometry of type (29b), the cycloadduct (10d) prefers a boat-like conformation of type (30b), compounds (9d–f) exist as a partially flattened chair of type (31b), and compound (12d) favours a boat-like geometry of type (32b).

A comparison of the pertinent torsion angles of compound (9d), obtained by X-ray analysis and calculated from spin–spin coupling constants, is made in Table 6. Although the agreement between the values is not perfect, it is clear that the A-ring of

**Table 4.** Coupling constants (Hz) of the A-ring-associated protons of compounds of type (27b) (measured in CDCl<sub>3</sub>)

(27b; Gl = 2,3,4,6-tetra-*O*-β-D-glucopyranosyl)

Compound	X	Y	$J_{a,b}$	$J_{a,c}$	$J_{b,c}$	$J_{c,d}$	$J_{d,e}$
(6d)		H <sub>d</sub>	18	≤1	7	7	4
(6e)		CO <sub>2</sub> Me	18	≤1	6		
(6f)		Ac	18	≤1	8		
(10d)	NPh	H <sub>d</sub>	15	9	9	11	4

**Table 5.** Coupling constants (Hz) of the A-ring-associated protons of compounds of type (28b)

(28b; Gl = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)

Compound	X	Y	$J_{a,b}$	$J_{a,c}$	$J_{b,c}$	$J_{c,d}$	$J_{d,e}$	$J_{e,f}$
(9d) <sup>a</sup>		H <sub>d</sub>	16	1.5	8	7	2	2
(9e) <sup>b</sup>		CO <sub>2</sub> Me	16	4	7			2
(9f) <sup>b</sup>		Ac	16	4	8			2
(12d) <sup>b</sup>		NPh	H <sub>d</sub>	17	8	11	10	4

<sup>a</sup> Measured in deuterioacetonitrile. <sup>b</sup> Measured in deuteriochloroform.

compound (9d) adopts a chair-like conformation both in the crystal state and in deuteriochloroform solution. This finding reinforces the belief that the common A-ring geometry of compounds (9a–f) is indeed represented by a chair-like arrangement of type (31).

An interesting feature of the conformational behaviour is the axial-like disposition of the glucopyranosyloxy substituents in compounds (6d–f), (9d–f), (10d), and (12d), a phenomenon which was noted earlier in related compounds.<sup>1–5,9</sup> As before, we suggest that the axial-like orientation is stabilised by a through-space interaction between the electron pairs on the O atom and the π\*-orbitals of the carbonyl groups. Certainly, the O(10)···C(2) and O(10)···C(8) interatomic distances in compound (9d) (2.88 Å and 2.83 Å, respectively, on the basis of the X-ray study) were less than the sum of the van der Waals radii of the atoms.

## Experimental

Dry solvents, referred to in the ensuing experiments, were prepared as follows: methanol was treated with magnesium and a few crystals of iodine, distilled, and stored over 3 Å molecule sieves; toluene, diethyl ether, and benzene were stored over sodium wire; DMSO was distilled under reduced pressure from calcium hydride and stored over 4 Å molecular sieves; dichloromethane was distilled from calcium chloride. Light petroleum refers to that fraction boiling in the range 40–60 °C. Prior to use as a solvent for the <sup>1</sup>H n.m.r. spectroscopic determination of cycloadducts, deuteriochloroform was kept over tin granules.

For chromatographic, spectroscopic, and other instrumental details, see Part 1.<sup>1</sup> A Kratos MS45 mass spectrometer was used to record chemical ionization (c.i.) mass spectra using ammonia as the carrier gas; fast atom bombardment (f.a.b.) negative ion mass spectra were determined using an A.E.I. MS9 instrument.

*Preparation of (E)-1-(2',3',4',6'-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3-trimethylsilyloxybuta-1,3-diene (1a).*—The title compound (1a) was prepared by the literature procedure<sup>5</sup>

**Table 6.** Selected torsion angles (°) of compound (9d) determined from X-ray analysis<sup>a</sup> and spin–spin coupling constants<sup>b</sup> (measured in CD<sub>3</sub>CN)

(9d; Gl = 2,3,4,6-tetra-*O*-β-D-glucopyranosyl)

	Angle (from X-ray)	Angle (from J)
H <sub>a</sub> ,H <sub>c</sub>	84	68
H <sub>b</sub> ,H <sub>c</sub>	35	31
H <sub>c</sub> ,H <sub>d</sub>	41	37
H <sub>d</sub> ,H <sub>e</sub>	58	65
H <sub>e</sub> ,H <sub>f</sub>	59	65

<sup>a</sup> The torsion angles are based on calculated hydrogen positions that were fixed by reference to the refined 'heavy' atom co-ordinates. <sup>b</sup> The spin–spin coupling constants ( $J$ ) were converted into torsion angles ( $\theta$ ) using the modified Karplus relationships:  $J = 11 \cos^2\theta$  (see L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, 1969, 2nd edn., p. 281).

but using a modified work-up. Thus a stirred mixture of fused zinc chloride (2.40 g, 17.6 mmol) and triethylamine (60 cm<sup>3</sup>, 430 mmol) was added a solution of the butenone (**23a**) (24.0 g, 57.7 mmol) in dry benzene (360 cm<sup>3</sup>) followed by trimethylsilyl chloride (30 cm<sup>3</sup>, 236 mmol). The mixture was stirred at 50–55 °C for 30 h and then concentrated. Dry diethyl ether (300 cm<sup>3</sup>) was added to the residue and the mixture was filtered. The filtered material was washed with diethyl ether (2 × 100 cm<sup>3</sup>) and the combined material was washed with diethyl ether (2 × 100 cm<sup>3</sup>) and the combined filtrates were concentrated. Purification of the residue by low-temperature silica gel chromatography [light petroleum–Et<sub>2</sub>O (1:1) as eluant; the column was jacketed with Me<sub>2</sub>CO–solid CO<sub>2</sub>] and recrystallisation of the product from diethyl ether–light petroleum gave the title compound (**1a**) (16.23 g, 58%), m.p. 98–100 °C (lit.,<sup>5</sup> 104–106 °C);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 1.99, 2.01, 2.02, and 2.05 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 3.75–3.81 (1 H, m, 5'-H), 4.09–4.17 (3 H, m, 6'-H and 4-H<sub>2</sub>), 4.25 (1 H, dd, *J* 12 and 3 Hz, 6'-H), 4.74 (1 H, d, *J* 8 Hz, 1'-H), 5.05–5.13 (2 H, m, 2'- and 4'-H), 5.21 (1 H, t, *J* 9 and 9 Hz, 3'-H), 5.61 (1 H, d, *J* 12 Hz, 2-H), and 6.64 (1 H, d, *J* 12 Hz, 1-H) (in an n.O.e.d. experiment, irradiation of the signal at  $\delta$  6.64 caused 6% and 3% enhancements of the signals at  $\delta$  4.74 and 4.12, respectively; irradiation of the signal at  $\delta$  5.61 caused 3% enhancements of the signals at  $\delta$  4.74 and 4.12; irradiation of the signal at  $\delta$  4.74 caused enhancements of 13%, 4%, 6%, 3%, and 8% of the signals at  $\delta$  6.64, 5.61, 5.21, 5.09, and 3.75–3.81, respectively; irradiation of the signal at  $\delta$  4.12 caused a 15% enhancement of that at  $\delta$  5.61).

*Crystal Data for Compound (1a).*—C<sub>21</sub>H<sub>32</sub>O<sub>11</sub>Si, *M* = 488.6. Orthorhombic, *a* = 7.883(2), *b* = 10.988(2), *c* = 30.055(7) Å, *V* = 2 603 Å<sup>3</sup>, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *Z* = 4, *D*<sub>c</sub> = 1.25 g cm<sup>-3</sup>. Refined unit-cell parameters were obtained by centering 18 reflections on a Nicolet R3m diffractometer. 2 042 Independent reflections ( $\theta \leq 58^\circ$ ) were measured with Cu-K $\alpha$  radiation (graphite monochromator) using the  $\omega$ -scan measuring routine; of these, 1 458 had  $|F_o| > 3\sigma(|F_o|)$  and were considered to be observed. The net count of two check reflections (the 1,2,3 and the 1,2,-3), measured every 50 reflections during the data collection, did not change significantly, indicating that no deterioration of the crystal had occurred. The data were brought to a uniform arbitrary scale, and Lorentz and polarisation corrections applied; no absorption correction was applied.

The structure was solved by conventional multiple-solution tangent refinement. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, *U*(H) = 1.2*U*<sub>eq</sub>(C), and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade, full-matrix least-squares to *R* = 0.065, *R*<sub>w</sub> = 0.069 [*w*<sup>-1</sup> =  $\sigma^2(F) + 0.001 46F^2$ ]. The maximum residual electron density in the final  $\Delta F$  map was 0.25 e Å<sup>-3</sup>. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.<sup>10,\*</sup>

*Reaction of Butan-2-one with Ethyl Formate and Sodium Methoxide.*—Sodium methoxide was prepared by the addition of sodium (23 g, 1 mol) in small pieces to dry methanol (200 cm<sup>3</sup>) during 1 h. The solvent was removed by evaporation and dry toluene (100 cm<sup>3</sup>) was added to the residue. Evaporation of the solvent was followed by the addition of a further quantity of

dry toluene (100 cm<sup>3</sup>) and re-evaporation. Dry diethyl ether (800 cm<sup>3</sup>) was added to the sodium methoxide and to the stirred mixture, cooled in an ice-bath, was added during 15 min a mixture of butan-2-one (100 cm<sup>3</sup>, 1.04 mol) and ethyl formate (100 cm<sup>3</sup>, 1.24 mmol). The mixture was allowed to warm up to room temperature, stirred overnight, and filtered. The filtered material was washed well with dry diethyl ether and dried (*in vacuo*; CaCl<sub>2</sub>) to give (*E*)-4-hydroxy-3-methylbut-3-en-2-one sodium salt (**22**)<sup>7</sup> (100 g, 82%);  $\nu_{\max}$ (KBr) 1 620sh, 1 590, and 1 550 cm<sup>-1</sup>;  $\lambda_{\max}$ (H<sub>2</sub>O) 289 nm ( $\epsilon$  14 300);  $\delta$ (60 MHz; D<sub>2</sub>O) 1.48 (3 H, s, 3-Me), 2.09 (3 H, s, 1-H<sub>3</sub>), and 8.97 (1 H, s, 4-H).

*Reaction of the Salt (22) with the Acetobromoglucose (21).*—To a stirred solution of the salt (**22**) (17.0 g, 139 mmol) in dry DMSO (120 cm<sup>3</sup>) was added the acetobromoglucose (**21**)<sup>6</sup> (40.0 g, 97 mmol) during 15 min. After 20 h, the mixture was poured over ice-cold water (500 cm<sup>3</sup>) and extracted with dichloromethane (6 × 200 cm<sup>3</sup>). The organic extract was washed with water (4 × 300 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), and evaporated. Recrystallisation of the product from diethyl ether gave (*E*)-3-methyl-4-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranosyloxy)but-3-en-2-one (**23b**) (7.00 g, 17%) as fine needles, m.p. 142–144 °C; [ $\alpha$ ]<sub>D</sub> -19° (0.7% in CHCl<sub>3</sub>);  $\nu_{\max}$ (KBr) 1 758 and 1 740 (together ester C=O), 1 667 (vinylogous ester C=O), and 1 655 cm<sup>-1</sup> (C=C);  $\lambda_{\max}$ (EtOH) 242 nm ( $\epsilon$  20 700);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 1.71 (3 H, d, *J* 1 Hz, 3-Me), 2.04, 2.05, 2.06, and 2.10 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.25 (3 H, s, 1-H<sub>3</sub>), 3.82–3.88 (1 H, m, 5'-H), 4.18 (1 H, dd, *J* 12.5 and 2 Hz, 6'-H), 4.31 (1 H, dd, *J* 12.5 and 5 Hz, 6'-H), 4.93 (1 H, d, *J* 7.5 Hz, 1'-H), 5.14–5.30 (3 H, m, 2'-, 3'-, and 4'-H), and 7.36 (1 H, apparent d, separation 1 Hz, 4-H) (in an n.O.e.d. experiment, irradiation of the signal at  $\delta$  7.36 caused a 13% enhancement of the signal at  $\delta$  4.93 and 5% enhancement of the signal at  $\delta$  2.25; irradiation of the signal at  $\delta$  4.93 caused an 18% enhancement of the signal at  $\delta$  7.36 and a 13% enhancement of the signal at  $\delta$  3.82–3.88); *m/z* (e.i.) 331 (C<sub>14</sub>H<sub>19</sub>O<sub>9</sub><sup>+</sup>) and 43 (C<sub>2</sub>H<sub>2</sub>O<sup>+</sup>, 100%) (Found: C, 52.8; H, 6.0. C<sub>19</sub>H<sub>26</sub>O<sub>11</sub> requires C, 53.0; H, 6.1%).

*Preparation of (E)-2-Methyl-1-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranosyloxy)-3-trimethylsilyloxybuta-1,3-diene (1b).*—(a) A mixture of fused zinc chloride (0.800 g, 5.87 mmol) and triethylamine (20 cm<sup>3</sup>, 143 mmol) was stirred for 1 h and to the dispersion was added a slurry of the butenone (**23b**) (8.00 g, 18.6 mmol) in dry benzene (160 cm<sup>3</sup>) followed by triethylsilyl chloride (10 cm<sup>3</sup>, 78.8 mmol). The mixture was stirred at 50 °C for 35 h, when the solvent was removed by evaporation and dry diethyl ether (100 cm<sup>3</sup>) was added to the residue. The insoluble material was removed by filtration and the filtrate was washed with water (4 × 50 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), and evaporated. The residue was recrystallised twice from diethyl ether–light petroleum to give the title compound (**1b**) (7.10 g, 76%), m.p. 98–100 °C; [ $\alpha$ ]<sub>D</sub> -18° (1.5% in CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{\max}$ (KBr) 1 755 and 1 740 (together ester C=O) and 1 657 cm<sup>-1</sup> (C=C);  $\lambda_{\max}$ (EtOH) 237 nm ( $\epsilon$  21 200);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 0.22 (9 H, s, Me<sub>3</sub>Si), 1.68 (3 H, d, *J* 1 Hz, 2-Me), 2.02, 2.03, 2.04, and 2.08 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 3.77–3.83 (1 H, m, 5'-H), 4.13 (1 H, dd, *J* 12 and 2 Hz, 6'-H), 4.20 and 4.32 (each 1 H, d, *J* 1 Hz, together 4-H<sub>2</sub>), 4.26 (1 H, dd, *J* 12 and 5 Hz, 6'-H), 4.75 (1 H, d, *J* 8 Hz, 1'-H), 5.09–5.28 (3 H, m, 2'-, 3'-, and 4'-H), and 6.70 (1 H, br s, 1-H) (in an n.O.e.d. experiment, irradiation of the signal at  $\delta$  6.70 caused a 13% enhancement of that at  $\delta$  4.75; irradiation of the signal at  $\delta$  4.75 caused a 32% enhancement of that at  $\delta$  6.70 and a 12% enhancement of that at  $\delta$  3.77–3.83; irradiation of the signal at  $\delta$  1.68 caused a 10% enhancement of that at  $\delta$  4.32); *m/z* (e.i.) 502 (*M*<sup>+</sup>), 331 (C<sub>14</sub>H<sub>19</sub>O<sub>9</sub><sup>+</sup>), and 43 (C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>, 100%) (Found: C, 52.7; H, 6.7. C<sub>22</sub>H<sub>34</sub>O<sub>11</sub>Si requires C, 52.55; H, 6.75%).

(b) To a stirred, cooled (CCl<sub>4</sub>–solid CO<sub>2</sub>) solution of the

\* Supplementary data (see section 5.6.3 of Instructions for Authors, in the January issue). Fractional co-ordinates of the hydrogen atoms and their isotropic thermal parameters and the anisotropic thermal parameters of the non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data centre.



butenone (**23b**) (5.00 g, 11.6 mmol) and triethylamine (3.3 cm<sup>3</sup>, 23.7 mmol) in dry dichloromethane (20 cm<sup>3</sup>) was added trimethylsilyl trifluoromethanesulphonate (2.7 cm<sup>3</sup>, 14 mmol). After 15 min, the solvent was removed by evaporation and the dark residue was subjected to low-temperature silica gel chromatography [light petroleum–Et<sub>2</sub>O (3:2) as eluant; the column was jacketed with Me<sub>2</sub>CO–solid CO<sub>2</sub>]. After recrystallisation from diethyl ether–light petroleum, the diene (**1b**) (4.50 g, 77%) was obtained as a white solid.

*Reaction of the Diene (1b) with p-Benzoquinone and Hydrolysis of the Cycloadduct (6d).*—To a stirred solution of the diene (**1b**) (0.251 g, 0.50 mmol) in dry benzene (2 cm<sup>3</sup>) in the dark was added freshly sublimed *p*-benzoquinone (0.054 g, 0.50 mmol). Removal of the solvent, after 20 h, left a residue which was very largely the cycloadduct (**6d**) on the basis of 300 MHz <sup>1</sup>H n.m.r. spectroscopy; there was no evidence for the presence of the cycloadduct (**7d**). Addition of dry diethyl ether to the residue and filtration gave (1*R*,6*R*,10*R*)-9-methyl-10-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-8-trimethylsiloxybicyclo-[4.4.0]deca-3,8-diene-2,5-dione (**6d**) (0.211 g, 69%). A sample, recrystallised from dichloromethane–diethyl ether, possessed m.p. 126–128 °C; [α]<sub>D</sub><sup>20</sup> +172° (0.3% in CH<sub>2</sub>Cl<sub>2</sub>); ν<sub>max</sub>(KBr) 1745 (ester C=O) and 1685 cm<sup>-1</sup> (enedione C=O); λ<sub>max</sub>(EtOH) 203 (ε 15 500) and 225sh nm (10 200); δ(300 MHz; CDCl<sub>3</sub>) 0.24 (9 H, s, Me<sub>3</sub>Si), 1.67 (3 H, br s, 9-Me), 1.95, 2.00, 2.05, and 2.07 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.14–2.21 (1 H, m, 7-H<sub>β</sub>), 3.09 (1 H, br d, separation 18 Hz, 7-H<sub>γ</sub>), 3.14 (1 H, dd, *J* 7 and 4 Hz, 1-H), 3.26 (1 H, t, *J* 7 and 7 Hz, 6-H), 3.55–3.61 (1 H, m, 5'-H), 4.09 (2 H, d, separation 4 Hz, 6'-H<sub>2</sub>), 4.31 (1 H, d, *J* 4 Hz, 10-H), 4.38 (1 H, d, *J* 8 Hz, 1'-H), 4.69 (1 H, t, *J* 8 and 8 Hz, 2'-H), 4.97 (1 H, 4, *J* 9 and 9 Hz, 4'-H), 5.02 (1 H, t, *J* 9 and 9 Hz, 3'-H), and 6.58 and 6.81 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (c.i.), 439 (7%), 438 (26), 368 (6), 367 (28), 366 (98), 263 (9), and 43 (C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>, 100) (Found: C, 54.9; H, 6.4. C<sub>28</sub>H<sub>38</sub>O<sub>10</sub>Si requires C, 55.05; H, 6.25%).

The cycloadduct (**6d**) (0.165 g, 0.27 mmol) was dissolved in THF (4 cm<sup>3</sup>) and 0.1M-hydrochloric acid (1 cm<sup>3</sup>) was added. After being stirred for 2.5 h under argon, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried (MgSO<sub>4</sub>) organic layer and recrystallisation of the residue from dichloromethane–diethyl ether gave (1*R*,6*R*,9*R*,10*S*)-9-methyl-10-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)bicyclo[4.4.0]dec-3-ene-2,5,8-trione (**9d**) (0.107 g, 74%) as needles, m.p. 142–144 °C; [α]<sub>D</sub><sup>20</sup> +9° (1.5% in CH<sub>2</sub>Cl<sub>2</sub>); ν<sub>max</sub>(KBr) 1750 (ester C=O), 1715 (ketone C=O), and 1690sh and 1670 cm<sup>-1</sup> (together enedione C=O); λ<sub>max</sub>(EtOH) 220 (ε 7600) and 302 nm(2800); δ(300 MHz; CDCl<sub>3</sub>) 1.09 (3 H, d, *J* 7 Hz, 9-Me), 1.96, 2.00, 2.08, and 2.09 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.37 (1 H, dd, *J* 16 and 8 Hz, 7-H<sub>β</sub>), 2.53 (1 H, dq, *J* 7 and 2 Hz, 9-H), 3.31 (1 H, dd, *J* 16 and 3 Hz, 7-H<sub>γ</sub>), 3.45–3.58 (3 H, m, 1-, 5'-, and 6-H), 4.08 (1 H, dd, *J* 12 and 5 Hz, 6'-H), 4.19–4.24 (2 H, m, 1'- and 6'-H), 4.66 (1 H, t, separation 2 Hz, 10-H), 4.70–4.76 and 4.97–5.05 (1 and 2 H, each m, together 2'-, 3'-, and 4'-H), and 6.81 and 6.90 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); δ(300 MHz; CD<sub>3</sub>CN; line-narrowed) 1.00 (3 H, d, *J* 7 Hz, 9-Me), 1.93, 2.07, 2.08, and 2.20 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.45 (1 H, ddd, *J* 16, 8, and 1 Hz, 7-H<sub>β</sub>), 2.76 (1 H, ddq, *J* 7, 2, and 1 Hz, 9-H), 3.04 (1 H, dd, *J* 16 and 1.5 Hz, 7-H<sub>γ</sub>), 3.58 (1 H, ddd, *J* 7, 2, and 1 Hz, 1-H), 3.67–3.76 (2 H, m, 5'- and 6-H), 4.08–4.18 (2 H, m, 6'-H<sub>2</sub>), 4.35 (1 H, d, *J* 8 Hz, 1'-H), 4.59 (1 H, t, *J* 2 and 2 Hz, 10-H), 4.65 (1 H, dd, *J* 10 and 8 Hz, 2'-H), 4.59 (1 H, t, *J* 10 and 10 Hz, 4'-H), 5.12 (1 H, t, *J* 10 and 10 Hz, 3'-H), 6.82 (1 H, dd, *J* 10 and 1 Hz, 4-H), and 6.92 (1 H, d, *J* 10 Hz, 4-H); *m/z* (e.i.) 331 (C<sub>14</sub>H<sub>19</sub>O<sub>9</sub><sup>+</sup>) and 43 (C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>, 100%) (Found: C, 57.7; H, 5.4. C<sub>25</sub>H<sub>30</sub>O<sub>13</sub> requires C, 55.75; H, 5.6%).

*Crystal Data for Compound (9d).*—C<sub>25</sub>H<sub>30</sub>O<sub>13</sub>, *M* = 538.5. Orthorhombic, *a* = 9.053, *b* = 12.951(3), *c* = 22.914(4) Å, *V* = 2 687 Å<sup>3</sup>, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *Z* = 4, *D*<sub>c</sub> = 1.33 g cm<sup>-3</sup>. Refined unit-cell parameters were obtained by centering 16 reflections on a Nicolet R3m diffractometer. 2 085 Independent reflections (θ ≤ 58°) were measured with Cu-K<sub>α</sub> radiation (graphite monochromator) using the ω-scan measuring routine; of these 1 865 had |*F*<sub>o</sub>| > 3σ(|*F*<sub>o</sub>|) and were considered to be observed. The net count of two check reflections (the 0, -2, -1 and the 0,2,0), measured every 50 reflections during the data collection, did not change significantly, indicating that no deterioration of the crystal had occurred. The data were brought to a uniform arbitrary scale, and Lorentz and polarisation corrections applied; no absorption correction was applied.

Several attempts at conventional multiple-solution tangent refinement, using automatically selected starting terms, failed to reveal any meaningful structural fragments. The structure was finally solved using two Σ1 terms, the 5 principal contributors to the list of negative quartets, and 12 automatically selected reflections. Δ*E* Map recycling of the fifth-ranked solution gave the positions of all non-hydrogen atoms. These atoms were refined anisotropically. The positions of the hydrogen atoms were idealised, C–H = 0.96 Å, assigned isotropic thermal parameters, *U*(H) = 1.2*U*<sub>eq</sub>(C), and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade, full-matrix least-squares to *R* = 0.039, *R*<sub>w</sub> = 0.044 [*w*<sup>-1</sup> = σ<sup>2</sup>(*F*) + 0.000 70*F*<sup>2</sup>]. The maximum residual electron density in the final Δ*F* map was 0.21 e Å<sup>-3</sup>. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.<sup>10,\*</sup>

*Reaction of the Diene (1b) with Methoxycarbonyl-p-benzoquinone and Hydrolysis of the Cycloadduct (6e).*—A solution of the diene (**1b**) (0.251 g, 0.50 mmol) and methoxycarbonyl-*p*-benzoquinone<sup>11</sup> (0.083 g, 0.50 mmol) in dry benzene (2 cm<sup>3</sup>) was kept overnight in the dark. The solvent was then evaporated off and the residue was found to be very largely the cycloadduct (**6e**) on the basis of 300 MHz <sup>1</sup>H n.m.r. spectroscopy; there was no evidence for the presence of the diastereoisomer (**7e**). Addition of dry diethyl ether and filtration gave (1*S*,6*R*,10*S*)-methyl 9-methyl-2,5-dioxo-10-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-8-trimethylsiloxybicyclo-[4.4.0]deca-3,8-diene-1-carboxylate (**6e**) (0.239 g, 72%). The sample, after recrystallisation from dichloromethane–diethyl ether, showed m.p. 158–159 °C; [α]<sub>D</sub><sup>20</sup> +200° (0.1% in CH<sub>2</sub>Cl<sub>2</sub>); ν<sub>max</sub>(KBr) 1755 and 1740sh (together ester C=O), 1700 and 1680 cm<sup>-1</sup> (together enedione C=O); λ<sub>max</sub>(EtOH) 204 (ε 13 800) and 223 nm (10 100); δ(300 MHz; CDCl<sub>3</sub>) 0.20 (9 H, s, Me<sub>3</sub>Si), 1.68 (3 H, br s, 9-Me), 1.96, 2.00, 2.04, and 2.07 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 3.09 (1 H, br d, separation 18 Hz, 7-H<sub>γ</sub>), 3.56–3.62 (1 H, m, 5'-H), 3.77 (3 H, s, OMe), 3.81 (1 H, d, *J* 8 Hz, 6-H), 4.10 (2 H, d, separation 4 Hz, 6'-H<sub>2</sub>), 4.42 (1 H, d, *J* 8 Hz, 1'-H), 4.68 (1 H, t, *J* 9 and 9 Hz, 2'-H), 4.68 (1 H, s, 10-H), 4.96 (1 H, t, *J* 9 and 9 Hz, 4'-H), 5.05 (1 H, t, *J* 9 and 9 Hz, 3'-H), and 6.54 and 6.85 (each 1 H, d, *J* 10 Hz, together 3- and 4-H) (the signal for the 7-H<sub>β</sub> was partly obscured by the MeCO signal at δ 2.07); *m/z* (c.i.) 686 (MNH<sub>4</sub><sup>+</sup>, 100%) (Found: C, 53.6; H, 6.1. C<sub>30</sub>H<sub>40</sub>O<sub>15</sub>Si requires C, 53.9; H, 6.05%).

Conc. hydrochloric acid (2 drops) was added to a stirred

\* *Supplementary data* (see section 5.6.3 of Instructions for Authors in the January issue). Fractional atomic co-ordinates of the hydrogen atoms and their isotropic thermal parameters, the bond lengths and bond angles, and the anisotropic thermal parameters of the non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

solution of the cycloadduct (**6e**) (0.100 g, 0.15 mmol) in chloroform (2 cm<sup>3</sup>). After 15 min, the mixture was poured onto water and extracted with dichloromethane. Evaporation of the dried (MgSO<sub>4</sub>) organic layer and crystallisation of the residue from dichloromethane–light petroleum gave (1*S*,6*R*,9*R*,10*S*)-methyl 9-methyl-2,5,8-trioxo-10-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)bicyclo[4.4.0]dec-3-ene-1-carboxylate (**9e**) (0.038 g, 43%). After recrystallisation from dichloromethane–diethyl ether–light petroleum, the sample possessed m.p. 82–84 °C;  $[\alpha]_D^{25} + 34^\circ$  (0.18% in CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{\max}$ (KBr) 1755br (ester C=O) and 1680 cm<sup>-1</sup> (enedione C=O);  $\lambda_{\max}$ (EtOH) 226 nm ( $\epsilon$  9700);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 1.12 (3 H, d, *J* 7 Hz, 9-Me), 1.96, 2.00, 2.06, and 2.10 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.27 (1 H, dd, *J* 16 and 7 Hz, 7-H<sub>β</sub>), 2.75 (1 H, dq, *J* 7 and 2 Hz, 9-H), 3.18 (1 H, dd, *J* 16 and 4 Hz, 7-H<sub>α</sub>), 3.54–3.62 (1 H, m, 5'-H), 3.86 (3 H, s, CO<sub>2</sub>Me), 3.96 (1 H, dd, *J* 7 and 4 Hz, 6-H), 4.09–4.22 (2 H, m, 6'-H<sub>2</sub>), 4.23 (1 H, d, *J* 8 Hz, 1'-H), 4.67–4.77 (1 H, m, 2'-H), 4.95 (1 H, br d, *J* 2 Hz, 10-H), 4.96–5.08 (2 H, m, 3'- and 4'-H), and 6.77 and 6.90 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (f.a.b., –ve ion) 596 (*M*<sup>-</sup>, 100%). (The sample, which was unstable, failed to give an acceptable elemental analysis.)

**Reaction of the Diene (1b) with Acetyl-*p*-benzoquinone and Hydrolysis of the Cycloadduct (6f).**—A solution of the diene (**1b**) (0.251 g, 0.50 mmol) and acetyl-*p*-benzoquinone<sup>12</sup> (0.075 g, 0.50 mmol) in dry benzene (2 cm<sup>3</sup>) was stirred overnight in the dark. The solvent was then evaporated off and the residue was found to be very largely the cycloadduct (**6f**) on the basis of 300 MHz <sup>1</sup>H n.m.r. spectroscopy; there was no evidence for the presence of the diastereoisomer (**7f**). Addition of diethyl ether, cooling of the solution, and collection of the insoluble material by filtration gave (1*R*,6*R*,10*S*)-1-acetyl-9-methyl-10-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-8-trimethylsilyloxy-bicyclo[4.4.0]deca-3,8-diene-2,5-dione (**6f**) (0.213 g, 65%). The sample, after recrystallisation from dichloromethane–diethyl ether, showed m.p. 134–136 °C;  $[\alpha]_D^{25} + 196^\circ$  (0.5% in CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{\max}$ (KBr) 1755 (ester C=O), 1705 (ketone C=O), and 1680 and 1670 cm<sup>-1</sup> (together enedione C=O);  $\lambda_{\max}$ (EtOH) 203 ( $\epsilon$  15500) and 222 nm (10800);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 0.18 (9 H, s, Me<sub>3</sub>Si), 1.67–1.72 (3 H, m, 9-Me), 1.95, 1.99, 2.03, and 2.06 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.34 (3 H, s, MeCO), 3.08 (1 H, br d, separation 18 Hz, 7-H<sub>γ</sub>), 3.60 (1 H, dt, *J* 10, 3, and 3 Hz, 5'-H), 3.90 (1 H, d, *J* 8 Hz, 6-H), 4.09 (2 H, d, separation 4 Hz, 6'-H<sub>2</sub>), 4.45 (1 H, d, *J* 8 Hz, 1'-H), 4.66 (1 H, dd, *J* 9 and 8 Hz, 2'-H), 4.68 (1 H, s, 10-H), 4.95 (1 H, t, *J* 9 and 9 Hz, 4'-H), 5.06 (1 H, t, *J* 9 and 9 Hz, 3'-H), and 6.45 and 6.81 (each 1 H, d, *J* 10 Hz, together 3- and 4-H) (the signal for the 7-H<sub>β</sub> was obscured by the MeCO signals); *m/z* (c.i.) 438 (32%), 378 (12), 377 (40), 367 (16), 366 (100), and 305 (13) (Found: C, 55.1; H, 6.1. C<sub>30</sub>H<sub>40</sub>O<sub>14</sub>Si requires C, 55.2; H, 6.15%).

Conc. hydrochloric acid (2 drops) was added to a stirred solution of the cycloadduct (**6f**) (0.100 g, 0.15 mmol) in dichloromethane (2 cm<sup>3</sup>). After 15 min, the solution was poured onto water and extracted with dichloromethane. Evaporation of the dried (MgSO<sub>4</sub>) organic layer and crystallisation of the residue from dichloromethane–light petroleum gave (1*R*,6*R*,9*R*,10*S*)-1-acetyl-9-methyl-10-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)bicyclo[4.4.0]dec-3-ene-2,5,8-trione (**9f**) (0.054 g, 61%). After recrystallisation from ethyl acetate–light petroleum, the sample possessed the following properties: m.p. 81–84 °C;  $[\alpha]_D^{25} + 14^\circ$  (0.23% in CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{\max}$ (KBr) 1760 (ester C=O), 1730 (ketone C=O), and 1675 cm<sup>-1</sup> (enedione C=O);  $\lambda_{\max}$ (EtOH) 226 nm ( $\epsilon$  9600);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 1.10 (3 H, d, *J* 7 Hz, 9-Me), 1.96, 2.00, 2.06, and 2.07 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.28 (1 H, dd, *J* 16 and 8 Hz, 7-H<sub>β</sub>), 2.41 (1 H, dq, *J* 7 and 2 Hz, 9-H), 2.46 (3 H, s, MeCO), 3.20 (1 H, dd, *J* 16 and 4 Hz, 7-H<sub>γ</sub>), 3.58–3.64 (1 H, m,

5'-H), 4.00 (1 H, dd, *J* 12 and 5 Hz, 6'-H), 4.23 (1 H, dd, *J* 12 and 3 Hz, 6'-H), 4.26 (1 H, d, *J* 8 Hz, 1'-H), 4.67–4.77 (1 H, m, 2'-H), 4.93–5.10 (3 H, m, 10-, 3'-, and 4'-H), and 6.74 and 6.91 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (f.a.b., –ve ion), 580 (*M*<sup>-</sup>, 100%). (The sample, which was unstable, failed to give an acceptable elemental analysis.)

**Reaction of the Diene (1b) with *N*-Phenylmaleimide and Hydrolysis of the Cycloadduct (10d).**—A mixture of the diene (**1b**) (0.200 g, 0.40 mmol) and *N*-phenylmaleimide (0.069 g, 0.40 mmol) in dry benzene (2 cm<sup>3</sup>) was stirred at room temperature for 4 days. Removal of the solvent left a residue which was mainly the cycloadduct (**10d**) by 300 MHz <sup>1</sup>H n.m.r. spectroscopy; there was no evidence for the presence of the diastereoisomer (**11c**). Addition of dry diethyl ether to the residue and filtration gave (1*R*,2*R*,3*R*)-4-methyl-*N*-phenyl-3-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-5-trimethylsilyloxy-cyclohex-4-ene-1,2-dicarboximide (**10d**) (0.230 g, 87%). The sample, after recrystallisation from dichloromethane–light petroleum, showed m.p. 161–163 °C;  $[\alpha]_D^{25} + 71^\circ$  (0.9% in CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{\max}$ (KBr) 1750sh and 1740 (together ester C=O), 1710 (imide C=O), and 1675 cm<sup>-1</sup> (C=C);  $\lambda_{\max}$ (EtOH) 210sh nm ( $\epsilon$  16200);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 0.24 (9 H, s, Me<sub>3</sub>Si), 1.47, 1.96, 2.02, and 2.09 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 1.76 (3 H, d, *J* 2 Hz, 4-Me), 2.55 (1 H, dd, *J* 15 and 9 Hz, 6-H<sub>γ</sub>), 2.79 (1 H, br apparent ddd, separations 15, 9, and 2 Hz, 6-H<sub>β</sub>), 3.22 (1 H, dd, *J* 11 and 4 Hz, 2-H), 3.35 (1 H, apparent q, separation 10 Hz, 1-H), 3.66–3.73 (1 H, m, 5'-H), 4.10 (1 H, dd, *J* 12 and 3 Hz, 6'-H), 4.18 (1 H, dd, *J* 12 and 5 Hz, 6'-H), 4.63 (1 H, d, *J* 4 Hz, 3-H), 4.64 (1 H, d, *J* 8 Hz, 1'-H), 4.82 (1 H, dd, *J* 9 and 8 Hz, 2'-H), 5.02 (1 H, t, *J* 9 and 9 Hz, 4'-H), 5.16 (1 H, t, *J* 9 and 9 Hz, 3'-H), and 7.30–7.55 (5 H, m, Ph); *m/z* (c.i.) 256 (41%), 255 (25), 169 (48), 119 (26), 117 (66), 109 (42), 108 (100), 81 (23), 80 (56), 75 (93), and 73 (39) (Found: C, 56.7; H, 6.3; N, 2.1. C<sub>32</sub>H<sub>41</sub>NO<sub>13</sub>Si requires C, 56.9; H, 6.1; N, 2.05%).

The cycloadduct (**10d**) (0.125 g, 0.185 mmol) was dissolved in THF (4 cm<sup>3</sup>) containing 0.1M-hydrochloric acid (1 cm<sup>3</sup>). After 2 h, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried (MgSO<sub>4</sub>) organic layer and recrystallisation of the residue from dichloromethane–diethyl ether gave (1*R*,2*R*,3*S*,4*R*)-4-methyl-5-oxo-*N*-phenyl-3-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)cyclohexane-1,2-dicarboximide (**12d**) (0.086 g, 77%) as needles, m.p. 208–210 °C;  $[\alpha]_D^{25} - 110^\circ$  (0.2% in CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{\max}$ (KBr) 1745 (ester C=O) and 1710 cm<sup>-1</sup> (imide and ketone C=O);  $\lambda_{\max}$ (EtOH) 201 ( $\epsilon$  12000) and 219 nm (8100);  $\delta$ (300 MHz; CDCl<sub>3</sub>) 1.24 (3 H, d, *J* 7 Hz, 4-Me), 1.57, 1.96, 2.03, and 2.09 (each 3 H, s, together 4 × MeCO<sub>2</sub>), 2.29 (1 H, dq, *J* 7 and 2 Hz, 4-H), 2.67 (1 H, dd, *J* 17 and 11 Hz, 6-H<sub>α</sub>), 2.92 (1 H, dd, *J* 17 and 8 Hz, 6-H<sub>β</sub>), 3.32 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.39–3.53 (1 H, m, 1-H), 3.70–3.77 (1 H, m, 5'-H), 4.13 (1 H, dd, *J* 12 and 5 Hz, 6'-H), 4.26 (1 H, *J* 12 and 3 Hz, 6'-H), 4.77 (1 H, d, *J* 8 Hz, 1'-H), 4.84 (1 H, dd, *J* 4 and 2 Hz, 3-H), 4.90 (1 H, dd, *J* 10 and 8 Hz, 2'-H), 5.06 (1 H, t, *J* 10 and 10 Hz, 4'-H), 5.21 (1 H, t, *J* 10 and 10 Hz, 3'-H), and 7.39–7.58 (5 H, m, Ph); *m/z* (c.i.) 367 (45%), 366 (100), 306 (20), 274 (31), and 273 (89) (Found: C, 56.6; H, 5.6; N, 2.0. C<sub>29</sub>H<sub>33</sub>NO<sub>13</sub>·0.5H<sub>2</sub>O requires C, 56.85; H, 5.6; N, 2.3%).

**Reaction of the Diene (1a) with Tetracyanoethylene** (With Dr. C. M. Raynor).—A solution of the diene (**1a**) (0.489 g, 1.00 mmol) and tetracyanoethylene (0.128 g, 1.00 mmol) in dry benzene (20 cm<sup>3</sup>) was stirred for 3 h. Evaporation left a residue which comprised mainly a 67:33 mixture of the cycloadducts (**24a**) and (**25a**) according to 300 MHz <sup>1</sup>H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at  $\delta$  0.29 and 0.31, attributed to the trimethylsilyl groups of compounds (**24a**) and (**25a**) respectively, and of the double triplets at  $\delta$  2.98 and 3.01, ascribed to the 6-hydrogen atoms of

compounds (**24a**) and (**25a**) respectively]. Addition of diethyl ether to the residue and filtration gave (3S)-3-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranosyloxy)-5-trimethylsilyloxycyclohex-4-ene-1,1,2,2-tetracarbonitrile (**24a**). The sample, after recrystallisation from dichloromethane–light petroleum, was isolated as a cream solid (0.258 g, 42%) with m.p. 165–167 °C (decomp.);  $[\alpha]_D^{20} + 20^\circ$  (1% in  $\text{CH}_2\text{Cl}_2$ );  $\nu_{\text{max}}$  (KBr) 1755 (ester C=O) and 1670  $\text{cm}^{-1}$  (C=C);  $\lambda_{\text{max}}$  (EtOH) 300 ( $\epsilon$  490), 392 (290), and 410 nm (270);  $\delta$ (300 MHz;  $\text{CDCl}_3$ ) 0.29 (9 H, s,  $\text{Me}_3\text{Si}$ ), 2.04, 2.07, 2.11, and 2.13 (each 3 H, s, together  $4 \times \text{MeCO}_2$ ), 2.98 (1 H, dt,  $J$  18, 1, and 1 Hz, 6-H), 3.14 (1 H, dt,  $J$  18, 2, and 2 Hz, 6-H), 3.78–3.85 (1 H, m, 5'-H), 4.22 (1 H, dd,  $J$  12 and 5 Hz, 6'-H), 4.26 (1 H, dd,  $J$  12 and 3 Hz, 6'-H), 4.93 (1 H, br s, 3-H), 4.95 (1 H, d,  $J$  8 Hz, 1'-H), 5.08–5.10 (1 H, m, 4-H), 5.16 and 5.17 (each 1 H, t,  $J$  10 and 10 Hz, together 2'- and 4'-H), and 5.27 (1 H, t,  $J$  10 and 10 Hz, 3'-H);  $m/z$  (c.i.,  $\text{Me}_3\text{CH}$  as carrier gas) 331 ( $\text{C}_{14}\text{H}_{19}\text{O}_9^+$ , 8%), 169 (7), and 42 ( $\text{C}_2\text{H}_2\text{O}^+$ , 100) (Found: C, 52.3; H, 5.1; N, 8.8; Si, 4.6.  $\text{C}_{27}\text{H}_{32}\text{N}_4\text{O}_{11}\text{Si}$  requires C, 52.6; H, 5.25; N, 9.1; Si, 4.55%).

*Reaction of the Diene (1b) with Tetracyanoethylene.*—A solution of the diene (**1b**) (0.200 g, 0.37 mmol) and tetracyanoethylene (0.047 g, 0.37 mmol) in dry benzene (2  $\text{cm}^3$ ) was stirred for 20 min. Evaporation left a residue which comprised an 80:20 mixture of the cycloadducts (**24b**) and (**25b**) according to 300 MHz  $^1\text{H}$  n.m.r. spectroscopy [the ratio was estimated from the integrals of the broad singlets at  $\delta$  4.83 and 4.88, attributed to the 3-hydrogen atoms of compounds (**25b**) and (**24b**) respectively]. Addition of diethyl ether to the residue and filtration gave (3R)-4-methyl-3-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranosyloxy)-5-trimethylsilyloxycyclohex-4-ene-1,1,2,2-tetracarbonitrile (**24b**) (0.171 g, 69%). The sample, after recrystallisation from dichloromethane–light petroleum, was isolated as needles with m.p. 178 °C (decomp.);  $[\alpha]_D^{20} + 4^\circ$  (1% in  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  (KBr) 1755 (ester C=O) and 1680  $\text{cm}^{-1}$  (C=C);  $\lambda_{\text{max}}$  (EtOH) 204 nm ( $\epsilon$  8300);  $\delta$ (300 MHz;  $\text{CDCl}_3$ ) 0.28 (9 H, s,  $\text{Me}_3\text{Si}$ ), 1.7 (3 H, br s, 4-Me), 2.03, 2.06, 2.10, and 2.13 (each 3 H, s, together  $4 \times \text{MeCO}_2$ ), 2.97 (1 H, br d, separation 18 Hz, 6-H), 3.13 (1 H, apparent dt, separations 18, 2, and 2 Hz, 6-H), 3.80–3.86 (1 H, m, 5'-H), 4.23 (1 H, dd,  $J$  12 and 5 Hz, 6'-H), 4.30 (1 H, dd,  $J$  12 and 3 Hz, 6'-H), 4.86 (1 H, br s, 3-H), 5.06 (1 H, d,  $J$  8 Hz, 1'-H), 5.10–5.18 (2 H, m, 2'- and 4'-H), and 5.27 (1 H, t,  $J$  9 and 9 Hz, 3'-H);  $m/z$  (c.i.) 331 ( $\text{C}_{14}\text{O}_{19}\text{O}_9^+$ , 21%), 169 (55), 109 (45), 75 (26), 73 (77), and 43 ( $\text{C}_2\text{H}_3\text{O}^+$ , 100) (Found: 53.1; H, 5.1; N, 8.6.  $\text{C}_{28}\text{H}_{34}\text{N}_4\text{O}_{11}\text{Si}$  requires C, 53.3; H, 5.45; N, 8.9%).

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## References

- 1 Part I, R. C. Gupta, C. M. Raynor, R. J. Stoodley, A. M. Z. Slawin, and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1773.
- 2 Preliminary communication, R. C. Gupta, A. M. Z. Slawin, R. J. Stoodley, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1986, 1116.
- 3 R. U. Lemieux, *Pure Appl. Chem.*, 1971, **25**, 527; R. U. Lemieux, S. Koto, and D. Voisin, *Am. Chem. Soc. Symp. Series*, 1979, **87**, 17; A. J. Kirby, 'The Anomeric Effect and Related Stereoelectronic Effects at Oxygen,' Springer-Verlag, New York, 1983.
- 4 F. Bernardi, N. D. Epiotis, R. L. Yates, and H. B. Schlegel, *J. Am. Chem. Soc.*, 1976, **98**, 2385.
- 5 R. C. Gupta, P. A. Harland, and R. J. Stoodley, *Tetrahedron*, 1984, **40**, 4657.
- 6 R. U. Lemieux, in 'Methods in Carbohydrate Chemistry,' eds. R. L. Whistler and M. L. Wolfrom, Academic Press, New York, 1963, vol. 2, p. 221.
- 7 R. Kaushal, S. Sorani, and S. S. Deshpande, *J. Ind. Chem. Soc.*, 1942, **19**, 107.
- 8 H. Emde, D. Domsch, H. Feger, U. Frick, A. Götz, H. H. Hergott, K. Hofmann, W. Kober, K. Krägeloh, T. Oesterle, W. Steppan, W. West, and G. Simchen, *Synthesis*, 1982, 1.
- 9 R. C. Gupta, D. A. Jackson, R. J. Stoodley, and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1985, 525.
- 10 G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, University of Gottingen, Federal Republic of Germany, 1978.
- 11 J. Cason, *Org. React.*, 1948, **4**, 354.
- 12 M. C. Kloetzel, R. P. Dayton, and B. Y. Abadir, *J. Org. Chem.*, 1955, **20**, 38.

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