Asymmetric Diels–Alder Reactions. Part 1. Diastereofacial Reactivity of (*E*)-3-Trimethylsilyloxybuta-1,3-dienyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside towards Cyclic Dienophiles[1]

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The title diene (**5a**) reacted with *p*-benzoquinone in benzene at ambient temperature to give an 89:11 mixture of (1*R*,6*R*,10*S*)-10-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)oxy]-8-trimethylsilyoxybicyclo[4.4.0]deca-3,8-diene-2,5-dione (**9a**) and its (1*S*,6*S*,10*R*)-diastereoisomer (**10a**). The stereostructure of the major cycloadduct was established by its conversion into (1*R*,6*R*,10*S*)-10-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)oxy]bicyclo[4.4.0]decane-2,5,8-trione (**12**), the structure of which was determined by *X*-ray crystallography. The diene (**5a**) showed a similar diastereofacial selectivity in its reactions with 2-methoxycarbonyl-*p*-benzoquinone [to give an 88:12 mixture of the cycloadducts (**9b**) and (**10b**)], 2-acetyl-*p*-benzoquinone [to yield a 75:25 mixture of the cycloadducts (**9c**) and (**10c**)], *N*-phenylmaleimide [to afford an 86:14 mixture of the cycloadducts (**15a**) and (**16a**)], maleimide [to produce an 85:15 mixture of the cycloadducts (**15b**) and (**16b**)], and maleic anhydride [to furnish mainly the cycloadduct (**15c**)]. In every instance, the major cycloadduct could be isolated in a pure state by crystallisation. Under mildly acidic conditions, it underwent hydrolysis resulting in the conversion of its *O*-silyl enol moiety into the ketone function. On the basis of c.d. spectroscopy, the ketones (**11a**—**c**) [derived from the respective cycloadducts (**9a**—**c**)] possessed the same absolute stereochemistry at positions 1, 6, and 10. The ketone (**17c**), formed by hydrolysis of the cycloadduct (**15c**), was transformed by the action of aniline and acetic anhydride into the ketone (**17a**), which was also obtained from the cycloadduct (**15a**) by hydrolysis. The conformational properties of the cycloadducts and their hydrolysis products were assessed by 300 MHz ^{1}H n.m.r. spectroscopy.

The Diels–Alder reaction[2] has played a substantial role in the development of synthetic, mechanistic, and theoretical organic chemistry.[3] The remarkable stereo- and regio-selectivities which are associated with the cycloaddition, coupled with the multiplicity of structural variations that are permitted to the diene and dienophile components, are responsible for its exceptional synthetic value.

Striking success in the use of the reaction to control absolute stereochemistry is of relatively recent vintage.[4] In this context, the temporary attachment of a homochiral auxiliary to the dienophile moiety, rather than the diene function, has been the more rewarding option. Indeed, the repertoire of such homochiral dienes available to the synthetic chemist is very limited; of the acyclic representatives, only Trost's diene (**1**)[5] has been especially effective. Thus it reacted with acrylaldehyde in the presence of boron trifluoride–ether complex to give, following reduction and hydrolysis, the *cis*-cyclohexanol (**2**) with an enantiomeric excess of 50%. Notably, the corresponding reaction with juglone in the presence of boron triacetate occurred with seemingly complete asymmetric induction to give the cycloadduct (**3**).

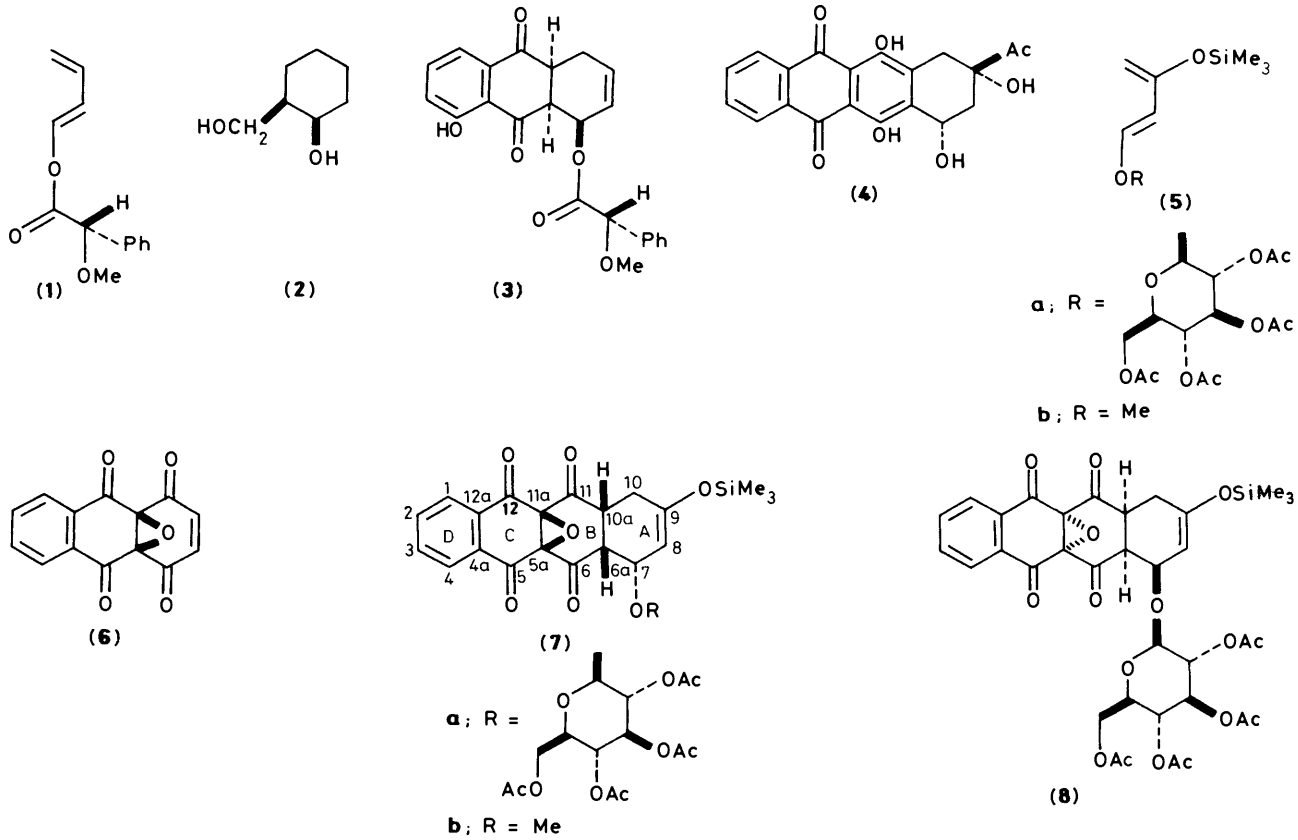
In work relating to the total synthesis of (+)-4-demethoxydaunomycinone (**4**), we had occasion to prepare the D-glucose-based diene (**5a**).[6] It reacted with the epoxy tetraone (**6**) to give one major cycloadduct, readily isolated by taking advantage of its insolubility in diethyl ether. Since the corresponding reaction of the dienophile (**6**) with Danishefsky's diene (**5b**) had been shown unequivocally to occur by way of the least-hindered *endo* transition state to give the racemic modification of the cycloadduct (**7b**)[7],‡ the major cycloadduct arising from compounds (**5a**) and (**6**) possessed the stereostructure (**7a**) or (**8**). By virtue of its transformation into (+)-4-demethoxydaunomycinone (**4**), the major cycloadduct was assigned the stereostructure (**7a**).[6] In this paper, we examine the diastereofacial reactivity of the diene (**5a**) towards the epoxy tetraone (**6**) and related cyclic dienophiles.

Results and Discussion

Previously,[6] it was found that the diene (**5a**) reacted with compound (**6**) in benzene at *ca.* 5 °C to give predominantly an 80:20 mixture of the cycloadducts (**7a**) and (**8**). The ratio was estimated by 300 MHz ^{1}H n.m.r. spectroscopy ($CDCl_3$) from the integrals of the doublets (*J* 18 Hz) at δ 2.73 and 2.84 [attributed to the 10α-hydrogen atoms of compounds (**8**) and

† Part of this work was carried out in the Department of Organic Chemistry at the University of Newcastle upon Tyne.

‡ Following previous practice, we have used the Brockmann system of numbering and lettering (H. Brockman, *Fortschr. Chem. Org. Naturst.*, 1983, **21**, 121) to describe compounds (**7a** and **b**) and their derivatives. Earlier and throughout this work, the αβ-notation is applied in the standard manner to the aglycones of the major cycloadducts of the diene (**5a**) and their derivatives; the descriptors are used in an opposite sense to describe the aglycones of the minor cycloadducts and their derivatives (because their absolute configuration is inverted). Cycloadducts of the diene (**5b**) and their derivatives are, of course, produced as racemic modifications. Only single enantiomers are represented in this paper, which, arbitrarily, correspond to the major cycloadducts of the diene (**5a**) and their derivatives; the αβ-notation is applied to these representations in the standard manner.



(**7a**), respectively] and of the double doublets (*J* 7.5 and 4 Hz) at δ 3.07 and 3.10 [attributed to the 6a-hydrogen atoms of compounds (**7a**) and (**8**), respectively]. The assignment was unequivocal in the case of the cycloadduct (**7a**) because the material had been isolated in a pure state and fully characterised. However, the assignment was not definitive in the case of the minor cycloadduct (**8**).

In the present study, the reaction of the diene (**5a**) with the oxirane (**6**) was conducted in benzene at *ca.* 20 °C in alkali-washed glassware. When the reaction was complete, the solvent was evaporated off. According to 300 MHz ^{1}H n.m.r. spectroscopy, the residue comprised a 75:25 mixture of the cycloadducts (**7a**) and (**8**) together with other materials. Trituration of the residue with diethyl ether and filtration afforded the major cycloadduct (**7a**) (43% yield). Concentration of the filtrate and subjection of the resultant foam to repeated fractionation by h.p.l.c. led to the isolation of the minor cycloadduct (**8**) in a slightly impure state. After recrystallisation, the last-cited compound was obtained (4.5% yield) as an analytically pure pale cream solid. Its 300 MHz ^{1}H n.m.r. spectrum incorporated signals at δ 2.72 and 3.16, substantiating the earlier assignment.

It was of interest to determine whether the diene (**5a**) would show a similar diastereofacial reactivity towards other cyclic dienophiles. *p*-Benzoquinone was selected for an initial study because of its high reactivity, although the experiences of Danishefsky and his co-workers[8] with its cycloadduct with the diene (**5b**) (the cycloadduct could not be purified and underwent aromatisation during acidic hydrolysis) were a cause for concern.

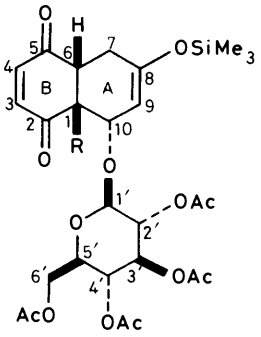
The diene (**5a**) reacted with *p*-benzoquinone in benzene at ambient temperature to give mainly an 89:11 mixture of cycloadducts, tentatively assigned the stereostructures (**9a**) and (**10a**).* The stereostructures of the cycloadducts were assumed on the basis that their formation would involve *endo* transition states; by analogy with the reaction involving compounds (**5a**) and (**6**), the major cycloadduct was considered to possess the stereostructure (**9a**). Addition of diethyl ether to the crude product gave the major cycloadduct (**9a**) in 46% yield. A single recrystallisation provided the material in an analytically pure state. Efforts to purify the minor cycloadduct (**10a**) were without avail, the material being unstable to chromatography (including h.p.l.c.).

The unrecrystallised cycloadduct (**9a**) underwent hydrolysis in tetrahydrofuran (THF) containing dilute hydrochloric acid to give, after recrystallisation, the enetrione (**11a**) in 45% yield based upon the diene (**5a**).

The crystals of compounds (**9a**) and (**11a**) were not suitable for *X*-ray analysis. However, the trione (**12**), obtained in 83% yield after recrystallisation by subjecting the enetrione (**11a**) to the action of zinc in acetic acid, was amenable to *X*-ray study. The molecular structure, which was readily solved using direct methods (see Experimental section for crystal data and other information), is shown in the Figure, together with its crystallographic numbering. Refined atomic co-ordinates are included in Table 1, while bond lengths and bond angles are available from the Cambridge Crystallographic Data Centre.

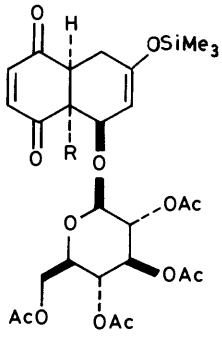
The *X*-ray study confirmed that the major cycloadduct arising from the reaction of the diene (**5a**) with *p*-benzoquinone possessed the stereostructure (**9a**). Thus the diene (**5a**) had displayed a similar diastereofacial reactivity towards both the epoxy tetraone (**6**) and *p*-benzoquinone.

* To facilitate comparisons, the numbering and lettering shown in structure (**9**) are used in this paper to describe the cycloadducts of the dienes (**5a** and **b**) and *p*-benzoquinone, 2-methoxycarbonyl-*p*-benzoquinone, and 2-acetyl-*p*-benzoquinone; derivatives of the aforecited compounds are labelled in an analogous manner.



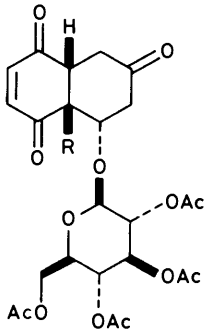
(9)

a; R = H
b; R = CO_2Me
c; R = Ac



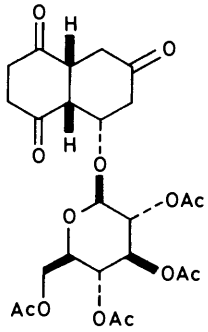
(10)

a; R = H
b; R = CO_2Me
c; R = Ac

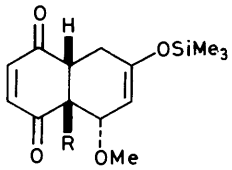


(11)

a; R = H
b; R = CO_2Me
c; R = Ac

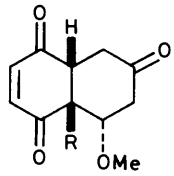


(12)



(13)

a; R = H
b; R = CO_2Me
c; R = Ac



(14)

a; R = H
b; R = CO_2Me
c; R = Ac

In view of the apparent difference in behaviour between the cycloadduct (**9a**) and that derived from *p*-benzoquinone and the diene (**5b**), we reinvestigated the reaction leading to the latter cycloadduct. In benzene at ambient temperature, the diene (**5b**) reacted with *p*-benzoquinone to give the racemic modification of the cycloadduct (**13a**) in 66% yield after recrystallisation in an analytically pure state. The (±)-cycloadduct (**13a**) was converted into the pure (±)-enetrione (**14a**) in 90% yield after recrystallisation when subjected to the action of dilute hydrochloric acid in THF. Clearly, Danishefsky's findings[8] were the consequence of using inappropriate conditions for the cycloaddition and hydrolysis reactions.

It was of interest to examine the reaction of the diene (**5a**) with unsymmetrical *p*-benzoquinones and, in this context, 2-methoxycarbonyl-*p*-benzoquinone[9] and 2-acetyl-*p*-benzoquinone[10] were selected for study. Although, in principle, eight cycloadducts are possible in each case, it was anticipated[11,12] that the cycloadducts (**9b** and **c**) would predominate. Thus the methoxycarbonyl and acetyl moieties were expected to render the 2,3-double bonds of the quinones more reactive than their 5,6-counterparts. They were also expected to control the regiochemical outcome of the cycloaddition reactions. Finally, it was envisaged that the dione moieties would dominate any

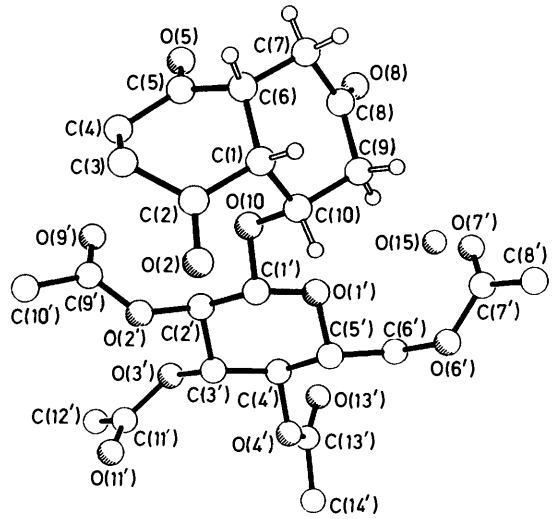


Figure. The molecular structure of compound (**12**)

Table 1. Fractional atomic co-ordinates (× 10^4) and temperature factors ($Å^2$; × 10^3)

Atom	*x*	*y*	*z*
C(1)	742(11)	7 439(5)	2 115(2)
C(2)	1 328(13)	8 469(6)	1 884(2)
O(2)	302(11)	8 860(5)	1 621(2)
C(3)	3 195(14)	8 973(7)	1 998(3)
C(4)	4 743(12)	8 080(7)	2 028(3)
C(5)	4 209(13)	7 094(8)	2 273(2)
O(5)	5 331(10)	6 349(6)	2 344(2)
C(6)	2 212(11)	7 099(6)	2 347(2)
C(7)	1 687(14)	6 029(6)	2 650(2)
C(8)	1 135(11)	5 141(6)	2 353(2)
O(8)	1 760(11)	4 191(4)	2 376(2)
C(9)	−308(11)	5 466(6)	2 039(2)
C(10)	218(9)	6 530(5)	1 816(2)
O(10)	1 840(6)	6 342(3)	1 555(1)
C(1′)	1 306(8)	6 135(5)	1 152(2)
O(1′)	445(8)	5 060(3)	1 142(1)
C(2′)	3 067(9)	6 120(5)	884(2)
O(2′)	3 785(6)	7 240(3)	859(1)
C(3′)	2 515(9)	5 766(4)	456(2)
O(3′)	4 235(6)	5 545(3)	226(1)
C(4′)	1 379(10)	4 706(5)	459(2)
O(4′)	662(6)	4 515(3)	54(1)
C(5′)	−303(10)	4 803(5)	749(2)
C(6′)	−1 399(11)	3 715(6)	790(2)
O(6′)	−3 147(7)	3 917(4)	1 040(1)
C(7′)	−3 282(14)	3 377(7)	1 408(2)
O(7′)	−2 080(11)	2 717(5)	1 516(2)
C(8′)	−5 079(13)	3 742(9)	1 625(2)
C(9′)	5 612(10)	7 418(5)	967(2)
O(9′)	6 700(7)	6 722(4)	1 087(2)
C(10′)	6 108(11)	8 633(6)	922(2)
C(11′)	4 708(9)	6 250(6)	−82(2)
O(11′)	3 885(8)	7 107(4)	−147(2)
C(12′)	6 353(12)	5 788(7)	−309(2)
C(13′)	972(11)	3 498(5)	−117(2)
O(13′)	1 682(10)	2 745(4)	57(2)
C(14′)	211(12)	3 451(6)	−536(2)
O(15)	627(38)	995(14)	1 208(5)

secondary orbital effects and therefore that the *endo* transition states would be favoured.

In a preliminary study, the cycloaddition of the diene (**5b**) with 2-methoxycarbonyl-*p*-benzoquinone was investigated. When conducted in benzene at room temperature, the reaction gave rise to one major cycloadduct (67% yield) which, on the basis of 300 MHz ^{1}H n.m.r. spectroscopy, was assigned the (±)-stereostructure (**13b**). Thus the presence of two one-proton doublets (*J* 10 Hz) at δ 6.67 and 6.85 established that the diene (**5b**) had added to the 2,3-double bond of the *p*-benzoquinone. The appearance of the 10-H signal, at δ 4.46 as a doublet (*J* 6 Hz) (due to coupling with the 9-hydrogen atom at δ 5.18), revealed the vicinal relationship of the methoxy and methoxycarbonyl moieties [in the (±)-cycloadduct (**13a**), the 10-hydrogen atom resonated as a double doublet at δ 4.05 due to coupling with the 9-hydrogen atom at δ 5.14 (*J* 5.5 Hz) and the 1-hydrogen atom at δ 3.10 (*J* 4 Hz)]. Finally, the coupling constants of 6- and 7α-H and 6- and 7β-H of the (±)-cycloadduct (**13b**) were very similar to the corresponding values for the (±)-cycloadduct (**13a**), implying a common conformational as well as configurational relationship between the two compounds.

In THF containing dilute hydrochloric acid the (±)-cycloadduct (**13b**) underwent hydrolysis to give the (±)-enetrione (**14b**) in 69% yield after recrystallisation. The 300 MHz ^{1}H n.m.r. spectrum of the last-cited compound featured the 10-H signal as a triplet (*J* 3 and 3 Hz) at δ 4.37 due to coupling with the 9-hydrogen atoms [in the (±)-enetrione (**14a**), the 10-H signal appeared as an apparent quartet (separation 3 Hz) at δ 4.10 owing to equal coupling with the 9- and 1-hydrogen atoms]. Again, the coupling constants of the 6- and 7α-H and 6- and 7β-H of the (±)-enetrione (**14b**) were very similar to those of the (±)-enetrione (**14a**), reinforcing the conformational and configurational similarity of the two compounds.

In benzene at *ca.* 20 °C, the diene (**5a**) reacted with 2-methoxycarbonyl-*p*-benzoquinone to give mainly an 88:12 mixture of the cycloadducts (**9b**) and (**10b**); addition of diethyl ether to the mixture and filtration gave the major cycloadduct in 75% yield. Compound (**9b**) was obtained in a pure state after recrystallisation. Attempts to purify the minor cycloadduct (**10b**) were unrewarding, the material decomposing when subjected to h.p.l.c. The constitutional and configurational similarity of the cycloadduct (**9b**) to its (±)-relative (**13b**) were established by 300 MHz ^{1}H n.m.r. spectroscopy. Thus the 3- and 4-H signals appeared as doublets (*J* 10 Hz) at δ 6.51 and 6.81, whereas the 10-hydrogen atom resonated as a doublet (*J* 5.5 Hz) at δ 4.84.

Acidic hydrolysis of the unrecrystallised cycloadduct (**9b**) gave the enetrione (**11b**) in 59% yield after recrystallisation [based upon the diene (**5a**)]. The high-field ^{1}H n.m.r. spectrum of this compound featured the 10-H signal as an apparent quartet (separation 3 Hz) at δ 4.85.

A single cycloadduct (75% yield) was also isolated from the reaction of the diene (**5b**) with 2-acetyl-*p*-benzoquinone in benzene at *ca.* 5 °C. High-field ^{1}H n.m.r. spectroscopy left little doubt that the material possessed the (±)-stereostructure (**13c**). Thus the spectrum incorporated a one-proton doublet (*J* 7 Hz) at δ 4.50 for the 10-hydrogen atom and two one-proton doublets (*J* 10 Hz) at δ 6.59 and 6.85 for the 3- and 4-hydrogen atoms.

Although converted into a mixture of products when subjected to the standard hydrolysis conditions, the (±)-cycloadduct (**13c**) was transformed into the (±)-enetrione (**14c**) (50% yield after recrystallisation) under milder acidic conditions. In the 300 MHz ^{1}H n.m.r. spectrum of compound (**14c**), the 10-hydrogen atom absorbed as a triplet (*J* 3 and 3 Hz) at δ 4.42.

In benzene at ambient temperature, the diene (**5a**) reacted with 2-acetyl-*p*-benzoquinone to give mainly a 75:25 mixture of the cycloadducts (**9c**) and (**10c**). The major cycloadduct, isolated by virtue of its poor solubility in diethyl ether, was obtained in 43% yield. Attempts to isolate the minor cycloadduct (**10c**) using h.p.l.c. were unsuccessful, owing to the lability of the compound. In the cycloadduct (**9c**), the 3- and 4-H signals appeared as doublets (*J* 10 Hz) at δ 6.48 and 6.82 and the 10-hydrogen atom resonated as a doublet (*J* 6 Hz) at δ 4.82.

Acidic hydrolysis of the unrecrystallised cycloadduct (**9c**) gave the enetrione (**11c**) in 32% yield after recrystallisation [based upon the diene (**5a**)] in an analytically pure state. In the ^{1}H n.m.r. spectrum of the last-cited compound, the 10-H signal appeared as a triplet (*J* 3 and 3 Hz) at δ 4.84.

A comparison of the circular dichroism (c.d.) spectra of the enetriones (**11a**—**c**) left little doubt about their stereochemical similarity. Thus in acetonitrile, compound (**11a**) showed positive dichroisms at 225 (Δε + 12.14) and 242 nm (Δε + 5.46). Under corresponding conditions, the enetrione (**11b**) possessed positive dichroisms at 228 (Δε + 12.32) and 242 nm (Δε + 4.60) whereas compound (**11c**) featured positive dichroisms at 228 (Δε + 4.02), 245 (Δε + 0.37), and 280 nm (Δε + 1.68). Clearly, there was little question that the major cycloadducts arising from the reactions of the diene (**5a**) with 2-methoxycarbonyl-*p*-benzoquinone and 2-acetyl-*p*-benzoquinone possessed the stereostructures (**9b** and **c**). Again, the diastereofacial reactivity of the diene (**5a**) towards the substituted *p*-benzoquinones had paralleled that observed with *p*-benzoquinone and the epoxy tetraone (**6**).

It was of interest to examine the diastereofacial reactivity of the diene (**5a**) towards heterocyclic five-membered dienophiles. In benzene at ambient temperature, the diene (**5a**) reacted with *N*-phenylmaleimide to give mainly an 86:14 mixture of cycloadducts. Addition of diethyl ether to the mixture and filtration gave the major cycloadduct in 58% yield. Although not unambiguously established, the stereostructure (**15a**) was assumed for the major cycloadduct by analogy with the earlier results. When the filtrate [obtained after removal of the cycloadduct (**15a**)] was concentrated and the residue subjected to purification by h.p.l.c., the minor cycloadduct (**16a**) was isolated in a pure state in 6% yield.

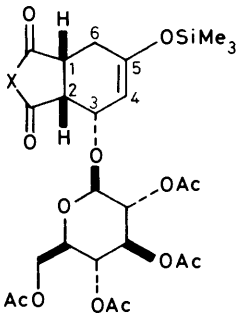
Acidic hydrolysis of the major cycloadduct (**15a**) provided the ketone (**17a**) in 85% yield. When the material obtained after removal of the major cycloadduct (**15a**) was subjected to acidic hydrolysis and the product fractionated by silica gel chromatography, the ketone (**18a**) was obtained in 7% yield [based upon the diene (**5a**)].

Mainly an 85:15 mixture of cycloadducts was produced from the reaction of the diene (**5a**) with maleimide in benzene. The usual work-up procedure led to the isolation of the major cycloadduct, considered to possess the stereostructure (**15b**), in 37% yield. Acidic hydrolysis of the crude cycloadduct and recrystallisation of the product gave the ketone (**17b**) in 61% yield.

The diene (**5a**) reacted with maleic anhydride in benzene to give a mixture of products.* Again, addition of diethyl ether to the mixture and recrystallisation of the insoluble material provided a cycloadduct, assumed to possess the stereostructure (**15c**), in 52% yield. When subjected to acidic hydrolysis, the cycloadduct (**15c**) was transformed into the ketone (**17c**) in 81% yield after recrystallisation.

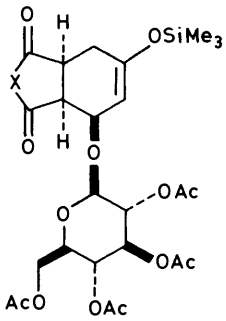
A comparison of the 300 MHz ^{1}H n.m.r. spectral properties of the major cycloadducts (**15a**—**c**) (all of which were isolated in a pure state) with those of the minor cycloadducts (**16a** and **b**) [compound (**16a**) was obtained pure; compound (**16b**) was a constituent of a mixture and its presence was inferred from ^{1}H n.m.r. spctroscopy] revealed some diagnostic differences. In

* The ratio reported in ref. 1 is unreliable.



(15)

a; X = NPh
b; X = NH
c; X = O



(16)

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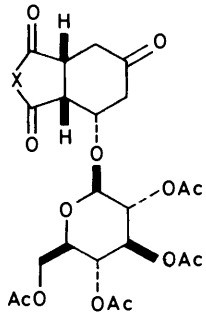
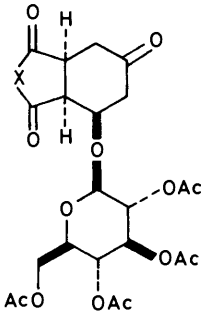
b; X = NH



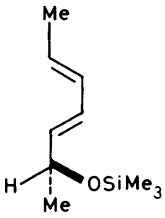
(17)

a; X = NPh
b; X = NH
c; X = O



(18)

a; X = NPh
b; X = NH
c; X = O



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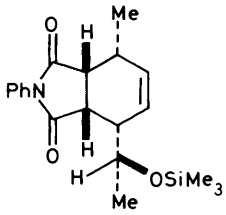

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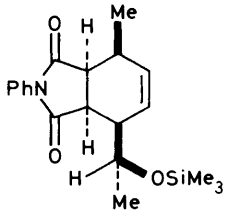

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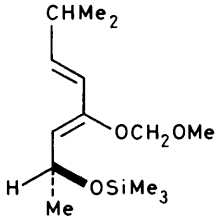

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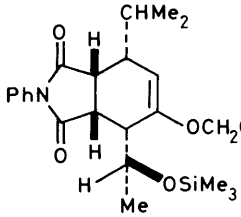

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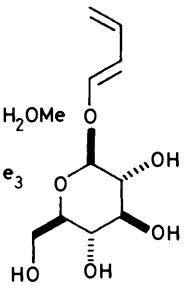

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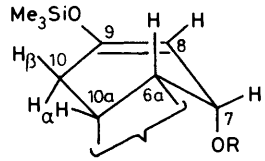

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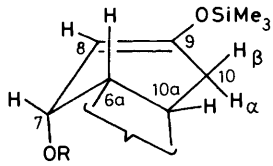


(26)

particular, the signals for the trimethylsilyl moieties of the major cycloadducts were at higher field (in the δ 0.21—0.25 region) than those of the minor cycloadducts (in the δ 0.30—0.33 region). It is noteworthy that the signals for the trimethylsilyl groups of the major cycloadducts (**7a**) and (**9a**—**c**) were also at higher fields than those attributed to their counterparts (**8**) and (**10a**—**c**). These observations supported the view that the major cycloadducts emerging from the reactions of the diene (**5a**) with *N*-phenylmaleimide, maleimide, and maleic anhydride possessed the stereostructures (**15a**—**c**).

A comparison of the c.d. spectra of the ketones (**17a** and **b**) left little doubt about their stereochemical similarity. Thus in acetonitrile, the former compound showed negative dichroisms at 295 (Δε −4.35), 303 (Δε −3.50), and 312sh nm (Δε −1.53), whereas the latter compound displayed similar negative dichroisms at 292 (Δε −3.07), 303 (Δε −2.51), and 312sh nm (Δε −1.10). By contrast, the ketone (**18a**) displayed positive dichroisms at 297 (Δε +3.20), 304 (Δε +2.52), and 312sh nm (Δε +1.16). Finally, a chemical correlation between the ketones (**17a** and **c**) was established. Thus the latter compound reacted with aniline in dichloromethane at low temperature to give a mixture of products which was transformed into the ketone (**18a**) (20% yield after SiO_2 chromatography) by the action of acetic anhydride and pyridine. Clearly, the three chiral centres associated with the aglycone moieties of compounds (**15a**—**c**) possessed the same absolute configuration.

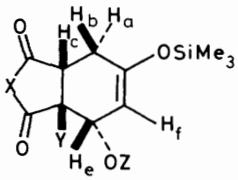
The foregoing findings are of synthetic and mechanistic interest. In the former context, an operationally simple route to functionalised homochiral *cis*-decalins and cyclohexenes is delineated. In the latter association, the diastereofacial reactivity of the diene (**5a**) is notable. Generally, only modest diastereoselection is observed in uncatalysed Diels–Alder reactions involving chiral acylic dienes and achiral cyclic dienophiles.[13] Recently, however, Franck and his co-workers found[14] that the diene (**19**) (in racemic form) reacted with *N*-phenylmaleimide to give an 88:12 mixture of the cycloadducts (**20**) and (**21**). Subsequently, McDougal's group reported[15] that the diene (**22**) (in racemic form) gave exclusively the cycloadduct (**23**) with *N*-phenylmaleimide. Of course, in compounds (**19**) and (**22**), the chiral centre is adjacent to the diene moieties and it is destined to become an integral part of any product. With compound (**5a**), the nearest chiral centre is separated from the diene moiety by an oxygen atom; furthermore, there is the possibility of removing the chiral auxiliary from any product.

In a recent development, Lubineau and Queneau prepared[16] the diene (**24**) and noted that it reacted with methacrylaldehyde in water to give a 60:40 mixture of cycloadducts. Interestingly, the sugar moiety could be removed from the cycloadduct mixture (after reduction of the aldehydic and olefinic moieties) by enzymic hydrolysis with β-glucosidase.

Conformation Considerations.—Previously, rings *A* of the epoxy tetraones (**7a** and **b**) were considered to adopt the sofa-like geometry (**25**) on the basis of ^1H n.m.r. spectroscopy.[6,7] It was of interest therefore to compare the conformational properties of rings *A* of the related cycloadducts prepared in this study.

In the case of the epoxy tetraone (**8**), the proton coupling constants $J_{10\beta,10a}$ and $J_{10\alpha,10a}$ were 6.5 and ≤ 1 Hz whereas $J_{6a,10a}$ and $J_{6a,7}$ were 6 and 4.5 Hz. These values, which can be equated to respective torsion angles of *ca.* 40°, 80°, 40°, and 50° by using a modified Karplus relationship[17] (J^0 11; J^{180} 12 Hz), are very similar to those observed in compound (**7a**). Clearly, ring *A* of the epoxy tetraone (**8**) favours the sofa-like geometry (**26**) and, apart from the mirror-image relationship, it is virtually identical with that of compound (**7a**).

Table 2. Coupling constants (Hz) of the ring-*A*-associated protons of compounds of type (**27**)



(**27**)

Compound	X	Y	Z	$J_{a,b}$	$J_{a,c}$	$J_{b,c}$	$J_{c,d}$	$J_{d,e}$	$J_{e,f}$	$J_{b,f}$
(**9a**)	CH=CH	H_d	Gl[a]	18	≤1	7	7	5	5	≤1
(**13a**)	CH=CH	H_d	Me	18.5	≤1	7.5	7.5	4	5.5	1
(**9b**)	CH=CH	CO_2Me	Gl	18	≤1				5.5	≤1
(**13b**)	CH=CH	CO_2Me	Me	18	≤1	8			6.5	1.5
(**9c**)	CH=CH	Ac	Gl	19	≤1	7.5			6	≤1
(**13c**)	CH=CH	Ac	Me	18	≤1	8			6	1.5
(**15a**)	NPh	H_d	Gl	16	10	8.5	10	5	7	2.5
(**15b**)	NH	H_d	Gl	17	10	8	10	4.5	7	3
(**15c**)	O	H_d	Gl	18	11	4.5	11	4.5	7	2.5

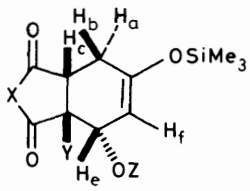
[a] Gl = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl.

A comparison of the coupling constants of the ring-*A*-associated protons of the cycloadducts (**9a**—**c**) and (**13a**—**c**) [labelled H_a—H_f as depicted in the generalised formula (**27**)] is made in Table 2. Again, the values strongly suggest that a common conformation, denoted by the generalised structure (**28**), is adopted. This geometry is very similar to that taken up by rings *A* of compounds (**7a** and **b**) and (**8**). In the case of compounds (**9a**) and (**13a**), where Y represents a hydrogen atom (*i.e.* H_d), the result is not surprising. However, it is noteworthy that, in spite of the presence of an axial-like methoxycarbonyl or acetyl group, the geometry is maintained in compounds (**9b** and **c**) and (**13b** and **c**). Cooper and Sammes reported[12] a similar conformational bias in the case of compound (**29**).

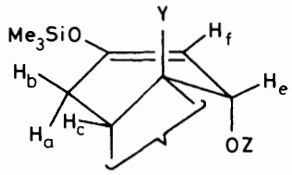
The coupling constants of the ring-*A*-associated protons of compounds (**15a**—**c**) are also summarised in Table 2. In the case of compound (**15c**), the values are consistent with the adoption of a boat-like conformation of type (**30**). Thus the torsion angle between H_a and H_c is estimated to be *ca.* 165°, between H_b and H_c *ca.* 50°, between H_c and H_d *ca.* 0°, and between H_d and H_e *ca.* 50°. With compounds (**15a** and **b**), a slight conformational distortion of ring *A* towards a twist-boat-like geometry of type (**31**) is apparent. Thus $J_{b,c}$ is *ca.* 8 Hz, consistent with a torsion angle between H_b and H_c of *ca.* 30°. The presence of a large long-range coupling (*J* 2.5—3 Hz) between H_b and H_f in compounds (**15a**—**c**), implying a **W**-like disposition of the protons[18] [no such sizeable coupling was observed in the cycloadducts (**7a** and **b**), (**8**), (**9a**—**c**), and (**13a**—**c**)] is also in accord with the boat-like geometry. Clearly, the fusion of the five-membered ring (presumably near planar) necessitates a near-eclipsed relationship of H_c and H_d and a consequential boat-like disposition of ring *A*.

The coupling constants of ring-*A*-associated protons of the cycloadduct (**16a**) were very similar to those of its diastereoisomeric counterpart (**15a**) indicating that the ring *A* geometries of the two compounds were identical (rings *A* bear an enantiomeric relationship).

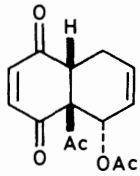
Previously, the ring *A* conformations of the epoxy pentaones (**32a** and **b**) and the dihydroxy triones (**33a** and **b**) were compared.[6,7] It was suggested that a sofa-like geometry of type (**34**) represented the average conformation of the former compounds, whereas a chair-like geometry of type (**35**) was preferred in the latter compounds. It was therefore of interest to compare the behaviour of the related compounds prepared in this study.



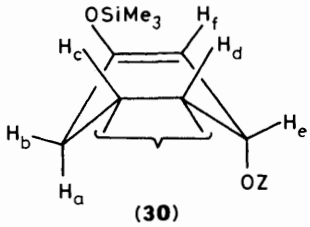
(**27**)



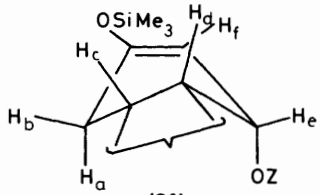
(**28**)



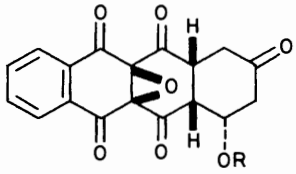
(**29**)



(**30**)

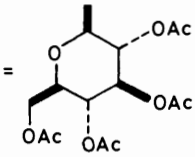


(**31**)



(**32**)

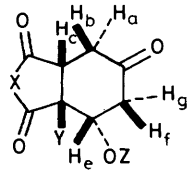
a; R =



b; R = Me

A comparison of the coupling constants of the ring-*A*-associated protons of compounds (**11a**—**c**), (**12**), and (**14a**—**c**)

Table 3. Coupling constants (Hz) of the ring-*A*-associated protons of compounds of type (**36**)

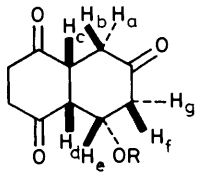


(**36**)

Compound	X	Y	Z	$J_{a,b}$	$J_{a,c}$	$J_{b,c}$	$J_{c,d}$	$J_{d,e}$	$J_{e,f}$	$J_{e,g}$	$J_{f,g}$	$J_{a,f}$
(**11a**)	CH=CH	H_d	Gl[a]	16	3	8	8	3	3	3	16	2
(**14a**)	CH=CH	H_d	Me	16	2	8	8	3	3	3	16	3
(**11b**)	CH=CH	CO_2Me	Gl	16	3	7			3	3	16	2
(**14b**)	CH=CH	CO_2Me	Me	16	2	7			3	3	16	2
(**11c**)	CH=CH	Ac	Gl	17	3.5	7			3	3	17	2
(**14c**)	CH=CH	Ac	Me	16	2	8			3	3	16	3
(**12**)	CH_2CH_2	H_d	Gl	16	2	8	8	3	3	3.5	16	2
(**17a**)	NPh	H_d	Gl	16.5	11	9	10	4	3	2.5	19	0
(**17b**)	NH	H_d	Gl		10	10	10	4.5	3	3	19	0
(**17c**)	O	H_d	Gl	17	9	11	11	4	3	3	18	0

[a] Gl = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl.

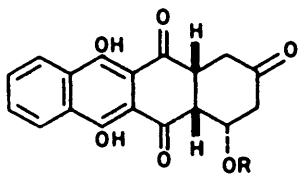
Table 4. Selected torsion angles (°) of compound (**12**) determined from *X*-ray analysis[a] and spin–spin coupling constants[b]



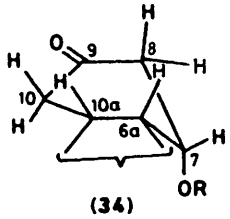
(**12**) R = 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl

	Angle (from *X*-ray)	Angle (from *J*) (J^0 = 11 Hz)	Angle (from *J*) (J^0 = 14 Hz)
H_a,H_c	76	65	68
H_b,H_c	44	31	41
H_c,H_d	50	31	41
H_d,H_e	55	59	62
H_e,H_f	70	59	62
H_e,H_g	49	56	60

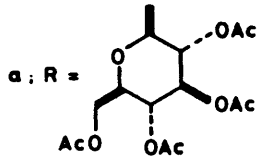
[a] The torsion angles are based on calculated hydrogen positions fixed by reference to the refined 'heavy' atomic co-ordinates. [b] The spin–spin coupling constants (*J*) were converted into torsion angles (θ) by using the Karplus relationship: [17] $\cos\theta = (J/J^0)^{1/2}$.



(**33**)

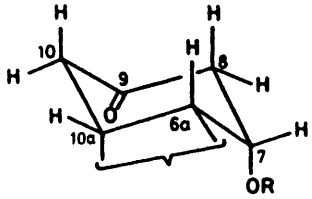


(**34**)

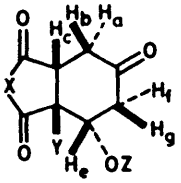


a ; R =

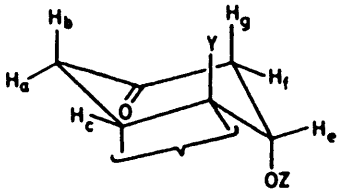
b ; R = Me



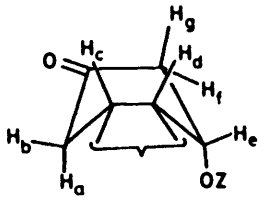
(**35**)



(**36**)



(**37**)



(**38**)

[labelled H_a—H_g as shown in the generalised formula (**36**)] is made in Table 3. The values are quite similar to those reported for the dihydroxy triones (**33a** and **b**), leaving little doubt that rings *A* of these compounds possess a common geometry. However, we suggest that the partially flattened chair (**37**) is a more apt representation of the average ring *A* conformation than that previously proposed [*i.e.* (**35**)]. In particular, the values of $J_{b,c}$ and $J_{c,d}$ (*ca.* 8 Hz) are indicative of torsion angles between H_b and H_c and between H_c and H_d of *ca.* 30°. The presence of a sizeable long-range coupling (*J* 2—3 Hz) between H_a and H_f, implying a **W**-relationship,[18] reinforces the view that the protons in question possess a near-diequational relationship.

A comparison of the pertinent torsion angles of compound (**12**), obtained by *X*-ray analysis and calculated from spin–spin coupling constants, is made in Table 4. Although the agreement between the values is only modest,* it is clear that ring *A* of compound (**12**) adopts a chair-like conformation in both the crystal state and in deuteriochloroform solution. This finding reinforces the belief that the common ring-*A*-geometry of the

* When J^0 14 Hz, rather than J^0 11 Hz, is used in the Karplus equation, the angles calculated from spin–spin coupling constants are in better agreement with those determined by *X*-ray analysis.

compounds under discussion is indeed represented by a chair-like arrangement.

The coupling constants of the ring-*A*-associated protons of compounds (**17a**—**c**) showed some marked differences from those of the compounds just discussed. Thus $J_{a,c}$, $J_{b,c}$, and $J_{c,d}$ were quite similar (in the 9—11 Hz region) in each instance, indicative of torsion angles of *ca.* 150—165° between H_a and H_c, *ca.* 0—25° between H_b and H_c, and *ca.* 0—20° between H_c and H_d. Again, it is clear that a boat-like geometry, as depicted by the generalised structure (**38**), represents the average conformational situation.

In the case of compound (**18a**), the coupling constants of the ring-*A*-associated protons were very close to those of its counterpart (**17a**), indicating a common ring-*A* geometry for the diastereoisomers (rings *A* bear a mirror-image relationship).

An interesting feature of the conformational behaviour is the axial-like disposition of the ring-*A*-associated oxy substituent [located at position 7 in compound (**8**), at position 10 in compounds (**9a**—**c**), (**11a**—**c**), (**12**), (**13a**—**c**), and (**14a**—**c**), and at position 3 in compounds (**15a**—**c**), (**16a**), (**17a**—**c**), and (**18a**)]. Earlier we noted[6,7] a similar phenomenon in the case of compounds (**7a** and **b**), (**32a** and **b**), (**33a** and **b**), and their derivatives. We suggested that the axial-like orientation was stabilised by a through-space interaction between the electron pairs on the oxygen atom and the antibonding σ* orbitals of the ring-*B* carbonyl groups. In support of this suggestion, it was noted that the O(7)–C(11) and O(7)–C(6) interatomic distances in compound (**32b**) were 2.687 and 2.74 Å, respectively, on the basis of *X*-ray studies. A similar through-space interaction is believed to be responsible for the axial-like disposition of the oxy substituent associated with rings *A* of the compounds described in this study. Certainly, the O(10)–C(2) interatomic distance in compound (**12**) (2.8 Å on the basis of the *X*-ray study) was substantially less than the sum of the van der Waals radii of the atoms.

Experimental

Cycloadditions were carried out in oven-dried glassware which had been pre-washed with dilute sodium hydroxide solution followed by distilled water. Dry benzene was prepared by distillation of the solvent from sodium wire; dry diethyl ether was obtained by leaving the solvent over sodium wire and then distilling it from lithium aluminium hydride. Light petroleum refers to that fraction boiling in the range 40—60 °C. Prior to use as a solvent for the ^{1}H n.m.r. spectral determination of cycloadducts, deuteriochloroform was filtered through a bed of sodium carbonate.

Column chromatography was effected under pressure on Merck Kieselgel H (Type 60). T.l.c. was performed on Schleicher and Schull plastic plates coated with silica gel (F1 500 LS 254); the plates were initially examined under u.v. light and the spots were then located with iodine vapour. Preparative h.p.l.c. was carried out using a column (20 × 0.8 cm) of Partisil 10 silica, a LDC Constametric III pump, and a LDC Spectromonitor III or a Cecil CE212 variable wavelength detector. Evaporations refer to the removal of solvents at ≤ 40 °C using a Buchi rotary evaporator. M.p.s were determined by using either a Kofler hot-stage apparatus or a Buchi 512 apparatus. Optical rotations were measured at *ca.* 20 °C with a Thorn Automation Type 243 polarimeter. C.d. spectra were recorded with a Roussel-Jouan Dichrographe III. I.r. spectra were determined with a Hilger and Watts Infrascan or a Perkin-Elmer 580 spectrometer. Either a Unicam SP 800 or a Cary 188 spectrometer was employed to determine u.v. spectra. ^{1}H N.m.r. spectra were measured at 300 MHz with a Bruker WM300 WB or a Varian XL300 spectrometer. Electron impact (e.i.) mass spectra were determined with an A.E.I. MS9 instrument operating at 70 eV; chemical ionisation (c.i.) spectra were recorded with a Kratos MS45 spectrometer (isobutane as carrier gas).

Reaction of the Diene (**5a**) *with the Epoxy Tetraone* (**6**).—A solution of the diene (**5a**) (0.976 g, 2 mmol) and the epoxy tetraone (**6**) (0.508 g, 2 mmol) in dry benzene (75 cm^3) was left at room temperature for 18 h. Evaporation left a residue which was considered to be mainly a 75:25 mixture of the cycloadducts (**7a**) and (**8**) on the basis of 300 MHz ^{1}H n.m.r. spectroscopy [the ratio was estimated from the integrals of the doublets (*J* 18 Hz) at δ 2.72 and 2.84, attributed to the 10α-hydrogen atoms of compounds (**8**) and (**7a**), respectively, and of the double doublets (*J* 7 and 4 Hz) at δ 3.08 and 3.16, ascribed to the 6a-hydrogen atoms of compounds (**7a**) and (**8**), respectively]. Dry diethyl ether was added to the residue and the insoluble material (0.640 g, 43% yield), which was (5a*S*,6a*R*,7*S*,10a*R*,11a*R*)-5a,11a-epoxy-5a,6a,7,10,10a,11a-hexahydro-7-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)oxy]-9-trimethylsilyloxynaphthacene-5,6,11,12-tetraone (**7a**) on the basis of 300 MHz ^{1}H n.m.r. spectroscopy, was collected by filtration.

The filtrate, obtained after removal of compound (**7a**), was concentrated and the resultant orange foam (0.840 g) was subjected to h.p.l.c. After two purifications using a 1:99 mixture of isopropyl alcohol and dichloromethane as the mobile phase and a third purification using a 5:95 mixture of ethyl acetate and dichloromethane as the mobile phase, an orange solid (0.109 g) was obtained. It was recrystallised from dichloromethane–diethyl ether–hexane to give (5aR,6aS,7R,10aS,11aS)-5a,11a-*epoxy*-5a,6a,7,10,10a,11a-*hexahydro*-7-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-9-*trimethylsilyloxynaphthacene*-5,6,11,12-*tetraone* (**8**) [0.067 g, 4.5% yield based upon the diene (**5a**)] as a pale cream solid, m.p. 182—184 °C (decomp.); $[\alpha]_D$ − 76° (0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 755, 1 745 and 1 735 (ester C=O), 1 695 (ketone C=O), and 1 655 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 230 (ε 19 900), 264sh (6 600), and 307 nm (2 400); δ(300 MHz; $CDCl_3$) 0.30 (9 H, s, $SiMe_3$), 1.84, 1.96, 1.97, and 2.18 (each 3 H, s, together 4 × MeCO), 2.72br (1 H, d, *J* 18 Hz, 10-H_α), 3.16 (1 H, dd, *J* 7 and 4 Hz, 6a-H), 3.60 (1 H, ddd, *J* 9.5, 5, and 2.5 Hz, 5′-H), 3.76br (1 H, t, *J* 6.5 and 6.5 Hz, 10a-H), 4.14 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.26 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.42 (1 H, d, *J* 8 Hz, 1′-H), 4.57 (1 H, dd, *J* 9.5 and 8 Hz, 2′-H), 4.93 (1 H, t, *J* 9.5 and 9.5 Hz, 4′-H), 4.94 (1 H, dd, *J* 6 and 4.5 Hz, 7-H), 4.98 (1 H, d, *J* 6 Hz, 8-H), 5.11 (1 H, t, *J* 9.5 and 9.5 Hz, 3′-H), 7.75—7.85, 8.02—8.07, and 8.12—8.17 (2, 1, and 1 H, each m, together 1-, 2-, 3-, and 4-H) (the signal for 10-H_β was partly obscured by the signal at δ 2.18); *m/z* (c.i.) 542 (30%), 541 (33%), 450 (22%), 379 (57%), 378 (54%), and 331 (100%) (Found: C, 56.7; H, 4.9. $C_{35}H_{38}O_{16}Si$ requires C, 56.6; H, 5.2%)

Reaction of the Diene (**5a**) *with* p-*Benzoquinone and Hydrolysis of the Major Cycloadduct*.—To a stirred solution of the diene (**5a**) (0.489 g, 1 mmol) in dry benzene (10 cm^3) was added freshly sublimed *p*-benzoquinone (0.108 g, 1 mmol). After 2 days in the dark, the mixture was concentrated to leave a residue which was mainly an 89:11 mixture of the cycloadducts (**9a**) and (**10a**) on the basis of 300 MHz ^{1}H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at δ 0.21 and 0.23, attributed to the trimethysilyl groups of compounds (**9a**) and (**10a**), respectively, and of the doublets (*J* 18 Hz) at δ 2.94 and 2.98, ascribed to the 7α-hydrogen atoms of compounds (**9a**) and (**10a**), respectively]. Trituration of the residue with dry diethyl ether and filtration gave (1R,6R,10S)-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-8-*trimethylsilyloxybicyclo*-[4.4.0]*deca*-3,8-*diene*-2,5-*dione* (**9a**) (0.276 g, 46% yield) as an off-white solid. A sample, recrystallised from dichloromethane–light petroleum, was obtained as colourless needles (0.252 g, 42%), m.p. 156—157 °C (decomp.); $[\alpha]_D$ + 179° (1.0% in

CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 and 1 740 (ester C=O), and 1 695 and 1 675 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 230sh (ε 11 700 and 306 nm (370); δ(300 MHz; $CDCl_3$) 0.21 (9 H, s, $SiMe_3$), 1.94, 1.98, 2.02, and 2.06 (each 3 H, s, together 4 × MeCO), 2.94br (1 H, d, *J* 18 Hz, 7-H_α), 3.15br (1 H, dd, *J* 7 and 5 Hz, 1-H), 3.25br (1 H, t, *J* 7 and 7 Hz, 6-H), 3.56—3.61 (1 H, m, 5′-H), 4.05 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.16 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.38 br (1 H, t, *J* 5 and 5 Hz, 10-H), 4.41 (1 H, d, *J* 8 Hz, 1′-H), 4.74 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 4.97 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.01 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.05br (1 H, d, separation 5 Hz, 8-H), 6.52 (1 H, dd, *J* 10 and 1 Hz, 3- or 4-H), and 6.75 (1 H, d, *J* 10 Hz, 4- or 3-H) (the signal for 7-H_β was partly obscured by the signal at δ 2.06); *m/z* (e.i.) 248 (M^+ − $C_{14}H_{20}O_{10}$) and 43 ($C_2H_3O^+$, base peak) (Found: C, 54.1; H, 6.0; Si, 4.5. $C_{27}H_{36}O_{13}Si$ requires C, 54.35; H, 6.05; Si, 4.7%).

The unrecrystallised cycloadduct (**9a**) (1.80 g) was dissolved in THF (45 cm^3) containing 0.1M hydrochloric acid (5 cm^3). After 3 h, the mixture was diluted with chloroform and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from chloroform–light petroleum gave (1R,6R,10S)-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*bicyclo*[4.4.0]*dec*-3-*ene*-2,5,8-*trione* (**11a**) [1.45 g, 45% yield based upon the diene (**5a**)] as colourless needles, m.p. 135—137 °C; $[\alpha]_D$ + 53° (1% in $CHCl_3$); c.d. (MeCN) 225 (Δε + 12.14) and 242 nm (Δε + 5.46); $\nu_{max.}$(KBr) 1 755 (ester C=O) and 1 675 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 222 (ε 13 100) and 302 nm (1 900); δ(300 MHz; $CDCl_3$) 1.94, 1.97, 1.98, and 2.10 (each 3 H, s, together 4 × MeCO), 2.37 (1 H, dd, *J* 16 and 8 Hz, 7-H_β), 2.45 (1 H, dd, *J* 16 and 3 Hz, 9-H_β), 2.89 (1 H, dm, separation 16 Hz, 7-H_α), 3.28br (1 H, dd, *J* 8 and 3 Hz, 1-H), 3.31 (1 H, ddd, *J* 16, 3, and 2 Hz, 9-H_α), 3.46 (1 H, dt, *J* 8, 8, and 3 Hz, 6-H), 3.58—3.63 (1 H, m, 5′-H), 4.10 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.13 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.39 (1 H, d, *J* 8 Hz, 1′-H), 4.56br (1 H, apparent q, separation 3 Hz, 10-H), 4.72 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 4.95 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.04 (1 H, t, *J* 9 and 9 Hz, 3′-H), 6.65 (1 H, dd, *J* 10 and 1 Hz, 3- or 4-H), and 6.83 (1 H, d, *J* 10 Hz, 4- or 3-H); *m/z* (e.i.) 176 (M^+ − $C_{14}H_{20}O_{10}$, base peak) (Found: C, 54.9; H, 5.3. $C_{24}H_{28}O_{13}$ requires C, 54.95; H, 5.35%).

Reaction of the Enetrione (**11a**) *with Zinc–Acetic Acid.*—To a stirred solution of the enetrione (**11a**) (1.20 g, 2.29 mmol) in acetic acid (40 cm^3) was added activated zinc (1.45 g, 22.2 mmol) while the temperature of the mixture was kept below 20 °C. After 3.5 h, water was added and the mixture was extracted twice with chloroform. The organic layers were combined and washed sequentially with water, aqueous sodium hydrogen carbonate, and water. Evaporation of the dried ($MgSO_4$) chloroform solution and crystallisation of the residue from chloroform–light petroleum gave (1R,6R,10S)-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*bicyclo*[4.4.0]*decane*-2,5,8-*trione* (**12**) (1.00 g, 83%) as colourless crystals, m.p. 148—150 °C; $[\alpha]_D$ − 36° (1% in $CHCl_3$); $\nu_{max.}$(KBr) 1 740 (ester C=O) and 1 715 cm^{-1} (ketone C=O); δ(300 MHz; $CDCl_3$) 1.96, 1.99, 2.06, and 2.11 (each 3 H, s, together 4 × MeCO), 2.29 (1 H, dd, *J* 16 and 8 Hz, 7-H_β), 2.38 (1 H, dd, *J* 16 and 3.5 Hz, 9-H_β), 2.56—2.96 (5 H, m, 2- and 3-H_2, 7-H_α), 3.05 (1 H, dd, *J* 8 and 3 Hz, 1-H), 3.27 (1 H, apparent dt, *J* 16, 2, and 2 Hz, 9-H_α), 3.45 (1 H, apparent dt, *J* 8, 8, and 2 Hz, 6-H), 3.61—3.67 (1 H, m, 5′-H), 4.07 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.18 (1 H, dd, *J* 12 and 6 Hz, 6′-H), 4.38 (1 H, d, *J* 8 Hz, 1′-H), 4.72 (1 H, apparent q, separation 3 Hz, 10-H), 4.78 (1 H, dd, *J* 9.5 and 8 Hz, 2′-H), 4.94 (1 H, t, *J* 9.5 and 9.5 Hz, 4′-H), and 5.11 (1 H, t, *J* 9.5 and 9.5 Hz, 3′-H); *m/z* (e.i.) 178 (M^+ − $C_{14}H_{20}O_{10}$) and 43 ($C_2H_3O^+$, base peak) (Found: C, 54.4; H, 5.6. $C_{24}H_{30}O_{13}$ requires C, 54.75; H, 5.7%).

X-Ray Crystal Structure Data.—$C_{24}H_{30}O_{13}\cdot 0.5H_2O$, M = 535.5. Orthorhombic, a = 6.930(1), b = 12.005(2), c = 32.909(4) Å, U = 2 738 $Å^3$, space group $P2_12_12_1$, Z = 4, D_c = 1.30 g cm^{-3}. Refined unit-cell parameters were obtained by centering 18 reflections on a Nicolet R3m diffractometer; 2 155 independent reflections (θ ⩽ 58°) were measured with Cu-K_α radiation (graphite monochromator) using the ω-scan measuring routine. Of these, 1 642 had $|F_0| > 3\sigma(|F_0|)$ and were considered to be observed. The net count of two check reflections (the −122 and the −124), 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 were applied; no absorption correction was applied.

Several attempts at conventional multiple solution tangent refinement failed to reveal any meaningful structural fragments. The structure was finally solved by resorting to random start tangent refinement coupled with ΔE map recycling. The non-hydrogen atoms were refined anisotropically. A ΔF map revealed the presence of a water molecule of estimated occupancy 0.5. The protons of the water of crystallisation were located from a ΔF map. The group was refined as a rigid body. The methyl groups were refined as rigid bodies. The positions of the remaining hydrogen atoms were idealised, d(C–H) = 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to 'ride' on their parent carbon atoms. Refinement was performed by block-cascade, full-matrix least-squares techniques to R = 0.058, R_w = 0.062 [$w^{-1} = \sigma^2(F) + 0.001\,47F^2$]. The maximum residual electron density in the final ΔF map was 0.29 e $Å^{-3}$. Computations were carried out with an Eclipse S140 computer using the SHELXTL program system.[19]

The fractional co-ordinates of the hydrogen atoms and their anisotropic thermal parameters , the bond lengths and bond angles, and the isotropic thermal parameters of the non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.*

Reaction of the Diene (**5b**) *with* p-*Benzoquinone and Hydrolysis of the Cycloadduct.*—A solution of the diene (**5b**) (90% purity; 0.250 g, 1.3 mmol) and freshly sublimed *p*-benzoquinone (0.130 g, 1.2 mmol) in dry benzene (5 cm^3) was left for 18 h at room temperature in the dark. Evaporation left a residue which was very largely the cycloadduct (**13a**), on the basis of 300 MHz ^1H n.m.r. spectroscopy. Crystallisation of the material from light petroleum gave (1RS,6RS,10SR)-10-*methoxy*-8-*trimethylsilyloxybicyclo*[4.4.0]*deca*-3,8-*diene*-2,5-*dione* (**13a**) (0.223 g, 66%) as pale yellow crystals, m.p. 57—58 °C; $\nu_{max.}$(KBr) 1 680 and 1 660 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 228sh nm (ε 10 700); δ(300 MHz; $CDCl_3$) 0.24 (9 H, s, Me_3Si), 2.10br (1 H, dd, *J* 18.5 and 7.5 Hz, 7-H_β), 3.02br (1 H, d, *J* 18.5 Hz, 7-H_α), 3.08 (3 H, s, MeO), 3.10 (1 H, ddd, *J* 7.5, 4, and 1 Hz, 1-H), 3.24 (1 H, dt, *J* 7.5, 7.5, and 1 Hz, 6-H), 4.05 (1 H, dd, *J* 5.5 and 4 Hz, 10-H), 5.14 (1 H, dt, *J* 5.5, 1, and 1 Hz, 9-H), 6.68 (1 H, dd, *J* 10 and 1 Hz, 3- or 4-H), and 6.80 (1 H, d, *J* 10 Hz, 4- or 3-H); δ(300 MHz; C_6D_6) 0.16 (9 H, s, Si Me_3), 1.76br (1 H, dd, *J* 18 and 7 Hz, 7-H_β), 2.30br (1 H, t, *J* 7 and 7 Hz, 6-H), 2.69 (1 H, dd, *J* 6 and 4 Hz, 1-H), 2.78 (3 H, s, OMe), 3.10br (1 H, d, *J* 18 Hz, 7-H_α), 3.90 (1 H, dd, *J* 5 and 4 Hz, 10-H), 4.99 (1 H, dd, *J* 5 and 1 Hz, 9-H), 6.30 (1 H, dd, *J* 10.5 and 1 Hz, 3-or 4-H), and 6.36 (1 H, d, *J* 10.5 Hz, 4- or 3-H); *m/z* (e.i.) 280 (M^+, base peak) (Found: C, 59.8; H, 7.5; Si, 9.6. $C_{14}H_{20}O_4Si$ requires C, 60.0; H, 7.2; Si, 10.0%).

The cycloadduct (**13a**) (0.060 g, 0.21 mmol) was dissolved in freshly distilled THF (10 cm^3) containing 0.1M hydrochloric

* For details see Instructions for Authors (1988) in *J. Chem. Soc. Perkin Trans. 1*, 1988. Issue 1.

acid 1 cm^3). After 90 min, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer left a residue which was crystallised from dichloromethane–diethyl ether–light petroleum to give (1RS,6RS,10SR)-10-*methoxybicyclo*[4.4.0]*dec*-3-*ene*-2,5,8-*trione* (**14a**) (0.040 g, 90%) as colourless needles, m.p. 110—112 °C; $\nu_{max.}$(KBr) 1 710 (ketone C=O) and 1 680 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 222 nm (ε 6 800); δ(300 MHz; $CDCl_3$) 2.25 (1 H, dd, *J* 16 and 8 Hz, 7-H_β), 2.45 (1 H, dd, *J* 16 and 3 Hz, 9-H_β), 2.87 1 H, dt, *J* 16, 3, and 3 Hz, 9-H_α), 3.14 (3 H, s, MeO), 3.34 (1 H, dt, *J* 16, 2, and 2 Hz, 7-H_α), 3.36 (1 H, dd, *J* 8 and 3 Hz, 1-H), 3.48 (1 H, dt, *J* 8, 8, and 2 Hz, 6-H), 4.10 (1 H, apparent q, separation 3 Hz, 10-H), 6.75 and 6.88 (each 1 H, d, *J* 10.5 Hz, together 3- and 4-H); *m/z* (e.i.) 208 (M^+, base peak) (Found: C, 63.1; H, 5.7. $C_{11}H_{12}O_4$ requires C, 63.45; H, 5.75%).

Reaction of the Diene (**5b**) *with* 2-*Methoxycarbonyl*-p-*benzoquinone and Hydrolysis of the Cycloadduct*.—A solution of the diene (**5b**) (90% purity, 0.250 g, 1.3 mmol) and 2-methoxycarbonyl-*p*-benzoquinone (0.210 g, 1.25 mmol) in dry benzene (5 cm^3) was left in a refrigerator for 0.5 h. Evaporation left a syrup which was very largely the cycloadduct (**13b**) on the basis of 300 MHz ^1H n.m.r. spectroscopy. Addition of light petroleum and filtration gave *methyl* (1SR,6RS,10SR)-10-*methoxy*-2,5-*dioxo*-8-*trimethylsilyloxybicyclo*[4.4.0]*deca*-3,8-*diene*-l-*carboxylate* (**13b**) (0.284 g, 67%) as a pale yellow solid, m.p. 57—59 °C; $\nu_{max.}$(KBr) 1 750 (ester C=O), 1 700, 1 680, and 1 660 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 226sh nm (ε 9 800); δ(300 MHz; $CDCl_3$) 0.23 (9 H, s, $SiMe_3$), 2.04br (1 H, dd, *J* 18 and 8 Hz, 7-H_β), 3.02br (1 H, d, *J* 18 Hz, 7-H_α), 3.10 (3 H, s, MeO), 3.78 (3 H, s, CO_2Me), 3.80 (1 H, d, *J* 8 Hz, 6-H), 4.46 (1 H, d, *J* 6 Hz, 10-H), 5.18 (1 H, dt, *J* 6, 1.5, and 1.5 Hz, 9-H), 6.67 and 6.85 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (c.i.) 338 (M^+, 20%), 306 ($M^+ - CH_4O$, 43%), 279 ($M^+ - C_2H_3O_2$, 55%), 157 (88%), 147 (41%), 141 (53%), 78 (57%), 75 (83%), and 73 ($C_3H_9Si^+$, 100%) (Found: C, 56.9; H, 6.9; Si, 8.3. $C_{16}H_{22}O_6Si$ requires C, 56.8; H, 6.55; Si, 8.3%).

A solution of the cycloadduct (**13b**) (4.60 g, 13.6 mmol) in THF (50 cm^3) at 0 °C was treated with 0.05M hydrochloric acid (15 cm^3). After 1 h, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from dichloromethane–diethyl ether gave *methyl* (1SR,6RS,10SR)-10-*methoxy*-2,5,8-*trioxobicyclo*[4.4.0]*dec*-3-*ene*-1-*carboxylate* (**14b**) (2.50 g, 69%) as a colourless solid, m.p. 144—146 °C; $\nu_{max.}$(KBr) 1 745 (ester C=O), 1 715 (ketone C=O), 1 700 and 1 670 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 225 nm (ε 9 900); δ(300 MHz; $CDCl_3$) 2.21 (1 H, dd, *J* 16 and 7 Hz, 7-H_β), 2.77 (1 H, dd, *J* 16 and 3 Hz, 9-H_β), 2.82 (1 H, ddd, *J* 16, 3, and 2 Hz, 9-H_α), 3.15 (3 H, s, MeO), 3.25 (1 H, dt, *J* 16, 2, and 2 Hz, 7-H_α), 3.88 (3 H, s, CO_2Me), 3.99 (1 H, dd, *J* 7 and 2 Hz, 6-H), 4.37 (1 H, t, *J* 3 and 3 Hz, 10-H), 6.74 and 6.91 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (e.i.) 266 (M^+) and 85 (base peak) (Found: C, 58.6; H, 5.3. $C_{13}H_{14}O_6$ requires C, 58.65; H, 5.25%).

Reaction of the Diene (**5a**) *with* 2-*Methoxycarbonyl*-p-*benzoquinone and Hydrolysis of the Major Cycloadduct*.—To a solution of the diene (**5a**) (5.00 g, 10.2 mmol) in dry benzene (60 cm^3) was added 2-methoxycarbonyl-*p*-benzoquinone (1.75 g, 10.5 mmol). Evaporation of the solvent after 5 h left a residue which was mainly an 88 : 12 mixture of the cycloadducts (**9b**) and (**10b**) according to 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at δ 0.21 and 0.24, attributed to the trimethylsilyl groups of compounds (**9b**) and (**10b**), respectively, and of the doublets (*J* 18 Hz) at δ 2.92 and 3.03, attributed to the 7α-hydrogen atoms of compounds (**9b**) and (**10b**), respectively]. Dry diethyl ether was added to the residue and the insoluble material (5.00 g, 75%), which was *methyl* (1R,6R,10S)-2,5-*dioxo*-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-8-*trimethylsilyloxybicyclo*[4.4.0]*deca*-3,8-*diene*-1-*carboxylate* (**9b**), was collected by filtration. A sample, recrystallised from dicholoromethane–diethyl ether–hexane, showed m.p. 152—153 °C; $[\alpha]_D$ + 227° (1% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester C=O), 1 710, 1 685, and 1 670 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 230sh nm (ε 9 600); δ(300 MHz; $CDCl_3$) 0.21 (9 H, s, $SiMe_3$), 1.96, 2.00, 2.04, and 2.08 (each 3 H, s, together 4 × MeCO), 2.92br (1 H, d, *J* 18 Hz 7-H_α), 3.59—3.65 (1 H, m, 5′-H), 3.79 (3 H, s, CO_2Me), 4.07 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.17 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.48 (1 H, d, *J* 8 Hz, 1′-H), 4.78 (1 H, t, *J* 8 and 8 Hz, 2′-H), 4.84 (1 H, d, *J* 5.5 Hz, 10-H), 4.96—5.14 (3 H, m, 6-, 3′-, and 4′-H), 6.51 and 6.81 (each 1 H, d, *J* 10 Hz, together 3- and 4-H) (the 7β-H signal was obscured by the MeCO signals, and the 6-H signal was partly obscured by the MeO signal); *m/z* (c.i.) 655 (MH^+, 9%), 654 (M^+, 6%), 332 (18%), and 331 ($C_{14}H_{19}O_9^+$, 100%) (Found: C, 52.9; H, 5.7; Si, 4.3. $C_{29}H_{38}O_{15}Si$ requires C, 53.2; H, 5.85; Si, 4.3%).

The unrecrystallised cycloadduct (**9b**) (5.00 g) was dissolved in THF (75 cm^3) and treated with 0.1M hydrochloric acid (15 cm^3). After 2 h, the solution was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave *methyl* (1R,6R,10S)-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)-*oxy*]-2,5,8-*trioxobicylo*[4.4.0]*dec*-3-*ene*-1-*carboxylate* (**11b**) [3.50 g, 59% yield based upon the diene (**5a**)] as colourless needles, m.p. 145—146 °C; $[\alpha]_D$ + 95° (1.7% in CH_2Cl_2); c.d. (MeCN) 228 (Δε + 12.32), 242 (Δε + 4.60), and 253sh nm (Δε + 2.82); $\nu_{max.}$(KBr) 1 740br (ester C=O) and 1 680 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 227 nm (ε 9 000); δ(300 MHz; $CDCl_3$) 1.96, 2.00, 2.01, and 2.13 (each 3 H, s, together 4 × MeCO), 2.20 (1 H, dd, *J* 16 and 7 Hz, 7-H_β), 2.78 (1 H, dd, *J* 16 and 3 Hz 9-H_β), 2.89 (1 H, ddd, *J* 16, 3, and 2 Hz, 9-H_α), 3.23 (1 H, ddd, *J* 16, 3, and 2 Hz, 7-H_α), 3.60—3.67 (1 H, m, 5′-H), 3.86 (3 H, s, CO_2Me), 3.93 (1 H, dd, *J* 7.5 and 3 Hz, 6-H), 4.10 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.18 (1 H, dd, *J* 12 and 5.5 Hz, 6′-H), 4.42 (1 H, d, *J* 8 Hz, 1′-H), 4.73 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 4.85 (1 H, apparent t, separation 3 Hz, 10-H), 4.95 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.03 (1 H, t, *J* 9 and 9 Hz, 3′-H), 6.64 and 6.88 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (e.i.) 462, 235 ($M^+ - C_{14}H_{19}O_{10}$), and 43 ($C_2H_3O^+$, base peak) (Found: C, 53.3; H, 5.1. $C_{26}H_{30}O_{15}$ requires C, 53.6; H, 5.2%).

Reaction of the Diene (**5b**) *with* 2-*Acetyl*-p-*benzoquinone and Hydrolysis of the Cycloadduct*.—A solution of the diene (**5b**) (90% purity; 0.500 g, 2.6 mmol) and 2-acetyl-*p*-benzoquinone (0.376 g, 2.5 mmol) in dry benzene (10 cm^3) was left at 5 °C for 30 min. Evaporation left a syrup which was predominantly the cycloadduct (**13c**) on the basis of 300 MHz ^1H n.m.r. spectroscopy. Addition of hexane to the syrup induced the precipitation of a yellow solid which was collected by filtration. The resultant (1RS,6RS,10SR)-1-*acetyl*-10-*methoxy*-8-*trimethylsilyloxybicyclo*[4.4.0]*deca*-3,8-*diene*-2,5-*dione* (**13c**) (0.301 g, 75%) showed m.p. 78—80 °C; $\nu_{max.}$(KBr) 1 720 (ketone C=O), 1 700, 1 675, and 1 665 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 226sh (ε 12 900) and 358 nm (500); δ(300 MHz; $CDCl_3$) 0.23 (9 H, s, $SiMe_3$), 2.02br (1 H, dd, *J* 18 and 8 Hz, 7-H_β), 2.44 (3 H, s, MeCO), 3.05 (1 H, d, *J* 18 Hz, 7-H_α), 3.13 (3 H, s, MeO), 3.88br (1 H, d, *J* 8 Hz, 6-H), 4.50 (1 H, d, *J* 6 Hz, 10-H), 5.17 (1 H, dt, *J* 6, 1.5, and 1.5 Hz, 9-H), 6.59 and 6.85 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (c.i.) 322 (M^+, 2%), 280 (20%), and 279 ($M^+ - C_2H_3O$, 100%) (Found: C, 59.4; H, 6.8; Si, 8.7. $C_{16}H_{22}O_5Si$ requires C, 59.6; H, 6.9; Si, 8.7%).

The cycloadduct (**13c**) (0.161 g, 0.50 mmol) was dissolved in THF (5 cm^3) and to the ice-cooled solution was added

0.01M hydrochloric acid (2 cm^3). After 1 h, the solution was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and recrystallisation of the product from dichloromethane–diethyl ether–hexane gave (1RS,6RS,10SR)-1-*acetyl*-10-*methoxybicyclo*[4.4.0]*dec*-3-*ene*-2,5,8-*trione* (**14c**) (0.062 g, 50%) as a cream solid, m.p. 106—108 °C; $\nu_{max.}$(KBr) 1 710 (ketone C=O) and 1 670 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 223 nm (ε 11 700); δ(300 MHz; $CDCl_3$) 2.20 (1 H, dd, *J* 16 and 8 Hz, 7-H_β), 2.46 (3 H, s, MeCO), 2.60 (1 H, dd, *J* 16 and 3 Hz, 9-H_β), 2.84 (1 H, dt, *J* 16, 2.5, and 2.5 Hz, 9-H_α), 3.18 (3 H, s, OMe), 3.27 (1 H, dt, *J* 16, 2, and 2 Hz, 7-H_α), 3.96 (1 H, dd, *J* 8 and 3 Hz, 6-H), 4.42 (1 H, t, *J* 3 and 3 Hz, 10-H), 6.74 and 6.93 (each 1 H, d, *J* 10 Hz, together 3-and 4-H); *m/z* (c.i.) 250 (M^+, 6%), 218 ($M^+ - CH_4O$, 11%), 208 ($M^+ - C_2H_2O$, 32%), and 207 ($M^+ - C_2H_3O$, 100%) (Found: C, 62.1; H, 5.5. $C_{13}H_{14}O_5$ requires C, 62.4; H, 5.6%).

Reaction of the Diene (**5a**) *with* 2-*Acetyl*-p-*benzoquinone and Hydrolysis of the Major Cycloadduct.*—A solution of the diene (**5a**) (0.489 g, 1.0 mmol) and 2-acetyl-*p*-benzoquinone (0.150 g, 1.0 mmol) in dry benzene (10 cm^3) was left overnight at *ca.* 5 °C. Evaporation left a residue which was mainly a 75:25 mixture of the cycloadducts (**9c**) and (**10c**) by 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the doublets (*J* 18 Hz) at δ 2.98 and 3.05, attributed to the 7-hydrogen atoms of compounds (**9c**) and (**10c**), respectively, and of the doublets (*J* 8 Hz) at δ 3.86 and 3.90, attributed to the 6-hydrogen atoms of compounds (**9c**) and (**10c**), respectively]. Addition of dry diethyl ether and filtration gave (1R,6R,10S)-1-*acetyl*-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-8-*trimethylsilyloxybicyclo*[4.4.0]*deca*-3,8-*diene*-2,5-*dione* (**9c**) (0.274 g, 43%). A sample recrystallised from dichloromethane–diethyl ether–hexane possessed m.p. 76—77 °C; $[\alpha]_D$ + 234° (1% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester C=O), 1 710 (ketone C=O), and 1 675 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 230sh nm (ε 11 000); δ(300 MHz; $CDCl_3$) 0.22 (9 H, s, $SiMe_3$), 1.98, 2.02, 2.05, and 2.10 (each 3 H, s, together 4 × $MeCO_2$), 2.40 (3 H, s, MeCO), 2.98br (1 H, d, *J* 18 Hz, 7-H_α), 3.61—3.67 (1 H, m, 5′-H), 3.86 (1 H, d, *J* 8 Hz, 6-H), 4.09 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.18 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.52 (1 H, d, *J* 8 Hz, 1′-H), 4.77 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 4.82 (1 H, d, *J* 6 Hz, 10-H), 5.00 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.08 (1 H, t, *J* 9 and 9 Hz, 3′-H), 5.09br (1 H, d, *J* 6 Hz, 9-H), 6.48 and 6.82 (each 1 H, d, *J* 10 Hz, together 3-and 4-H) (the 7β-H signal was partly obscured by the signal at δ 1.98); *m/z* (c.i.) 363 (93%), 362 (100%), 331 (82%), and 290 (87%) (Found: C, 54.3; H, 6.1; Si 4.3. $C_{29}H_{38}O_{14}Si$ requires C, 54.55; H, 6.0; Si, 4.4%).

The unrecrystallised cycloadduct (**9c**) (0.250 g) was dissolved in THF (5 cm^3) and treated with 0.1M hydrochloric acid (1.5 cm^3). After 2 h, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and recrystallisation of the residue from methanol–diethyl ether–light petroleum gave (1R,6R,10S)-1-*acetyl*-10-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*bicyclo*[4.4.0]*dec*-3-*ene*-2,5,8-*trione* (**11c**) [0.150 g, 32% based upon the diene (**5a**)] as colourless crystals, m.p. 110—112 °C; $[\alpha]_D$ + 68° (0.5% in CH_2Cl_2); c.d. (MeCN) 228 (Δε + 4.02), 245 (Δε + 0.37), and 280 nm (Δε + 1.68); $\nu_{max.}$(KBr) 1 750 (ester C=O), 1 720 (ketone C=O), and 1 680 cm^{-1} (enone C=O); $\lambda_{max.}$(EtOH) 228 (ε 9 000) and 300 nm (800); δ(300 MHz; $CDCl_3$) 1.97, 2.00, 2.02, and 2.12 (each 3 H, s, together 4 × $MeCO_2$), 2.18 (1 H, dd, *J* 16.5 and 7 Hz, 7-H_β), 2.37 (3 H, s, MeCO), 2.63 (1 H, dd, *J* 17 and 3 Hz, 9-H_β), 2.89 (1 H, ddd, *J* 17, 3, and 2 Hz, 9-H_α), 3.23 (1 H, ddd, *J* 17, 3.5, and 2 Hz, 7-H_α), 3.61—3.67 (1 H, m, 5′-H), 3.85 (1 H, dd, *J* 7 and 3.5 Hz, 6-H), 4.11 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.17 (1 H, dd, *J* 12 and 5.5 Hz, 6′-H), 4.43 (1 H, d, *J* 8 Hz, 1′-H), 4.73 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 4.84 (1 H, t, *J* 3 and 3 Hz, 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), 6.65 and 6.90 (each 1 H, d, *J* 10 Hz, together 3- and 4-H); *m/z* (e.i.) 218 ($M^+ - C_{14}H_{20}O_{10}$) and 43 ($C_2H_3O^+$, base peak) (Found: C, 55.1; H, 5.2. $C_{26}H_{30}O_{14}$ requires C, 55.1; H, 5.3%).

Reaction of the Diene (**5a**) *with* N-*Phenylmaleimide and Hydrolysis of the Cycloadducts.*—(*a*) A solution of the diene (**5a**) (0.489 g, 1.0 mmol) and *N*-phenylmaleimide (0.173 g, 1.0 mmol) in dry benzene (10 cm^3) was left at room temperature for 3 days. Evaporation left a residue which was considered to be an 86:14 mixture of the cycloadducts (**15a**) and (**16a**) on the basis of 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at δ 0.25 and 0.34, attributed to the trimethylsilyl groups of compounds (**15a**) and (**16a**), respectively, and of the doublets (*J* 8 Hz) at δ 4.66 and 4.62, ascribed to the 1′-hydrogen atoms of compounds (**15a**) and (**16a**), respectively]. Dry diethyl ether was added to the residue and the insoluble material (0.384 g, 58%), which was (1R,2R,3S)-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-5-*trimethylsilyloxycyclohex*-4-*ene*-1,2-N-*phenyldicarboximide* (**15a**), was collected by filtration. After recrystallisation from dichloromethane–diethyl ether–hexane, the sample (0.342 g, 52%) showed m.p. 162—163 °C; $[\alpha]_D$ + 79° (1.0% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester C=O), 1 710 (imide C=O), and 1 645 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 216sh nm (ε 13 900); δ(300 MHz; $CDCl_3$) 0.25 (9 H, s, $SiMe_3$), 1.58, 1.95, 2.00, and 2.08 (each 3 H, s, together 4 × MeCO), 2.51 (1 H, dd, *J* 16 and 10 Hz, 6-H_α), 2.79 (1 H, ddd, *J* 16, 8.5, and 2.5 Hz, 6-H_β), 3.17 (1 H, dd, 10 and 5 Hz, 2-H), 3.35 (1 H, dt, *J* 10, 10, and 8.5 Hz, 1-H), 3.61—3.67 (1 H, m, 5′-H), 4.06 (1 H, dd, *J* 12.5 and 2.5 Hz, 6′-H), 4.20 (1 H, dd, *J* 12.5 and 5 Hz, 6′-H), 4.66 (1 H, d, *J* 8 Hz, 1′-H), 4.77 (1 H, dd, *J* 7 and 5 Hz, 3-H), 4.81 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 5.03 (1 H, t, *J* 9 and 9 Hz, 4′-H), 5.12 (1 H, t, *J* 9 and 9 Hz, 3′-H), 5.18 (1 H, dd, *J* 7 and 2.5 Hz, 4-H), and 7.30—7.55 (5 H, m, Ph); *m/z* (c.i.) 493 (13%), 361 (12%), 332 (17%), and 331 ($C_{14}H_{19}O_9^+$, 100%) (Found: C, 56.0; H, 6.0; N, 2.1; Si, 4.0. $C_{31}H_{39}NO_{13}Si$ requires C, 56.25; H, 5.95; N, 2.1; Si, 4.25%).

The filtrate, obtained after removal of the cycloadduct (**15a**), was concentrated to leave a pale yellow foam (0.224 g). Purification of a portion (0.188 g) of this foam by h.p.l.c., using a 1:99 mixture of isopropyl alcohol and dichloromethane as the mobile phase, gave a colourless syrup (0.064 g) which crystallised on addition of dichloromethane–hexane. The resultant white solid [0.042 g, 6% based upon the diene (**5a**)], which was (1S,2S,3R)-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-5-*trimethylsilyloxycyclohex*-4-*ene*-1,2-N-*phenyldicarboximide* (**16a**), showed m.p. 183—184 °C; $[\alpha]_D$ − 137° (0.25% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 750 (ester C=O), 1 710 (imide C=O), and 1 635 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 216sh nm (ε 15 200); δ(300 MHz; $CDCl_3$) 0.33 (9 H, s, $SiMe_3$), 1.93, 1.99, 2.04, and 2.12 (each 3 H, s, together 4 × MeCO), 2.53 (1 H, dd, *J* 16.5 and 10 Hz, 6-H_α), 2.65 (1 H, dd, *J* 16.5 and 7 Hz, 6-H_β), 3.15br (1 H, d, *J* 10 Hz, 2-H), 3.42 (1 H, dt, *J* 10, 10, and 7 Hz, 1-H), 3.59—3.66 (1 H, m, 5′-H), 4.15 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.25 (1 H, dd, *J* 12 and 4.5 Hz, 6′-H), 4.62 (1 H, d, *J* 8 Hz, 1′-H), 4.95 (1 H, dd, *J* 9 and 8 Hz, 2′-H), 5.06—5.17 (4 H, m, 3-, 3′-, 4-, and 4′-H), and 7.28—7.54 (5 H, m, Ph); *m/z* (c.i.) 493 (11%), 463 (15%), 332 (16%), and 331 ($C_{14}H_{19}O_9^+$, 100%) (Found: C, 56.0; H, 5.9; N, 2.1. $C_{31}H_{39}NO_{13}Si$ requires C, 56.25; H, 5.95; N, 2.1%).

The cycloadduct (**15a**) (0.993 g, 1.5 mmol) was left in THF (50 cm^3) containing 0.1M hydrochloric acid (15 cm^3) for 4 h. The solution was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from dichloromethane–diethyl ether gave (1R,2R,3S)-5-*oxo*-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*cyclohex*-4-*ene*-1,2-N-*phenyldicarboximide* (**17a**) (0.748 g, 85%) as colourless needles, m.p. 205—207 °C; $[\alpha]_D$ − 62° (0.75% in CH_2Cl_2); c.d. (MeCN) 295 (Δε − 4.35),

303 ($\Delta\varepsilon$ − 3.59), and 312sh nm ($\Delta\varepsilon$ − 1.53); $\nu_{max.}$(KBr) 1 750 (ester C=O) and 1 710 cm^{-1} (imide C=O); $\lambda_{max.}$(EtOH) 206 (ε 12 000) and 215 nm (10 900); δ(300 MHz; $CDCl_3$) 1.56, 1.96, 2.01, and 2.12 (each 3 H, s, together 4 × MeCO), 2.34 (1 H, dd, *J* 19 and 2.5 Hz, 4-H_β), 2.91 (1 H, dd, *J* 16 and 11 Hz, 6-H_α), 2.94 (1 H, dd, *J* 16 and 9 Hz, 6-H_β), 3.03 (1 H, dd, *J* 19 and 3 Hz, 4-H_α), 3.26 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.37 (1 H, dt, *J* 11, 11, and 9 Hz, 1-H), 3.67—3.73 (1 H, m, 5′-H), 4.11 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.17 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.66 (1 H, d, *J* 8 Hz, 1′-H), 4.82 (1 H, apparent q, separation 3 Hz, 3-H), 4.90 (1 H, dd, *J* 9.5 and 8 Hz, 2′-H), 4.99 and 5.16 (each 1 H, t, *J* 9.5 and 9.5 Hz, together 3′-and 4′-H), 5.30 (1 H, s, 0.5 CH_2Cl_2), and 7.33—7.53 (5 H, m, Ph); *m/z* (e.i.) 589 (M^+) and 43 ($C_2H_3O^+$, base peak) (Found: C, 54.2; H, 4.8; N, 2.2. $C_{28}H_{31}NO_{13}\cdot0.5CH_2Cl_2$ requires C, 54.15; H, 5.05; N, 2.2%).

A solution of the cycloadduct (**16a**) in deuteriochloroform was monitored from time to time by 300 MHz ^1H n.m.r. spectroscopy. Over 7 days the material was transformed into a new product, the spectrum of which matched that of compound (**18a**) [see (*b*)].

(*b*) A solution of the diene (**5a**) (0.245 g, 0.5 mmol) and *N*-phenylmaleimide (0.090 g, 0.5 mmol) in dry benzene (3 cm^3) was left at room temperature for 3 days. The residue obtained on evaporation was triturated with dry diethyl ether and the insoluble material (0.215 g, 64%) [which was the cycloadduct (**15a**) on the basis of 300 MHz ^1H n.m.r. spectroscopy] was collected by filtration. The filtrate was concentrated and the residue was dissolved in THF (7 cm^3) containing 0.1M hydrochloric acid (2 cm^3). After 2 h, the solution was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and purification of the residue by silica gel column chromatography (elution with Et_2O to remove impurities followed by elution with EtOAc) gave two fractions.

The first-eluted material [0.010 g, 3% based upon the diene (**5a**)] was identical with the ketone (**17a**) on the basis of 300 MHz ^1H n.m.r. spectroscopy.

The second-eluted material was crystallised from dichloromethane–diethyl ether–light petroleum and then from dichloromethane–ethanol to give (1S,2S,3R)-5-*oxo*-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*cyclohex*-4-*ene*-1,2-N-*phenyldicarboximide* (**18a**) [0.020 g, 7% based upon the diene (**5a**)] as colourless needles, m.p. 174—175 °C; $[\alpha]_D$ + 16° (0.5% in CH_2Cl_2); c.d. (MeCN) 284 ($\Delta\varepsilon$ + 2.91), 297 ($\Delta\varepsilon$ + 3.20), 304 ($\Delta\varepsilon$ + 2.52), and 312sh nm ($\Delta\varepsilon$ + 1.16); $\nu_{max.}$(KBr) 1 750 (ester C=O) and 1 710 cm^{-1} (imide C=O); $\lambda_{max.}$(EtOH) 207 (ε 12 200) and 215 nm (10 600); δ(300 MHz; $CDCl_3$) 1.97, 1.98, 2.01, and 2.04 (each 3 H, s, together 4 × MeCO), 2.37 (1 H, dd, *J* 18 and 2 Hz, 4-H_β), 2.79 (1 H, dd, *J* 17.5 and 9.5 Hz, 6-H_α), 2.82 (1 H, dd, *J* 18 and 3.5 Hz, 4-H_α), 2.90 (1 H, dd, *J* 17.5 and 9 Hz, 6-H_β), 3.23 (1 H, dd, *J* 9.5 and 3 Hz, 2-H), 3.44 (1 H, apparent q, separation 9.5 Hz, 1-H), 3.65—3.70 (1 H, m, 5′-H), 4.05 (1 H, dd, *J* 12 and 2.5 Hz, 6′-H), 4.20 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.54 (1 H, d, *J* 8 Hz, 1′-H), 4.86 (1 H, dd, *J* 9.5 and 8 Hz, 2′-H), 4.91 (1 H, apparent t, separation 3 Hz, 3-H), 5.03 (1 H, t, *J* 9.5 and 9.5 Hz, 4′-H), 5.17 (1 H, t, *J* 9.5 and 9.5 Hz, 3′-H), and 7.33—7.55 (5 H, m, Ph); *m/z* (e.i.) 589 (M^+) and 43 ($C_2H_30^+$, base peak) (Found: C, 57.0; H, 5.2; N, 2.3. $C_{28}H_{31}NO_{13}$ requires C, 57.05; H, 5.25; N, 2.4%).

Reaction of the Diene (**5a**) *with Maleimide and Hydrolysis of the Major Cycloadduct.*—(*a*) A solution of the diene (**5a**) (0.245 g, 0.5 mmol) and maleimide (0.048 g, 0.5 mmol) in dry benzene (10 cm^3) was left at room temperature for 3 days. Evaporation left a residue which comprised mainly an 85:15 mixture of the cycloadducts (**15b**) and (**16b**) on the basis of 300 MHz ^1H n.m.r. spectroscopy [the ratio was estimated from the integrals of the singlets at δ 0.23 and 0.30, ascribed to the trimethylsilyloxy groups of compounds (**15b**) and (**16b**), respectively, and of the double doublets (*J* 17 and 10 Hz) at δ 2.37 and 2.42, attributed to the 6α-hydrogen atoms of compounds (**15b**) and (**16b**), respectively]. Crystallisation of the material from dry diethyl ether gave (1R,2R,3S)-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-5-*trimethylsilyloxycyclohex*-4-*ene*-1,2-*dicarboximide* (**15b**) (0.018 g, 37%), m.p. 165—167 °C; $[\alpha]_D$ + 104° (0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 3 230 (NH), 1 750 (ester C=O), and 1 725 cm^{-1} (imide C=O); δ(300 MHz; $CDCl_3$) 0.23 (9 H, s, $SiMe_3$) 1.98, 2.01, 2.08, and 2.09 (each 3 H, s, together 4 × MeCO), 2.37 (1 H, dd, *J* 17 and 10 Hz, 6-H_α), 2.72 (1 H, ddd, *J* 17, 8, and 3 Hz, 6-H_β), 3.01 (1 H, dd, *J* 10 and 4.5 Hz, 2-H), 3.25 (1 H,dt, *J* 10, 10, and 8 Hz, 1-H), 3.61—3.68 (1 H, m, 5′-H), 4.05 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.20 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.54 (1 H, d, *J* 8 Hz, 1′-H), 4.60 (1 H, dd, 7 and 4.5 Hz, 3-H), 4.87 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.02 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.12 (1 H, dd, *J* 7 and 3 Hz, 4-H), 5.14 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 8.09br (1 H, s, NH); δ(300 MHz; C_6D_6) 0.12 (9 H, s, $SiMe_3$), 1.67, 1.68, 1.75, and 2.12 (each 3 H, s, 4 × MeCO), 2.24 (1 H, dd, *J* 16.5 and 10 Hz, 6-H_α), 2.43 (1 H, dd, *J* 10 and 4.5 Hz, 2-H), 2.50 (1 H, dd, *J* 10 and 7 Hz, 1-H), 2.83 (1 H, ddd, *J* 16.5, 7, and 2.5 Hz, 6-H_β), 3.16—3.22 (1 H, m, 5′-H), 3.98 (1 H, dd, *J* 12.5 and 2.5 Hz, 6′-H), 4.24 (1 H, dd, *J* 12.5 and 4.5 Hz, 6′-H), 4.27 (1 H, d, *J* 8 Hz, 1′-H), 4.32 (1 H, dd, *J* 6.5 and 4.5 Hz, 3-H), 5.01 (1 H, dd, *J* 6.5 and 2.5 Hz, 4-H), 5.07 (1 H, dd, *J* 9.5 and 8 Hz, 2′-H), 5.18 and 5.38 (each 1 H, t, *J* 9.5 and 9.5 Hz, together 3′-and 4′-H), and 8.31br (1 H, s, NH); *m/z* (e.i.) 288 ($M^+ - C_{14}H_{19}O_{10}$) and 43 ($C_2H_3O^+$, base peak) (Found: C, 51.3; H, 5.7; N, 2.3; Si, 4.7. $C_{25}H_{35}NO_{13}Si$ requires C, 51.25; H, 6.0; N, 2.4; Si, 4.8%).

(*b*) The afore-cited reaction was repeated: the diene (**5a**) (0.489 g, 1 mmol) and maleimide (0.105 g, 1.1 mmol) were left in dry benzene (20 cm^3) for 3 days. Evaporation left a residue which was dissolved in THF (15 cm^3) containing 0.1M hydrochloric acid (5 cm^3). After 2 h, the mixture was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave (1R,2R,3S)-5-*oxo*-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*cyclohexane*-1,2-*dicarboximide* (**17b**) [0.315 g, 61% based upon the diene (**5a**] as colourless crystals, m.p. 207—209 °C; $[\alpha]_D$ − 58° (0.95% in CH_2Cl_2); c.d. (MeCN) 283 ($\Delta\varepsilon$ − 2.70), 292 ($\Delta\varepsilon$ − 3.07), 303 ($\Delta\varepsilon$ − 2.51), and 312sh nm ($\Delta\varepsilon$ − 1.10); $\nu_{max.}$(KBr) 3 230 (NH), 1 750 (ester C=O), and 1 715 cm^{-1} (imide C=O); $\lambda_{max.}$(EtOH) 202 nm (ε 4 900); δ(300 MHz; $CDCl_3$) 1.99. 2.02, 2.07, and 2.10 (each 3 H, s, together 4 × MeCO), 2.28 (1 H, dd, *J* 19 and 2.5 Hz, 4-H_β), 2.79—2.85 (2 H, m, 6-H_2), 2.96 (1 H, dd, *J* 19 and 3 Hz, 4-H_α), 3.11 (1 H, dd, *J* 10 and 3.5 Hz, 2-H), 3.28 (1 H, apparent q, separation 10 Hz, 1-H), 3.67—3.73 (1 H, m, 5′-H), 4.09 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.16 (1 H, dd, *J* 12 and 5.5 Hz, 6′-H), 4.59 (1 H, d, *J* 8 Hz, 1′-H), 4.68 (1 H, apparent q, separation 3 Hz, 3-H), 4.91 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 4.98 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.19 (1 H, t, *J* 10 and 10 Hz, 3′-H), and 8.39br (1 H, s, NH); *m/z* (e.i.) 299 and 43 ($C_2H_3O,^+$ base peak) (Found: C, 51.5; H, 5.2; N, 2.6. $C_{22}H_{27}NO_{13}$ requires C, 51.45; H, 5.25; N, 2.75%).

Reaction of the Diene (**5a**) *with Maleic Anhydride and Hydrolysis of the Major Cycloadduct.*—A solution of the diene (**5a**) (0.489 g, 1.0 mmol) and freshly sublimed maleic anhydride (0.098 g, 1.0 mmol) in dry benzene (10 cm^3) was left for 18 h at room temperature. Evaporation left a residue which comprised mainly the cycloadduct (**15c**) and other, unidentified materials. Addition of dry diethyl ether to the residue and filtration gave (1R,2R,3S)-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]-8-*trimethylsilyloxycyclohex*-4-*ene*-1,2-*dicarboxylic anhydride* (**15c**) (0.304 g, 52%) in an almost pure state. After crystallisation from dichloromethane–diethyl ether–

hexane, the sample (0.250 g, 42%) showed m.p. 212—213 °C; $[\alpha]_D$ + 82° (0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 775 (anhydride C=O), 1 750 (ester C=O), and 1 650 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 206 nm (ε 6 800); δ(300 MHz; $CDCl_3$) 0.21 (9 H, s, $SiMe_3$) 1.98, 2.02, 2.07, and 2.12 (each 3 H, s, together 4 × MeCO), 2.41 (1 H, dd, *J* 18 and 11 Hz, 6-H_α), 2.79 (1 H, ddd, *J* 18, 4.5, and 2.5 Hz, 6-H_β), 3.22 (1 H, dd, *J* 11 and 4.5 Hz, 2-H), 3.46 (1 H, dt, *J* 11, 11, and 4.5 Hz, 1-H), 3.63—3.69 (1 H, m, 5′-H), 4.11 (1 H, dd, *J* 12 and 3 Hz, 6′-H), 4.18 (1 H, dd, *J* 12 and 5 Hz, 6′-H), 4.55 (1 H, d, *J* 8 Hz, 1′-H), 4.57 (1 H, dd, *J* 7 and 4.5 Hz, 3-H), 4.89 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.02 (1 H, t, *J* 10 and 10 Hz, 4′-H), 5.12 (1 H, dd, *J* 7 and 2.5 Hz, 4-H), and 5.15 (1 H, t, *J* 10 and 10 Hz, 3′-H); *m/z* (e.i) 586 (M^+) and 43 ($C_2H_3O^+$, base peak) (Found: C, 51.1; H, 5.8; Si, 4.9. $C_{25}H_{34}O_{14}Si$ requires C, 51.2; H, 5.85; Si, 4.8%).

The recrystallised cycloadduct (**15c**) (0.158 g, 0.27 mmol) was dissolved in THF (10 cm^3) containing 0.1M hydrochloric acid (1 cm^3). After 2 h, the solution was diluted with dichloromethane and washed with water. Evaporation of the dried ($MgSO_4$) organic layer left a residue which was recrystallised from dichloromethane–diethyl ether–hexane to give (1R,2R,3S)-5-*oxo*-3-[(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl*)*oxy*]*cyclohexane*-1,2-*dicarboxylic anhydride* (**17c**) (0.112 g, 81%) as a white solid, m.p. 218—220 °C; $[\alpha]_D$ − 69° (0.5% in CH_2Cl_2); $\nu_{max.}$(KBr) 1 785 (anhydride C=O), 1 750 (ester C=O), and 1 720 cm^{-1} (ketone C=O); $\lambda_{max.}$(EtOH) 208 nm (ε 1 050); δ(300 MHz; $CDCl_3$) 2.00, 2.03, 2.11, and 2.12 (each 3 H, s, together 4 × MeCO), 2.35 (1 H, dd, *J* 18 and 3 Hz, 4-H_β), 2.88 (1 H, dd, *J* 17 and 9 Hz, 6-H_α), 2.95 (1 H, dd, *J* 17 and 11 Hz, 6-H_β), 2.98 (1 H, dd, *J* 18 and 3 Hz, 4-H_α), 3.33 (1 H, dd, *J* 11 and 4 Hz, 2-H), 3.56 (1 H, dt, *J* 11, 11, and 9 Hz, 1-H), 3.67—3.73 (1 H, m, 5′-H), 4.16—4.18 (2 H, m, 6′-H_2), 4.62 (1 H, d, *J* 8 Hz, 1′-H), 4.70 (1 H, apparent q, separation 3.5 Hz, 3-H), 4.92 (1 H, dd, *J* 10 and 8 Hz, 2′-H), 5.02 (1 H, t, *J* 10 and 10 Hz, 4′-H), and 5.20 (1 H, t, *J* 10 and 10 Hz, 3′-H); *m/z* (e.i.) 514 (M^+), 441, 395, 394, 352, and 331 ($C_{14}H_{19}O_9^+$) (Found: C, 51.1; H, 4.8. $C_{22}H_{26}O_{14}$ requires C, 51.35; H, 5.1%).

Reaction of the Oxo Anhydride (**17c**) with *Aniline followed by Acetic Anhydride*.—A cooled (Me_2CO–solid CO_2) solution of aniline (0.009 g, 0.1 mmol) in dichloromethane (2 cm^3) was added to a similarly cooled solution of the oxo anhydride (**17c**) (0.051 g, 0.1 mmol) in dichloromethane (5 cm^3). The mixture was left at *ca.* −20 °C for 3 h and the solvent was removed by evaporation. The product was dissolved in a 3:1 mixture of acetic anhydride and pyridine (5 cm^3). After 18 h, a few drops of water were added to the mixture which, after a further 15 min, was partitioned between dichloromethane and dilute hydrochloric acid. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Purification of the residue by silica gel column chromatography [elution with Et_2O (to remove impurities) followed by elution with EtOAc–Et_2O (1:1)] gave a solid (0.012 g, 20%) which was the oxo maleimide (**17a**) on the basis of 300 MHz ^1H n.m.r. spectroscopy.

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