The Photochemistry of Ketones derived from Carbohydrates. Part 9.[1] Formation of *O*- and *C*-Ribofuranoside Derivatives by Photodecarbonylation of *O*- and *C*-Glycosides of *lyxo*-Hexopyranos-4-ulose Derivatives

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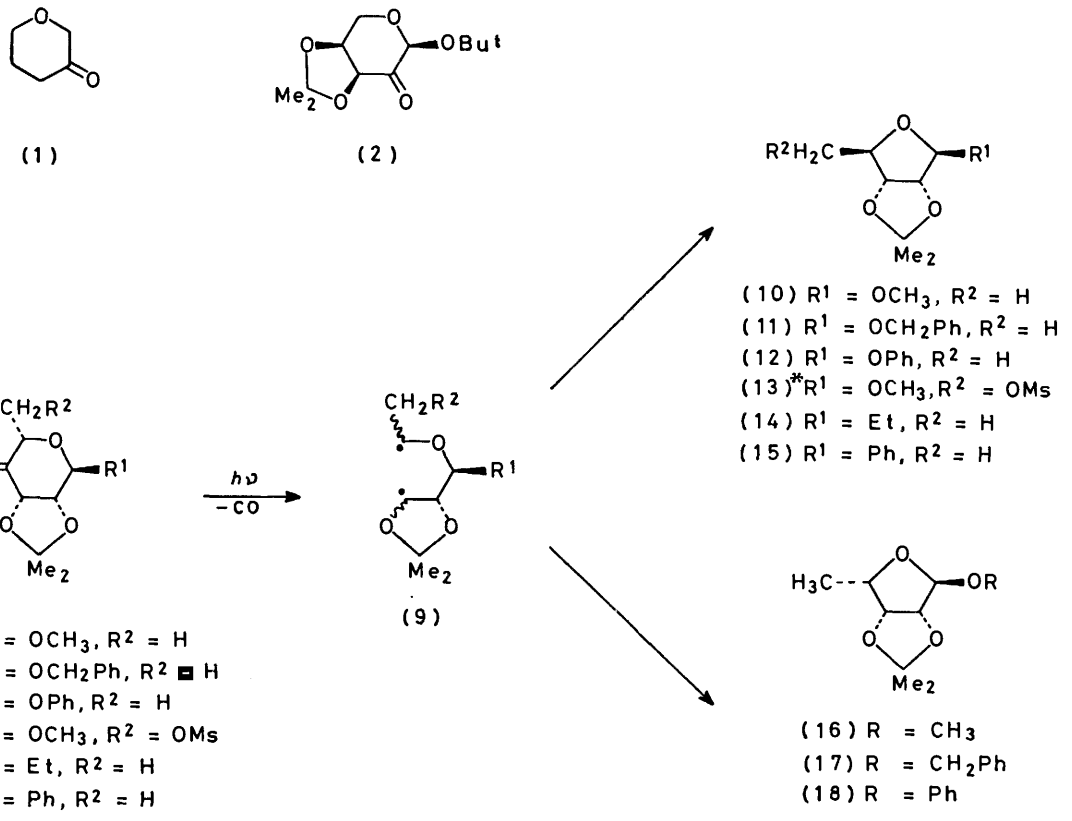
The syntheses of 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosyl-4-ulose-ethane (7) and -benzene (8), and the assignment of their anomeric configurations by ^1H and ^{13}C n.m.r. spectroscopy, are described. The preparations of a number of *O*-glycosid-4-ulose derivatives [(4)—(6) and (19)] related stereochemically to these *C*-glycosides are also reported. Irradiation of all these 4-ulose derivatives in solution with u.v. light causes them to decarbonylate and form as the sole non-polar photoproducts the respective *O*- and *C*-furanosides with preponderantly the β-D-*ribo*-structure.

WE have found that some pyranosulose derivatives which possess a tetrahydropyran-3-one ring structure (1) undergo photochemical decarbonylation in solution. The pyranosid-2-ulose derivatives [*e.g.* (2)] upon loss of carbon dioxide ring-contract to furanosides or give olefins,[1] whereas the pyranosid-4-ulose derivatives [*e.g.* (3)] give only furanosides.[2] As part of our research programme we plan to see if this result is true for all pyranosidulose derivatives with the tetrahydropyran-3-one structure and also to find if it holds for a range of blocking groups. As a first step in this programme we report the results for six 4-ulose derivatives which are stereochemically related to the α-L-*lyxo*-ketone (3). In later papers we will report on 4-ulose derivatives with different stereochemical configurations.

RESULTS AND DISCUSSION

All the hexopyranos-4-ulose derivatives described in this paper were prepared specifically for the photochemical investigation. Compounds (4) and (5) were synthesised without difficulty by sequential isopropylidenation [3] and ruthenium tetraoxide oxidation [4] of the respective benzyl and phenyl α-L-rhamnopyranosides, both of which were prepared by standard procedures.[5,6]

Treatment of methyl α-D-mannopyranoside 6-mesylate in the same reaction sequence gave (6) but the isopropylidenation step proved troublesome. The 2,3-positions were acetonated only by using 2,2-dimethoxypropane in dimethylformamide containing toluene-*p*-sulphonic acid,[7] but oxidation with ruthenium tetraoxide was straightforward giving a crystalline, fully



*Drawn as the enantiomer

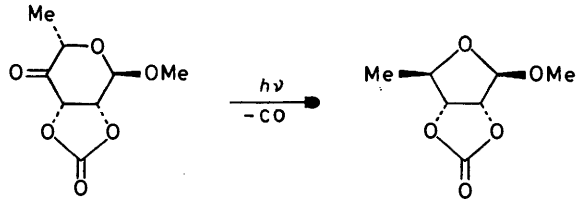
TABLE 1

220 MHz ^{1}H N.m.r. δ and J/Hz values for 2,3,4-tri-*O*-acetyl-6-deoxy-α- and -β-L-mannopyranosylethanes (21) and (22) in $CDCl_3$

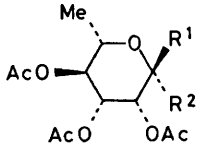
Compound	H-1	H-2	H-3	H-4	H-5	H-6	CH_2		CH_3	OAc
							B	A		
(21)	3.76 (ddd, $J_{1,2}$ 1.6, $J_{1,A}$ 9.0, $J_{1,B}$ 5.0)	5.22—5.15 (m)		5.02 (t, $J_{4,5}$ 8.8, $J_{4,3}$ 9.0)	3.71 (dq, $J_{5,6}$ 6.4, $J_{5,4}$ 8.8)	1.20 (d, $J_{6,5}$ 6.4)	1.61 (m)	1.81 (m)	0.96 (t, J 7.0)	2.08 2.00 1.96
					d (8.8)	Ird				
	dd (9,2)						Ird			
	dd (5,2)							Ird		
				d (9.0)	Ird					
(22)	3.4—3.6	5.35 (dd, $J_{2,1}$ 1.0, $J_{2,3}$ 3.0)	4.91 (dd, $J_{3,4}$ 10.0)	5.06 (t, $J_{4,5}$ 10.0)	3.4—3.6	1.20 (d, $J_{6,5}$ 6.0)	1.50 (m)		0.89 (t, J 7.0)	2.10 1.99 1.92
	Ird	d(3)	dd	d(10)	Ird					

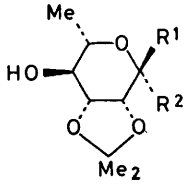
Ird = Irradiation carried out at designated chemical shift in a double-resonance experiment.

characterised 4-ulose derivative (6). Few pyranose derivatives with leaving groups at the 6-position have been oxidised at C-4 [8] because of the problem of elimination.[9] The 6-*O*-benzoyl analogue of mesylate (6) is a closely related rare example which was successfully prepared by chromium trioxide–pyridine oxidation.[8] Dimethyl sulphoxide in acetic anhydride gave only a 4-(methylthio)methyl ether. In the present study we found that the 6-*O*-*p*-tolylsulphonyl analogue of (6) could not be oxidised to give an adequately characterised pyranos-4-ulose suitable for photochemical study. The structures of (4)—(6) follow from their elemental compositions and their m.s., n.m.r., and i.r. spectral features. In particular the pattern of the proton resonances for H-1, -2, and -3 of (4) and (5) are very similar to those of the more common methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (3).



(19) (20)





(21) R^1 = Et, R^2 = H
(22) R^1 = H, R^2 = Et
(23) R^1 = Ph, R^2 = H
(24) R^1 = H, R^2 = Ph

(25) R^1 = Et, R^2 = H
(26) R^1 = H, R^2 = Et
(27) R^1 = Ph, R^2 = H
(28) R^1 = H, R^2 = Ph

In the preparation of (19) the only difficult step in the reaction sequence was the 2,3-carbonylation of methyl α-L-rhamnopyranoside. The well established method using phosgene [10] gave only 12% of the required product and the newer method of Ishido *et al.*[11] using 1,1'-carbonyldi-imidazole proved little better, giving a 15% yield. However treating methyl α-L-rhamnopyranoside with 1.1 mol equiv. of bis(ethoxythiocarbonyl) disulphide as described by Doane *et al.*[12] was more satisfactory, since the cyclic 2,3-carbonate was produced in 30% yield. Oxidation of this material with ruthenium tetraoxide was accomplished in high yield to give (19) as a crystalline, fully analysed product. As far as we are aware this is the first example of a pyranosidulose carbonate derivative.

The ^{1}H n.m.r. spectrum was less well resolved than that of the isopropylidene analogue (3), because the resonances for H-2 and -3 were deshielded relative to these signals in (3), causing H-1, -2, and -3 to have similar chemical shifts.

The most time-consuming operation in the syntheses of (7) and (8) was the formation of the *C*-glycosidic linkage and the subsequent separation and assignment of anomeric configuration. Bonner's method [13] of preparation was used, acetochlororhamnopyranose being condensed with either ethyl- or phenyl-magnesium bromide.

The rhamnopyranosylethane triacetate anomers (21) and (22), which resulted from the condensation with the former Grignard reagent, were present in the mixture in a 1.6 : 1 ratio, as shown by g.l.c. The major isomer was anticipated to have the α-L-configuration since condensations with acetylated pyranosyl halides appear to produce *C*-glycosides with the 1,2-*trans*-configuration.[14] In later work, where non-participating blocking groups have been used with furanosyl halides [15,16] and pyranosyl halides,[17] larger amounts of *C*-glycosides with the 1,2-*cis*-configuration have been formed. The anomeric mixture was separated by fractional crystallisation into (21) and (22). These compounds possessed identical elemental compositions and their ^{1}H 220-MHz n.m.r. spectra recorded in Table 1 exhibited signals for one *C*-methyl, one *C*-ethyl, and three acetoxy-groups. Signals for five pyranosyl ring protons were also present and these appeared in two groups, the chemically similar α-alkoxy H-1 and -5 protons resonating between δ 3.4 and 3.8 and the acetoxy-methine protons H-2, -3, and -4

resonating between δ 4.9 and 5.4. By recourse to several double-resonance experiments outlined in Table 1 most of the vicinal couplings in the pyranosyl ring were obtained.

The minor component ($[\alpha]_D^{22}$ +17°) had vicinal couplings $J_{1,2}$ 1.0, $J_{2,3}$ 3.0, $J_{3,4}$ 10.0, and $J_{4,5}$ 10.0 Hz. The last three values indicate a $^1C_4$ conformation for the rhamnopyranosyl ring in agreement with the results which Vliegenthart and his co-workers [18] found for rhamnoside derivatives. Thus this material probably has the β-L-configuration, as anticipated, in which the bulky ethyl group is equatorially orientated. The major component ($[\alpha]_D^{22}$ +1.0°) possessed $J_{1,2}$ 1.6, $J_{3,4}$ 9.0, and $J_{4,5}$ 8.8 Hz. The last two vicinal couplings indicate that the rhamnopyranosyl ring has a slightly flattened $^1C_4$ conformation which would arise in the α-L-anomer (21) owing to the size of the axial (or quasi-axial) ethyl group. The optical rotations agree with the assignment of the α-L- and β-L-configurations (21) and (22), respectively, to the major and minor products.

The ^{13}C n.m.r. spectra of these isomers confirms the stereochemistry proposed. Signals were observed for all the carbon atoms, although specific assignments to the rhamnosyl ring carbon atoms could not be made with certainty. The resonances for C-6 of the equatorial methyl groups occurred at δ 17.78 p.p.m. in both (21) and (22), whereas the signal of the methylene carbon of the ethyl group resonated at δ 21.92 for (21) and at 23.79 p.p.m. for (22), which is consistent with an equatorially disposed ethyl group in the latter compound and a more sterically crowded axial (or quasi-axial) arrangement for the former.[19] The Σδ values for the carbon atoms in the rhamnopyranosyl ring were informative.[20] For (22) and (21) they were respectively δ 366.26 and 356.45 p.p.m. which suggest a less sterically crowded arrangement for (22), in keeping with a compound possessing two equatorial alkyl groups as found in the β-L-anomer (22).

Compounds (21) and (22) were deacetylated and then partially blocked at the 2,3-positions with acetone to give (25) and (26) respectively which were characterised spectroscopically. The α-L-anomer (25) was converted with ruthenium tetraoxide to an unstable syrup which was shown to be the 4-ulose derivative (7) from its $\lambda_{max.}$ (273 nm) and its $\nu_{max.}$ (1 735 cm^{-1}) (indicative of a ketone) and its strong *m/e* peak at 199 $(M - 15)^{+\cdot}$. Signals for all the protons in the 100-MHz ^1H n.m.r. spectrum, except for those of the methylene of the ethyl residue, could readily be analysed by first-order methods, as indicated in Table 2. Since H-1 was deshielded less than the other ring protons it appeared upfield from them leaving H-2, -3, and -5 grouped together and not easy to assign. However the signal for H-2 was eventually picked out by decoupling it from H-1. In this fashion the H-3 and -5 signals were also exposed and analysed.

The conformation adopted by (7) differs from that of the triacetate (21) from which it was derived. The most reasonable Dreiding model that can be constructed for this 4-ulose derivative has dihedral angles $\phi_{1,2}$ and $\phi_{2,3}$ which measure 160 and 10° respectively. These agree closely with the angles calculated [21] from the $J_{1,2}$ 8.0 and $J_{2,3}$ 8.0 Hz values measured in its ^1H n.m.r. spectrum in Table 2.

The anomeric mixture of rhamnopyranosylbenzene triacetates (23) and (24) formed in the reaction between phenylmagnesium bromide and acetorhamnopyranosyl chloride could not be separated. Consequently the mixture was sequentially deacetylated and acetonated to give a product which was successfully fractionated on silica gel into two compounds (27) and (28). Both had identical elemental compositions and a hydroxyl-absorption at 3 500 cm^{-1}.

The major component had $[\alpha]_D^{22}$ −23° and $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ vicinal couplings of 6.0, 6.0, and 6.5 Hz respectively (see Table 3) whereas the minor product had $[\alpha]_D^{22}$ +1.0° and vicinal couplings of 2.5, 5.5, and 7.0 Hz. The major product was expected [14] to have the α-L-configuration (27) and application of Hudson's rule supports this view. The minor product therefore has the β-L-configuration (28) and the values for $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ corroborate this conclusion since they are very similar to those measured for the β-ethyl analogue (26) (see Table 3).

Oxidation of the α-L-compound (27) gave an unstable

TABLE 2

100-MHz ^1H N.m.r. δ and *J*/Hz for 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosyl-4-ulose-ethane and -benzene in $CDCl_3$

Compound	H-1	H-2	H-3	H-5	H-6	Me_2	Substituent
(7)	3.26 (dt, $J_{1,2}$ 8.0, $J_{1,A}$ 8.0, $J_{1,B}$ 4.4) Ird	4.40 (t, $J_{2,3}$ 8.0, $J_{2,1}$ 8.0) d (8.0)	4.64 (dd, $J_{3,2}$ 8.0 $J_{3,5}$ 1.0)	4.29 (q, $J_{5,6}$ 7.2)	1.36 (d, $J_{6,5}$ 7.2)	1.38 (s) 1.44 (s)	CH_3 1.02 (t) CH_AH_B 1.60 (m)
(8)	4.72 (d, $J_{1,2}$ 6.0)	4.64 (dd, $J_{2,3}$ 7.5, $J_{2,1}$ 6.0)	4.34 (d, $J_{3,2}$ 7.5)	4.26 (q, $J_{5,6}$ 6.0)	1.40 (d, $J_{6,5}$ 6.0)	1.36 (s) 1.50 (s)	Ph 6.9—7.4 (m)

TABLE 3

Vicinal couplings (Hz) for 6-deoxy-2,3-*O*-isopropylidene α- and β-L-mannopyranosyl-ethane and -benzene in $CDCl_3$

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{5,6}$
(27)	6.0	6.0	6.5	6.0
(28)	2.5	5.5	7.0	6.0
(26)	2.5	6.0	6.0	6.0
(25)		Not resolved		

syrup which could be formulated as the 4-ulose derivative (8), from $\nu_{max.}$ at 1 745 cm^{-1} (C=O), the *m/e* peak at 247 for the $M - 15$ ion, and a satisfactory ^1H n.m.r. spectrum (Table 2) that yielded values for vicinal couplings between ring protons similar to those found in the spectrum of the ethyl analogue (7).

All the 4-ulose derivatives studied were irradiated as *ca.* 1% solutions in benzene at 22 and 60° with the full arc from a 450-W medium-pressure mercury lamp. The temperature affected the photochemistry of compounds (7) and (8) only. Consequently for these compounds the high temperature experiments will be discussed in addition to those carried out at 22°.

The photolyses were monitored chromatographically, t.l.c. being used for the mesylate (6) and g.l.c. for the other 4-ulose derivatives. This showed that materials less polar than the isopropylidenated uloses were formed. Irradiations were continued to maximise the product yield, which usually coincided with complete reaction of the ketone.

The benzyl and phenylglycosides of 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranos-4-ulose (4) and (5), which are most closely related to the model ketone (3), each yielded two photoproducts with very similar g.l.c. retention times. These were considered to be isomeric furanosides by analogy with the photoproducts (10) and (16) obtained from (3). The two photoproducts from the benzyl glycosidulose (4) were present in a 1 : 10 ratio and they were isolated by distillation at reduced pressure in 40% yield. The major component, which was freed from the minor one by preparative g.l.c., was formulated as benzyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (11) from its elemental composition, and the first-order analysis of its ^1H n.m.r. spectrum shown in Table 4. The minor component exhibited a signal at δ 5.08 in the spectrum of the photoproduct mixture with an intensity equal to one-tenth of a proton. This was thought to be the signal of the anomeric proton of the α-L-*lyxo*-isomer (17) because it was shielded by 0.07 p.p.m. relative to the anomeric proton of (11) (see Table 4). This difference is identical to that found between the resonances of the anomeric protons of the methyl glycofuranosides of these two sugars [*i.e.* (10) and (16)].[22]

The two photoproducts formed from the phenyl glycosidulose (5) were isolated by distillation but they could not be separated. The n.m.r. spectrum of the distilled mixture indicated that they were formed in a 9 : 2 ratio and from the prominent resonances recorded in Table 4, the major product was assigned structure (12). The minor component, with an anomeric proton signal at δ 5.62 [deshielded by 0.06 p.p.m. relative to this proton in (12)] was assumed to be the α-L-lyxofuranoside isomer (18).

The influence that protecting groups have upon the course of these photochemical reactions has been studied. From ketone (19) in which the *O*-2,*O*-3 positions are blocked with a carbonyl group, in place of an isopropylidene residue, a photoproduct was isolated in 22% yield by preparative layer chromatography. It was shown to be methyl 2,3-*O*-carbonyl-5-deoxy-β-D-ribofuranoside (20) by i.r., m.s., and n.m.r. spectroscopy (see Table 4).

The effect of replacing the C-5 methyl group with a blocked hydroxymethyl group was investigated with the 6-*O*-methylsulphonyl derivative (6). One non-polar photoproduct was formed from this compound and this was isolated by column chromatography in 43% yield. It was formulated as the 5-*O*-mesyl-L-riboside derivative (13) from its elemental analysis, and 220-MHz ^1H n.m.r. spectrum given in Table 4. The enantiomer of this compound is known [23] and its physical constants compare closely with those of (13). It yielded L-ribose upon demesylation and hydrolysis. Efforts to examine the photochemistry of the tosyl analogue of (6) were thwarted because this 4-ulose proved too reactive to be isolated.

TABLE 4

^1H N.m.r. parameters (δ; *J*/Hz) for *O*- and *C*-glycosides of 2,3-*O*-isopropylidene-β-D-ribofuranosides in $CDCl_3$

Compound	H-1	H-2	H-3	H-4	H-5	Me_2	1-Substituent
(10) [a]	4.80 (s, $J_{1,2}$ <0.5)	4.50 (d, $J_{2,3}$ 6.0)	4.36 (d, $J_{3,4}$ <1.0)	4.20 (q, $J_{4,5}$ 7.0)	1.20 (d, $J_{5,4}$ 7.0)	1.41, 1.25 (2s)	3.25 (s)
(11a) [a]	5.15 (s, $J_{1,2}$ <0.5)	4.74 (d, $J_{2,3}$ 6.0)	4.55 (d, $J_{3,4}$ <0.5)	4.42 (q, $J_{4,5}$ 7.0)	1.35 (d, $J_{5,4}$ 7.0)	1.48, 1.32 (2s)	4.75 (d), 4.48 (d, *J* 12), 7.3 (m)
(12) [a]	5.68 (s, $J_{1,2}$ <0.5)	4.91 (d, $J_{2,3}$ 6.5)	4.60 (d, $J_{3,4}$ <1.0)	4.43 (q, $J_{4,5}$ 7.0)	1.26 (d, $J_{5,4}$ 7.0)	1.50, 1.34 (2s)	7.1 (m)
(13) [b,c]	4.98 (s, $J_{1,2}$ <0.5)	4.61 (d, $J_{2,3}$ 6.0)	4.69 (d, $J_{3,3}$ <1)	4.41 (dd, $J_{4,5}$ 7.0, $J_{4,5}$ 8.0)	4.20 (d, 5-H), 4.21 (d, 5′-H)	1.47, 1.32 (2s)	3.34 (s)
(20) [a]	5.04 (s, $J_{1,2}$ <0.5)	4.99 (d, $J_{2,3}$ 6.5)	4.85 (d, $J_{3,4}$ <1)	4.48 (q, $J_{4,5}$ 7.0)	1.35 (d, $J_{5,4}$ 7.0)		3.32 (s)
(15) [b]	4.74 (d, $J_{1,2}$ 5.0)	4.56 (dd, $J_{2,3}$ 7.0)	4.36 (dd, $J_{3,4}$ 5.0)	4.11 (dq, $J_{4,5}$ 6.5)	1.38 (d, $J_{5,4}$ 6.5)	1.56, 1.72 (2s)	7.2 (m)
(14) [b]	3.71 (dt, $J_{1,2}$ 4.8, $J_{1,A}$ 6.5, $J_{1,B}$ 6.5)	4.32 (dd, $J_{2,3}$ 7.3)	4.22 (dd, $J_{3,4}$ 5.0)	3.89 (qd, $J_{4,5}$ 6.0)	1.31 (d, $J_{5,4}$ 6.0)	1.53, 1.34 (2s)	1.0 (t, *J* 7.5), 1.7 (m)

[a] 100 MHz. [b] 220 MHz. [c] δ 3.08 (CH_3SO_2).

The *C*-glycosiduloses (7) and (8) differed most markedly from the model compound (3) since they do not have an oxygen atom at C-1. Thus the electronic effects in (7) and (8) would be different from those present in all the other glycosiduloses studied and furthermore, because the erstwhile anomeric effect is absent in these pyranosyluloses, conformational changes would also occur. Consequently these compounds might have been expected to exhibit photochemistry different from that which we have found for the *O*-glycosides. Upon irradiation at 60°, (7) and (8) each gave one g.l.c.-detectable photoproduct in similar high yields (65%). These were the only compounds in this study which gave improved yields at high temperatures. At 22° the conversions of ketones (7) and (8) into products were only 30 and 40% respectively.

The product from the ethyl compound (7) was isolated by preparative g.l.c., whereas that from the phenyl compound (8) was purified by fractional distillation under reduced pressure. The assignment of gross structures (14) and (15) respectively to these materials from their 220 MHz ^{1}H n.m.r. spectra was relatively easy. However, determination of the stereochemistry was initially less straightforward. *O*-Glycofuranosides with the β-D-*ribo*-structure have couplings in the following range $J_{1.2}$ <0.5, $J_{2.3}$ 6.0—7.5, $J_{3.4}$ <1.0 Hz, as shown in Table 4, whereas the ring proton couplings in the *C*-glycofuranosides (14) and (15) are $J_{1.2}$ *ca.* 5.0, $J_{2.3}$ *ca.* 7.0, and $J_{3.4}$ 5.0 Hz. At first sight it appeared that these *C*-glycosides possessed the alternative configurations at C-4 and C-1, *viz.* the β-L-*lyxo*-structure. Moffatt and his co-workers [16] have, however, shown that *C*-glycosides with 2,3-*O*-isopropylidene-β-D-ribofuranosyl structures have $J_{1.2}$ 3.5—4.5, $J_{2.3}$ 6.0—7.0, and $J_{3.4}$ 3.5—5.0 Hz. Thus (14) and (15) can be formulated as 2,3-*O*-isopropylidene-β-D-ribofuranosyl-ethane, and -benzene respectively.

The same ring-contracted products as those produced in benzene solutions were formed from all these ketones when they were irradiated in n-pentane, t-butyl alcohol, or methanol. Solutions of ketones (4) and (5) in the alcohols yielded additional trace amounts of materials, which i.r. spectroscopy indicated were esters, presumably arising from a non-decarboxylated keten intermediate, a result which closely parallels the photolysis of (3) in these solvents. Such products were not detected in irradiated alcoholic solutions of the other ketones. Photoreductions in methanol, of the type found with the 3-ulose derivatives, [24] were not observed with any of the ketones in this study.

Thus this investigation shows that ketones (4)—(8) and (19) undergo the same photochemical decarbonylation reaction in solution as the stereochemically related ketone (3). Presumably diradicals of the type (9) are involved in all cases, which stereoselectively ring-close to give furanosides with the β-D-*ribo*-structure, preferentially to the α-L-*lyxo*-structure, in which there is an unfavourable '*cis*' interaction between the C-4 methyl group and the C-3 and possibly the C-2 substituents.

Olefins, which could be formed by intramolecular hydrogen atom transfer [25] in radicals of the type (9) were not produced. Thus the difference noted earlier [1] between the photoreactions of 4-ulose derivatives with the α-L-*lyxo*-stereochemistry and 2-ulose derivatives, which form considerable amounts of olefins, is maintained with the compounds studied in this work.

EXPERIMENTAL

Unless stated otherwise, optical rotations were measured on chloroform solutions with a Bellingham and Stanley polarimeter, u.v. absorption spectra were measured with a Perkin-Elmer 402 spectrometer on ethanol solutions, and i.r. spectra were measured on solids dispersed in potassium bromide discs and on gums smeared on sodium chloride plates with a Perkin-Elmer Infracord model 137. ^{1}H N.m.r. spectra were measured on samples dissolved in $CDCl_3$ with Varian Associates EM360 or HA220MH or JEOL MH100 instruments. ^{13}C N.m.r. spectra were measured on chloroform solutions with tetramethylsilane as internal reference on a JEOL FX60 instrument operating in the Fourier-transform mode.

Column chromatography was carried out on Kieselgel 60 (70—230 mesh) and t.l.c. on Kieselgel G_{254}. Varian Aerograph models 2700 with flame ionisation and thermal conductivity detectors were used for g.l.c. Retention times of a component are expressed as R_t in min or relative to a compound X when R_x is used.

Benzyl 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose* (4).—L-Rhamnose (10 g) was heated with benzyl alcohol (150 ml) in benzene (100 ml) in the presence of Amberlite resin IR-120 (H^+) (2.5 g) for 8 h at 95° under a Dean and Stark apparatus.[26] The syrup obtained on work up gave, after chromatography, benzyl α-L-rhamnopyranoside (R_F 0.4, EtOAc) (5.6 g, 36%), m.p. 76—78°, $[\alpha]_D^{22}$ −58.3° (*c* 0.8, H_2O), δ(D_2O) 4.84 (d, $J_{1.2}$ 1.5 Hz), 3.92 (dd, $J_{2.3}$ 2 Hz), 3.42 (t, $J_{4.3} = J_{4.5} = 9.0$ Hz), 3.5—3.8 (2 H, H-3, -5), 1.28 (d, $J_{6.5}$ 6.5 Hz), 4.50 and 4.65 (2d, J_{gem} 12.0 Hz), 7.36 (s, Ph).

The rhamnoside (5 g) was acetalated with acetone (100 ml) containing copper(II) sulphate (0.4 g) and sulphuric acid (1 ml) during 12 h at 21°. The usual work-up gave, after crystallisation from butan-2-ol, *benzyl* 2,3-O-*isopropylidene*-α-L-*rhamnopyranoside* (4.1 g, 71%), m.p. 69—71°, $[\alpha]_D^{22}$ −54.2° (*c* 1.1), δ 5.00 (s, H-1), 4.12 (d, $J_{2.3}$ 6.0 Hz), 4.04 (t, $J_{3.4}$ 6.0 Hz), 3.32 (dd, $J_{4.5}$ 9.0 Hz), 3.68 (dq, $J_{5.6}$ 6.0 Hz), 3.08br (s, OH), 1.50 and 1.32 (2s, Me_2C), 4.68 and 4.46 (2d, J_{gem} 12.0 Hz, CH_2Ph), and 7.28 (s, Ph) (Found: C, 64.9; H, 7.7. $C_{16}H_{22}O_5$ requires C, 65.3; H, 7.55%).

The free hydroxy-group of the isopropylidenated rhamnoside (3 g) was oxidised with ruthenium, tetraoxide in the usual manner.[4] After 1 h, g.l.c. on 10 ft 10% SE30 at 220° revealed that the alcohol with R_t 10.6 min had been transformed into a ketone with R_t 9.8 min.

The usual work-up followed by chromatography gave the pure 4-*ulose* (4) (2.3 g, 77%) (R_F 0.95, CH_2Cl_2–EtOAc, 3 : 1), $[\alpha]_D^{22}$ −76.5° (*c* 1.0), $\nu_{max.}$ 1 730 cm^{-1} (C=O), $\lambda_{max.}$ 251, 257, and 263 nm, δ (100 MHz) 4.86 (s, H-1), 4.30 (2 H, s, H-2, -3), 4.16 (q, $J_{5.6}$ 6.2 Hz), 1.36 (d, Me), 1.32 and 1.44 (2s, Me_2C), 4.42 and 4.62 (2d, J_{gem} 10.5 Hz, CH_2Ph), and 7.12 (s, Ph), *m/e* 291 $(M - 1)^{+\cdot}$ and 277 $(M - 15)^{+\cdot}$ (Found: C, 66.0; H, 6.95. $C_{16}H_{20}O_5$ requires C, 65.75; H, 6.9%).

Phenyl 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose* (5).—An anomeric mixture of 1,2,3,4-tetra-

O-acetyl-L-rhamnose (20 g) was fused with phenol (20 g) in the presence of zinc chloride (5 g) at 125° for 0.5 h under a pressure of 15 mmHg according to the method of Helferich.[6] Work-up followed by recrystallisation from ethanol gave phenyl 2,3,4-tri-*O*-acetyl-α-L-rhamnoside as needles (4.0 g, 18%), m.p. 123—125°, $[\alpha]_D^{22}$ −79° (*c* 1.3), δ (100 MHz) 5.34 (s, H-1), 5.32 (d, $J_{2,3}$ 3.0 Hz), 5.42 (dd, $J_{3,4}$ 9.5 Hz), 5.04 (t, $J_{4,5}$ 9.5 Hz), 3.92 (dq, $J_{5,6}$ 6.5 Hz), 1.18 (d, Me, $J_{6,5}$ 6.5 Hz), 2.12, 2.00, and 1.98 (3s, 3Ac), and 6.8—7.3 (m, Ph).

The rhamnoside triacetate (3.2 g) was deacetylated by the Zemplen method and the syrupy phenyl rhamnoside (1.9 g) so formed was dissolved in acetone (25 ml) containing sulphuric acid. After 24 h at room temperature the solution was neutralised, evaporated, and chromatographed to give phenyl 2,3-*O*-isopropylidene-α-L-rhamnoside (1.2 g, 55%), δ (60 MHz) 5.87 (s, H-1), 4.48 (d, $J_{2,3}$ 6.0 Hz), 4.35 (t, $J_{3,4}$ 6.0 Hz), 3.50 (dd, $J_{4,5}$ 9.0 Hz), 3.92 (dq, $J_{5,6}$ 6.5 Hz), 1.27 (d, $J_{6,5}$ 6.5 Hz), 1.43 and 1.60 (2s, Me_2C), 7.6—6.9 (m, Ph), and 3.0—2.8 (OH).

Oxidation of the product (1 g) gave the title 4-*ulose* (5) (0.45 g, 44%), m.p. 142—144° (crystallised during 4 weeks from propan-2-ol), $[\alpha]_D^{22}$ −129° (*c* 2.1, CH_2Cl_2), $\nu_{max.}$ 1 740 cm^{-1} (C=O), $\lambda_{max.}$ 261, 267, and 274 nm, δ (60 MHz) 5.82 (s, H-1), 4.73 (2- H, s, H-2, -3), 4.36 (q, $J_{5,6}$ 7.0 Hz), 1.38 (d, $J_{6,5}$ 7.0 Hz), 1.45 and 1.57 (2s, Me_2C), and 7.6—7.1 (m, Ph) (Found: C, 64.45; H, 6.4. $C_{15}H_{18}O_5$ requires C, 64.75; H, 6.5%).

Methyl 6-*Deoxy*-2,3-O-*carbonyl*-α-L-lyxo-*hexopyranosid*-4-*ulose* (19).—A solution of methyl α-L-rhamnopyranoside (10 g) and bis(ethoxycarbonyl) disulphide [12] (18 g) in acetone (40 ml) containing dimethyl sulphoxide (4 ml) and triethylamine (25 ml) was left at ambient temperature for 2 h. The small amount of solid that was formed was filtered off and the solution evaporated to low volume, water (10 ml) added and the product extracted into dichloromethane (20 ml × 3). The combined extracts were evaporated to afford a gum which was triturated with light petroleum (b.p. 40—60°). The solid mass was recrystallised from ethyl acetate–light petroleum to furnish methyl 2,3-*O*-carbonyl-α-L-rhamnopyranoside (3.9 g, 30%), m.p. 160—162°, $[\alpha]_D^{22}$ −71.3° (*c* 1.1, CH_2Cl_2), $\nu_{max.}$ 3 500 and 1 850 cm^{-1} (OH and cyclic carbonate), δ (100 MHz) 4.88 (s, H-1), 4.5—4.7 (2 H, m, H-2, -3), 3.50 (dd, $J_{4,3}$ 5.5 Hz), 3.72 (dq, $J_{5,4}$ 8.5 Hz), 1.34 (d, $J_{6,5}$ 6.0 Hz), 2.88 (s, OH), and 3.38 (s, OMe).

The product was oxidised with ruthenium tetraoxide in dichloromethane to give, after recrystallisation from ethyl acetate–light petroleum (b.p. 60—80°), the 4-*ulose derivative* (19) (2.3 g, 90%), m.p. 96—98°, $[\alpha]_D^{22}$ −125° (*c* 1.0, CH_2Cl_2), $\nu_{max.}$ 1 850 and 1 750 cm^{-1} (cyclic carbonate and ketone C=O), $\lambda_{max.}$ 273 nm (ε 2 080), δ (60 MHz) 4.85—5.15 (3 H, m, H-1, -2, -3), 4.41 (q, $J_{5,6}$ 7.0 Hz), 1.56 (d, $J_{6,5}$ 7.0 Hz), and 3.60 (s, OMe) (Found: C, 47.7; H, 5.05. $C_8H_{10}O_6$ requires C, 47.55; H, 5.0%).

Methyl 2,3-O-*Isopropylidene*-6-O-*methylsulphonyl*-α-D-lyxo-*hexopyranosid*-4-*ulose* (6).—Methyl α-D-mannopyranoside (20 g) was selectively sulphonylated in the usual way [27] to give methyl 6-*O*-methylsulphonyl-α-D-mannopyranoside (23 g) as a gum, δ (60 MHz) 3.50 (s, OMe) and 3.37 (s, SO_2Me). The sulphonate (23 g) dissolved in the minimum amount of *NN*-dimethylformamide was treated with 2,2-dimethoxypropane (200 ml) containing toluene-*p*-sulphonic acid (0.5 g). Work-up and recrystallisation from propan-2-ol gave the 2,3-*O*-isopropylidene derivative (18 g, 56% overall), m.p. 100—102°, $[\alpha]_D^{22}$ +39° (*c* 0.6), δ (60 MHz) 4.96 (s, H-1), 3.3—3.9 (3 H, m), 4.1—4.3 (2 H, m), 4.4—4.6 (2 H, m), 3.40 (s, OMe), 3.08 (s, SO_2Me), and 1.36 and 1.52 (2s, Me_2C) (Found: C, 42.45; H, 6.2; S, 10.2. $C_{11}H_{20}O_8S$ requires C, 42.3; H, 6.45; S, 10.25%).

The isopropylidene derivative (4.0 g) was oxidised with ruthenium tetraoxide [from the dioxide (4.3 g)] in a mixture of dichloromethane (12 ml) and carbon tetrachloride (60 ml) to give, after recrystallisation from propan-2-ol, *methyl* 2,3-O-*isopropylidene*-6-O-*methylsulphonyl*-α-D-lyxo-*hexopyranosid*-4-*ulose* (6) (2.2 g, 50%), m.p. 114—116°, $[\alpha]_D^{22}$ +10.7° (*c* 0.6), $\nu_{max.}$ 1 750 cm^{-1} (C=O), δ (220 MHz; C_6D_6) 4.57 (s, H-1), 4.2—4.4 (m, H-2, -3), 4.0—4.2 (m, H-5, -6, -6′), 2.90 (s, OMe), 2.20 (s, SO_2Me), and 1.08 and 1.42 (2s, Me_2C) (Found: C, 42.5; H, 5.85; S, 10.4. $C_{11}H_{18}O_8S$ requires C, 42.6; H, 5.85; S, 10.3%).

6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosyl*-4-*ulose*-*ethane* (7).—2,3,4-Tri-*O*-acetyl-L-rhamnosyl chloride (28 g, 0.09 mol) in ether (500 ml) was added during 1 h to ethylmagnesium bromide (0.99 mol) in diethyl ether (500 ml) and the mixture was heated under reflux for 5 h. The product obtained on work-up was treated with acetic anhydride (800 ml) containing sodium acetate (20 g) at 100° for 3 h. A small quantity of the anomeric mixture of acetates was fractionated into two peaks, which were in a ratio 1.6 : 1, by g.l.c. on 10 ft of 10% SE30 at 170°. The crystals so obtained were used to seed a solution of the bulk of material in diethyl ether–light petroleum (b.p. 40—60°). The first crystals which separated were 1-*ethyl*-1-*deoxy*-2,3,4-*tri*-O-*acetyl*-α-L-*rhamnosylethane* (21) (4.1 g, 15%), m.p. 42—44°, $[\alpha]_D^{22}$ +1.0° (*c* 2.0). For the 220-MHz ^1H n.m.r. spectrum and double-resonance experiments, see Table 1, δ(^{13}C) 69.44, 71.71, 76.83, 71.14, 67.73, 17.78 (C-1 to -6), 21.92 and 10.07 (CH_2CH_3), and 20.79 (CH_3CO) (Found: C, 55.3; H, 7.45. $C_{14}H_{22}O_7$ requires C, 55.6; H, 7.35%).

The second crop of crystals was the β-L-anomer (22) (1.2 g, 4%), m.p. 74—76°, $[\alpha]_D^{22}$ +17.0° (*c* 1.6). For the 220-MHz ^1H n.m.r. spectrum and double-resonance experiments, see Table 1, δ(^{13}C) 71.22, 74.47, 78.29, 72.68, 69.60, 17.78 (C-1 to -6), 23.79 and 9.90 (CH_2CH_3), and 20.70 (CH_3CO).

The α-L-triacetate (4.1 g) was deacetylated to give the *C*-glycoside (2.0 g, 84%), which was acetonated during 24 h at 21° with acetone containing sulphuric acid to give 2,3-*O*-isopropylidene-α-L-rhamnopyranosylethane (1.8 g, 61%), δ (100 MHz) 3.0—4.4 (m, H-1, -2, -3, -4, and -5), 1.26 (d, $J_{6,5}$ 6.0 Hz), 1.28 and 1.42 (2s, Me_2), and 0.98 and 1.60 (t and m, CH_3CH_2).

The partially protected *C*-rhamnoside (1.5 g) was oxidised with ruthenium tetraoxide in carbon tetrachloride. When t.l.c. indicated that all the alcohol of R_F 0.4 (CH_2Cl_2–EtOAc, 3 : 1) had been changed into ketone of R_F 0.9 the reaction was worked up and the product purified by distillation to give 2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosyl-4-ulose-ethane (7) as an unstable clear syrup (0.8 g, 53%), $[\alpha]_D^{22}$ −15° (*c* 0.6), $\nu_{max.}$ 1 735 cm^{-1} (C=O), $\lambda_{max.}$ 273 nm (ε 50), *m/e* 215 $(M + 1)^+$, 214 $(M^{+\cdot})$, 199 $(M - 15)^+$. For 100-MHz n.m.r. spectrum and double-resonance experiments see Table 2.

6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosyl*-4-*ulosebenzene* (8).—2,3,4-Tri-*O*-acetyl-L-rhamnosyl chloride (15 g, 0.05 mol) was treated with phenylmagnesium bromide (0.5 mol) in ether and the product acetylated as described for the ethyl analogue. Column chromatography afforded an anomeric acetate mixture (12 g, 70%), which was

deacetylated and acetonated in the usual way. The products were fractionated on silica gel with light petroleum (b.p. 40—60°)–diethyl ether (2 : 1) into 2,3-*O*-isopropylidene-α-L-rhamnopyranosylbenzene (27) (3.5 g, 27%), $[\alpha]_D^{22}$ −23.2° (*c* 2.2), δ (100 MHz) 4.70 (d, $J_{1,2}$ 6.0 Hz), 4.36 (t, $J_{2,3}$ 6.0 Hz), 4.10 (dd, $J_{3,4}$ 6.5 Hz), 3.4—3.8 (m, H-4, -5), 1.30 (d, Me, $J_{6,5}$ 6.0 Hz), 1.32 and 1.52 (2s, Me_2C), 2.7 (s, OH), and 6.9—7.4 (m, Ph) (Found: C, 67.75; H, 7.6. $C_{15}H_{18}O_4$ requires C, 68.15; H, 7.65%), and the β-L-anomer (28) (1.0 g, 8%), m.p. 110—112°, $[\alpha]_D^{22}$ +1.1° (*c* 6.0), δ (100 MHz) 4.62 (d, $J_{1,2}$ 2.5 Hz), 4.26 (dd, $J_{2,3}$ 5.5 Hz), 3.98 (dd, $J_{3,4}$ 7.0 Hz), 3.2—3.7 (m, H-4, -5), 1.34 (d, Me, $J_{6,5}$ 6.0 Hz), 1.24 and 1.44 (2s Me_3C), 3.5 (s, OH), and 7.3—7.4 (m, Ph) (Found: C, 68.2; H, 7.5. $C_{15}H_{18}O_4$ requires C, 68.15; H, 7.65%).

The isopropylidenated α-L-rhamnosylbenzene (2 g) was oxidised in the usual way and the product purified on silica gel (CH_2Cl_2–EtOAc, 3 : 1) to give, as an unstable oil, 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosyl-4-ulosebenzene (8) (0.73 g, 37%), $\nu_{max.}$ 1 745 cm^{-1} (C=O), *m/e* 262 ($M^{+\cdot}$), 261 ($M - 1$)$^+$, 247 ($M - 15$)$^+$. The 220-MHz ^1H n.m.r. parameters are recorded in Table 2.

General Procedures for Irradiations.—Solutions of the ulose derivatives with volumes <100 ml were irradiated at 22 and 60° in quartz tubes situated 3 cm from the centre of a water-cooled 450-W medium-pressure mercury lamp. Solutions with volumes over 100 ml were irradiated in the annular space of a standard photolysis well at 20°. All solutions were agitated during their irradiation by the passage of nitrogen gas. The progress of the reactions was monitored by g.l.c. on 5 ft × 1/8 in of 5% OV101 on Chromosorb W, unless stated to the contrary. When photolysis was complete the solvent was evaporated under reduced pressure and the residue purified as described.

Irradiations in Benzene.—(a) *Benzyl* 6-*deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose* (4). A 1% benzene solution (80 ml) of (4) at 22° was irradiated for 3 h. G.l.c. (208°) of the photolysate revealed 10% of unchanged (4) and two products of R_4 0.48 and 0.51 in the ratio of 1 : 10. The residue remaining after solvent evaporation was distilled at 120° and 0.22 mmHg to give an oil (0.37 g, 40%) which exhibited two anomeric proton signals at δ 5.15 and 5.08 in a ratio of 10 : 1. Purification of this material by preparative g.l.c. on 10 ft × 3/8 in of 10% SE30 gave a small sample of uncontaminated *benzyl* 5-*deoxy*-2,3-O-*isopropylidene*-β-D-*ribofuranoside* (11), m.p. 37—39°, ^1H n.m.r. (100 MHz) parameters in Table 4 (Found: C, 67.9; H, 7.6. $C_{15}H_{20}O_4$ requires C, 68.2; H, 7.6%).

(b) *Phenyl* 6-*deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose* (5). A 1% benzene solution (20 ml) of (5) was irradiated for 4 h. G.l.c. analysis (180°) of the photolysate showed that 95% of (5) had reacted and that one peak had been formed (R_5 0.61) with an area equivalent to *ca.* 40% of reacted (5). The residue (0.23 g), which remained after solvent evaporation, showed two signals for anomeric protons in the n.m.r. spectrum at δ 5.68 and 5.62 in a ratio of 9 : 2. Distillation of the crude product at 160° and 0.2 mmHg gave a clear syrup, which was preponderantly phenyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (12) as indicated by the n.m.r. parameters given in Table 4, contaminated with some of the α-L-*lyxo*-isomer (18).

The products (12) and (18) (50 mg) were hydrolysed with aqueous hydrochloric acid (1.0M) at 70° during 6 h. Paper chromatography (butan-1-ol–ethanol–water, 4 : 1 : 5 v/v) of the neutralised hydrolysate showed an intense spot at R_F 0.48 identical with 5-deoxyribose and a weak one at R_F 0.41 which was the same as 5-deoxylyxose.

Treatment of these sugars with 2,4-dinitrophenylhydrazine gave a red oily product, which was dissolved in water and washed with ethyl acetate. From the concentrated aqueous solution crystalline 5-deoxy-D-ribose hydrazone, m.p. 147—149° (lit.,[28] 151—152°), separated.

(c) *Methyl* 6-*deoxy*-2,3-O-*carbonyl*-α-L-lyxo-*hexopyranosid*-4-*ulose* (19). A 1% benzene solution (20 ml) of (19) was irradiated for 4 h. After this period g.l.c. analysis on 10 ft × 3/8 in of 10% SE30 at 140° showed that only 10% (19) remained and one major peak had been formed with R_{19} 0.57. The material left after solvent evaporation was purified by preparative layer chromatography on silica gel (dichloromethane–ethyl acetate, 3 : 2) to give the preponderant photoproduct (R_F 0.8), methyl 5-deoxy-2,3-*O*-carbonyl-β-D-ribofuranoside (20) (39 mg, 22%), $\nu_{max.}$ 1 820 cm^{-1} (cyclic carbonate), *m/e* 159 ($M - 15$)$^+$, n.m.r. parameters recorded in Table 4.

The photoproduct was saponified with aqueous sodium hydroxide and then hydrolysed with aqueous hydrochloric acid which gave a sugar with a paper chromatographic mobility (R_F 0.48; butanol–ethanol–water, 4 : 1 : 5 v/v) identical with that of 5-deoxyribose.

(d) *Methyl* 2,3-O-*isopropylidene*-6-O-*methylsulphonyl*-α-D-lyxo-*hexopyranosid*-4-*ulose* (6). A 2% benzene solution (100 ml) of (6) was irradiated in the annular space of a photolysis well for 0.5 h, when t.l.c. on silica gel (benzene–ethyl acetate, 2 : 1) revealed complete reaction of (6) and the formation of a single mobile product, R_F 0.8. The gum (2.1 g) obtained by solvent evaporation gave, after column chromatography on silica gel, *methyl* 2,3-O-*isopropylidene*-5-O-*methylsulphonyl*-β-L-*ribofuranoside* (13) (0.8 g, 43%), m.p. 75—77°, $[\alpha]_D^{22}$ +57° (*c* 3.0) (lit.,[22] 78—79°), $[\alpha]_D^{20}$ −53°, *m/e* 267 (M − Me)$^+$, 251 (M − OMe)$^+$, 173 (M − CH_2OMs)$^+$ (Found: C, 42.8; H, 6.4; S, 11.3. $C_{10}H_{18}O_7S$ requires C, 42.6; H, 6.4; S, 11.3%).

Compound (13) was heated with sodium benzoate in dimethylformamide and worked up to give the 5-*O*-benzoyl derivative in 86% yield with m.p. 115—117°, $\nu_{max.}$ 1 740 cm^{-1}. The benzoate was deacylated and hydrolysed with aqueous acid, which gave L-ribose, R_F 0.30 on paper with butan-1-ol–acetic acid–water (4 : 1 : 5), m.p. 84—86° (lit.,[29] 85—87°), R_F 0.30. The sugar yielded L-ribose *p*-bromophenylhydrazone, m.p. 169—171° (lit.,[29] 170—172°).

(e) 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosyl*-4-*ulose*-*ethane* (7). A 1% solution of (7) in benzene (30 ml) was irradiated for 30 min at 22° when g.l.c. at 155° showed one peak of R_7 0.36 representing 30% of reacted (7). In a similar irradiation conducted at 60° the same product was formed in 65% yield. After removal of the solvent under reduced pressure the residue was subjected to preparative g.l.c. which afforded 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosylethane (14), $[\alpha]_D^{20}$ +2.0° (*c* 1.3), *m/e* 185 (M − 1)$^+$ and 171 (M − Me)$^+$, and n.m.r. parameters recorded in Table 4.

(*f*) 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosyl*-4-*ulosebenzene* (8).—A 1% benzene solution (50 ml) of compound (8) was irradiated at 22° for 0.5 h when g.l.c. at 170° showed complete reaction and the formation of one major product with R_8 0.42, representing a *ca.* 40% yield. A similar irradiation, carried out at 60°, gave the same product in 60% yield. This was isolated, by distillation of the residual gum formed after solvent evaporation, as a

yellow oil (0.22 g, 49%). It was characterised as 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosylbenzene (15), $[\alpha]_D^{22}$ −82° (*c* 1.0), *m/e* 219 $(M - Me)^{+\cdot}$, and n.m.r. parameters in Table 4.

Irradiation in Other Solvents.—The ketones (4)—(8) and (19) were all irradiated in methanol as 1% solutions (20—50 ml). The photoproducts formed from ketones (6)—(8) and (17) were the same as those produced in benzene. Ketone (4) produced, in addition to the furanosides (11) and (17), a small quantity (*ca.* 5%) of a product with R_4 1.15. This was isolated by preparative g.l.c. and found to have $\nu_{max.}$ 1 745 cm^{-1}. Ketone (5) yielded the furanosides (12) and (18) and two other products in low yields, *ca.* 8 and 4%, respectively, with R_5 1.06 and 1.27. These were isolated by g.l.c. and found to possess $\nu_{max.}$ 1 740 cm^{-1}. Similar products were obtained from (4) in t-butyl alcohol.

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