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PHOTOLYTIC DECOMPOSITION OF D-GLUCOFURANOSYL PHENYL SULPHONE ACETATES*

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ABSTRACT

Irradiation of phenyl 2,3,5,6-tetra-*O*-acetyl-α-D-glucofuranosyl sulphone (**4**) in benzene with u.v. light gave sulphur dioxide, biphenyl, the 2,3,5,6-tetra-*O*-acetyl derivatives of 1,4-anhydro-D-glucitol (**7**), α-D-glucofuranosylbiphenyl (**5**), and its β-D anomer (**6**), and three isomeric 1,2,4,5,8,9,11,12-octa-*O*-acetyl-3,6:7,10-dianhydrododecitols (**8**). Irradiation of the β-D anomer of **4** gave similar results.

RESULTS AND DISCUSSION

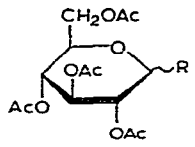
Pyranose and furanose derivatives undergo an extensive range of reactions at their anomeric centres. A large number of these reactions occur *via* carbocations, whereas there have been few reports of reactions involving free-radical intermediates[2]. Photochemical methods constitute important routes to free radicals; consequently, our interest in the photochemistry of carbohydrate derivatives prompted us to investigate decompositions of glycosyl derivatives which would yield radical centres at anomeric carbon atoms.

Recently, we showed[1] that u.v. irradiation of solutions of D-glucopyranosyl phenyl sulphone acetates (**1**) in benzene gave *C*-D-glucopyranosyl products (*e.g.*, **2** and **3**) which could be accounted for by a free-radical mechanism. We now report an extension of that work to furanosyl sulphones.

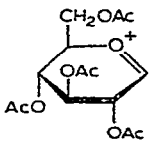
U.v. irradiation of a 2.5% solution in benzene of phenyl 2,3,5,6-tetra-*O*-acetyl-α-D-glucofuranosyl sulphone[3] (**4**) in the annular space of a quartz, water-cooled, photolysis well for 18 h with a 450-watt, medium-pressure, mercury-arc lamp gave sulphur dioxide and several non-gaseous products which were separated by column chromatography into four fractions (*A–D*) (R_F 1.0, 0.8, 0.7, and 0.35). Fraction *A* (1.2 g) was shown by its p.m.r. spectrum to comprise only aromatic materials, half of which was biphenyl (g.l.c. analysis).

Syrupy and crystalline components were obtained from fraction *B* (0.6 g) and shown to be anomeric 4-(2,3,5,6-tetra-*O*-acetyl-D-glucofuranosyl)biphenyls (**5** and **6**)

*Photochemistry of Carbohydrate Derivatives: Part II[1].



1 R = $PhSO_2$
2 R = *p*-PhC_6H_4
3 R = 2,3,4,6-tetra-O-acetyl-D-glucopyranosyl



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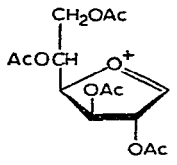

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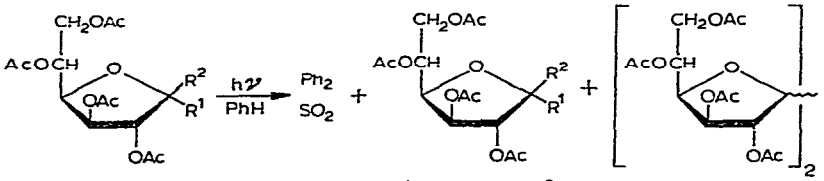


4 R^1 = $PhSO_2$, R^2 = H
9 R^1 = H, R^2 = $PhSO_2$

5 R^1 = *p*-PhC_6H_4, R^2 = H
6 R^1 = H, R^2 = *p*-PhC_6H_4
7 R^1 = R^2 = H

8

from their elemental analyses and u.v., i.r., p.m.r., and mass spectra. The *para*-substituted biphenyl structure was assigned to these compounds on the basis of the position of their u.v. absorption maxima at 253 nm, which resembled more closely that (λ_{max} 253 nm)[4] for 4-methylbiphenyl than those (249 and 237 nm, respectively) for the 3- and the 2-isomers[5]. *para*-Substitution was not unexpected in these products, since photolysis of the pyranosyl sulphone analogue (**1**) also afforded the *para*-D-glucosylbiphenyl anomers[1] (**2**).

Compounds **5** and **6** were different from the pyranosyl biphenyls (**2**) and, consequently, they were tentatively assigned furanosyl structures, which was reasonable since retention of ring size was expected in this reaction. The presence of the furanosyl ring in these compounds was confirmed by the p.m.r. spectra, which were analysed by first-order methods, as shown in Table I. Apart from the signals for nine aromatic protons and four acetoxy groups, there were signals from seven other protons which were assigned as shown. The magnitude of the *vicinal* couplings for H-2,3,4,5,6,6′ were the same for compounds **5** and **6**, and the *geminal* couplings for H-6,6′ were also identical. The values for $J_{2,3}$ and $J_{3,4}$ were 1.0 and 3.5 Hz, respectively, which suggests that both compounds contain D-glucofuranosyl rings. However, the $J_{1,2}$ values were different, being larger (4.0 Hz) in the crystalline product than in the syrupy product (2.0 Hz). Thus, the latter must be the β-D-glucofuranosyl anomer (**6**) and the former the α-D-glucofuranosyl anomer[6] (**5**), a conclusion confirmed by their respective optical rotations (−38° and +27°).

Inspection of the chemical shifts for the acetoxy signals recorded in Table I for **5** and **6** reveals that there is another feature which is dependent upon the anomeric configuration. The α-D anomer (**5**) possesses one methyl resonance at δ 1.72, significantly up-field from the other signals. This observation is contrary to that made

TABLE 1

P.M.R. PARAMETERS[a] OF SOME TETRA-*O*-ACETYL-D-GLUCOFURANOSYL DERIVATIVES MEASURED IN $CDCl_3$

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*Ar*	*Ac*
5[b]	5.44 d	5.52 q	5.60 q	4.66 q	5.38 o	4.72 q	4.29 q	7.3–7.7 m	2.10
	$J_{1,2}$ 4.0	$J_{2,3}$ 1.0	$J_{3,4}$ 3.5	$J_{4,5}$ 9.5	$J_{5,6}$ 5.5	$J_{6,6'}$ 12.5	$J_{6',5}$ 2.5	9H	2.07
									2.00
									1.72
6[c]	5.09 d	5.18 q	5.50 q	4.48 q	5.55 o	4.78 q	4.32 q	7.3–7.7 m	2.17
	$J_{1,2}$ 2.0	$J_{2,3}$ 1.0	$J_{3,4}$ 3.5	$J_{4,5}$ 9.5	$J_{5,6}$ 5.5	$J_{6,6'}$ 12.5	$J_{6',5}$ 2.5	9H	2.10
									2.04
									1.96
7[b]	4.31 q	5.22 m	5.44 q	4.14 q	5.24 o	4.60 q	4.12 q		2.10
	$J_{1,2}$ 5.0	$J_{2,3}$ 1.0	$J_{3,4}$ 3.5	$J_{4,5}$ 9.5	$J_{5,6}$ 5.5	$J_{6,6'}$ 12.5	$J_{6',5}$ 2.5		2.00
	3.82 q								2.04
	$J_{1',1}$ 10.5, $J_{1',2}$ 2.0								2.04

[a] δ in p.p.m., and J in Hz. [b] Measured at 100 MHz. [c] Measured at 60 MHz.

for the anomers of tetra-*O*-acetyl-D-glucopyranosylbiphenyl[1] (**2**) and *C*-D-glucopyranosylflavonoids[7] which exhibit a shift to higher field for the AcO-2 signal in the spectrum of the β-D anomers. Hillis and Horn[7] concluded that this effect arose because the planes of the aromatic and pyranosyl rings exist perpendicular to each other for steric reasons, so that, in the β-D-pyranosyl anomer, the methyl group of AcO-2 is situated over the plane of the aromatic ring in its diamagnetic region. Application of this reasoning to the D-glucofuranosyl systems shows that AcO-2 will be deshielded in the α-D rather than in the β-D compound, because in five-membered rings *vicinal* substituents are close to each other only in the *cis* configuration. This method therefore constitutes a useful additional way of assigning anomeric configurations in pyranosyl and furanosyl aryl peracetates.

The product in fraction *C* was separated by g.l.c. from contaminating starting-material and characterised as 2,3,5,6-tetra-*O*-acetyl-1,4-anhydro-D-glucitol (**7**) from its p.m.r. spectrum (see Table I) and by deacetylation to give the known 1,4-anhydro-D-glucitol. It is noteworthy that the sizes of the *vicinal* and *geminal* couplings in the spectrum of **7** were very similar to those of the other furanosyl products (**5** and **6**).

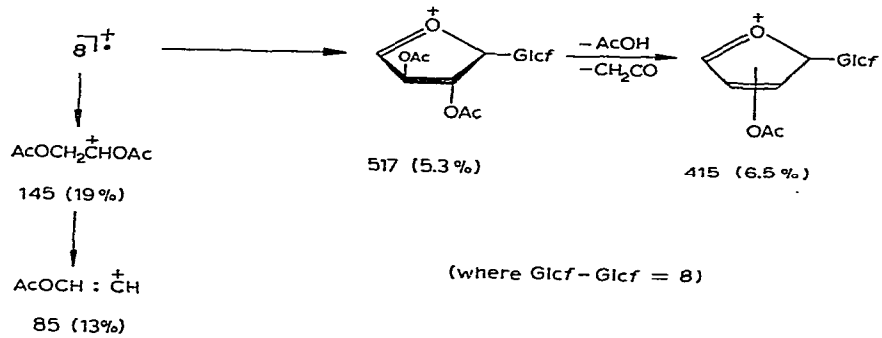
The final fraction *D* comprised compounds of high molecular weight (Rast), which contained neither sulphur nor aromatic substituents. The t.l.c. mobility and the 60-MHz p.m.r. spectrum of this fraction were similar to those found for the dimers (**3**) formed in the photolysis of the pyranosyl sulphones (**1**); consequently, bi-D-glucosyl structures of the type **8** were assigned to these compounds.

All the major peaks in the mass spectrum of fraction *D* could be accounted for by five fragmentation pathways (see Experimental) which have been devised to explain the cracking patterns of acetoxy[8] and aryl[9] hexosyl tetra-acetates. This evidence, in conjunction with the molecular ion at *m/e* 662 and the intense ion at *m/e* 331, supports the view that these compounds are dimers of hexosyl tetra-acetates linked at their anomeric centres.

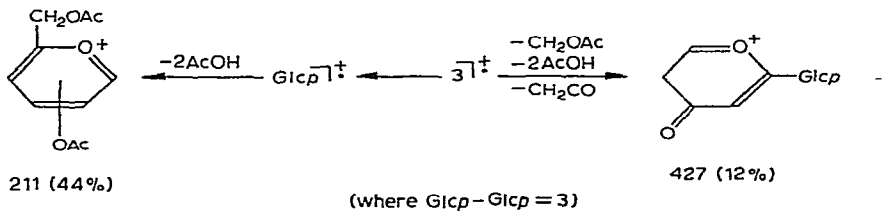
There are three significant differences between the mass spectra of fraction *D* and the pyranosyl dimers (**3**), which indicate that the former comprises furanosyl derivatives. Firstly, the *m/e* 331 ion (**10**) in the spectrum of **3** was only 9% of the base peak, whereas the 331 ion in the spectrum of fraction *D* was abundant (94%). This large difference in intensity suggests that the ion responsible had structure **11**, since furanosyl derivatives are known to lose substituents situated at carbon atoms adjacent to the ring oxygen atoms more readily than pyranosyl derivatives. Secondly, the ions shown in Scheme 1, which arise *via* a related fragmentation pathway, but on this occasion involving cleavage between C-4 and C-5, also indicate that furanosyl rings are present. Thirdly, it is also significant that two fragmentation processes, which Biemann *et al.*[8] have shown are important for pyranosyl acetates and that we[1] have found to give rise to prominent ions at *m/e* 427 and 211 in the spectrum of **3** (see Scheme 2), were not important in the spectrum of fraction *D*.

Fraction *D* was shown to contain three components by g.l.c. analysis of the trimethylsilyl ether derivatives of the polyols obtained by deacetylation of the fraction. Consequently, it is probably composed of an isomeric mixture of 1,2,4,5,8,9,11,12-

octa-*O*-acetyl-3,6:7,10-dianhydrododecitols having the D-*gluco*-D-*galacto*-L-*erythro*, D-*gluco*-L-*altro*-L-*erythro*, and D-*gluco*-L-*ido*-L-*erythro* structures which correspond to the *ββ*-, *αβ*-, and *αα*-linked bi-D-glycofuranosyl octa-acetates.



Scheme 1



Scheme 2

Irradiation of the *β*-D-furanosyl compound **9** gave sulphur dioxide and, according to t.l.c. evidence, a similar spectrum of products to those obtained from the *α*-D anomer.

These results show that u.v. irradiation of solutions of **4** and **9** in benzene affords the same type of photoproducts as those obtained when **1** was irradiated[1]. Furthermore, they show that the integrity of the D-glucosyl ring of the sulphone is maintained during these transformations. A free-radical mechanism proposed earlier to explain the products from the pyranosyl sulphone will accommodate these observations. Thus, **4** and **9** probably fragment upon u.v. irradiation into sulphur dioxide, phenyl radicals, and D-glucofuranosyl tetra-acetate radicals (not necessarily concertedly[10]). The phenyl radicals would react with the benzene to give a phenylcyclohexadienyl radical, which is either oxidised to biphenyl or, because of its relatively longer life, undergoes a combination reaction with a D-glucofuranosyl radical to give, after oxidation, the D-glucofuranosylbiphenyl acetates **5** and **6**. The D-glucofuranosyl radicals could react in at least two other ways, either they could abstract a hydrogen atom and produce the 1,4-anhydride (**7**) or they could dimerise to give the anomeric mixture of bi-D-glucosyls (**8**).

EXPERIMENTAL

U.v. spectra were measured for ethanolic solutions with a Perkin–Elmer Spectrophotometer model 402, i.r. spectra (for solids dispersed in potassium bromide or for gums smeared on sodium chloride discs) with a Perkin–Elmer Infracord model 137, p.m.r. spectra with Varian A60D or HA220 or Jeol JMN-MH-100 instruments, and mass spectra with an AEI MS902 instrument. Optical rotations were determined for chloroform solutions with a Bellingham and Stanley polarimeter.

Silica Gel G (Merck) was used for t.l.c. with the following solvent systems: *A*, benzene–ethyl acetate (2:1) and *B*, ethyl acetate–methanol (1:1), and the compounds were located either under u.v. light or with a sulphuric acid–ethanol spray reagent. For g.l.c., either a Varian Aerograph instrument model 202B was employed with hydrogen carrier-gas and a thermal conductivity detector, using columns *A* (10 ft × 0.25 in.) or *B* (20 ft × 0.375 in.) packed with Chromosorb W (60–80 mesh) impregnated with 15% SE52, or a Perkin–Elmer F11 instrument with nitrogen carrier-gas, using column *C* (6 ft × 0.125 in.) packed with 5% SE52 on the same support.

*Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-*D*-glucofuranoside.* — To a boiling solution of D-glucose diphenyl dithioacetal (28.5 g) in ethanol (500 ml), mercuric oxide (8.1 g) was added with stirring followed by a hot, ethanolic solution of mercuric chloride (10.2 g). After 15 min, the reaction mixture was cooled, the precipitate filtered off, and the solution concentrated to ~25 ml. Water was added to precipitate unreacted dithioacetal (2.1 g), which was filtered off, and the solution was concentrated to a syrup (18 g), R_F (solvent *B*) 0.6 (major) and 0.5 (minor). A solution of this syrup in hot ethyl acetate (200 ml) was cooled, which caused an oil to separate that contained the material with R_F 0.5. The solution was decanted and evaporated, giving a residue (16 g) which afforded phenyl 1-thio-α-D-glucofuranoside (11 g, 60%), m.p. 116–119° (from ethanol–pentane); lit.[3] m.p. 121°. P.m.r. data: δ (D_2O) 7.3–7.7 (m, Ph), 5.84 (d, $J_{1,2}$ 4.0 Hz), 3.5–4.6 (m, H-2,3,4,5,6,6′).

The mother liquor yielded a syrup (1.9 g) which was used in the preparation of the β-D anomer described below.

The phenyl thiofuranoside (6.4 g) was acetylated in the usual way, giving the tetra-acetate (9.8 g, 95%) as a syrup.

*Phenyl 2,3,5,6-tetra-*O*-acetyl-α-*D*-glucofuranosyl sulphone* (**4**). — A solution of the foregoing thiofuranoside (6.8 g) in acetic acid (180 ml) was boiled under reflux with aqueous potassium permanganate (5%, 75 ml). The solution was decolourised with sodium metabisulphite and the sulphone **4** (5.3 g, 72%) was precipitated with water and had m.p. 126–128° (from ethanol); lit.[3] m.p. 129°; λ_{max} 259, 266, and 273 nm (ε 1,000, 1,500, and 1,200, respectively). P.m.r. data: δ 7.4–8.1 (m, Ph), 5.16 (d, $J_{1,2}$ 6.0 Hz), 5.90 (q, $J_{2,3}$ 2.0 Hz), 5.68 (q, $J_{3,4}$ 4.0 Hz), 4.93 (q, $J_{4,5}$ 9.0 Hz), 5.24 (m, H-5), 4.52 (q, $J_{6,5}$ 2.0, $J_{6,6'}$ 12.5 Hz), 4.16 (q, $J_{6',5}$ 4.5 Hz), 2.20, 2.16, 2.04, 2.02 (4s, 4AcO).

*Phenyl 1-thio-β-*D*-glucofuranoside.* — The foregoing α-thiofuranoside (5.0 g) was stirred in boiling hydrochloric acid (50mM) (150 ml) for 20 min. The solution was

neutralised and the water evaporated to give a syrup (4.9 g) which was dissolved in ethyl acetate (100 ml). This solution was filtered at room temperature and left for 3 days to allow some α-D-furanoside (2.2 g) to crystallise. The mother liquor was concentrated to give a syrup (2.6 g) which contained 30% of the required β-D anomer, as estimated from its p.m.r. spectrum. This material was combined with the syrup (1.9 g) obtained from the mother liquor remaining from the α-D-furanoside preparation described above. From the combined syrup (4.5 g), a further 2.0 g of the α-D anomer was removed by repeated crystallisations from ethyl acetate. The p.m.r. spectrum of the residual oil (2.5 g) exhibited a doublet at δ 5.84 (J 4.0 Hz) for H-1 of the α-D anomer and a more intense doublet at δ 5.36 ($J_{1,2}$ 2.0 Hz) which was assigned to H-1 of the β-D anomer. The intensities of these signals showed that 60% of the β-D-furanoside was present in the anomeric mixture.

*Phenyl 2,3,5,6-tetra-*O*-acetyl-β-*D*-glucofuranosyl sulphone* (**9**). — The foregoing mixture of phenyl thiofuranosides, enriched in the β-D anomer, was acetylated in the usual way to give an anomeric mixture of acetates which could not be separated. Consequently, this mixture was oxidised with potassium permanganate as described above, the product was extracted into chloroform, and the syrup (4.8 g), R_F (solvent *A*) 0.6 (major) and 0.7 (minor) (*cf.* α-D-sulphone, R_F 0.7), obtained upon evaporation was fractionated by column chromatography on silica gel (solvent *A*) to afford **9** as a syrup (1.5 g), R_F (solvent *A*) 0.6; λ_{max} 259, 266, and 273 nm (ε 1,000, 1,500, and 1,200). P.m.r. data: δ 7.6–8.2 (m, Ph), 4.97 (d, $J_{1,2}$ 2.5 Hz), 5.72 (q, $J_{2,3}$ 0.5 Hz), 5.42 (q, $J_{3,4}$ 4.5 Hz), 4.47 (q, $J_{4,5}$ 9.5 Hz), 5.30 (sept, $J_{5,6}$ 2.0 Hz), 4.68 (q, $J_{6,6'}$ 12.5 Hz), 4.07 (q, $J_{6',5}$ 5.0 Hz), 2.14, 2.07, 1.98, 1.88 (4s, 4AcO).

U.v. irradiations. — (*a*) *Phenyl 2,3,5,6-tetra-*O*-acetyl-α-*D*-glucofuranosyl sulphone* (**4**). The α-D-sulphone **4** (6.5 g) was irradiated for 18 h as a 2.5% solution in benzene in the annular space of a quartz photolysis well. The reaction mixture was stirred and protected from atmospheric oxygen by passing nitrogen through the solution during irradiation. The presence of sulphur dioxide was detected in the effluent gas with a Draeger–Normalair tube.

Concentration of the photolysate solution gave a syrup (7.3 g) which on examination by t.l.c. (solvent *A*) showed three spots *A*, *B*, and *C* (R_F 1.0, 0.8, and 0.7) when visualised with u.v. light, and three spots *B*, *C*, and *D* of equal intensities (R_F 0.8, 0.7, and 0.35) when visualised with the spray reagent. The crude product was fractionated by column chromatography on silica gel. Elution with benzene gave fraction *A* as a solid (1.2 g), which g.l.c. analysis showed contained biphenyl (0.6 g). Elution with solvent *A* gave three more fractions *B* (0.6 g), *C* (2.22 g), and *D* (1.25 g).

A portion of fraction *B* was obtained crystalline after g.l.c. (column *B* at 260°), and with this specimen the bulk of the fraction was nucleated and crystallised from 2-propanol, to give pure 4-(2,3,5,6-tetra-*O*-acetyl-α-D-glucofuranosyl)biphenyl (**5**, 80 mg), m.p. 151–152°, $[\alpha]_D$ +27° (*c* 1.0); ν_{max} 1750 cm^{-1} (Ac); λ_{max} 210 and 253 nm (ε 27,000 and 21,000). For p.m.r. data, see Table I.

Anal. Calc. for $C_{26}H_{28}O_9$: C, 64.5; H, 5.8. Found: C, 64.6; H, 5.9.

The major component remaining in the 2-propanol mother liquor was sepa-

rated by preparative g.l.c. on column *B* at 290° and shown to be 4-(2,3,5,6-tetra-*O*-acetyl-β-D-glucofuranosyl)biphenyl (**6**), $[\alpha]_D$ −38° (*c* 1.0); ν_{max} 1,750 cm^{-1} (Ac); λ_{max} 210 and 253 nm (ε 27,000 and 21,000). For p.m.r. data, see Table I.

The product in fraction *C* was separated from the unreacted sulphone present by g.l.c. on column *A* at 150° and characterised as 2,3,5,6-tetra-*O*-acetyl-1,4-anhydro-D-glucitol (**7**), ν_{max} 1750 cm^{-1} (Ac). P.m.r. data are reported in Table I.

Upon deacetylation, this syrupy acetate gave crystalline 1,4-anhydro-D-glucitol, m.p. 112–114° (lit.[3] m.p. 114–115°) undepressed on admixture with an authentic sample.

Fraction *D* was an oil. P.m.r. data: δ 5.0–5.6 (m, 6H), 4.0–4.8 (m, 8H), 1.9–2.2 (m, 24H, 8AcO).

Anal. Calc. for $C_{28}H_{38}O_{18}$: C, 50.8; H, 5.8; mol. wt., 662. Found: C, 50.4; H, 6.1; mol. wt., 570 (Rast), 662 (mass spectrometry).

Its mass spectrum showed peaks typical of polyacetoxy derivatives, for example, base peak at *m/e* 43 (Ac^+), and the peaks at 103 (12%) and 145 (12%) for the di- and tri-acetoxonium ions Ac_2OH^+ and Ac_3O^+, respectively. The following five major fragmentation-pathways, which accounted for the most-intense ions, were observed:

$$M \xrightarrow{-AcO} 603\ (0.8\%) \xrightarrow{-2AcOH} 483\ (5.3\%)$$

$$M \xrightarrow{-2AcOH} 542\ (5.1\%) \xrightarrow{-AcOH} 482\ (5.3\%) \xrightarrow{-AcOH} 422\ (5.0\%)$$

$$542\ (5.1\%) \xrightarrow{-CH_2CO} 500\ (5.3\%) \xrightarrow{-CH_2CO} 458\ (5.0\%)$$

$$482\ (5.3\%) \xrightarrow{-CH_2CO} 440\ (13.0\%)$$

$$M \xrightarrow{-AcOCH_2\dot{C}HOAc} 517\ (5.3\%) \xrightarrow{-AcOH} 457\ (4.5\%) \xrightarrow{-CH_2CO} 415\ (5.0\%)$$

$$M \xrightarrow{-0.5M\cdot} 331\ (94\%) \xrightarrow{-2AcOH,\ -CH_2CO} 169\ (79\%)$$

$$103 \xleftarrow{-CH_2CO} AcOCH_2\overset{+}{C}HOAc \xrightarrow{-AcOH} 85\ (14\%)$$

The oil was deacetylated and the polyol mixture so formed was trimethylsilylated in the usual fashion[1]. G.l.c. analysis on column *C* at 240° showed three compounds, *T* 15, 18, and 20 min, in the ratios of 3:1:3.

(*b*) *Phenyl 2,3,5,6-tetra-*O*-acetyl-β-D-glucofuranosyl sulphone* (**9**). A 2.5% benzene solution of **9** (100 mg) was irradiated in a quartz tube (diameter, 1 cm) fixed to the side of the photolysis well. T.l.c. analysis showed that products were formed similar to those produced during the irradiation of the α-D anomer.

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REFERENCES

1 Part I: P. M. COLLINS AND B. R. WHITTON, *J. Chem. Soc. Perkin I*, (1974) in the press.
2 I. M. SARKAR, J. C. ARTHUR, JR., AND O. HINOJOSA, *Carbohyd. Res.*, 6 (1968) 333; P. J. BAUGH, K. KERSHAW, AND G. O. PHILLIPS, *J. Chem. Soc., B*, (1970) 1482.
3 E. ZISSIS, A. L. CLINGMAN, AND N. K. RICHTMYER, *Carbohyd. Res.*, 2 (1966) 461.
4 A. BURAWOY AND E. SPINNER, *J. Chem. Soc.*, (1955) 2085.
5 E. A. BRAUDE AND W. F. FORBES, *J. Chem. Soc.*, (1955) 3776.
6 B. CAPON AND D. THACKER, *Proc. Chem. Soc.*, (1964) 369.
7 W. E. HILLIS AND D. H. S. HORN, *Aust. J. Chem.*, 16 (1963) 147.
8 K. BIEMANN, D. C. DEJONGH, AND H. K. SCHNOES, *J. Amer. Chem. Soc.*, 85 (1963) 1763.
9 M. ARITOMI, T. KOMORI, AND T. KAWASAKI, *Ann.*, 734 (1970) 91.
10 N. KHARASCH AND A. I. A. KHODAIR, *Chem. Commun.*, (1967) 98.