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CYCLOADDITION "4 + 2" REACTIONS OF LEVOGLUCOSENONE

DAVID D. WARD AND FRED SHAFIZADEH*
Wood Chemistry Laboratory, Department of Chemistry, University of Montana, Missoula, MT 59812 (U.S.A.)

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ABSTRACT

The reactions of levoglucosenone with a variety of dienes ranging from 1,3-butadiene to 1,3-diphenylisobenzofuran have been investigated and found to provide a variety of multicyclic products in good yield. With the exception of furan, the adducts were formed by the "4 + 2" cycloaddition reaction. The structures of these products are discussed on the basis of their p.m.r. and c.m.r. data. 3-Bromolevoglucosan reacts with 1,3-butadiene to provide the expected product.

INTRODUCTION

As a part of our program on the pyrolytic conversion of biomass to fuel and chemicals, we have been concerned with synthetic applications of levoglucosenone (**1**) (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) that may be obtained by the pyrolysis of waste paper. Preparation of a variety of modified sugars from this compound, including deoxy, keto, unsaturated, oxidized, *O*- and *C*-substituted, and brominated derivatives have been already described[2–4]. In this study, we have explored applications of Diels–Alder or "4 + 2" cycloadditions[5], which are of special interest because of the possibilities for extension of the carbon skeleton of the sugar molecule by addition with a variety of organic compounds, and the polymerization and copolymerization of the products.

RESULTS AND DISCUSSION

Refluxing of **1** with an excess of dicyclopentadiene** for 3 h at 168° resulted in the ready formation of the adduct **2**. Isolation of the product, and purification by column chromatography, yielded a colorless, crystalline material of sharp melting-point. Dreiding models show that the tetracyclic system is extremely rigid and somewhat strained. The four possible isomers of **2** are depicted.

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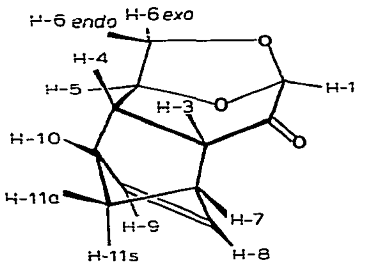
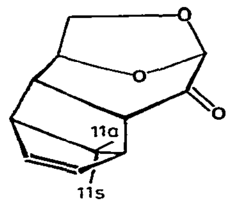
*To whom inquiries should be addressed

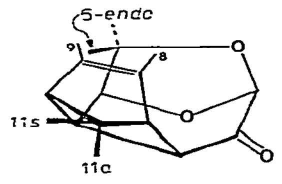
Cyclopentadiene, a volatile material of low boiling point (41°), readily dimerizes to an endo dimer of high boiling point (170°). Depolymerization may be achieved by fractional distillation[6]. Refluxing **1 with an excess of 1,3-cyclopentadiene (T, 42°) did not result in any reaction.



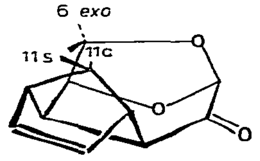
2a



2b



2c



2d

This observation was supported by results of examination of the p.m.r. spectrum of **2**, which showed long-range coupling, a phenomenon requiring specific geometry and strict rigidity. Two multiplets were observed, at δ 5.98 and 6.24, due to H-8 and H-9*, respectively (see Fig. 1 and Table I). These appear as doublets of doublets (in an AB type of pattern) unless expanded, at which point a more-complex multiplet was observed due to long-range coupling. Separation of these multiplets by 0.260 p.p.m. has been explained in terms of the anisotropy of the C=O group (to be discussed later), and it can only occur if the double bond lies endo to the parent ring. Coupling between H-1 and H-3, as seen in **1**, was not observed here, as these protons are no longer coplanar. Coupling between protons 5,6-*exo* and 6-*endo* was consistent with that observed for **1**, suggesting that little steric change had occurred in this region of the molecule. Were the conformation as depicted in **2c**, H-6*endo* would be strongly shielded, because of the anisotropy[7] and close proximity to the C=C bond, but this was not observed. The value of $J_{3,4}$ (5 Hz) indicated that the dihedral angle between H-3 and H-4 was zero. No distinct coupling between H-4 and H-5 was observed, either during decoupling experiments or on spectral expansion; this suggested that the dihedral angle between H-4 and H-5 must be close to 70–75°. For this to occur, the cyclopentadiene ring must be attached "under" the parent ring, as depicted in **2a**. Were **2d** the correct structure, the dihedral angle between H-4 and H-5 should be of the order of 35–40°, suggesting that $J_{4,5}$ should be ~5–6 Hz, which was not observed in Dreiding models.

Carbon atoms 3, 4, and 7–11 (in **2**) form the skeleton of norbornene, in which long-range coupling has been found to be most pronounced. Considerable controversy

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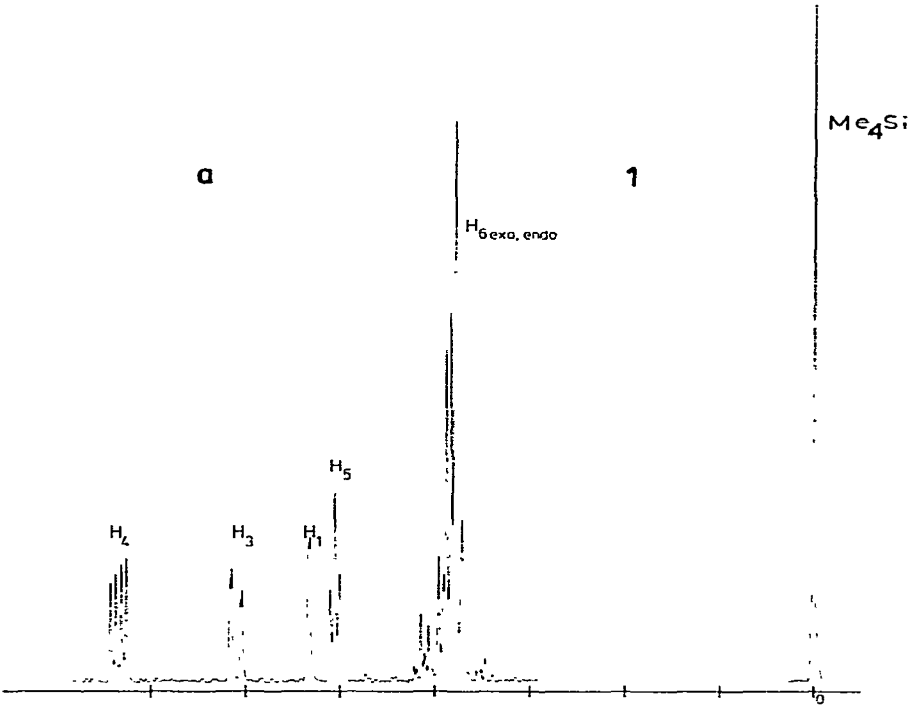
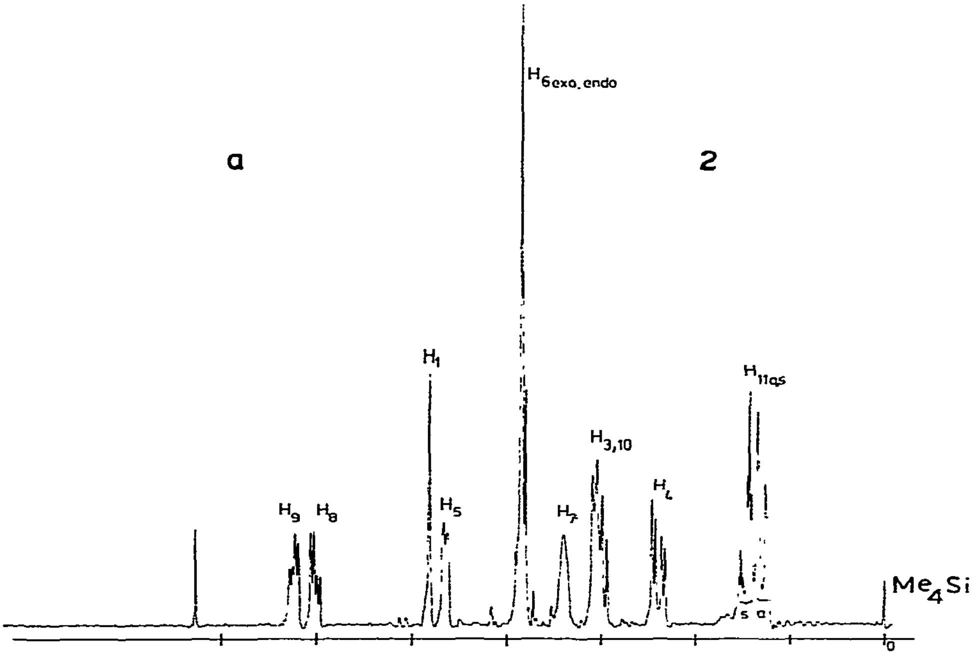
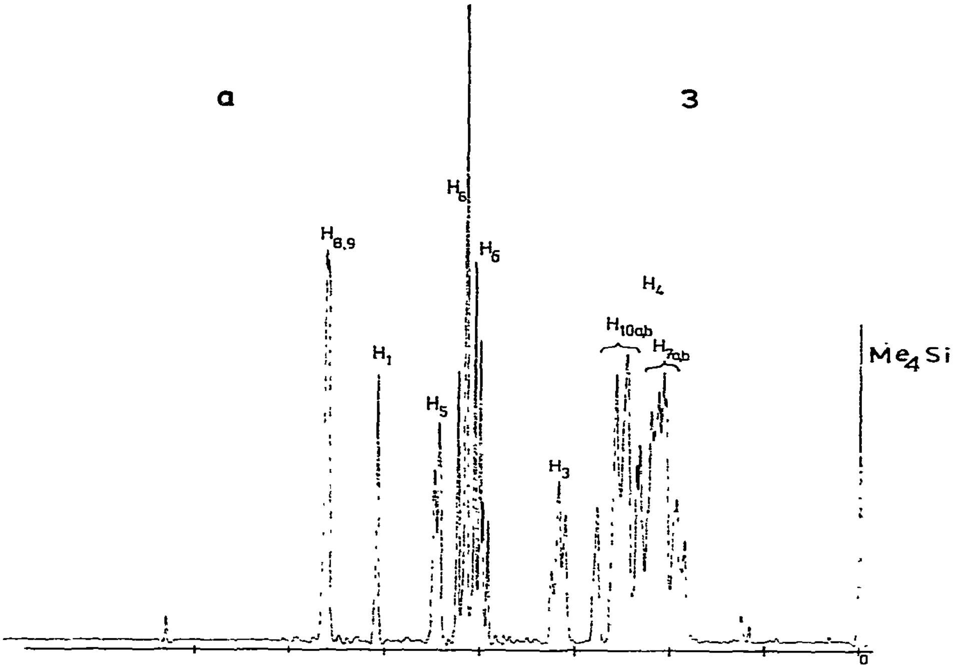
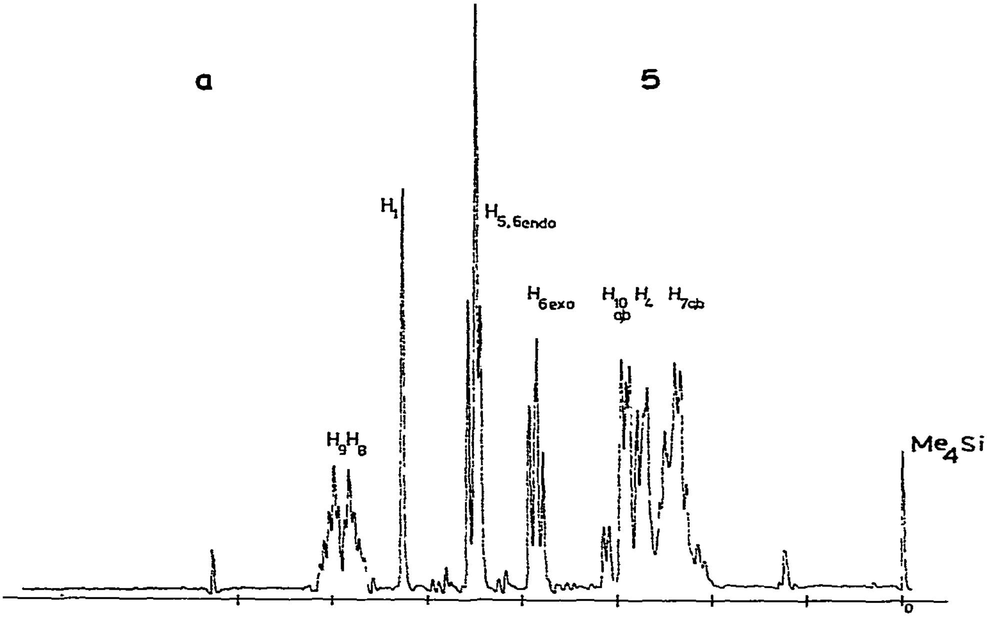
*The numbering system for the ring systems of these levoglucosenone adducts is unconventional. It is self-consistent, and has been used in order to simplify the p.m.r. and c.m.r. discussion.


a
1
$H_{6exo, endo}$
Me_4Si
H_5
H_4
H_3
H_1
0


$H_{6exo, endo}$
a
2
H_1
H_{11as}
$H_{3,10}$
H_4
H_9
H_8
H_5
H_7
Me_4Si
s
a
0


a
3
H8,9
H1
H5
H6
H6
H4
H10a,b
H7a,b
Me4Si
0


a
5
H1
H5,6endo
H6exo
H10 a,b
H4
H7a,b
H9H8
Me4Si
0

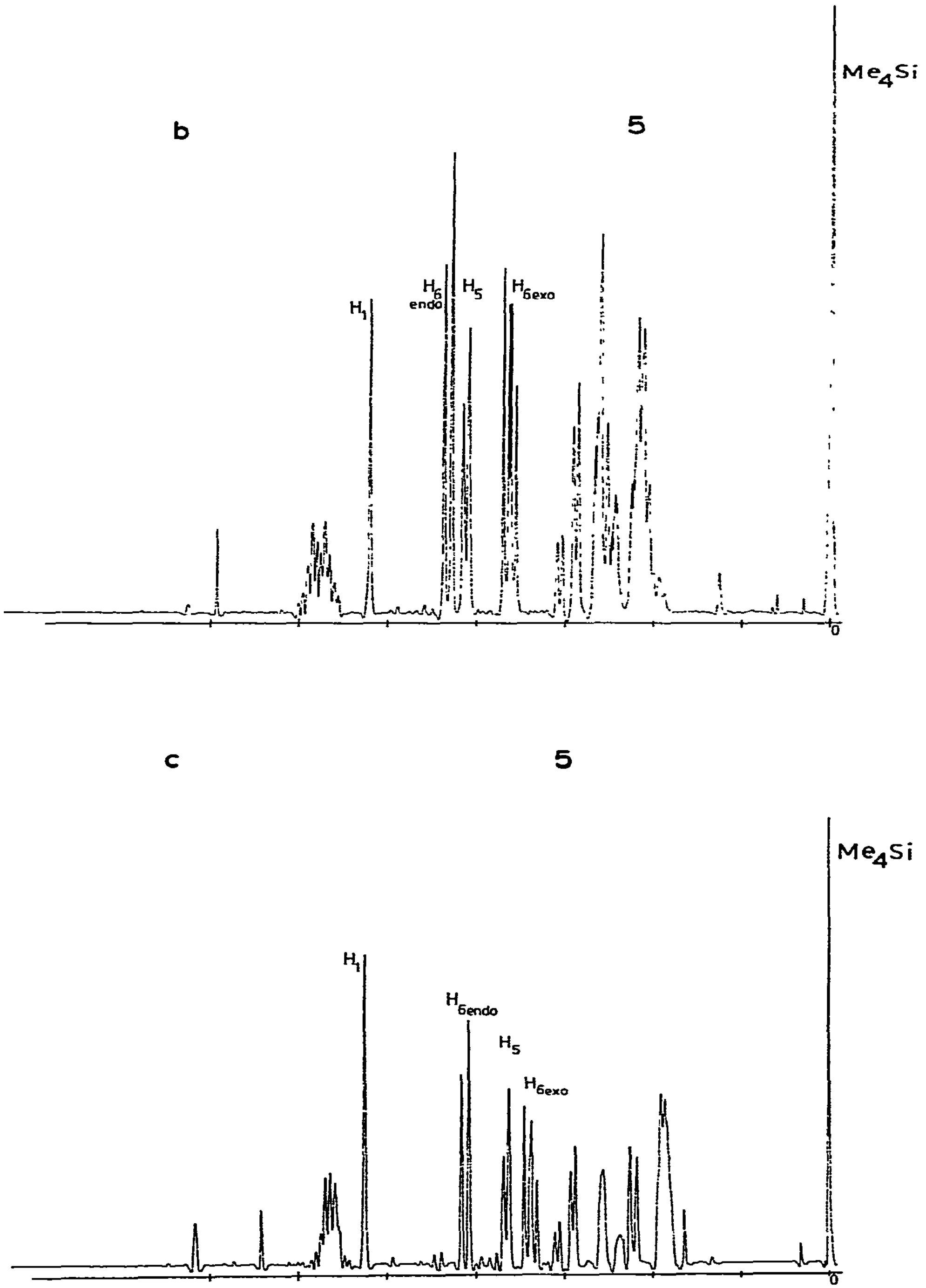


Fig. 1. ^{1}H-N.m.r. spectra of levoglucosenone (1), cyclopentadiene adduct (2), butadiene adduct (3), and the butadiene adduct (5) of 3-bromolevoglucosenone in (a) $CDCl_3$, (b) 1:1, $CDCl_3$–C_6D_6, and (c) C_6D_6; all at 90 MHz.

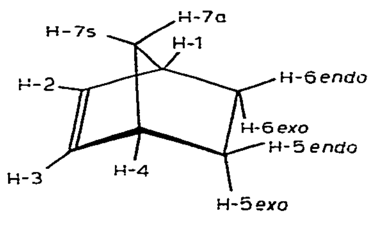
TABLE I

^{1}H-N.M.R. PARAMETERS FOR LEVOGLUCOSENONE (1) AND SOME CYCLOADDITION ADDUCTS[a],[b]

Compound	H-1	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11	Other
1	7.32	6.09	5.38	5.04	3.89 *exo* 3.75 *endo*						
2	4.77 (s)	2.99 (m) 3.18 (m)	2.39 (dd) 2.79–1.93	4.62 (d)	3.77 (dd) *exo* 3.85 (d) *endo*	3.34 (m) w/2 8 Hz 2.30–1.93	5.98 (dd)	6.24 (dd)	2.99 (m) 2.79–2.30	1.14 (m) 11s 1.24 (m) 11a	
3	5.11 (s)	w/s 14 Hz	?	4.63 (d)	4.20 (d) *endo* 4.00 (d) *exo*		5.64m w/2 5.5 Hz				
5	5.27 (s)		2.77 (d)	4.49 (d)	4.54 (d) *endo* 3.86 (dd) *exo*	2.80 (d) 7a 3.02 (dd) 7b	5.83 (m)	6.00 (m)	2.56–2.16 (m) 10a,b		
8	4.86 (s)	2.75 (dd)	2.09 (d)	4.53 (dd)	3.81 (m) *exo* *endo*	3.21 (m)	6.08 (ddd)	6.40 (ddd)	2.65 (dd)		
9[c]	4.84 (s)	3.24 (d)	2.56 (d)	4.70 (dd)	3.61 (dd) *endo* 3.72 (dd) *exo*						
10	5.10	3.02 (dd) 3a 2.60 (d) 3b	3.52 (d)	4.80 (m)	4.16 (dd) *endo* 4.14 (dd) *exo*		6.18 (dd)	6.22 (dd)	7.34 (m)		7.35 (m) 14 H phenolic

[a] δ Values; 90 MHz; solvent CDCl$_3$; reference Me$_4$Si. For coupling constants, see the Experimental section. [b] Key: d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; m = multiplet. [c] 100-MHz Spectrum.

has arisen in the literature over the proton absorptions (bridge head, and those at C-5 and C-6) in the p.m.r. spectra of norbornenyl compounds. Using a variety of norbornenes, both substituted and deuterated, Franzus *et al.*[8] invoked a geometric argument suggesting that the "syn" proton is situated at the diamagnetic–paramagnetic border of the bond system. Small changes in this position would cause it to be either shielded or deshielded. Marchand and Rose[9] studied a variety of monodeuterated norbornenes, and concluded that it is hazardous to assign the configuration of protons 7a and 7s of norbornene (corresponding to 11a and 11s in **2**) based on presumed, anisotropic effects of the C=C bond, or to utilize chemical-shift information for assignments in the case of substituted norbornenes. However, they found that, in the absence of complicating effects caused by the presence of other anisotropic groups, *in general* the *anti*-bridge protons absorbed at higher field than the *syn*-bridge protons. This phenomenon, which also appears in $J_{1,7s}$ and $J_{1,7a}$ has proved useful in assigning the position of protons 11a and 11s in our compound.



Norbornene

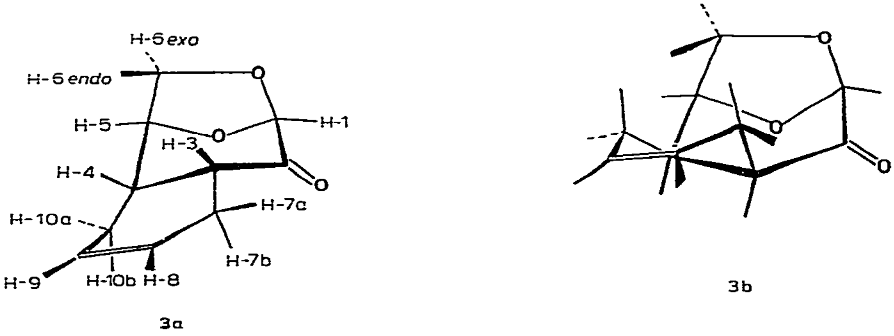
Expansion of the multiplet observed at δ 1.49–1.16 allowed a more accurate analysis of the coupling involved in protons 11a and 11s. Irradiation of the multiplet due to H-9, at δ 6.24, sharpened the triplets due to coupling between 9,11a; 7,11s; 10,11a; and 10,11s, allowing their measurement; this also resulted in partial collapse of the multiplet resulting from 9,11a and 9,11s coupling. Irradiation of the multiplet at δ 3.34 caused partial collapse of the multiplet at δ 1.41, as well as partial collapse of the multiplet at δ 5.98, allowing the assignment of the resonance at δ 3.34 to H-7, and confirming the 7,11s coupling-constant of 2.02 Hz. Similarly, coupling due to 7,11a was confirmed as being 1.5 Hz.

In norbornene, coupling between 7s and 5-*exo*, 6-*exo* has been observed as being ~2–3 Hz, whereas no coupling was observed[9] between 7s and 5-*endo*, 6-*endo*. For **2**, no coupling was observed between 11s and 3,4; this is strong evidence that the C=C bond is "syn" to the parent ring. Furthermore, we have used this, together with the evidence reported by Franzus *et al.*[8] and Marchand and Rose[9], to base our assertion that the resonance due to proton 11s is observed at δ 1.41 rather than δ 1.24. (There are larger coupling-constants between 7, 10, and 11s relative to 7, 10, and 11a.) Furthermore, the chemical shifts for 11s,11a (δ 1.41 and δ 1.24, respectively) are very similar to those reported for norbornenes[8,9]: 7s, 7a (δ 1.33 and 1.06, respectively).

The magnetic dissimilarity of protons 8 and 9, the similarity in the resonances observed for protons 6-*exo* and 6-*endo* relative to **1**, and the lack of observable coupling between protons 11s, 3, and 4 have convinced us that the conformation of the molecule of **2** is as depicted in **2a**.

Because of the results obtained by using cyclopentadiene, 1,3-butadiene was next examined. Treatment of **1** with neat 1,3-butadiene in a sealed ampoule at 120–130° produced a mixture of two isomeric compounds in the ratio of 3:2. These two isomers were observable in both the p.m.r. and c.m.r. spectra, but proved inseparable either by fractional recrystallization or by g.l.c. analysis. The isomeric nature of this mixture was confirmed by its giving a correct micro-analysis. Increasing the reaction temperature to 160° resulted, however, in the formation of a single isomer, as observed from the p.m.r. and c.m.r. spectra, and when the reaction temperature was increased to 200° or higher, polymerization occurred.

Unlike that of **2**, the tricyclic structure of the molecule of **3** is somewhat flexible. Models showed that the parent pyranoid ring may exist in a partial boat or partial chair conformation, and that carbon atoms 3, 4, and 7–10 (which make up the new ring) can, by the nature of this reaction, lie only in such a position as to form a boat. Conformational flexibility through carbon atoms 7 and 10 allows the C=C bond to lie either *endo* or *exo* to the plane of the parent ring. As it is possible for the new ring to be fused above or below the parent ring, there are two geometric isomers, each giving rise to four conformers. Thus, there are eight possible structures (unlikely to be observed) for this molecule. Dreiding models showed little resistance to conformational change, indicating a low, conformational-energy barrier.



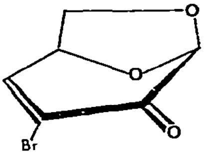
3a

3b

Both forms shown with the new ring exo to the parent ring

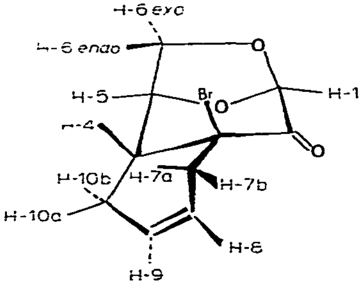
From p.m.r.-spectral analysis, it seemed probable that the conformation of this compound is best represented as in **3a** for the following reasons (see Fig. 1 and Table I). Protons 8 and 9 appear as a narrow multiplet with no observable wings (w/2 = 5.5 Hz), indicating their magnetic similarity; this seems to indicate that they are spatially arranged as in **3a**. If the C=C bond were to lie *endo* to the parent ring (*i.e.*, folded under, or over, it), a greater magnetic nonequivalence between protons 8 and 9 would have been expected, because of anisotropic effects due to the presence of the C=O group (to be discussed presently). Lack of coupling between protons 4 and 5 suggests that isomer **3a** is more plausable than **3b**, as models of **3b** suggest a coupling constant ($J_{4,5}$) of ~5 Hz, which was not observed. Furthermore, in the *endo* conformation of **3b** (*i.e.*, with the C=C bond folded back over the parent ring), models show that H-6*endo* and the C=C bond lie within 0.05–0.08 nm. This would probably cause two immediate effects in the p.m.r. spectrum: H-6*endo* would be very strongly shielded, relative to that observed in **1** (anisotropy[7] of C=C) and steric compression would decrease the bond angle between H-6*endo* and H-6*exo*, thus increasing $J_{6,exo,endo}$ relative to that of **1**. Neither of these effects was observed.

In an effort to locate the resonance position of H-3 in **3**, 3-bromolevoglucosenone[10] (**4**) was treated with 1,3-butadiene in a similar fashion.



4

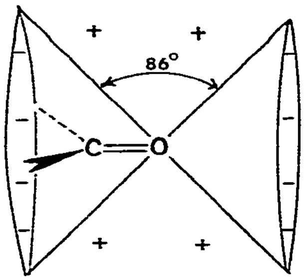
In this instance, the reaction occurred readily, yielding an oil. The p.m.r. and c.m.r. analysis of this compound, **5**, proved very interesting (see Fig. 1). Examination of the ^{1}H-n.m.r. spectrum of **5** in $CDCl_3$ shows protons 8 and 9 to be magnetically nonequivalent, more so than observed for **3a**. For this to occur, it would seem that the rings must be oriented as depicted (*i.e.*, C=C lying *endo* to the parent ring).



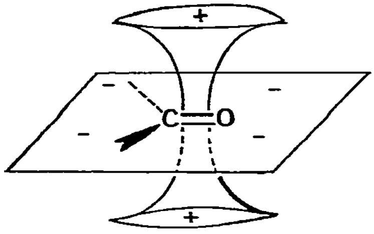
5

The magnetic nonequivalence of H-8 and H-9 could be due to either of two effects, an inductive effect due to Br, or the anisotropy of the C=O group. As the same effect, of similar magnitude, was observed for compound **2**, the inductive effect of Br was considered minimal.

In their excellent papers on the anisotropic effects of C=C and C=O functionalities, ApSimon *et al.*[11–13] invoked a modification of the conventional shielding



ApSimon's model



Conventional model

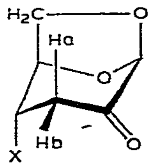
+ = region of shielding

− = region of deshielding

"cone" around the C=O group; this is contrary to that generally presented in most text-books on the subject of shielding[14] due to magnetic anistropy.

Use of ApSimon's model allowed us to explain (*a*) the shielded nature of H-8 relative to H-9 (0.17 p.p.m. in **5**, and 0.26 p.p.m. in **2**), and (*b*) the somewhat deshielded nature of H-3 in **3** (whereas, by using the conventional model, this proton should have been shielded). Similar results have been observed for other derivatives of levoglucosenone, but not explained[3,15]. In the spectrum of **5**, coupling was observed between H-4 and H-10a, but not between H-4, H-5, or H-4,H-10b; this, along with study of models, suggested dihedral angles of 75° and 100° for the foregoing protons, respectively (H-4,H-5, and H-4,H-10b), and this can occur only if the newly formed ring attaches itself below the plane of the pyranoid ring.

The chemical shift of H-3 (in **5**) was observed at δ 3.18. Had the newly formed ring been oriented above the plane of the pyranoid ring, it seems that the chemical shift of H-3 would be shifted somewhat up-field, and appear in a position similar to that observed for Hb, generally in the region of δ 2.45, for compounds of the type depicted below.



Allylic coupling observed between protons 8 and 10a,10b, as well as between protons 9 and 7a,7b, was consistent with that reported by Newsoroff and Sternhell[16]. Decoupling, and solvent change, further aided in coupling-constant identification

TABLE II

^{13}C CHEMICAL-SHIFT DATA FOR LEVOGLUCOSENONE AND DERIVATIVES[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-11*	*C-12*
1	100.81	186.07	126.49	147.94	71.77	66.61						
2	99.38	200.23	46.89	46.30	74.78	70.23	46.89	134.29	135.33	42.34	49.42	
3	101.84	202.05	40.71	38.24	77.39	67.37	24.19	124.73	124.08	20.55		
5	108.15	195.16	56.25	48.12	79.08	67.31	36.61	128.44	125.64	29.13		
8	99.62	200.40	46.86	43.23	77.84	69.39	35.64	133.91	132.18	32.77	27.41	22.10
9	100.24	196.51	52.43	48.11	72.40	68.08[b]						
10	101.64	199.06	35.05	40.58	75.43	67.44	154.10	106.71	110.42	141.89		

[a]All values in p.p.m., for solutions in $CDCl_3$, with Me_4Si as the reference standard. [b]For the rest, see the Experimental section.

and determination. Use of benzene-d_6 (see Fig. 1) very neatly spread apart the envelope of H-5 and H-6*endo* (observed for a solution in $CDCl_3$), allowing accurate measurement, and positive identification. Similar effects were observed with the multiplets of H-7a, H-7b, and H-4, allowing positive identification *via* decoupling.

As observed by Alder *et al.*[17,18], 4 + 2 cycloadditions generally occur in such a way as to form the "endo" product (*e.g.*, **2a**/**2c** and **5**), although there are some exceptions[19]. Unless sterically inhibited, the approaching diene is further stabilized by secondary, orbital interactions between the carbon atom of the C=O and C-2 or C-3 of the reacting diene[20a,b], leading to a preponderance of an *endo* product. The reactions of **1** with the variety of dienes examined showed no exception to this observation. It appears that the stereochemistry of compounds **2** and **5** are to be expected. The fact that, for **3**, the *exo* conformer was preponderant appears to result from the apparently low, conformational-energy barrier between the *endo* and *exo* conformers. The *endo* preference observed for **5** is probably due to the bulky nature of Br and its electronegative repulsion of C=C.

The c.m.r. spectra of compounds **3** and **5** both show the presence of ten carbon atoms (see Table II). Comparison of the proton-decoupled spectra of **1**, **3**, and **5** allowed the assignments therein to be made. Little change in the position of C-1 in **3** and **5**, relative to **1**, was observed. For **3**, deshielding of C-2 by 13.98 p.p.m., relative to **1**, was attributable to loss of the conjugation[21] present in **1**. For **5**, C-2 is somewhat less deshielded than its counterpart in **3**, because of the presence of Br at C-3. In both **3** and **5**, little change was observed in the resonance positions of C-5 and C-6 relative to **1**. Resonances for C-8 and C-9 in the spectra of both **3** and **5** were observed in the region of δ 125.0; this is consistent with that found for alkenes[22]. For **3**, there was very little difference in the resonance positions of C-8 and C-9. We have tentatively assigned C-8 as resonating at lower field than C-9, because of its closer proximity to the carbonyl function. For **5**, we have assigned C-8 as resonating at lower field for the same reason, as well as the presence of Br on C-3. The signals for C-7 and C-10 in both **3** and **5** appear as triplets in the off-resonance spectrum, and were assigned with C-7 appearing farthest downfield. For **5**, C-3 is readily assigned, as it is a quaternary carbon atom, and appears as a singlet in the off-resonance spectrum, at δ 156.25, leaving C-4 at δ 148.12. For **3**, C-3 was assigned as δ 140.70, leaving C-4 at δ 138.24; this is consistent with values observed for unsaturated, polycyclic ketones[23].

The c.m.r. spectrum of **2** contained ten resonances, whereas eleven were expected; their chemical shifts were assigned by comparison with those for compounds **1**, **3**, and **5**. Carbon atoms 1, 2, 8, and 9 were readily assigned, and are listed in Table II. Two triplets were observed in the off-resonance spectrum, at δ 70.23 and 49.42, corresponding to C-6 and C-11, C-6 being assigned the lower-field resonance, because of its close association to the two ring-oxygen atoms. Also, δ 49.42 is consistent with resonances observed for the bridge-head carbon atom in norbornenes. Atom C-5 was assigned to the resonance at δ 74.78, because of its similarity in position to C-5 of **3** and **5**. Carbon atoms 3, 4, 7, and 10 were left, to be assigned to the three remaining

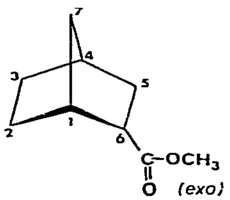
TABLE III

PUBLISHED ^{13}C DATA[22] FOR NORBORNANE, NORBORNENE, AND THEIR SUBSTITUTED DERIVATIVES **6** AND **7**, AS WELL AS SELECTED DATA FOR **2**

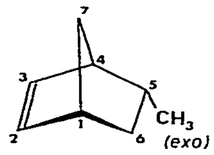
Carbon atom	*Compound*[a]				*Carbon atom*	*Compound*[a] **2**
	Norbornane	**6** *(exo)*	**7** *(exo)*	*Norbornene*		
1	36.8	40.8	42.7	42.2	3	46.89
2	31.1	25.1	137.2	135.5	4	46.30
3	31.1	29.0	136.2	135.5	7	46.89
4	36.8	37.5	48.7	42.2	8	134.29
5	31.1	32.3	33.0	25.5	9	135.33
6	31.1	46.0	35.0	25.5	10	42.34
7	38.7	40.4	45.0	48.8	11	49.42

[a]All values in p.p.m.

resonances, at δ 46.89, 46.30, and 42.34. A quantitative, completely decoupled ^{13}C-spectrum of this compound (long delay-periods between pulses) showed the area of the resonance at δ 46.89 to be almost twice that of the other two, suggesting the presence of two carbon atoms. By comparison of data published for norbornane, norbornane substituted at C-6(C-2) by -C(=O)OCH$_3$ (**6**), norbornene, and norbornene substituted at C-5 by Me (**7**), the remaining resonances were assigned.



6*



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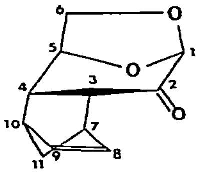


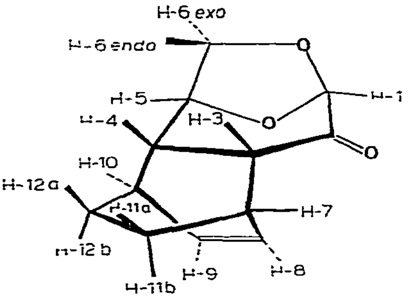
2

* Numbered unconventionally.for ease of discussion and comparison.

Atom C-10 of **2** is farthest from the C=O functionality, and would be expected to be least influenced; thus we have assigned this to the resonance at δ 42.34. Atom C-7 of **2** is very similar to C-1 of **6**, and by using Table III and interpolating the data, it would seem that oxidation of norbornane to norbornene causes C-1 of norbornene to be shielded by 5.4 p.p.m., relative to norbornane. Adding this value to C-1 of **6** gives a value of 46.2 p.p.m.; this is very similar to the two resonances observed at δ 46.89 and 46.30 for **2**. Oxidation of norbornane to norbornene causes C-5 to be shielded by 4.6 p.p.m. (see Table III). The effect on C-5 of norbornane on substitution of C-6 by -C(=O)-OCH$_3$ (*exo*) is to deshield C-5 by 2.2 p.p.m. Thus, considering C-5 of **7**, substitution of C-6 by -C(=O)OCH$_3$ (*exo*) would theoretically deshield C-5 by ~2.2 p.p.m., giving a calculated value of 35.2 p.p.m.

In view of this result, and the fact that the resonance at δ 46.89 appears to be due to two carbon atoms, we have tentatively assigned the resonances at δ 46.89 to C-3 and C-7, and C-4 was assigned to δ 46.30.

The ease of reaction between **1** and 1,3-cyclopentadiene led us to examine the reaction between **1** and 1,3-cyclohexadiene. Heating **1** in a 3.5-fold excess of 1,3-cyclohexadiene in a sealed tube at 200° resulted in a 96% conversion into the expected adduct **8**.



8

The p.m.r. spectrum of **8** (see Table I) again shows multiplets due to H-8 and H-9 separated by 0.32 p.p.m., with the expected, AB type of multiplet, as observed for **2** and **5**. Close examination of these two multiplets revealed that they are doublets of doublets of doublets, where $J_{8,9}$ = 7.56 Hz; this is of the order observed for bicyclo[2.2.2]oct-2-ene derivatives[24]. Coupling between protons 7,8 and 9,10 was observed to be 6.34 Hz, comparing well with literature values[24,25], whereas long-range, transoid, allylic coupling between 8,10 and 7,9 was 1.23 Hz, indicating that protons 7, 8, 9, and 10 are coplanar[16,25]. As with **2**, no 1,3 coupling was observed, H-1 appearing as a singlet, at δ 4.87. Irradiation of a doublet at δ 2.63 resulted in partial collapse of the H-9 multiplet (J 6.34 Hz), allowing assignment of H-10 to this resonance. Similar treatment of the broad multiplet at δ 3.21 caused major collapse of the multiplet due to H-8, and collapse of the doublet (J 3.53 Hz) at δ 2.74. We therefore assigned the multiplet at δ 3.21 to H-7 and the doublet of doublets at δ 2.74 to H-3. No coupling between protons 10 and 4, or 4 and 5, was observed, consistent with the dihedral angle between 4,5 and 4,10 of ~70–75°; this is strong evidence that the new ring was formed below the plane of the parent ring, as depicted, rather than above it. Furthermore, a chemical shift of δ 2.75 for H-3 also supports this contention, as previously explained. Had the new ring been formed above the plane of the parent ring, 4,5 coupling on the order of 3–4 Hz should have been observed. It also seems that steric hindrance between C-6 and the approaching 1,3-

cyclohexadiene would prevent reaction in this manner. Coupling between protons 3 and 10 (J 3.41 Hz) was observed; this is consistent with a dihedral angle between protons 3 and 7 of ~50°, as observed with Dreiding models. Unlike the cyclopentadiene adduct **2**, this compound, with its six-membered ring, shows marginal flexibility, allowing the parent, levoglucosenone ring to assume either a partial boat, or partial chair, conformation. A dihedral angle between protons 3 and 7 of 50° is consistent with the parent ring's being in a chair conformation.

One "anomaly" was, however, observed. Coupling between protons 3 and 4 was observed to be 10.56 Hz; this is very difficult to explain, as the dihedral angle (from models) appears to be on the order of 10°, and this is an even larger coupling-constant than would have been expected had protons 3 and 4 been *trans*-diaxial.

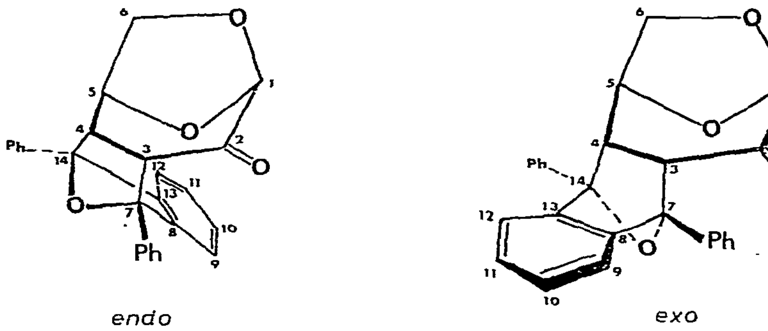
The c.m.r. spectrum of compound **8** indicated the presence of twelve carbon atoms, twelve distinct signals being observed. The chemical shifts are tabulated in Table II. Assignments for carbon atoms 1, 2, 5, 6, 8, and 9 caused no difficulty, compared to the compounds previously discussed. Resonances at δ 46.86 and 43.23 were assigned to C-3 and C-4, respectively, by comparison with the values obtained for **2**. An off-resonance spectrum showed the resonances appearing at δ 35.64, 32.77, 27.41, and 22.10 as two doublets and two triplets, respectively. We thus assigned δ 32.77 and 35.64 to C-10 and C-7, respectively, C-4 being somewhat deshielded, due to its position relative to C=O. Similarly, δ 27.41 and 2.10 were assigned to C-11 and C-12.

1,3-Diphenylisobenzofuran, long known to be a very reactive diene, has been used for a variety of 4 + 2 cycloaddition reactions. Because of its high reactivity with a wide variety of dienes, it has frequently been used as a trapping agent for transient, double bonds[27] in strained systems. It has been allowed to react with a variety of substituted propenes[28,29], to give high yields of stereospecific products.

This led us to examine the reactivity of 1,3-diphenylisobenzofuran towards levoglucosenone. Boiling of a solution of **1** in benzene containing a two-fold excess of 1,3-diphenylisobenzofuran under reflux for 3 h resulted in the precipitation of crystalline material on cooling. After filtering, and recrystallizing from benzene–hexane, an analytically pure, white, crystalline material (**9**) was obtained.

P.m.r. analysis of **9** showed a very simple spectrum with regard to the parent ring: H-1 appears as the expected singlet, and H-3 and H-4 as doublets coupled by 8.0 Hz, at δ 3.24 and 2.56, respectively. No coupling was observed between protons 4 and 5; H-5 appears as a doublet of doublets, coupled to both the 6*exo* and 6*endo* protons, by 5.2 and 1.7 Hz, respectively. Protons 6*exo* and 6*endo* are seen to couple by 10 Hz. A large multiplet centered at δ 7.35, w/2 70 Hz, and integrating to 14 protons, is due to the aromatic regions of this molecule.

In view of the lack of coupling between protons 4 and 5, it seemed that attachment of the isobenzofuran ring to the parent compound occurs below the ring, for reasons discussed earlier. However, it is not yet possible to decide whether the isobenzofuran ring is attached *endo* or *exo* to the parent ring. Kelley and McNutt[29] allowed both isobenzofuran and 1,3-diphenylisobenzofuran to react with 4,4-dimethyl-2-buten-1-one, and obtained high stereoselectivity with isobenzofuran, which gives an *exo*-adduct. The stereochemistry of the 1,3-diphenylisobenzofuran adduct was not defined. In view of this observation, and the bulky nature of the diene, it would seem reasonable to assume that an *exo* product was formed, as depicted.



endo *exo*

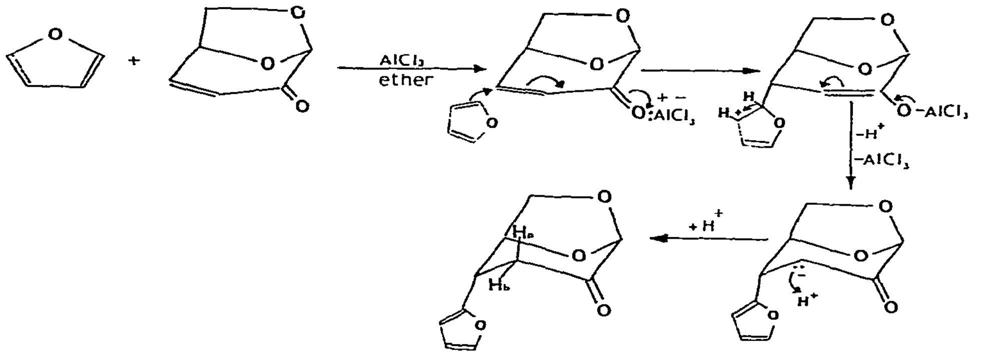
9

The c.m.r. spectrum of **9** was complicated, and proved useless for structural determination. Twenty-six carbon atoms are present in this compound, but only twenty-one lines were discernible in the spectrum. The chemical shifts of carbon atoms 1–6 were not too difficult to assign (see Table II). Carbon atoms 7, 8, 13, and 14 are quaternary, and, as such, appear as singlets in the off-resonance spectrum. We have assigned resonances δ 90.73 and 91.25 to C-7 and C-14, and the resonances at δ 47.07 and 146.78 were to C-8 and C-13, respectively. On comparison with those published for similarly structured compounds[22], these assignments seemed reasonable. Resonances at δ 135.63 and 134.46 appear to be C-1 of the two phenyl substituents; δ 130.31, 129.14 (*ortho* carbon atoms); δ 128.32, 127.62 (*meta* carbon atoms); δ 126.98, 126.51 (*para* carbon atoms) of the same substituents; these shifts agree well with published data[22]. Other absorbances were observed at δ 119.79, 117.79, 117.28, and 97.96, but were not assigned.

Despite the reaction of 1,3-diphenylisobenzofuran, initial attempts to achieve reaction with unsubstituted furan proved unproductive, and heating of a mixture of furan and levoglucosenone in a sealed tube at 130 to 200° caused no reaction. Examination of the literature revealed that a wide variety of cycloaddition reactions have been performed with furan. Eggelts *et al.*[30] reported the preparation of 7-oxabicyclo[2.2.1]heptene derivatives from furan and such reactive dienophiles as acryloyl chloride, ethyl propiolate[31], and dimethyl acetylenedicarboxylates[21], although, in many cases, the reaction appears to be slow. Such reactions have shown dramatic increases in rate[21,30,31] on using a Lewis-acid catalyst, such as $AlCl_3$.

Reaction at room temperature of levoglucosenone with furan in diethyl ether, using aluminum chloride as the catalyst, did not produce the desired Diels–Alder adduct. Instead, a β-addition compound was obtained. Such a reaction between αβ-unsaturated ketones and aromatic compounds has been reported[32] as a Friedel–

Crafts type of acylation; however, in this instance, it was unexpected, because of the successful applications of Lewis-acid catalysts by others in the 4 + 2 addition.



10

Substitution of the furan ring occurred at C-2, as expected in cases of electrophilic substitution; this was indicated by both the p.m.r. and c.m.r. spectra of the product. The p.m.r. spectrum showed multiplets at δ 7.34, 6.29, and 6.18, typical of 2-substituted furan. Similarly, the c.m.r. spectrum of the furan portion of this molecule was consistent with published data[22] (see Tables I and II). It seems probable that attachment of the furan ring to the parent levoglucosenone occurs below the plane of the parent ring, as the p.m.r. resonances for H-1, 3a, 3b, 4, 5, and $6_{exo,endo}$ are very similar to those reported[3] for similarly substituted levoglucosenone adducts; decoupling experiments provided further confirmation.

Treatment of levoglucosenone with $AlCl_3$ in ether had no effect, and the starting material was recovered quantitatively.

The foregoing data indicate interesting possibilities for incorporation of sugar units within the carbon skeleton of organic compounds by the 4 + 2 cycloaddition reaction of various dienes with levoglucosenone.

EXPERIMENTAL

General. — P.m.r. (90 MHz) and c.m.r. (22.5 MHz) spectra were recorded with a Jeol FX-900 instrument, except for the 100-MHz spectra, recorded with a Jeol-100 instrument. I.r. spectra were recorded with a Beckman Aculab II spectrophotometer. G.l.c. analyses were performed in a Varian series 1800 chromatograph equipped with an H.P. 3380A digital integrator. Mass-spectral analyses were made with a Varian M.A.T. III spectrometer. All t.l.c. assays were conducted on plates of Baker-flex silica gel, IB2-F (J. T. Baker Chemical Co.). Silica used for column separations was supplied by E. Merck (Silica gel 60, cat. 7734; 70–230 mesh, ASTM).

Reaction of levoglucosenone with cyclopentadiene. — A solution of levoglucosenone (**1**) (0.22 g, 1.75 mmol) in dicyclopentadiene (10 mL) was boiled for 3 h under reflux (T 168°, which decreased as depolymerization occurred). T.l.c. of the reaction mixture on silica, eluted with 1:1 hexane–ethyl acetate, showed 3 spots; R_F 0.58 (trace), 0.50 (major), 0.45 (trace). The mixture was then passed through a column (2 × 50 cm) of silica gel eluted with 1:1 hexane–ethyl acetate, to remove most of the remaining cyclopentadiene. The 3 fractions were separated in a second column. The fraction having R_F 0.58 proved to be an unidentified hydrocarbon, and the fraction having R_F 0.45 was unreacted levoglucosenone. The middle fraction, R_F 0.50, contained the product (**2**), which, on removal of the solvent, crystallized as a white solid: yield 0.162 g (47.8%), m.p. 61.5–62.5°; ν_{max}^{KBr} 3020 (HC=CH), 2950, 2885, 2845 (CH), 1705 (C=O, nonconjugated), 1630 (C=C), and 1100 cm^{-1} (COC); ^{1}H-n.m.r. (90 MHz, $CDCl_3$–Me_4Si): δ 6.24 (dd, 1 H, H-9, $J_{8,9}$ 6 Hz), 5.98 (dd, 1 H, H-8, $J_{8,9}$ 6, $J_{7,8}$ 3 Hz), 4.77 (s, 1 H, H-1), 4.62 (slightly broadened d, 1 H, H-5, $J_{5,6exo}$ 4, $J_{5,6endo}$ ~0.5 Hz), 3.85 (broadened d, 1 H, H-6*endo*, $J_{6endo,exo}$ 7, $J_{5,6endo}$ 0.5 Hz), 3.77 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7, $J_{5,6exo}$ 4 Hz), 3.34 (m, 1 H, H-7, poorly resolved, w/2 8 Hz), 2.99 (m, 2 H, H-10 + H-3, $J_{3,4}$ 8.5, $J_{3,7}$ 3.0 Hz; resolution of H-7, H-9 + H-10 coupling is poor), 2.39 (dd, 1 H, H-4, $J_{3,4}$ 8.5, $J_{4,10}$ 3.17 Hz), 1.41 (m, 1 H, H-11s, $J_{7,11s}$ 2.02 Hz, $J_{8,11s} = J_{9,11s} =$ 0.5 Hz, $J_{11a,11s}$ 8.5 Hz), and 1.24 (m, 1 H, H-11a, $J_{7,11a} = J_{10,11a} =$ 1.5 Hz, $J_{8,11a} = J_{9,11a} =$ ~0.2 Hz, $J_{11a,11s}$ 8.5 Hz); c.m.r. (22.5 MHz, $CDCl_3$–Me_4Si): δ 200.23 (C-2), 135.33 (C-8), 134.29 (C-9), 99.38 (C-1), 74.78 (C-5), 70.23 (C-6), 49.42 (C-11), 46.89 (C-7 and C-3), 46.30 (C-4), and 42.34 (C-10): *m/z*: parent ion 192 (16%), 164 ($M^{+\cdot}$ — CO, 5.5%), 146 ($164^{+\cdot}$ — H_2O, 5%), 118 ($146^{+\cdot}$ — CO, 80%), and 117 ($146^{+\cdot}$ — HCO·, 100%).

Anal. Calc. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.20. Found: C, 68.72; H, 6.28.

Reaction of levoglucosenone with butadiene. — A mixture of levoglucosenone (0.500 g, 3.97 mmol) with a five-fold excess of condensed 1,3-butadiene was sealed in a Pyrex tube, heated in an autoclave for 3 h at 160°, and cooled. The mixture formed long, needle-like crystals, and in t.l.c. on plates of silica eluted with 1:1 ethyl acetate–hexane gave only one spot, R_F 0.55. Evaporation of the excess of 1,3-butadiene yielded **3** as a yellow oil that crystallized readily from hexane, producing long, colorless, needle-like crystals (0.678 g, 95%), m.p. 62–63°; ν_{max}^{KBr} 3005 (C–H stretch), 2945, 2807, 2280, 1730 (C=O), 1655, and 1412 (C=C), and 1100 cm^{-1} (COC); ^{1}H-n.m.r. (90 MHz, $CDCl_3$–Me_4Si): δ 5.64 (m, 2 H, w/2 5.5 Hz, H-8 + H-9), 5.11 (s, 1 H, H-1), 4.46 (d, 1 H, H-5, $J_{5,6exo}$ 4.88 Hz), 4.20 (d, 1 H, H-6*endo*, $J_{6ndo,exo}$ 7.33 Hz), 4.00 (dd, 1 H, H-6*exo*, $J_{5,6exo}$ 4.88, $J_{6endo,exo}$ 7.33 Hz), 3.18 (m, 1 H, H-3, $J_{3,4}$ 4, $J_{3,7b}$ 9, $J_{3,7a}$ 0.5 Hz, w/2 14 Hz), 2.79–1.93 (m, 5 H, H-10a,b, H-7a,b, H-4; from decoupling experiments, it appears that the upper half of this multiplet is due to H-7a + b and, perhaps, H-4, and that the lower half, δ 2.79–2.30, is due to H-10a + b); c.m.r. (22.5 MHz, $CDCl_3$–Me_4Si): δ 202.05 (C-2, C=O), 124.73 (C-8, C=C), 124.08 (C-9, C=C), 101.84 (C-1, CH), 77.39 (C-5, CH_2), 67.37 (C-6, CH_2), 40.71 (C-3, CH), 38.24 (C-4, CH), 24.19 (C-7, CH_2), and 20.55 (C-10, CH_2); *m/z*: parent ion 180 (3.5%), 152 ($M^{+\cdot}$ — CO or C_2H_4, 3%), 134 ($152^{+\cdot}$ — H_2O, 25%), 106 ($134^{+\cdot}$ — CO or C_2H_4, 67%), 91 ($106^{+\cdot}$ — CH_3, 100%), and 78 ($106^{+\cdot}$ — C_2H_4 or CO; this might also be derived from $91^{+\cdot}$ — CH·, 82%).

Anal. Calc. for $C_{10}H_{12}O_3$: C. 66.66: H. 6.66; O, 26.66. Found: C, 66.72; H, 6.77; O, 26.51.

Reaction of 3-bromolevoglucosenone with 1,3-butadiene. — 3-Bromolevoglucosenone (**4**; 0.245 g, 1.94 mmol) plus a three-fold excess of 1,3-butadiene was heated for 3 h at 90°, cooled, kept for 16 h at room temperature, and then heated for a further 7.5 h at 90°. Evaporation of the excess of butadiene gave a brownish oil which was added to a column (2 × 20 cm) of silica gel and eluted with 4:1 hexane–ethyl acetate, to provide 0.322 g (64%) of **5** as a straw-colored oil; t.l.c. (silica plates) R_F 0.5: ν_{max}^{neat} 3045 (C–H stretch, *cis*, disubst. alkene), 2972, 2900, 2844 (C–H stretch), 1740 (C=O stretch), 1635 (C=C stretch), 1115, and 1085 cm^{-1} (COC stretch); ^{1}H-n.m.r. (90 MHz; $CDCl_3$–Me_4Si): δ 6.00 (distorted m, 1 H, H-9, $J_{8,9}$ 10.63, $J_{9,10b}$ 7.56, $J_{9,7b}$ 1, $J_{9,7a}$ 3 Hz), 5.83 (distorted m, 1 H, H-8, $J_{8,9}$ 10.63, $J_{8,7b}$ 5.37, $J_{8,10b}$ ~1. $J_{8,10a}$ 3 Hz), 5.27 (s, 1 H, H-6*endo*, $J_{6endo,exo}$ 7.36 Hz). 4.49 (d. 1 H, H-5, $J_{5,6exo}$ 5.82 Hz), 3.86 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.36, $J_{5,6exo}$ 5.82 Hz). 3.02 (broadened dd, 1 H, H-7b, $J_{7a,b}$ 16.10, $J_{8,7b}$ 5.37, $J_{9,7b}$ ~1 Hz), 2.80 (broad d. 1 H, H-7a, $J_{7a,b}$ 16.10, $J_{9,7a}$ 3 Hz), 2.77 (d, 1 H, H-4, $J_{4,10a}$ 6.83 Hz), and 2.56–2.16 (m, 2 H, H-10a,b); ^{1}H-n.m.r. (90 MHz; benzene-d_6–Me_4Si): δ 5.55 (m, 2 H, H-8,9, w/2 38 Hz), 5.24 (s. 1 H, H-1), 4.13 (d, 1 H, H-6*endo*, $J_{6endo,exo}$ 7.36 Hz), 3.71 (d, 1 H, H-5, $J_{5,6exo}$ 5.85 Hz), 3.40 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.36, $J_{5,6exo}$ 5.85 Hz). 2.98 (dd, H-7b, $J_{7a,b}$ 16.10 $J_{8,7b}$ 5.36 Hz), 2.45 (broad d, 1 H, H-7a, $J_{7a,b}$ 16.10, $J_{9,7a}$ 3 Hz), 2.24 (d, 1 H. H-4, $J_{4,10a}$ 6.83 Hz), and 1.89 (m, 2 H, H-10a,b, w/2 15 Hz): c.m.r. (22.5 MHz, $CDCl_3$–Me_4Si): δ 195.16 (C-2), 128.44 (C-8), 125.64 (C-9), 108.15 (C-1). 79.08 (C-5), 67.31 (C-6), 56.25 (C-3), 48.12 (C-4), 36.31 (C-7), and 29.13 (C-10).

Anal. Calc. for $C_{10}H_{11}BrO_3$: C, 46.35; H, 4.28; Br, 30.87. Found: C, 46.41: H, 4.20; Br, 30.63.

Reaction of levoglucosenone with 1,3-cyclohexadiene. — A mixture of levoglucosenone (0.339 g, 2.69 mmol) with 1,3-cyclohexadiene (0.9 mL, 9.50 mmol) was sealed in a Pyrex tube, and heated for 3 h at 200°. T.l.c. of the mixture, whose color had changed from light straw to deep red-brown, showed 3 spots, R_F 0.93, 0.71, and 0.57 (starting enone) in 1:1 ethyl acetate–hexane. Evaporation of the excess of 1,3-cyclohexadiene gave 0.916 g of a crude oil that could not be crystallized, despite repeated efforts. Chromatography on a column (2 × 50 cm) of silica eluted with 3:1 ethyl acetate–hexane gave four compounds, R_F 0.75, 0.46, 0.40, and 0.23. The compounds having R_F 0.46 and 0.40 were not u.v.-active, and those having R_F 0.46 and 0.23 were present in traces only. G.l.c. on 3% of OV-17 on Gas Chrom Q (60–80 mesh) programmed at 8°/min from 50°: compounds of R_F 0.75 had RT 8.90, 9.51; ratio 1.64:1; that of R_F 0.40 had RT 17.9. The material having R_F 0.75 was a yellow oil having a terpenoid odor (0.100 g) and its g.l.c., p.m.r., and i.r. data showed that it was a mixture of hydrocarbons; that having R_F 0.40 was colorless, crystalline material (0.530 g, 96% yield based on initial levoglucosenone used), m.p. 44–45°; ν_{max}^{KBr} 3098 (HC=CH), 2935, 2880, 2500 (C–H), 1710 (C=O), and 1640 cm^{-1} (*cis* C=C); ^{1}H-n.m.r. (90 MHz, $CDCl_3$–Me_4Si): δ 6.40 (ddd, 1 H, H-9, $J_{8,9}$ 7.56, $J_{9,10}$ 6.35, $J_{7,9}$ 0.72 Hz), 6.08 (ddd, 1 H, H-8, $J_{8,9}$ 7.56, $J_{7,8}$ 6.35, $J_{8,10}$ 1.23 Hz), 4.86 (s, 1 H, H-1), 4.53 (dd, 1 H, H-5, $J_{5,7endo}$ 2.93, $J_{5,6exo}$ 3.17 Hz), 3.81 (m, 2 H, H-6*exo,endo*), 3.21 (m, 1 H, H-7, w/2 14 Hz), 2.75 (dd, 1 H, H-3, $J_{3,4}$ 10.56, $J_{3,7}$ 3.41 Hz), 2.65 (dd, 1 H, H-10, $J_{9,10}$ 6.34, $J_{7,9}$ 1.23 Hz), 2.09 (d, 1 H, H-4, $J_{3,4}$ 10 Hz), and 1.69–1.20 (m, 4 H, H-11a,11b,12a,12b); c.m.r. (22.5 MHz, $CDCl_3$–Me_4Si): δ 200.40 (C-2), 133.91 (C-8), 132.18 (C-9, 99.62 (C-1), 77.84 (C-5), 69.39 (C-6), 46.86 (C-3), 43.23 (C-4), 35.64 (C-7), 32.77 (C-10), 27.41 (C-11), and 22.10 (C-12); *m/z*: 206 (parent ion, 12%), 178 ($206^{+\cdot}$ — CO or C_2H_4, 12%), 160 ($178^{+\cdot}$ — H_2O, 15%), 132 ($160^{+\cdot}$ — CO or C_2H_4, 32%), 117 ($132^{+\cdot}$ — CH·, 73%), 103 (132 $-^{+\cdot}$ C_2H_4 and/or 117^{+} — CH·, 87%), and 91 (100%).

Anal. Calc. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.97; H, 6.81.

Reaction of levoglucosenone with 1,3-diphenylisobenzofuran. — Levoglucosenone (0.20 g, 1.59 mmol) was added to a solution of 1,3-diphenylisobenzofuran (0.43 g, 1.59 mmol) in benzene (5 mL), and the mixture was heated under reflux for 3 h at 77°, cooled, and kept overnight at room temperature; a crystalline material had then precipitated. This was filtered off, and recrystallized from benzene–hexane, to give white crystals of **9**; yield 0.56 g (90%), m.p. 174–175° (turned pale green at 168°, before melting at 174–175°); ν_{max}^{KBr} 3125 (C-H aromatic), 2995, 2950, 2890, (H-C-H stretch), 1728 (C=O), and 1105 cm^{-1} (COC); ^{1}H-n.m.r. (100 MHz; $CDCl_3$–Me_4Si): δ 7.35 (m, 14 H, phenolic, w/2 70 Hz), 4.84 (s, 1 H, H-1), 4.70 (dd, 1 H, H-5, $J_{5,6exo}$ 5.2, $J_{5,6endo}$ 1.7 Hz), 3.72 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 10, $J_{5,6exo}$ 5.2 Hz), 3.61 (dd, 1 H, H-6*endo*, $J_{6exo,endo}$ 10, $J_{5,6endo}$ 1.7 Hz), 3.24 (d, 1 H, H-3, $J_{3,4}$ 8.06 Hz), and 2.56 (d, 1 H, H-4, $J_{3,4}$ 8.06 Hz); c.m.r. (25 MHz; $CDCl_3$–Me_4Si): δ 48.11 (C-4), 52.43 (C-3), 68.08 (C-6), 72.40 (C-5), 100.24 (C-1), and 196.51 (C-2); [these are assigned to the parent ring: δ 91.25 + 90.73 (C-7 + C-14), δ 147.07 + 146.78 (C-8 + C-13) (these appear to be the four quaternary centers in the system, other than the carbonyl function)]; δ 135.63 + 134.46 appear to be the attachment carbon atoms of the phenyl substituents at C-7 and C-14; δ 130.31 + 129.14 (ortho carbon atoms in phenyl substituents); δ 128.32 + 127.62 (meta carbon atoms in phenyl substituents); and δ 126.98 + 126.51 (para carbon atoms in phenyl substituents). The following absorbances were also observed, but not assigned: δ 119.79, 117.79, 117.28, and 97.96; m.s.: this compound appears to undergo a retro-Diels–Alder reaction; the largest mass observed was 270 m.u., corresponding to 1,3-diphenylisobenzofuran; the mass spectrum is identical to that obtained for an authentic sample of 1,3-diphenylisobenzofuran.

Anal. Calc. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.08; O, 16.14. Found: C, 78.61; H, 5.23; O, 16.16.

Reaction of levoglucosenone with furan. — A solution of levoglucosenone (0.537 g, 4.26 mmol) in diethyl ether (2 mL) was treated with a small quantity of aluminum trichloride. A five-fold excess of furan was then added, and the mixture was stirred for 20 min at room temperature; thereafter, no further change was observed on t.l.c. plates (1 : 1 hexane–ethyl acetate). The final mixture showed three spots, corresponding to the starting enone (R_F 0.41), the Diels–Alder adduct (R_F 0.51), and an unknown compound (R_F 0.61, only a trace). Removal of the ether *in vacuo* gave a yellow oil which, on chromatography in a column (2 × 50 cm) of silica eluted with 1 : 1 hexane–ethyl acetate, produced **10** as a reddish-yellow oil (0.161 g, 19.7%). The product crystallized from $CDCl_3$, on long standing; ν_{max}^{neat} 3150, 3124 (olefinic C-H), 2980, 2915 (methylene stretch, strong), 1740 (C=O, v. strong), 1605 (C=C stretch), and 1117 cm^{-1} (COC, v. strong); ^{1}H-n.m.r. (90 MHz, $CDCl_3$–Me_4Si): δ 7.34 (m, 1 H, H-10, $J_{9,10}$ ~1.96 Hz (also, some very small long-range coupling from H-8 is observed), 6.29 (dd, 1 H, H-9, $J_{8,9}$ 3.18, $J_{9,10}$ 1.96 Hz), 6.18 (m, 1 H, H-8, $J_{8,9}$ 3.18 Hz), 5.10 (s, 1 H, H-1), 4.80 (m, 1 H, H-5, $J_{5,6exo}$ 6, $J_{5,6endo}$ 1, $J_{5,4}$ 0.5 Hz), 4.17 (dd, 1 H, H-6*endo*, $J_{5,6endo}$ ~1, $J_{6endo,exo}$ 7.33 Hz), 4.14 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.33, $J_{5,6exo}$ 6 Hz), 3.53 (d, 1 H, H-4, $J_{3a,4}$ 7.78, $J_{3b,4}$ <1 Hz), 3.02 (dd, 1 H, H-3a, $J_{3a,3b}$ 16.6, $J_{3a,4}$ 7.78 Hz), and 2.60 (d, 1 H, H-3b, $J_{3b,3a}$ 16.6 Hz); c.m.r. (22.5 MHz, $CDCl_3$–Me_4Si): δ 199.06 (C-2), 154.10 (C-7), 141.89 (C-10), 110.42 (C-9), 106.71 (C-8), 101.64 (C-1), 75.43 (C-5), 67.44 (C-6), 40.58 (C-4), and 35.05 (C-3); *m/z*: parent ion 194 (28%), 166 ($M^{\ddagger}$ — CO or C_2H_4, 21%), 148 ($166^{\ddagger}$ — H_2O, 13%), 120 ($148^{\ddagger}$ — CO or C_2H_4, 100%), 107 ($120^{\ddagger}$ — CH·, 74%), 94 (107^+ — CH·, or 120^+ — C_2H_2, 70%), and 83 (107^+ — C_2H_2, 71%).

Anal. Calc. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.97; H, 5.19.

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