# 3-Oxidopyrylium Adducts from the Pyrolysis of Cellulose

Richard H. Furneaux, Jennifer M. Mason,* and Ian J. Miller
Chemistry Division, DSIR, Private Bag, Petone, New Zealand

The major product from pyrolysis of acid-doped cellulose is levoglucosenone (1) which is now shown to undergo, under the conditions of its formation, deformylation to 3-oxidopyrylium (2). Five dimers [(7), (9), (11), (14) and either (10) or (16)] of this ylide (2), and an adduct (17) of it and levoglucosenone (1), have now been isolated from the product of phosphoric acid-catalysed pyrolysis of cellulose. Sealed tube pyrolysis of (1) yielded the adduct (17) and its isomer (18).

The pyrolysis of cellulose has been extensively studied because the tar produced is a potential chemical feedstock.[1,2] At temperatures above 300 °C and in the absence of catalysts, cellulose undergoes depolymerization by intramolecular transglycosylation to yield a mixture of anhydroglucoses, predominantly levoglucosan (1,6-anhydro-β-D-glucopyranose).[1] In the presence of Arrhenius acids, however, pyrolytic dehydration, rearrangement, and charring reactions are substantially accelerated. Thus, the pyrolysis of phosphoric acid-doped cellulose gave levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) (1) as the major tar constituent.[3-6] It is derived, at least formally, by double dehydration of levoglucosan, and can be obtained in yields of 2—12% from cellulose depending upon the scale of operation. Various minor dehydration and rearrangement products have also been characterized, including 2-furaldehyde, 1,4:3,6-dianhydro-α-D-glucopyranose, 5-hydroxymethyl-2-furaldehyde, and 2-furylhydroxymethyl ketone, but a significant portion (generally over 40%) of the tar comprises compounds of higher boiling point and lower chromatographic mobility which have not previously been investigated.

Pyrolytically produced compounds may undergo subsequent bimolecular condensation reactions. For instance, polymers resulting from the recondensation of levoglucosan have been found in the tar produced from untreated cellulose.[7] We have now examined the higher boiling tar fraction for discrete compounds in the hope that their identification would indicate the nature of condensation reactions occurring under acid-catalysed pyrolytic conditions.
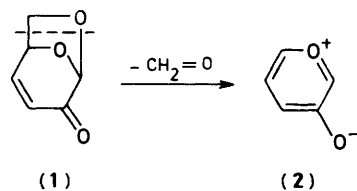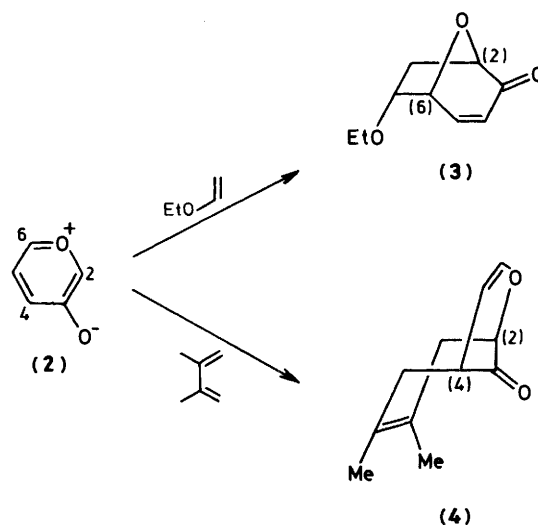

Scheme 1.

Levoglucosenone (1) could, as shown in Scheme 1, undergo pyrolytic deformylation to give 3-oxidopyrylium (2), the generation and *in situ* cycloaddition reactions of which, and its 2-alkyl-substituted analogues, have only recently been studied,[8,9] although certain aryl-substituted and aryl-fused 3-oxidopyryliums have been known for longer.[10] Analogues with nitrogen rather than oxygen in the ring, *i.e.* *N*-substituted 3-oxidopyridiniums, have by contrast been extensively investigated, largely by Katritzky and co-workers.[11]

From these studies it can be concluded that, for thermal cycloaddition reactions, 3-oxidopyrylium (2) can be regarded as

a 4π-electron component for addition across the 2- and 6-position, as demonstrated by its reaction with ethyl vinyl ether to give the bicyclic enone (3),[9b] but as a 6π-electron component for reaction across the 2- and 4-position, as demonstrated by its reaction with 2,3-dimethylbutadiene to give the bicyclic vinyl ether (4) (Scheme 2). Hence 3-oxidopyrylium (2) can condense with itself, with enes, or with dienes by thermally allowed electrocyclic reactions.

Scheme 2. [Products numbered as in ylide (2).]

Dimerization of (2) would be predicted to involve one ylide molecule acting as a 4π-, and one as a 6π-component, in a concerted [6π + 4π] reaction leading to four possible products (Scheme 3): two regioisomeric *endo*-adducts (5) and (8) with 2,2;4,6-and 2,6;4,2-bonding respectively between the monomers, and similarly two regioisomeric *exo*-adducts (11) and (14). Each contains a conjugated enone and a vinyl ether moiety. The *endo*-dimer (5) was the only product isolated by Hendrickson and Farina[8a] from generation and *in situ* condensation of 3-oxidopyrylium (2) at 0 °C. Dimerizations of various substituted oxidopyridinium species, in contrast, have yielded *exo*-dimers analogous to (11) and (14).[11]

The situation is further complicated by the potential for these initial dimers to undergo allylic rearrangements, under pyrolytic conditions. Each of the four primary dimers can give two rearranged dimers, one a bis-vinyl ether and the other a bis-enone. This is illustrated by the conversion of (8) into (9) and (10) (Scheme 3). Bonding of C-2 in (8) to C-9 rather than C-1 with concomitant allylic rearrangement gives (9), while the
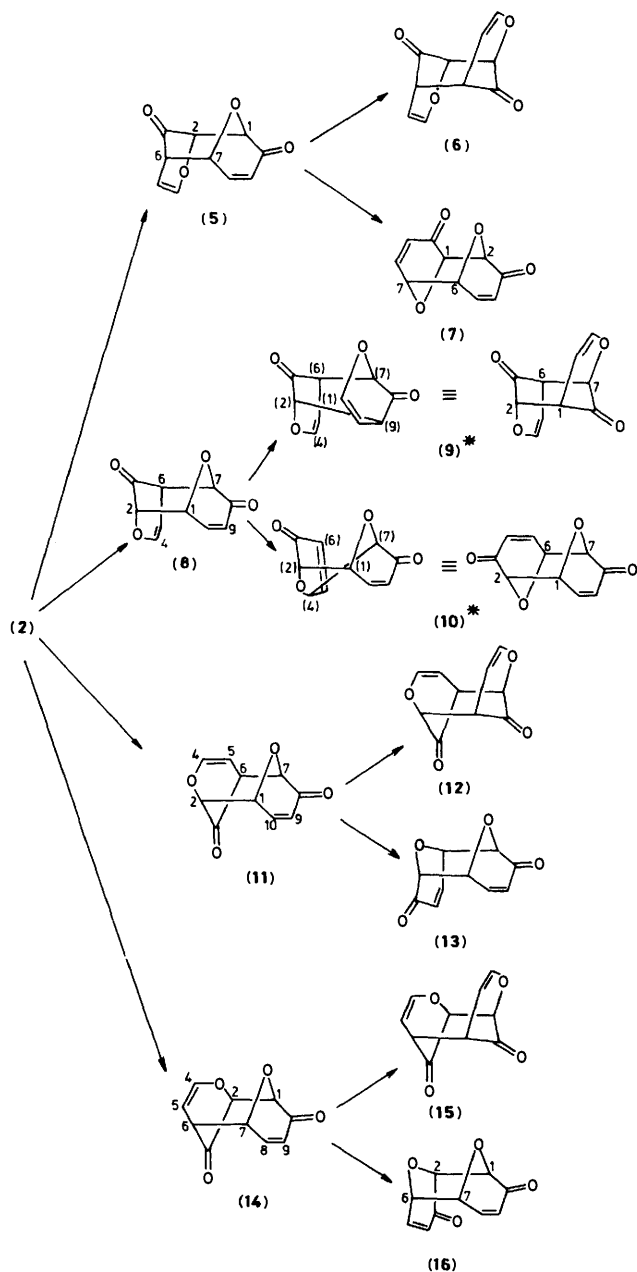
Scheme 3. * The structure on the left is numbered as in its precursor (8), while that on the right is numbered systematically

Results and Discussion

Compounds (7), (9), (11), (14), (17) and either (10) or (16) were produced by pyrolysis of cellulose impregnated with 2% by weight of phosphoric acid. The compounds were first detected as unidentified peaks in the g.l.c. trace of the pyrolysis tar (Figure 1). Preliminary work showed that their yields decreased
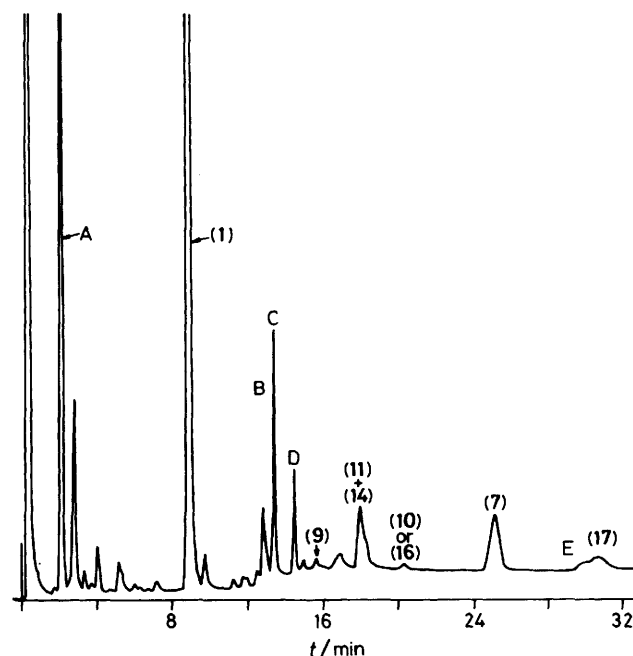

Figure 1. G.l.c. trace of pyrolysis tar (90—210 °C, 8 °C min⁻¹). A, 2-furaldehyde; B, levulinic acid; C, 1,4:3,6-dianhydro-α-D-gluco-pyranose; D, 5-hydroxymethyl-2-furaldehyde; E, levoglucosan; other compounds indicated by number

sharply if the sample size became too large. This critical sample size increased with increasing furnace temperature in the range 380—420 °C. For example, at 380 °C only samples of less than 0.5 g could be pyrolysed successfully, whilst at 420 °C samples of up to 2.5 g could be used. This observation suggested that rapid heating of the pyrolysis sample favoured production of the compounds under investigation. In the temperature and sample size range that favoured their production, typical g.l.c. peak area proportions for the pyrolysis products were (1):(7):(9):[(10) or (16)]: [(11) + (14)]: (17) = 100:12:1:-0.5:10:2. Since higher working temperatures allowed the successful pyrolysis of larger batches, the maximum convenient working temperature of our furnace (420 °C) was chosen for preparative work. At this temperature a sample size of 2.5 g was optimum.

The five compounds of interest were isolated from the

alternative rearrangement to form (10) involves bonding of C-7 in (8) to C-4 rather than C-6 with concomitant allylic rearrangement. Hendrickson and Farina[8a] have reported an example of this rearrangement: when the endo-dimer (5) was heated at 140 °C it was converted into the bis-enone dimer (7). Such rearrangements are not concerted thermal 1,3-alkyl shifts, since there is no inversion of configuration at the migrating carbon atom, and presumably therefore must proceed by a bond breaking–bond forming process.

In this paper we report that levoglucosenone (1) is pyrolytically deformylated to give 3-oxidopyrylium (2) (Scheme 1) during acid-catalysed pyrolysis of cellulose, and that we have isolated dimers (7), (9), (11), (14) and either (10) or (16) from the self-condensation of (2) (Scheme 3). An adduct (17) from the condensation of (2) with levoglucosenone (1) was also isolated.

(17)   (18)

Table 1. ¹H N.m.r. chemical shifts (δ values[a]) of adducts of 3-oxidopyrylium

	(7)[b]	(9)[c]	(10) or (16)[b]	(11)[c]	(14)[c]	(17)[b]	(18)[b]
			Compound				
1-H	4.18 (s)	3.23 (ddd)		5.22 (dd)	4.80 (d)	4.67 (ddd)	4.69 (d)
2-H	4.18 (s)	4.44 (dd)	3.91 (s)	4.45 (dd)	4.21 (dd)	2.53 (dddd)	2.86 (dd)
3-H						5.04 (dm)	4.75 (m)
4-H	6.40 (d)	6.48 (d)	6.38 (d)	6.78 (d)	6.80 (d)		
4-H$_{endo}$						3.95 (m)	3.90 (m)
4-H$_{exo}$						3.99 (m)	
5-H	7.17 (dd)	4.88 (dd)	7.02 (dd)	5.06 (dd)	5.04 (dd)		
6-H	4.26 (d)	3.23 (ddd)	4.55 (d)	2.97 (ddd)	3.15 (ddd)	5.21 (dd)	4.96 (s)
7-H	4.26 (d)	4.44 (dd)		4.37 (d)	4.86 (dd)		
8-H	7.17 (dd)				7.41 (dd)	3.03 (dd)	3.55 (dd)
9-H	6.40 (d)	6.48 (d)		6.22 (d)	6.17 (d)	5.26 (dddd)	5.13 (dd)
10-H		4.88 (dd)		7.30 (dd)		7.26 (dd)	7.24 (dd)
11-H						6.04 (dd)	6.12 (d)

[a] Relative to Me₄Si; (17) at 270 MHz, all others at 80 MHz. [b] CDCl₃. [c] [²H₆]Acetone.

Table 2. Selected observed coupling constants (Hz) of adducts of 3-oxidopyrylium

	(7)	(9)	(10) or (16)	(11)	(14)		(17)[b]	(18)
		Compound					Compound	
1,2		3.5[a]		2.9	2.9	1,2	2.2	7.8
1,7		4.3[a]				2,3	1.2	Small
1,10		6.5		4.2		2,8	8.3	10.4
2,3						2,9	0.7	
2,6		4.3[a]		2.4	2.4	8,9	0.7	7.8
2,7						9,10	4.5	4.7
2,8						10,11	9.8	9.8
4,5	10.2	5.8	10.2	5.7	5.7			
5,6	4.5	6.5	4.5	6.1	6.5			
6,7		3.5[a]		1.9	2.2			
7,8	4.5				4.3			
8,9	10.2				10.3			
9,10		5.8		10.2				

[a] These assignments may be interchanged. [b] For other coupling constants see Experimental section.

Table 3. ¹³C N.m.r. chemical shifts (δ/p.p.m.[a]) of adducts of 3-oxidopyrylium

	(7)[b]	(9)[d]	(10) or (16)[c]	(11)[b]	(14)[d]	(17)[b]	(18)[b]
C-1	76.7[e]	51.1		83.4[e]	81.3[e]	85.9[e]	84.2[e]
C-2	76.7[e]	83.5	73.3[e]	79.5[e]	76.6[e]	43.3	43.0
C-3	h	194.1				77.3[f]	74.0
C-4	130.8	146.5	128.5	143.5	148.6	68.8	69.5[f]
C-5	146.3	99.2	147.8	97.1	98.1		
C-6	67.6[e]	51.1	68.9[e]	50.5	50.7	99.9	99.5
C-7	67.6[e]	83.5		78.0[e]	87.4[e]	196.0[g]	196.4[g]
C-8	146.3			h	150.3	47.3	48.6
C-9	130.8	146.5		129.5	127.9	75.7[e,f]	69.8[e,f]
C-10	h	99.2		147.4	h	149.8	151.4
C-11						126.1	128.7
C-12		h		h	h	194.7[g]	194.6[g]

[a] At 20 MHz, relative to Me₄Si. [b] CDCl₃, [c] (CD₃)₂SO. [d] [²H₆]Acetone. [e,f,g] These assignments may be interchanged. [h] Carbonyl signals were not sufficiently intense to be detected.

pyrolysis tar by column chromatography on silica gel. The isolated yields of the compounds, based on cellulose, were in the range 0.012—0.056%. Their ¹H and ¹³C n.m.r. spectral data are listed in Tables 1—3.

Two of these products were the primary dimers, (11) and (14). They were only just separated by g.l.c., but samples were isolated pure by column chromatography. They had similar mass spectra, with molecular ion peaks at m/z 192. Their ¹³C n.m.r. spectra were similar, each showing the presence of eight

carbon atoms (not including carbonyl carbons whose resonances were not detected). Their i.r. spectra contained bands at 1 750, 1 690, and 1 640 cm⁻¹ assigned to unconjugated ketone, conjugated enone, and vinyl ether stretching frequencies respectively. From these data it was apparent that compounds (11) and (14) were close analogues of, but were not identical with, the known compound (5)[8b] and resulted from [6π + 4π] dimerizations of 3-oxidopyrylium (2).

The ¹H n.m.r. spectra of dimers (11) and (14) were fully

assigned, with the aid of selective decoupling experiments in the case of compound (11). Both dimers have 1,2- and 6,7-coupling constants in the range 1.9—2.9 Hz, which indicates that their central tetrahydropyranone rings are in the chair conformation, and hence that they are both exo-adducts. By contrast, the endo-dimer (5) has its central tetrahydropyranone ring in the boat conformation and consequently both $J_{1.2}$ and $J_{6.7}$ in this molecule were found to be ca. 9 Hz.[8b] A W-coupling[12] between 2-H and 6-H of 2.4 Hz was also observed for both (11) and (14). Evidently, vinyl ether moieties that result from coupling across the 2,4-positions of 3-oxidopyrylium species are perfectly orientated for such W-coupling, since analogous coupling has been observed in dimer (9) (see later), in dimer (5),[8b] in the adduct (4) (Scheme 2),[9b] and also in analogous oxidopyridinium dimers.[11]

The relative orientations of the enone and vinyl ether moieties that are shown for dimers (11) and (14) were determined by consideration of the proton–proton couplings in their ¹H n.m.r. spectra (Tables 1 and 2).

Three rearranged dimers (7), (9), and either (10) or (16), were isolated. Compound (7), the most abundant of all the dimers, was shown to be identical with the rearranged dimer isolated by Hendrickson and Farina[8b] by comparison of their g.l.c. and t.l.c. mobilities, m.p.s, and i.r. and ¹H n.m.r. spectra.

Compound (9) was a symmetrical dimer, since, as in the case of dimer (7), its mass spectrum revealed a molecular ion peak at m/z 192, while its ¹³C n.m.r. spectrum showed the presence of only four different carbon atoms apart from the carbonyl carbons, and only four distinct signals were present in the ¹H n.m.r. spectrum. The i.r. spectrum showed absorbances at 1 750 and 1 635 cm⁻¹ which were assigned to unconjugated ketone and vinyl ether functionalities respectively. These data suggest a dimer of ylide (2) with a structure composed of two vinyl ether moieties.

Preliminary single-crystal X-ray crystallographic data[13] indicated that compound (9) crystallized in the centrosymmetric space group $P2_1/c$ with 2 molecules per unit cell, which is sufficient to differentiate between the four possible bis-vinyl ether dimers in favour of the centrosymmetric dimer (9). The ¹H n.m.r. coupling pattern in (9) is unusual in that 1-H (like its equivalent 6-H) is coupled to two magnetically equivalent protons 2-H and 7-H, but by different paths. Thus $J_{1.2}$ is vicinal coupling, while $J_{1.7}$ is W-coupling analogous to that found in dimers (11) and (14). While the values (3.5 and 4.3 Hz) for these couplings could not be assigned specifically, the very presence of 1,2-coupling is sufficient to eliminate alternative structures (6) and (15).

The remaining dimer had i.r., ¹H and ¹³C n.m.r., and mass spectra almost identical with those of dimer (7). In particular, while the mass spectrum contained a molecular ion at m/z 192.042 consistent with $C_{10}H_8O_4$, the n.m.r. spectra contained only four proton and five carbon resonances, indicating a structure composed of two enone moieties, isomeric with that of compound (7). The ¹H n.m.r. spectrum showed no evidence of coupling between 1-H and 2-H, and 6-H and 7-H. This may be because 1-H and 2-H, and 6-H and 7-H, are magnetically equivalent, as in structure (16), or because the 1-H–2-H and 6-H–7-H dihedral angles are such that coupling would be weak, as in structure (10). For this remaining dimer we favour structure (10) since it has its central 1,4-dioxane ring in the chair form. An examination of Scheme 3 reveals that the other dimers obtained pyrolytically [i.e. (7), (9), (11), and (14)] have a central six-membered ring in the chair conformation, and we are tempted to ascribe the selective formation of these products to a greater thermodynamic stability of the isomers with central chair rather than boat conformations. So far, however, we have been unable to differentiate conclusively between the two alternatives.

As discussed in the Introduction, 3-oxidopyrylium (2) may act as a 4π-component in a cycloaddition reaction, being able to add an ene across its 2,6-positions. The remaining compound (17) isolated from the tar had a molecular ion peak at m/z 222 in its mass spectrum and its ¹³C n.m.r. spectrum showed the presence of eleven carbon atoms, including two carbonyl carbons (196.0 and 194.7 p.p.m.) and two alkene carbon atoms (149.8 and 126.1 p.p.m.). Its i.r. spectrum contained absorbances due to conjugated and unconjugated carbonyl groups (1 690 and 1 740 cm⁻¹). These data indicate that compound (17) is the product of a $[4_\pi + 2_\pi]$ cycloaddition reaction of 3-oxido-pyrylium (2) and levoglucosenone (1). There are eight stereo- and regio-isomers that may result from such an addition but the compound could be characterized from its ¹H n.m.r. spectrum. A coupling of 1.2 Hz between 2-H and 3-H indicated that the ylide (2) had approached from 'below' the pyranose ring of levoglucosenone (1).[14] The syn relationship of the pyranose ring and the 1,9-epoxy-bridge is reflected in the 1,2- and 8,9-coupling constants of 2.2 and 0.7 Hz.* The regiochemistry of the adduct (17) was deduced from the full ¹H n.m.r. coupling pattern, which included four long-range couplings, and was elucidated with the aid of decoupling and computer simulation experiments.

Isolation of the five aforementioned compounds from pyrolysis tar strongly suggests that 3-oxidopyrylium (2) is formed during pyrolysis. It could either be formed directly from cellulose or through secondary pyrolysis, the pyrolytic deformylation of levoglucosenone (1) (Scheme 1) being the most obvious route. Heating a solution of levoglucosenone (1) in a sealed tube yielded unchanged (1), adduct (17), and a further adduct (18).

A series of preliminary experiments showed that the yields of adducts (17) and (18) were dependent on the type of tube used (quartz was preferred over borosilicate glass since the latter gave increased charring and lower yields), and the concentration of the levoglucosenone (1) solution (dilution, down to 9%, increased the yield). The reaction rate increased with temperature in the range 190—230 °C, and with the concentration of (1). Figure 2 depicts the results of a typical preliminary run showing the relative concentrations of adducts (17) and (18), and levoglucosenone (1). In a preparative experiment, adducts (17) and (18) were isolated by column chromatography in 22% combined yield [(17):(18) = 4:3].

The adduct (18) was readily identified. Its mass and ¹³C n.m.r. spectra were similar to those of (17), indicating an isomeric structure. The stereochemistry of adduct (18) was deduced from its ¹H n.m.r. spectrum. As in adduct (17), coupling between 2-H and 3-H is weak, indicating that ylide (2) has approached from 'below' the pyranose ring of (1). In contrast to the situation in adduct (17), in adduct (18) coupling across the bridges between the levoglucosenone and oxido-pyrylium moieties is strong (ca. 8 Hz) indicating that the 1,9-epoxy-bridge is anti to the pyranose ring. The proton coupling pattern, which was elucidated with the aid of decoupling experiments, showed that adduct (18) had the same regiochemistry as adduct (17).

None of the dimers found in cellulose pyrolysate were formed in appreciable amounts in the sealed-tube pyrolysis experiments. This difference in product distribution is not remarkable considering the great disparity in experimental conditions, and that the relative amounts of dimers and levoglucosenone adducts would depend on the relative concentrations of

---

* From a consideration of molecular models, the adducts resulting from addition of 3-oxidopyrylium from 'above' the plane of the pyranose ring in (1) would have $J_{2.3}$ values of ca. 5 Hz. If the 1,9-epoxy-bridge and the pyranose ring were in an anti-relationship the 1,2- and 8,9-coupling constants would be ca. 8 Hz [cf. adduct (18), see later].
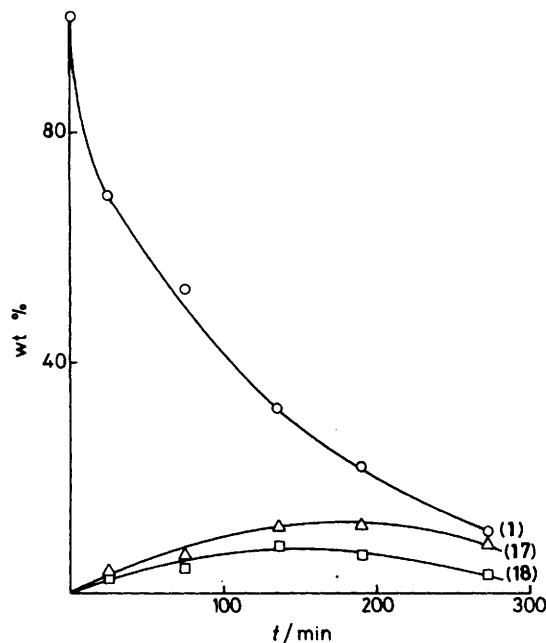
Figure 2. Thermolysis of levoglucosenone (1) (25%) in diphenyl ether at 215 °C

3-oxidopyrylium (2) and levoglucosenone (1). The formation of (17) and (18) on heating (1) is evidence, however, that levoglucosenone (1) is a precursor of ylide (2) under pyrolytic conditions.

Since substantial pyrolytic deformylation of levoglucosenone (1) occurs at temperatures as low as 215 °C (Figure 2), this reaction will competitively degrade (1) under the conditions of its pyrolytic synthesis from cellulose (300—400 °C). This, at least in part, accounts for the observation that while levoglucosan can be produced in up to 60% yield from uncatalysed pyrolysis of cellulose,[15] the best yield of levoglucosenone (1) from acid-catalysed pyrolysis is ca. 12%.[3]

Experimental

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer 580 spectrophotometer as KBr discs. Unless otherwise stated, ^1H and ^{13}C n.m.r. spectra were recorded on a Varian FT-80A instrument at 80 MHz and 20 MHz respectively. Mass spectra were recorded on a Kratos MS30 instrument and optical rotations were measured using a Perkin-Elmer 241 polarimeter. G.l.c. analysis was performed on a Pye GCD (equipped with a flame-ionization detector) temperature programmed from 90 or 110 up to 210 °C at 8 °C min^{-1}, and using a glass column (1.5 m × 2 mm i.d.) packed with 5% Pluronic F-68 (BASF)[16] on Gas-Chrom Q (100—120 mesh). T.l.c. analyses were performed on aluminium-foil-backed silica gel plates (Merck Cat No. 5554) with 1,2-dichloroethane–ethyl acetate (2:3) as developer. Column chromatography was performed according to the method of Still et al.[17] on silica gel (Kieselgel 60, 230—400 mesh, Merck). Pyrolysis of cellulose was performed in a preheated tube furnace (45 cm × 4.5 cm i.d.) equipped with two concentric glass liners (4.4 and 3.2 cm o.d.). A water-cooled condenser was attached to the outer of these. The sample for pyrolysis was held in an aluminium foil dish.

Preparation of Substrate for Pyrolysis.—Cellulose powder (Whatman CF-11; 150 g) was suspended in ethanol (ca. 400

cm^3) containing orthophosphoric acid (88%; 3.4 g). The solvent was removed under reduced pressure to yield cellulose containing 2% w/w orthophosphoric acid.

Preparation and Isolation of Cellulose Pyrolysis Products.—The above substrate (124 g) was pyrolysed in 2.5 g batches under flowing nitrogen (200 ml min^{-1}) at a furnace temperature of 420 °C. After each pyrolysis was complete (ca. 5 min) the inner glass tube was removed from the furnace and the tar that had condensed in the cool part of the tube was washed out with acetone. The combined washings were filtered and the solvent removed under reduced pressure. The tar was taken up in chloroform and the solution was washed in turn with saturated aqueous sodium hydrogen carbonate (twice) and then water. The organic phase was dried (sodium sulphate), filtered, and the solvent removed under reduced pressure to leave a dark syrup (8 g). Some compound (7) crystallized from the syrup on storage at 4 °C and was isolated by decantation. The decanted liquid contained 2-furaldehyde and levoglucosenone (1) which were largely removed by distillation (0.5 Torr; b.p. up to 72 °C). The distillation residue was fractionated by column chromatography with hexane–ethyl acetate (3:1) as eluant. The compounds of interest crystallized from pooled fractions (judged pure by g.l.c. examination) upon evaporation of the solvent, or upon trituration of the residues with diethyl ether, and they were further purified by washing with diethyl ether. Yields of compounds by weight from cellulose in order of their elution were: (9), 27 mg, 0.037%; (11), 40 mg, 0.056%; (10) or (16), 9 mg, 0.012%; (14), 12 mg, 0.017%; (17), 16 mg, 0.022%; and (7), 40 mg, 0.056% (including material crystallized from crude tar). Dimers (11) and (14) were not fully separated from residual levoglucosenone (1) and compounds (7) and (17) were not fully resolved, so that the recovery of these compounds from the tar was not quantitative. Therefore, the isolated yields do not indicate the relative amounts of the various compounds present in the tar. These products were characterized as follows.

(1α,2β,6β,7α)-11,12-*Dioxatricyclo*[5.3.1.1$^{2.6}$]*dodeca*-4,8-*diene*-3,10-*dione* (7).—White crystals, m.p. 200—204 °C (lit.,[8b] 200—205 °C); [α]$_D$ < 5° [c 0.1 in ethyl acetate–acetonitrile (1:1)]; m/z 192 (M$^+$, 55%), 163 (28), 135 (14), 110 (43), 109 (100), 97 (30), 96 (33), 81 (38), 79 (22), and 68 (74). This compound was shown to be identical with that reported by Hendrickson and Farina[8b] by comparison of their g.l.c. and t.l.c. mobilities, and i.r. and ^1H n.m.r. spectra, as well as by mixed m.p.

(1α,2β,6β,7α)-3,8-*Dioxatricyclo*[5.3.1.1$^{2.6}$]*dodeca*-4,9-*diene*-11,12-*dione* (9).—Pink rods, m.p. 165—168 °C (after recrystallization from acetone); ν$_{max.}$ 1 750 and 1 635 cm^{-1}; m/z 192 (M$^+$, 67%), 163 (23), 135 (16), 109 (68), 97 (39), 96 (38), and 68 (100) (Found: C, 62.2: H, 4.05. C$_{10}$H$_8$O$_4$ requires C, 62.50; H, 4.17%).

Compound (10) *or* (16).—White solid, m.p. 192—194 °C; ν$_{max.}$ 1 685 cm^{-1}; m/z 192 (M$^+$, 54%), 163 (18), 135 (15), 110 (17), 109 (74), 107 (30), 97 (29), 96 (31), 81 (23), 79 (49), and 68 (100) (Found: M$^+$, 192.042. C$_{10}$H$_8$O$_4$ requires M, 192.042).

(1α,2β,6β,7α)-3,11-*Dioxatricyclo*[5.3.1.1$^{2.6}$]*dodeca*-4,9-*diene*-8,12-*dione* (11).—White crystals, m.p. 158—160 °C; ν$_{max.}$ 1 750, 1 690, and 1 640 cm^{-1}; m/z 192 (M$^+$, 70%), 163 (13), 135 (14), 109 (50), 97 (32), 96 (32), 95 (11), 83 (21), 81 (36), 79 (39), 69 (23), and 68 (100) (Found: C, 62.55; H, 4.3%).

(1α,2β,6β,7α)-3,11-*Dioxatricyclo*[5.3.1.1$^{2.6}$]*dodeca*-4,8-*diene*-10,12-*dione* (14).—White solid, g.l.c. (110—210 °C; 8 °C min^{-1}); R$_t$ 16 min [(14); 90%], 6.8 min [(1), 3%], and 18 min [(7), 7%]; ν$_{max.}$ 1 750, 1 690, and 1 640 cm^{-1}; m/z 192 (M$^+$, 49%), 163 (16),

135 (17), 109 (69), 97 (64), 96 (27), 95 (39), 83 (49), 81 (74), 79 (32), 71 (49), 69 (46), and 68 (100) (Found: M^+, 192.042).

(1R)-(1α,2β,3α,6α,8β,9α)-5,13,14-*Trioxatetracyclo*-[7.3.1.1^{3,6}0^{2,8}]*tetradeca*-10-*en*-7,12-*dione* (**17**).—White needles, m.p. 194—198 °C (after recrystallization from ethanol); $[\alpha]_D$ + 42° (*c* 0.1 in ethanol); ^{1}H n.m.r., as listed in Tables 1 and 2; also $J_{1,9}$ 0.7 Hz, $J_{4_{exo},6}$ 0.4 Hz, $J_{3,4_{endo}}$ 1.1, $J_{4_{endo},4_{exo}}$ − 7.7 Hz, and $J_{1,11}$ 1.4 Hz (determined by decoupling and computer simulation); $\nu_{max.}$ 1 740 and 1 690 cm^{-1}; m/z 222 (M^+, 2%), 148 (73), 120 (99), 119 (64), 107 (19), 97 (22), 94 (30), 92 (31), and 91 (100) (Found: C, 59.25; H, 4.65. $C_{11}H_{10}O_5$ requires C, 59.49; H, 4.50%).

Thermolysis of Levoglucosenone (**1**).—(a) *Preliminary experiments.* Solutions containing varying proportions (9—100%) of (**1**)^6 in diphenyl ether or mesitylene, and with a small percentage of dibenzofuran as an internal standard, were sealed into capillary tubes. Several of these tubes were heated in an oven and were removed at various time intervals. Upon removal each tube was opened, the contents washed out with acetone (200 μl) and a sample analysed by g.l.c. (110—210 °C; 8 °C min^{-1}). The relative peak areas for (**1**) (R_t 4.8 min) and adducts (**18**) (R_t 20.3 min) and (**17**) (R_t 23.0 min) were normalized with respect to the peak area of dibenzofuran (R_t 7.8 min).

(b) *Preparative experiments.* A mixture of (**1**) (300 mg) and diphenyl ether (2.7 g) was sealed into two quartz tubes (80 × 5 mm i.d.) and held at 215 °C for 3 h. The reaction product was chromatographed on a column eluted with hexane–ethyl acetate (2:1). Adduct (**18**) (14 mg, 4.6%), a crystalline mixture of (**17**) and (**18**) (ratio 2:1; 40 mg, 13.4%), and adduct (**17**) (10 mg, 3.3%) were isolated from column fractions. Adduct (**17**) obtained by this route had the same m.p. ^{1}H n.m.r. spectrum, and t.l.c. and g.l.c. retention as the material obtained from pyrolysis tar.

(1S)-(1α,2α,3β,6β,8α,9α)]-5,13,14-*Trioxatetracyclo*-[7.3.1.1^{3,6}0^{2,8}]*tetradeca*-10-*ene*-7,12-*dione* (**18**).—Yellow rods, m.p. 202—204 °C (after recrystallization from ethanol); m/z 194 (M^+ − CO, 35%), 148 (25), 120 (96), 119 (89), 107 (23), 97 (23), 92 (24), and 91 (100) (Found: C, 58.9; H, 4.3. $C_{11}H_{10}O_5$ requires C, 59.46; H, 4.50%).

References

1 F. Shafizadeh, *J. Anal. Appl. Pyrolysis*, 1982, **3**, 283.
2 F. Shafizadeh, *Pure Appl. Chem.*, 1983, **55**, 705.
3 F. Shafizadeh and P. P. S. Chin, *Carbohydr. Res.*, 1976, **46**, 149.
4 F. Shafizadeh and P. P. S. Chin, *Carbohydr. Res.*, 1977, **58**, 79.
5 F. Shafizadeh, R. H. Furneaux, T. T. Stevenson, and T. G. Cochran, *Carbohydr. Res.*, 1978, **61**, 519.
6 F. Shafizadeh, R. H. Furneaux, and T. T. Stevenson, *Carbohydr. Res.*, 1979, **71**, 169.
7 F. Shafizadeh and Y. L. Fu, *Carbohydr. Res.*, 1973, **29**, 113.
8 J. B. Hendrickson and J. S. Farina, *J. Org. Chem.*, 1980, **45**, (a) 3359; (b) 3361.
9 P. G. Sammes and L. J. Street, (a) *J. Chem. Soc., Chem. Commun.*, 1982, 1056; (b) *J. Chem. Soc., Perkin Trans. 1*, 1983, 1261.
10 E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, 1964, **86**, 3814; H. H. Wasserman and D. L. Pavia, *Chem. Commun.*, 1970, 1459.
11 N. Dennis, B. Ibrahim, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 1*, 1976, (a) 2296; (b) 2307 and references therein.
12 L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd ed., Pergamon, Oxford, 1969, p. 334.
13 Unpublished results, G. J. Gainsford, Chemistry Division, DSIR.
14 T. T. Stevenson, M. G. Essig, F. Shafizadeh, L. H. Jensen, and R. E. Stenkamp, *Carbohydr. Res.*, 1983, **118**, 261.
15 F. Shafizadeh, R. H. Furneaux, T. G. Cochran, J. P. Scholl, and Y. Sakai, *J. Appl. Polym. Sci.*, 1979, **23**, 3525.
16 J. Hlavay, Á. Bartha, Gy. Vigh, M. Gazdag, and G. Szepesi, *J. Chromatogr.*, 1981, **204**, 59.
17 W. C. Still, M. Khan, and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.