Photochemistry of Carbohydrate Derivatives. Part I. Photolytic Decomposition of Glucopyranosyl Phenyl Sulphone Acetates

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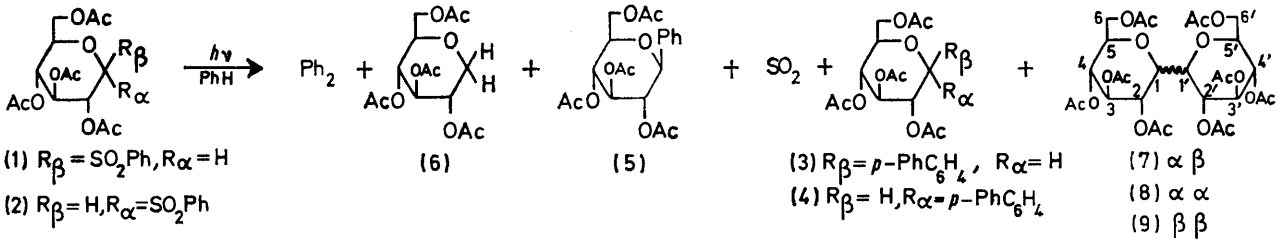
U.v. irradiation of either 2,3,4,6-tetra-*O*-acetyl-β-D-glucosyl phenyl sulphone or its α-anomer in benzene gave sulphur dioxide, biphenyl, the 2,3,4,6-tetra-*O*-acetyl derivatives of 1,5-anhydro-D-glucitol (6), α-D- and β-D-glucosylbiphenyl [(3) and (4)], and αβ-D-glucosylbenzene, and 1,3,4,5,8,9,10,12-octa-*O*-acetyl-2,6:7,11-dianhydro-D-*gluco*-L-*altro*-L-*erythro*-dodecitol, which can be considered as a 1-deoxy-derivative of αβ-D-trehalose octa-acetate.

The part played by the solvent in product formation was determined from the reaction in hexadeuteriobenzene. This gave pentadeuteriobiphenyl, compounds (3) and (4) tetradeuteriated in their aromatic residues, and 50% of compounds (6) deuteriated at C-1, preponderantly in the axial position.

A mechanism involving an intermediate carbonium ion has been excluded since irradiation in the presence of methanol gave no methyl glucosides. A free-radical mechanism is proposed, which accommodates all the products and accounts for the deuterium content of those formed in hexadeuteriated benzene.

THERE are only a few reported studies of sulphone photolyses. Cava *et al.*[1] have shown that certain endocyclic sulphones undergo ring contraction with concomitant extrusion of sulphur dioxide. Kharasch and Khodair,[2] on the other hand, found that irradiation of diphenyl sulphone in benzene gave no sulphur dioxide, biphenyl being the only identified product. Since glucosyl sulphone derivatives are readily available, a study of their photochemistry was undertaken in the hope that a route to *C*-aryl glycoside derivatives would be discovered.



SCHEME 1

U.v. irradiation of a 2·5% solution of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl phenyl sulphone [3] (1) (Scheme 1) in the annular space of a quartz photolysis well for 18 h with a 450 W medium-pressure mercury arc gave sulphur dioxide (*ca.* 80%) and several non-gaseous photo-products which were separated chromatographically on a column into four fractions, A, B, C, and D (R_F 1·0, 0·7, 0·5, and 0·3).

The n.m.r. spectrum of fraction A showed that it contained only aromatic compounds, one of which was volatile on g.l.c., and this was identified as biphenyl. It comprised 20% of the fraction; the remainder was not characterised.

Fraction B gave a crystalline compound which was shown to be β-D-glucopyranosylbiphenyl tetra-acetate (3) by comparison with an authentic sample prepared from acetobromoglucose and biphenyl-4-ylmagnesium bromide.[4] Its 100 MHz ^{1}H n.m.r. spectrum, which was partially analysed (see Table), exhibited signals for three hexopyranosyl protons in the low-field range (δ 5·06—5·47), which could be assigned to the acetoxy methine protons (H-2, -3, and -4), and four analysable signals at higher field (δ 3·85—4·43) assignable to H-1, -5, -6a, and -6b. The H-1 signal at δ 4·43 was a doublet split by 9·0 Hz which corroborated the β-structure. Of the four acetoxy-signals, three appeared in the range δ 1·98—2·07, and one was at δ 1·80. This low field signal must be due to the C-2 acetoxy-group, since Hillis and Horn [5] have shown that equatorial aromatic residues at C-1 in β-D-glucopyranosylarene acetates deshield adjacent acetoxy-groups.

G.l.c. separation of the mother liquor gave a major peak (t_R 24 min) due to compound (3) and several minor peaks, one of which had a retention time of 14 min, identical with that of tetra-*O*-acetyl-β-D-glucopyranosylbenzene (5).[6] The material constituting the major peak, which was collected, deposited a further crop of (3), leaving an oil similar to (3) in R_F value and u.v. and i.r. spectra, but possessing a more positive optical rotation. This suggested that the material was preponderantly the α-anomer (4), a view supported by the ^{1}H n.m.r. spectrum (see Table), which showed signals for

[1] M. P. Cava, R. H. Schlessinger, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1964, **86**, 3173.
[2] N. Kharasch and A. I. A. Khodair, *Chem. Comm.*, 1967, 98.
[3] W. A. Bonner and R. W. Drisko, *J. Amer. Chem. Soc.*, 1948, **70**, 2435.
[4] Yu. A. Zhdanov, L. I. Shcherbakova, R. V. Golovnya, *Doklady Akad. Nauk S.S.S.R.*, 1956, **107**, 259.
[5] W. E. Hillis and D. H. S. Horn, *Austral. J. Chem.*, 1963, **16**, 147.
[6] C. D. Hurd and W. A. Bonner, *J. Amer. Chem. Soc.*, 1945, **67**, 1972.

nine aromatic protons and seven hexopyranosyl protons, four in the region δ 5·0—5·7 and three in the range 3·80—4·33. Thus the anomeric proton signal must appear in the former group, at least 0·57 p.p.m. to lower field than the H-1 signal of the β-anomer, as would be expected [7] for an equatorial proton. The four acetoxy-signals are grouped in the region δ 2·00—2·10. Thus in this compound the C-2 acetoxy-group is not deshielded, which also indicates that the aromatic residue at C-1 is axial.[5] However, a signal at δ 1·80 indicated that 20% of the β-anomer contaminated this non-crystalline specimen.

M^+ — 2AcOH — CH_2CO), 458 (4%, M^+ — 2AcOH — $2CH_2CO$), 440 [4%, ion (14)], 427 [9%, ion (13)], and 211 [45%, ion (11)]. Structures for several of these ions were deduced by comparison with the mass spectra of the *C*-aryl glycoside tetra-acetates studied by Aritomi *et al.*[9] For example, ions (10), (13), and (14) are closely related to ions B′, F, and G, respectively, as described by these workers, and routes for the formation of ions with masses 500, 458, and 221 can be devised from the fragmentation schemes they describe.

A complete structural assignment for this compound was achieved by a first-order analysis of the signals from

^{1}H N.m.r. parameters (δ; *J* in Hz) for 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl derivatives in $CDCl_3$

Compound	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	Ac (singlets)
(3) [a,b]	4·43 (d) $J_{1,2}$ 9·0	5·06—5·47			3·85 (oct) $J_{5,4}$ 9·0 $J_{5,6a}$ 5·0	4·31 (q) $J_{6a,6b}$ 12·5	4·14 (q) $J_{6b,5}$ 2·5	2·07, 2·04, 1·98, 1·80
(4) [a,b]	5·0—5·7				3·80 (oct) $J_{5,4}$ 8·4 $J_{5,6a}$ 5·0	4·33 (q) $J_{6a,6b}$ 12·5 $J_{6a,5}$ 5·0	4·08 (q) $J_{6a,6b}$ 12·5 $J_{6b,5}$ 2·5	2·10, 2·10, 2·00, 2·00
(6) [c]	4·04 (q) $J_{1eq,1ax}$ 11·0 3·03 (t) $J_{1ax,2}$ 11·0	5·21 (sex) $J_{2,1eq}$ 6·0	5·28 (t) $J_{3,2}$ 10·0 $J_{3,4}$ 10·0	5·43 (t) $J_{4,5}$ 10·0	3·35 (oct) $J_{5,6a}$ 5·0	4·36 (q) $J_{6a,6b}$ 12·5	4·18 (q) $J_{6b,5}$ 2·0	2·16, 2·08, 2·02, 2·02
(7) [d]	4·04 (q) $J_{1,2}$ 5·5 $J_{1,1'}$ 2·5	5·26 (q) $J_{2,3}$ 8·0	5·65 (t) $J_{3,4}$ 8·0	4·97 (t) $J_{4,5}$ 8·0	4·08—4·24			2·14, 2·06, 2·04, 2·02, 1·98, 1·98, 1·97, 1·96
	3·83 (q) $J_{1',2'}$ 9·0 $J_{1',1}$ 2·5	5·24 (t) $J_{2',3'}$ 9·0	5·18 (t) $J_{3',4'}$ 9·0	5·02 (t) $J_{4',5'}$ 9·0	3·70 (sept) $J_{5',6a'}$ 6·0 $J_{5',6b'}$ 2·0	4·08—4·24		

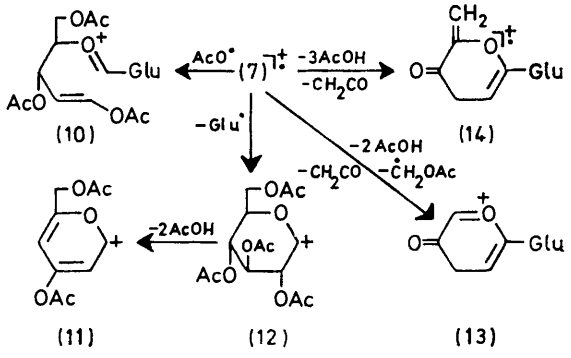
[a] Aromatic signals (m) appeared in range δ 7·3—7·7 (9H). [b] 100 MHz. [c] 220 MHz. [d] 300 MHz, kindly measured by Dr. D. Shaw, Varian Associates.

Fraction C was separated by preparative g.l.c. into equal amounts of the sulphone (1) and 1,5-anhydro-D-glucitol tetra-acetate (6). The 220 MHz ^{1}H n.m.r. spectrum of the latter, which was analysed completely by first-order methods as shown in the Table, was measured for comparison with the deuteriated analogue of (6), the preparation of which is described later.

Fraction D, which was composed of compounds containing no sulphur or aromatic residues, afforded one component in crystalline form. This had the empirical formula $C_{28}H_{38}O_{18}$ and a ^{1}H n.m.r. spectrum which showed that twenty-four of the hydrogen atoms were present in eight acetoxy-groups. These results suggest a dimeric structure, formed from two tetra-*O*-acetyl-glucopyranosyl rings, a view supported by the mass spectrum, which exhibited the most intense ion (*ca.* 10%) in the high mass region at *m/e* 331. Consequently the dimer must be readily bisected to give (12) as shown in Scheme 2, a reasonable observation if the two gluco-pyranosyl rings are joined at their anomeric carbon atoms as shown in structures (7)—(9).* Other prominent high mass ions appeared at 603 [1%, ion (10)], 500 (9%,

* Compounds (7)—(9) are treated for convenience in most of this discussion as biglucosyl derivatives. The carbon atoms in the two pyranosyl rings are numbered 1—6 and 1′—6′, and the C-1 and C-1′ are referred to as anomeric centres as is common in *C*-glycoside chemistry.[8]

the fourteen hexopyranosyl protons in the 300 MHz ^{1}H n.m.r. spectrum (see Table). Eight of these resonate upfield of δ 4·24, and the other six resonate downfield of



SCHEME 2

Glu = 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl ring

δ 4·97. The former group was assigned to the protons at C-5, -5′, -6, and -6′, and, also in keeping with the proposed *C*-glucosyl structure, C-1 and -1′; the latter

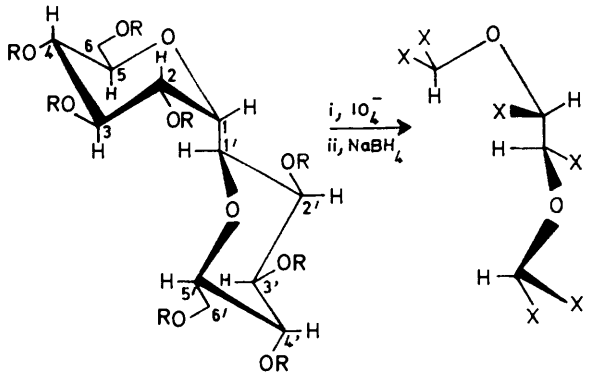
[7] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.

[8] L. J. Haynes, *Adv. Carbohydrate Chem.*, 1965, **20**, 357.

[9] M. Aritomi, T. Komori, and T. Kawasaki, *Annalen*, 1970, **734**, 91.

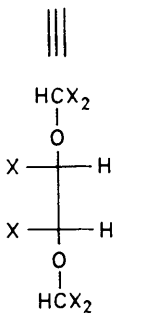
group was assigned to the protons attached to the ring carbon atoms, C-2, -2′, -3, -3′, -4, and -4′, which carry acetoxy-groups.

The anomeric configurations of the two pyranosyl rings, for which three linkages [αβ (7), αα (8), and ββ (9)]



(7a) R=Ac
(17) R=H

(18) X=CH_2OH
(19) X=CH_2OAc



(20) X=CH_2OAc

SCHEME 3

are possible, were established from this spectrum. A one-proton triplet (J 8·0 Hz) at δ 5·65 which was downfield of the signals of the remaining five low-field protons (δ 4·97—5·26) was assigned to H-3 on a glucopyranosyl ring that possessed a substituent at C-1 in the α-configuration [see (7a), Scheme 3]. This assignment was made because protons on six-membered rings suffer downfield shifts if they are *syn*-diaxial to an alkyl group.[10] All the other ring protons in this hexopyranosyl unit, except H-5, were assigned as shown in the Table. Particularly significant was the quartet at high field (δ 4·04) which was coupled to H-2 by 5·5 Hz. This signal was assigned to H-1, thus confirming the α-configuration for this ring.

Since there was only one low-field triplet in the spectrum it was tentatively assumed that the other pyranosyl ring had the β-configuration, and this was confirmed by the analysis of the remaining five hexopyranosyl ring proton signals, which showed *inter alia* that $J_{1',2'}$ was 9·0 Hz (Table).

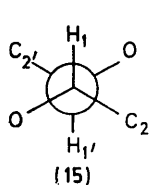
[10] R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.*, 1963, 806.
[11] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.
[12] G. Birch and A. C. Richardson, *Carbohydrate Res.*, 1968, **8**, 411.

Other features in the spectrum of the dimer support the configurations assigned to the anomeric centres: H-1′ resonates 0·21 p.p.m. to higher field than H-1, as expected for axial and equatorial protons,[7] and, owing to the deshielding influence of the C-1 axial substituent, H-5 resonates at least 0·38 p.p.m. to lower field than H-5′.[10] Furthermore the ring to which the α-configuration has been assigned exhibits $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ values of 8·0 Hz, whereas $J_{2',3'}$, $J_{3',4'}$, and $J_{4',5'}$ in the other ring are 9·0 Hz. This implies [11] that whereas the ring with the β-anomeric configuration has an undistorted $^4C_1$ conformation, the ring with the α-configuration is somewhat flattened, presumably owing to the bulk of the axial substituent at C-1.

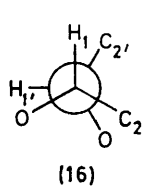
A space-filling model of this dimer reveals that two rotamers are possible about the sterically crowded C(1)–C(1′) bond, the antiperiplanar form (15) and the slightly twisted *gauche* form (16). The value of $J_{1,1'}$ (2·5 Hz) clearly shows that the latter conformer must be the one adopted.

It might be thought that the αβ-configuration could have been assigned immediately to dimer (7) because of its complex n.m.r. spectrum, since the alternative αα- and ββ-isomers, in certain conformations, possess C_2 symmetry, which would produce simple spectra (*e.g.* only four acetoxy-signals), as found in the spectrum of αα-trehalose octa-acetate.[12] However models of the ββ- (9) and (particularly) the αα- (8) isomers show that there is also crowding about the C(1)–C(1′) bonds in these compounds, leading to a preference for conformers that do not possess C_2 symmetry. Thus the complex ^1H n.m.r. spectrum observed does not necessarily exclude structures (8) and (9).

The anomeric configuration of the crystalline dimer (7) was also established by chemical means,[13] as shown in Scheme 3. The crystalline polyol (17) formed upon deacetylation of (7) was cleaved with sodium periodate and the aldehydic functions in the product were reduced with sodium borohydride to give an oily hexitol (18). Acetylation gave a crystalline product in 86% overall yield, which was characterised as the hexa-acetate (19)



(15)



(16)

(21)

with the *meso*-structure [see (20)], since it was optically inactive throughout the wavelength range 220—580 nm. The αα- and ββ-linked dimers (8) and (9) would have yielded hexa-acetates with gross structures similar to (19) but in optically active forms.

The syrupy fraction D which remained after dimer (7) had crystallised was examined for the αα- (8) and

[13] E. L. Jackson and C. S. Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 994; J. K. Hamilton, G. W. Huffman, and F. Smith, *ibid.*, 1959, **81**, 2173.

ββ- (9) dimers. The deacetylated syrup was trimethylsilylated and the silyl ethers were separated by g.l.c. into three components which had retention times of 16, 19, and 21 min. These were separately hydrolysed and then reacetylated. The silyl ether with t_R 16 min gave the crystalline dimer acetate (7), whereas the other two gave acetates which were oils with poorly resolved 60 MHz ^{1}H n.m.r. spectra. However these spectra did clearly show that there were eight acetoxy-groups and fourteen other protons in these compounds, having chemical shifts similar to those of (7), but in each there was one significant difference. The octa-acetate from the silyl ether with t_R 19·0 min exhibited a low-field two-proton triplet at δ 5·65, whereas the octa-acetate from the silyl ether with t_R 21·0 min did not exhibit a low-field triplet. Consequently the former compound was tentatively assigned the αα-structure (8) and the latter the ββ-structure (9).

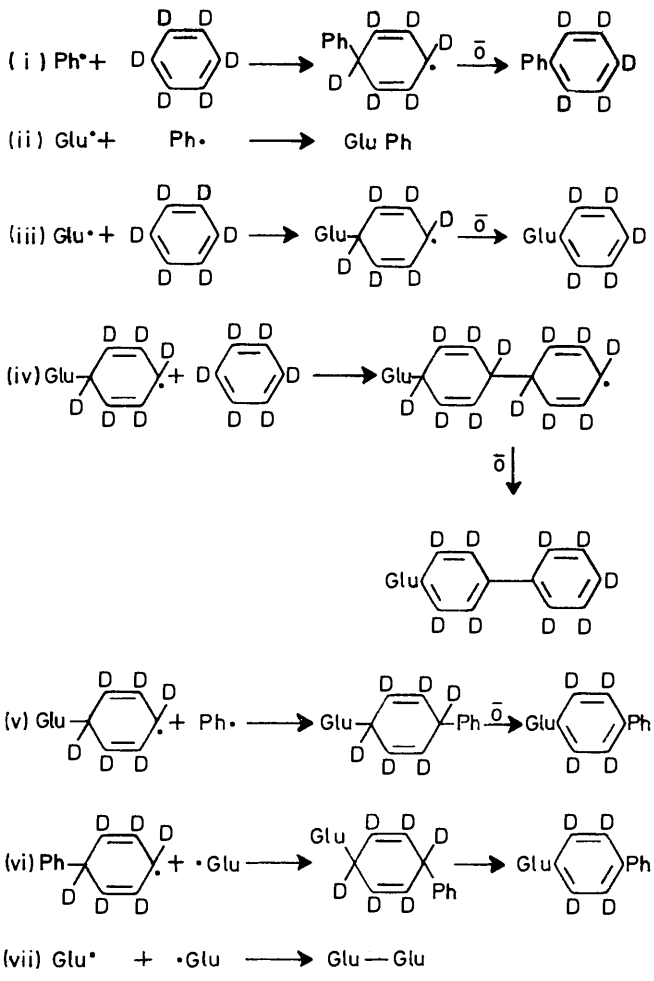
The distribution of the carbohydrate-containing products (3)—(9) formed in the irradiated solution was estimated by g.l.c. to be *ca.* 5 : 5 : 1 : 26 : 13 : 3 : 3, respectively.

Thus although the major carbohydrate product was the 1,5-anhydride (6), the photochemical reaction does afford a new method for preparing *C*-glycosides, which, while not competitive with the Grignard synthesis for glucosylbiphenyl, does offer a route to the glucosyl dimers that have not been prepared previously by standard methods.

The dimers (7)—(9), which can be considered as three anomeric forms of 2,3,4,6-tetra-*O*-acetyl-1-deoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucosyl)-D-glucose (*i.e.* octa-*O*-acetyl-1-deoxytrehalose), are dianhydride peracetates of acyclic polyols. The crystalline dimer (7), which has been referred to in the text as the αβ-biglucosyl acetate, is 1,3,4,5,8,9,10,12-octa-*O*-acetyl-2,6:7,11-dianhydro-D-*gluco*-L-*altro*-L-*erythro*-dodecitol, derived from a polyol with the stereochemistry shown in (21). To our knowledge, anhydrides formed from alditols with carbon chains of this length have not previously been reported, although Whistler and his co-workers [14] have produced a decitol deca-acetate by a photochemical method. An aldose derivative containing a carbon–carbon bond between pyranoid rings has also been reported [15] but in this case C-2 of one ring is linked to C-1 of the other.

U.v. irradiation of tetra-*O*-acetyl-α-D-glucosyl phenyl sulphone (2) [16] in benzene caused it to decompose giving the same products as the β-anomer. The quantities of each product were estimated by column chromatography to be similar to those obtained with the β-anomer.

Reactions at pyranosyl ring anomeric centres usually occur *via* carbonium ions, but these intermediates would not account for the products formed in this reaction. Furthermore irradiation of (1) in 1 : 1 benzene–methanol gave no methyl glycosides. A radical mechanism does account for all the products and some possible routes to them are shown in Scheme 4.



SCHEME 4

The part played by the solvent in the formation of three of these products was ascertained by running the reaction in hexadeuteriated benzene. The photoproducts were separated and their deuterium contents determined spectroscopically. The biphenyl was found to be pentadeuteriated, and the glucosylbiphenyl tetra-acetates (3) and (4) were tetradeuteriated in their aromatic substituents; 50% of the 1,5-anhydroglucitol tetra-acetate (6) was monodeuteriated at C-1, 40% at the C-1*ax* position and 10% at the C-1*eq* position. Thus the biphenyl must arise, as would be expected,[17] by phenylation of the solvent [Scheme 4 (i)] rather than phenyl radical dimerisation. The glucosylbenzene tetra-acetate could be formed either as shown in (ii) or as in (iii), but since the extent of deuteriation in this minor product was not estimated, neither route can be excluded. The deuterium content in the samples of glucosylbiphenyl tetra-acetate precludes route (iv) from

[14] R. L. Whistler and K.-S. Ong, *J. Org. Chem.*, 1971, **36**, 2575.
[15] R. J. Ferrier and N. Prasad, *J. Chem. Soc.* (*C*), 1969, 581.
[16] E. Zissis, A. L. Clingman, and N. K. Richtmyer, *Carbohydrate Res.*, 1966, **2**, 461.
[17] W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, p. 252; G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon, New York, 1960.

the three possible reactions (iv)—(vi) but this does not distinguish between the last two. Reaction (vi) is preferable because free radicals possessing an α-oxygen atom, such as a glucosyl radical, have relatively long lives.[18] Such radicals survive encounters with solvent molecules well enough to permit a significant amount of radical–radical combination to occur. For example, 1-alkoxy-1-methylethyl radicals dimerise to a greater extent than their 1-alkyl analogues,[19] and their extent of dimerisation is also unaffected by the hydrogen-atom-donating ability of the solvent.[20] This property also supports the dimerisation of glucosyl tetra-acetate radicals shown in reaction (vii) as the most reasonable route to the biglucosyl derivatives (7)—(9).

The deuteriated form of the 1,5-anhydride tetra-acetate (6) could be formed in two ways: either a glucosyl radical (Glu·) could abstract a deuterium atom from the hexadeuteriobenzene, or the radical could function as the oxidant in reaction (i), (iii), (v), or (vi). The undeuteriated 1,5-anhydride produced in the presence of hexadeuteriated benzene could be formed by hydrogen atom abstraction from the methyl groups in the acetoxy-residues or possibly as one product from a disproportionation of a pair of radicals.*

The reaction of the glucosyl phenyl sulphone tetra-acetate is similar in one respect to that of endocyclic aryl alkyl sulphones:[1] both classes of compound yield sulphur dioxide upon irradiation. However the mechanism for the photoinduced breakdown of the endocyclic sulphone is different, involving a concerted decomposition into sulphur dioxide and aromatic hydrocarbon.

The mechanism for the decomposition of the glucosyl phenyl sulphone is closer to that proposed by Kharasch and Khodair[2] for the photoreaction of diphenyl sulphone. However, there are again some marked differences. The diphenyl sulphones do not evolve sulphur dioxide, instead they are thought to give Ph· and $PhSO_2$· radicals. The latter apparently do not fragment into phenyl radicals and sulphur dioxide. The glucosyl phenyl sulphones, on the other hand, probably also give a pair of radicals (*i.e.* Ph· and $GluSO_2$·) initially, but in this case the glucosylsulphonyl radical does fragment into sulphur dioxide and a glucosyl tetra-acetate radical, a process presumably facilitated by the structure of the glucosyl radical.

If a free-radical mechanism were operating here, both α- and β-sulphones [(1) and (2)] would be expected to yield a similar spectrum of products, since it is known, for example, that cycloalkyl radicals retain their initial configuration for only a short time, rapidly giving either planar or inverting pyramidal radicals.[21,22] The latter are more probable for pyranosyl systems, since radicals possessing an α-oxygen atom are thought to be bent rather than planar.[23,24]

Product stereochemistry observed in chlorine and bromine atom transfer to cyclohexyl radicals is reported to be dependent upon the dissociation energies of the halogen bonds in the attacked reagents.[22] Cleavage of strong bonds leads to axial attack because bond making in the transition state is substantial; consequently torsional effects become dominant, making equatorial attack less favoured. A similar explanation † could account for the pyranosyl radical being deuteriated more extensively in the axial than in the equatorial position (4 : 1), since the dissociation energy[25] of a C–D bond in [$^2H_6$]benzene is greater than that of bonds to bromine and chlorine considered in ref. 22. However steric and electronic effects for hydrogen transfer will differ from those in halogen transfer reactions; consequently comparisons could be misleading.

Another difference with the pyranosyl system is the possibility of participation by the C-2 acetoxy-group.[24]

A more extensive investigation into the stereochemistry of the formation of monodeuteriated (6) and into the stereochemistry of the radical–radical combination reactions which lead to compounds (3), (4), and (7) is being undertaken.

EXPERIMENTAL

U.v. spectra were measured for ethanolic solutions with a Perkin-Elmer 402 spectrophotometer; i.r. spectra were measured on solids dispersed in potassium bromide discs and for gums smeared on sodium chloride plates, with a Perkin-Elmer Infracord 137; mass spectra were measured on an A.E.I. MS902 instrument with an ionising voltage of 70 eV; molecular weights were measured with a Mechrolab 301A vapour pressure osmometer; optical rotations were measured for solutions in chloroform with a Bellingham and Stanley polarimeter.

^{1}H N.m.r. spectra were usually determined for solutions in deuteriochloroform with a Varian A60D instrument; chemical shifts are expressed on the δ scale (Me_4Si standard) and J values in Hz. Some spectra were measured at higher field strengths with JEOL M100 and Varian HA100, HA200, and HA300 instruments.

G.l.c. was carried out either on a Varian-Aerograph 202 instrument with thermal conductivity detectors using

* The other product from a disproportionation would be 2,3,4,6-tetra-*O*-acetyl-D-*arabino*-hexenose, which, although not detected, has not been exluded as an initial reaction product. Compounds arising from 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl radicals *via* a β-scission (*e.g.* cleavage between C-5 and O-5 with concomitant formation of a carbonyl at C-1 and a radical centre at C-5) have also not been excluded as minor products in this reaction.

† This explanation will not hold if Glu· functions as the oxidant in Scheme 3, since C–D bond strengths in radical intermediates are low.[25]

[18] A. Ohno, N. Kito, and Y. Ohnishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 470.
[19] A. Ohno, and Y. Ohnishi, *Tetrahedron Letters*, 1969, 4405.
[20] J. W. Timberlake and M. L. Hodges, *Tetrahedron Letters*, 1970, 4147.
[21] P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, 1965, **87**, 2590; F. D. Greene, and N. W. Lowry, *J. Org. Chem.*, 1967, **32**, 875; L. Kaplan in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. II, p. 361.
[22] F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Amer. Chem. Soc.*, 1968, **90**, 5793.
[23] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124; R. O. C. Norman, *Chem. in Britain*, 1970, **6**, 66.
[24] A. L. J. Beckwith and P. K. Tindal, *Austral. J. Chem.*, 1971, **24**, 2099.
[25] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

hydrogen as carrier gas and columns packed with Chromosorb W (60—80 mesh) impregnated with 15% SE52 (A, 10 ft × 0·25 in; B, 20 ft × 0·375 in) or on a Perkin-Elmer F11 instrument using nitrogen as carrier gas and a flame ionisation detector, with a 6 ft × 0·125 in column (C) packed with Chromosorb W (80—100 mesh) impregnated with 5% SE52 or a 20 ft × 0·125 in column (D) packed with GasChrom Q impregnated with 5% OV-25 (a phenylated silicone oil).

T.l.c. was carried out on silica gel GF_{254} (Merck) and the materials were located visually either under u.v. light or with a sulphuric acid–ethanol spray reagent. Plates were developed with benzene–ethyl acetate (3 : 1).

2,3,4,6-*Tetra*-O-*acetyl*-β-D-*glucopyranosyl Phenyl Sulphone* (1).—Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside [26] (50 g) in acetic acid (1·25 l) was oxidised under reflux with aqueous potassium permanganate (5%; 530 ml). The solution was decolourised with sodium disulphite and the product precipitated with water; yield 50 g (95%), m.p. 188—189° (from propan-2-ol) (lit.,[3] 189°); $\lambda_{max.}$ 259, 266, and 273 nm (ε 1000, 1500, and 1200); δ 7·5—8·1 (m, Ph), 5·28 (m, H-1 and -2), 4·55 (m, H-3), 4·89 (m, H-4), 3·78 (m, H-5), 4·15 (m, H-6a and -6b), 2·11, and 1·95 (2 s, 2 AcO), and 1·99 (s, 2 AcO).

Phenyl 1-*Thio*-α-D-*glucopyranoside*.—A suspension of glucose diphenyl dithioacetal [16] (75 g) was stirred for 2 h in concentrated hydrochloric acid (750 ml) at 30°. The mixture was poured into ice–water, the unchanged acetal was filtered off (53 g), and the filtrate was neutralised with sodium hydrogen carbonate and then evaporated. The residue was extracted thrice with boiling ethyl acetate. Evaporation of the solution so obtained gave a syrup (2·9 g). The recovered starting material was recycled and three such runs gave more product (7·3 g). Crystallisation of the total crude product (10·2 g) from ethanol–n-pentane gave the crystalline phenyl thioglucoside (7·6 g, 19%), m.p. 153—156° (lit.,[16] 157°).

Phenyl 2,3,4,6-*Tetra*-O-*acetyl*-1-*thio*-α-D-*glucopyranoside*.—The foregoing thioglucoside (7 g) was acetylated with acetic anhydride (35 ml) in pyridine (35 ml) to give the tetra-acetate (95%), m.p. 90—92° (from propan-2-ol) (lit.,[16] 92°); δ 7·2—7·7 (m, Ph), 5·99 (d, $J_{1,2}$ 5·0), 5·07 (q, $J_{2,3}$ 9·5), 5·66 (t, $J_{3,4}$ 9·5), 5·13 (t, $J_{4,5}$ 9·5), 4·68 (m, H-5), 4·35 (q, $J_{6a,5}$ 4·5, $J_{6a,6b}$ 11·5), 4·04 (q, $J_{6b,5}$ 2·0), and 2·09, 2·06, 2·04, and 2·00 (4 s, 4 AcO).

2,3,4,6-*Tetra*-O-*acetyl*-α-D-*glucopyranosyl Phenyl Sulphone* (2).—The foregoing phenyl thioglucoside (10·8 g) was oxidised with potassium permanganate as described for the β-anomer to give the α-sulphone (2) (10·5 g) (from 82% propan-2-ol), m.p. 160—161° (lit.,[16] 162°); $\lambda_{max.}$ 259, 266, and 273 nm (ε 1000, 1500, and 1200); δ 7·6—8·1 (m, Ph), 5·27—5·53 (m, H-1 and -3), 6·13 (m, H-2), 5·15 (q, $J_{4,3}$ 9·0; $J_{4,5}$ 10·0), 4·72 (oct, $J_{5,6a}$ 4·5), 4·28 (q, $J_{6b,5}$ 2·0), 3·89 (q, $J_{6a,6b}$ 12·5), 2·12 and 2·00 (2 s, 2 AcO), and 2·07 (2 s, 2 AcO).

Photolyses.—(a) 2,3,4,6-*Tetra*-O-*acetyl*-β-D-*glucopyranosyl phenyl sulphone* (1). The β-sulphone (1) (6·5 g) was irradiated for 18 h as a 2·5% w/v solution in benzene in the annular space of a quartz photolysis well. The solution was stirred and nitrogen was passed through it during the irradiation.

The presence of sulphur dioxide was detected in the effluent gas with a Draeger–Normalair tube. It was estimated quantitatively [27] by passing into aqueous 2% sodium hydroxide, oxidising the sodium sulphite formed to sodium sulphate with hydrogen peroxide, and titrating the unchanged base. Only 45% of the theoretical amount of the sulphur dioxide, based upon sulphone (1) consumed, was accounted for in this way, but when a correction derived from a control experiment was applied for the sulphur dioxide which remained dissolved [28] in the benzene, 80% of the gas was accounted for.

Evaporation of the photolysate solution gave a syrup (7·3 g), which on t.l.c. showed three spots, A, B, and C (R_F 1·0, 0·7, and 0·5), under u.v. light, and three spots, B, C, and D, of equal intensities (R_F 0·7, 0·5, and 0·3) with the spray reagent [the sulphone (1) had R_F 0·5]. The syrup was deacetylated, the residue partitioned between water and chloroform, and the insoluble material filtered off.

The chloroform solution, which contained the non-carbohydrate fraction A (R_F 1·0), was evaporated to give an amorphous solid (1·8 g), the ^1H n.m.r. spectrum of which showed only aromatic signals, in the region δ 7·0—7·6. The product comprised biphenyl (20%) and non-volatile material (80%) as estimated by g.l.c. on column A at 150°. The biphenyl was collected and compared with authentic material.

The aqueous solution was evaporated and the carbohydrate fraction so obtained reacetylated to give a syrupy mixture of acetates (3·3 g), which was separated into three fractions by column chromatography (SiO_2): B, R_F 0·7 (0·77 g); C, R_F 0·5 (1·15 g); and D, R_F 0·3 (1·09 g).

A solution of fraction B in propan-2-ol deposited crystals of 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)biphenyl (3) (200 mg), m.p. and mixed m.p. 182—183° [with an authentic sample prepared from biphenyl-4-ylmagnesium bromide and acetobromoglucose (lit.,[4] 180°)], $[\alpha]_D$ −37° (*c* 1·3); $\nu_{max.}$ 1750 cm^{-1} (Ac); $\lambda_{max.}$ 210 and 253 nm (ε 27,000 and 20,000); *M* 488 (Calc. for $C_{26}H_{28}O_9$: 489); for n.m.r. data see Table.

G.l.c. of the mother liquor (column A; 260°) showed a major peak with t_R 24·0 min and several minor ones. One of these had t_R 14·0 min, identical with that of 2,3,4,6-tetra-*O*-acetyl-(αβ)-D-glucosylbenzene,[6] but it comprised less than 1·0% of the reaction products; consequently it was not collected. A syrupy specimen (110 mg) of the major component was collected and this yielded more crystalline β-D-glucosylbiphenyl tetra-acetate (3) (50 mg), leaving the α-anomer (4) (60 mg) as a syrup contaminated with less than 20% of (3): $[\alpha]_D$ +63° (*c* 1·0); $\lambda_{max.}$ 210 and 253 nm (ε 27,000 and 21,000); for n.m.r. data see Table; an acetoxy-signal at δ 1·80 (0·6H) indicated that *ca.* 20% of the β-anomer (3) was present.

Fraction C was separated on column A at 185° into equal amounts of two components with t_R 6·0 and 45 min, which were collected. The slower-running one was shown to be unchanged β-sulphone (1) and the other was crystallised from diethyl ether–n-pentane and identified as 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-glucitol (6), m.p. and mixed m.p. 71—73° [authentic (6) was prepared [29] by reduction of acetobromoglucose]; for n.m.r. parameters see Table.

Fraction D yielded crystals (0·5 g) of 1,3,4,5,8,9,10,12-*octa*-O-*acetyl*-D-gluco-L-altro-L-erythro-2,6:7,11-*dianhydro-dodecitol* (7) from isopropanol; m.p. 182°, R_F 0·3; *M* 638 (vapour phase osmometer) (Calc. for $C_{28}H_{38}O_{18}$: 622);

[26] C. B. Purves, *J. Amer. Chem. Soc.*, 1929, **51**, 3619.
[27] H. F. Johnstone and E. Taylor, *Ind. Eng. Chem. Anal.*, 1929, **1**, 197.
[28] 'International Critical Tables,' National Research Council of the U.S.A., McGraw-Hill, New York, 1928, **3**, 264.
[29] L. Zervas and C. Zioudrou, *J. Chem. Soc.*, 1956, 214.

m/e 500 (9%), 458 (4%), and the ions shown in Scheme 1; for n.m.r. parameters see Table (Found: C, 50·7; H, 5·8. $C_{28}H_{38}O_{18}$ requires C, 50·8; H, 5·8%).

The mother liquor, which appeared homogeneous on t.l.c. (R_F 0·3) was deacetylated and the hydroxy-products were treated with Tri-Sil *Z* (Pierce Chemical Co.) (1 ml). The trimethylsilyl ethers formed were fractionated on column C at 240° into three peaks with t_R 16, 19, and 21 min, in the ratio 5 : 1 : 1. The crystalline dimeric octa-acetate (7) was similarly converted into its octa-*O*-trimethylsilyl derivative and found to have t_R 16 min.

The three components were separated on column B at 290° (t_R 16, 19, and 21 min), and each was separately hydrolysed in 10% aqueous methanol at 65° and then acetylated with acetic anhydride in pyridine. The silyl ether with the shortest retention time gave more crystalline (7) (55 mg). The other silyl ethers (t_R 19 and 21 min) gave two syrupy acetates (60 and 30 mg, respectively), the n.m.r. spectra of which indicated that they were isomers of (7), both spectra exhibiting signals due to eight acetoxy-groups and fourteen other protons. Although these spectra could not be analysed in detail, that of the former syrup showed two protons as a triplet at δ 5·65, at lower field than the remaining twelve protons, whereas the spectrum of the latter syrup exhibited all fourteen protons in a group.

A sample of the crude photolysate was analysed by g.l.c. on column D, for which the detector response had been calibrated with known quantities of compounds (1) and (3)—(7). The following data were obtained: at 210° biphenyl t_R 3·0 min and 1,5-anhydroglucitol tetra-acetate (6) t_R 10·3 min; at 245° (6) t_R 5·3 min (26 parts), glucosylbenzene tetra-acetate (5) t_R 12·0 min (1 part), dimers (7) and (8) t_R 79·0 min (16 parts), dimer (9) t_R 90·0 min (3 parts), α-D-glucosylbiphenyl tetra-acetate (4) t_R 93 min (5 parts), and its β-anomer (3) t_R 101 min (5 parts).

(b) 2,3,4,6-*Tetra*-O-*acetyl*-α-D-*glucopyranosyl phenyl sulphone* (2). The α-pyranosyl sulphone (2) (6·5 g) was irradiated as described for its β-anomer to give a similar yield of crude product (7·4 g) which was separated into four fractions similar to those obtained previously: A (1·7 g), B (0·7 g), C (1·4 g), and D (1·0 g). These components were further separated as before and found to comprise the same compounds in similar proportions to those formed in the photolysis of the β-anomer.

(c) 2,3,4,6-*Tetra*-O-*acetyl*-β-D-*glucopyranosyl phenyl sulphone* (1) *in hexadeuteriobenzene*. The sulphone (1) (1·2 g) was irradiated for 7½ h in [$^2H_6$]benzene (95 ml) as described in (a). The crude product (1·4 g) was dissolved in ether, the insoluble material (0·2 g; R_F 0·0) was filtered off, and the solution was fractionated by preparative layer chromatography (p.l.c.) on two plates (1 m × 20 cm) coated with Kieselgel GF_{254}. The chromatograms were developed with benzene, dried, and redeveloped with benzene–ethyl avetate (3 : 1). This gave three bands, R_F 1·0, 0·7, and 0·5, which were visible under u.v. light.

Extraction of the most mobile band with acetone and chloroform afforded a yellow oil (160 mg) which contained biphenyl. This was isolated by g.l.c. and its deuterium content estimated by n.m.r. spectroscopy using a known weight of the sample and an equivalent quantity of ethanol in carbon tetrachloride. The ratio of the integrated areas of the aromatic proton signals and the methyl proton signals was 5 : 3.

An anomeric mixture of glucosylbiphenyl acetates (3) and (4) (170 mg) was extracted from the second band (R_F 0·7). The 60 MHz n.m.r. spectrum of this mixture exhibited signals equivalent to twelve acetate protons and seven carbohydrate chain and ring protons, but only five aromatic protons instead of the nine found for these products isolated in experiment (a). The mass spectrum of this fraction contained a series of peaks four mass units higher than those in the spectra of the non-deuteriated compounds (3) and (4). In particular the ions with masses 364·1310, 304, and 249 from the fully protonated material, which corresponded to structures C, D, and F, respectively, as described by Aritomi *et al.*,[9] appeared at 368·1561, 308, and 253 in the case of the deuteriated sample. Significantly the ion *m/e* 331, due to the 2,3,4,6-tetra-*O*-acetylglucopyranosyl cation (12), was of similar intensity in the spectrum of each sample.

Extraction of the band with R_F 0·5 gave a syrup (300 mg) from which partially deuteriated 1,5-anhydroglucitol tetra-acetate (6) was isolated by g.l.c. Its 220 MHz n.m.r. spectrum showed that the expected quartet at δ 4·04 (H-1*eq*) and triplet at δ 3·03 (1-H*ax*) had partially collapsed and decreased in intensity to 90% and 60%, respectively, of the intensity of the signal at 5·43 due to H-4 (see Table).

The glucosyl dimers could not be seen under u.v. light; their presence in the photoproduct was confirmed by extracting a broad band of silica gel (R_F 0·45—0·05). This afforded a syrup (210 mg) which was identical with the dimeric mixture obtained in (a).

Degradation of the Dimer Octa-acetate (7).—The crystalline biglucosyl acetate (7) (0·16 g) was deacetylated and the resulting polyol (17) was oxidised [13] with sodium periodate (0·51 g) in water (25 ml) containing sodium acetate (75 mg). The reaction was monitored by observing the change in optical rotation with a Bendix N.P.L. automatic polarimeter, which showed that the oxidation was complete in 2 h. After a further 2 h barium acetate (0·25 g) was added to precipitate the iodate and periodate ions. The solution was centrifuged and the supernatant liquor treated with sodium borohydride (0·15 g) for 2 h, and then Amberlite IR-120(H^+) ion exchange resin (*ca.* 5 ml). The water was evaporated off and borate ions were removed from the residue with methanol in the usual way. The hexitol (18) (64 mg) so obtained was treated with acetic anhydride in pyridine to give 1,4-*di*-O-*acetyl*-2,3-*bis*-O-(2-*acetoxy*-1-*acetoxymethylethyl*)*erythritol* (19) (0·11 g, 86%), which was recrystallised from propan-2-ol (yield 90 mg); m.p. 112—113°; [α] ±0° throughout wavelength range 220—580 nm, kindly measured by Dr. D. Marshall on a Fica Spectropol I, instrument, $\nu_{max.}$ 1750 cm^{-1} (Ac); δ 3·7—4·4 (16H, m), 1·94 (s, 2 AcO), 1·92 (s, 2 AcO), and 1·88 (s, 2 AcO) (Found: C, 50·6; H, 6·5. $C_{22}H_{34}O_{14}$ requires C, 50·6; H, 6·6%).

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