The Photochemistry of Ketones Derived from Carbohydrates.   Part III.[1] Type II Reactions of Some Pyranosid-2- and -3-ulose Derivatives

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Solutions of α- and β-anomers of methyl 3.4-*O*-isopropylidene-L-*erythro*-pentopyranosid-2-ulose [(2) and (4)] undergo type II elimination upon photolysis. giving 1.5-anhydro-3.4-*O*-isopropylidene-L-*erythro*-pent-2-ulose (3) and formaldehyde. The α-isopropyl analogue (1) behaves similarly. affording compound (3) and acetone.
      The type II reaction is shown to be strongly dependent upon the stereochemistry of the ring substituent which contains the hydrogen atom γ to the keto-group by the photolytic behaviour of the C-2 epimeric pair of methyl 4.6-*O*-benzylidene-2-*O*-methyl-α-D-hexopyranosid-3-uloses [(8) and (13)]. The *arabino*-isomer (8) eliminates the axial methoxy-group to give the 3-ulose derivatives (11) and (12) and formaldehyde. whereas the *ribo*-isomer (13) gives a 2.3-fused oxetanol derivative (15). Reductive cleavage of the oxetanol (15) with lithium aluminium hydride afforded the branched chain sugar derivative methyl 4.6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside (21).

WE have previously reported that pyranosid-4-uloses [1] and -2-uloses [2] undergo type I photochemical cleavage. We now report type II cleavages with this class of derivatives.[3]

Type II [4,5] photochemical cleavage of suitably substituted ketones involves an intramolecular γ-hydrogen atom abstraction by the oxygen atom of the excited carbonyl function. The diradical [5-8] formed in this process (*e.g.* Scheme 1, X = CH₂) either disproportion-
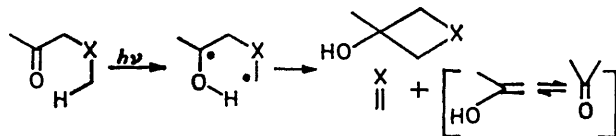
SCHEME 1

ates, yielding an olefin and the enolic [9] form of a ketone, or cyclises to form a cyclobutanol [6] derivative. Cyclisation to an oxetanol [10-12] can occur with α-alkoxyketones (*e.g.* X = O in Scheme 1) and this reaction path becomes more important than in the case where X = CH₂.

It was our intention to utilise this photochemical reaction with pyranosidulose derivatives to prepare new compounds; we also hoped that a study with the pyranosiduloses might increase our understanding of the stereochemical requirements of the type II process.

RESULTS AND DISCUSSION

Materials.—All the carbonyl compounds studied were obtained from suitable hydroxy precursors by conventional [13] oxidation with ruthenium tetroxide. Some have been reported previously but others are new; the structures of these will be discussed.

† Observation originally made by N. R. Williams and T. Turner. We thank our colleagues for discussions about this compound.

Isopropyl 3,4-*O*-isopropylidene-α-L-*erythro*-pentopyranosidulose (1) was prepared from the corresponding α-L-arabinopyranoside. Its structure was deduced from the molecular formula and spectral characteristics. Its conversion into L-ribose by reduction with lithium aluminium hydride and sequential acid hydrolysis showed that the carbonyl group was at position 2 and
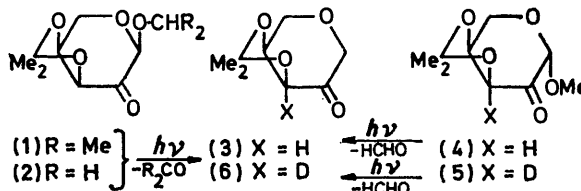
SCHEME 2

the unsplit H-1 signal in its n.m.r. spectrum confirmed this. The integrity of the α-configuration at the anomeric centre was established from the large negative optical rotation exhibited by the isopropyl 3,4-*O*-isopropylideneriboside reduction product.

Methyl 3,4-*O*-isopropylidene-α-L-*erythro*-pentopyranosidulose (2) was prepared from the corresponding arabinoside derivative. It was readily hydrated to yield a *gem*-diol † and the crystalline samples obtained were composed of about 50% of each form. Small quantities of the ulose (2), for photochemical studies, were freed from the corresponding diol by g.l.c.

The conformation of these α-L-pyranosiduloses is difficult to predict, unlike that of their β-L-anomers. For example, methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose, shown in the conformational formula (7; Rα = H, Rβ = OMe), and the t-butyl analogue [2] (7; Rα = H, Rβ = OBuᵗ) would be expected

[1] Part II, P. M. Collins and P. Gupta, *J. Chem. Soc.* (*C*), 1971, 1965.

[2] P. M. Collins, P. Gupta, and R. Iyer, *Chem. Comm.*, 1970, 1261.

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[5] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

[6] N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, 1958, **80**, 2913.

[7] P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 5898.

[8] N. C. Yang, S. P. Elliot, and B. Kim, *J. Amer. Chem. Soc.*, 1969, **91**, 7551.

[9] G. R. McMillan, J. G. Calvert, and J. N. Pitts, *J. Amer. Chem. Soc.*, 1964, **86**, 3602.

[10] P. Yates and A. G. Szabo, *Tetrahedron Letters*, 1965, 485.

[11] R. B. La Count and C. E. Griffin, *Tetrahedron Letters*, 1965, 1549.

[12] F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 311.

[13] P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc.* (*C*), 1966, 1131.

TABLE 1

N.m.r. parameters (τ values; J in Hz) for ring protons of some 3,4-O-isopropylidene-L-erythro-pentopyranosid-2-uloses in [^{2}H]chloroform

Compound		H-1	H-3	H-4	H-5	H-5'
(7)	R_β = OBu^t	4·91(s)	5·28(d)	5·45(o)	5·59(q)	5·94(q)
	R_α = H		$J_{3.4}$ 5·5	$J_{4.5}$ 2·0	$J_{5.5'}$ 13·5	
				$J_{4.5'}$ 1·5		
(7)	R_β = OMe	5·30(s)	5·25(d)	5·42(o)	5·76(q)	5·91(q)
	R_α = H		$J_{3.4}$ 5·8	$J_{4.5}$ 1·8	$J_{5.5'}$ 13·7	
				$J_{4.5'}$ 1·2		
(7)	R_α = OBu^t	4·93(d)	5·43(d)	5·23(sex)	6·0 (d)	
	R_β = H	$J_{1.3}$ 0·8	$J_{3.4}$ 7·5	$J_{4.5}$ 6·0		
				$J_{4.5'}$ 6·0		
(7) *	R_α = OPr^i	5·06(d)	5·41(q)	5·23(sex)	5·95 ~ 6·1	
	R_β = H	$J_{1.3}$ 0·8	$J_{3.4}$ 7·5	$J_{4.5}$ 6·0	Obscured by	
				$J_{4.5'}$ 6·0	aglycone	
					methine	
					proton	

* Measured at 100 MHz.

to exist predominantly in the $^4C_1$ conformation in which the alkoxy-group is axially disposed. In this conformation there are no unfavourable 1,3-diaxial interactions and the anomeric effect is satisfied.[14] The n.m.r. parameters for these compounds (see Table 1) are in broad agreement with this prediction since $J_{4,5ax}$ and $J_{4,5eq}$ are 1·8 and 1·2, and 2·0 and 1·5, respectively, for the two derivatives. These values are satisfactory for molecules

(7)
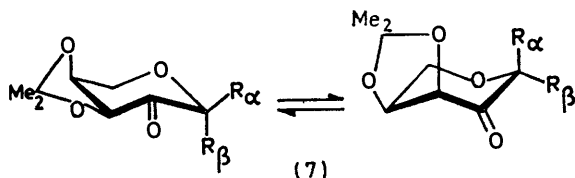
in a conformation in which the dihedral angles between H-4 and H-5ax and H-5eq are both ca. 60°. Such an arrangement would occur in molecules in the $^4C_1$ conformation, but not in the alternative $^1C_4$ form. On the other hand if isopropyl 3,4-O-isopropylidene-α-L-erythro-pentopyranosidulose (7; R_α = OPr^i, R_β = H) or its t-butyl analogue (7; R_α = OBu^t, R_β = H) adopted the $^1C_4$ conformation the alkoxy-group at C-1 would be in the favoured axial position, but this arrangement would be destabilised by a 1,3-syn-diaxial interaction.[14] This is relieved in the $^4C_1$ form but only at the expense of placing the C-1 alkoxy-group in the equatorial position. The n.m.r. parameters for these compounds are given in Table 1. The couplings $J_{4,5}$ and $J_{4,5'}$ are both larger in these anomers than in the β-compounds, and indicate that the dihedral angles between H-4 and H-5 and H-5' are ca. 30 and 150°. These values are not consistent with a molecule in either the $^1C_4$ or the $^4C_1$ conformation but suggest that some flexible intermediate form is adopted.

The structure of 1,5-anhydro-3,4-O-isopropylidene-L-erythro-pent-2-ulose (3) follows from its method of preparation (i.e. oxidation of 1,5-anhydro-3,4-O-isopropylidene-L-arabinitol), its molecular formula, and its spectral characteristics. The n.m.r. signals of this derivative could be completely assigned with the aid of

double-resonance studies (see Table 2); however there was one anomaly: whereas irradiation at the frequency of the H-4 quintet ($J_{4,5} = J_{4,5'} = 3\cdot4$ Hz, $J_{4,3} = 6\cdot8$ Hz) caused collapse of the H-3 doublet, irradiation at the frequency of the H-3 doublet had no effect upon the H-4 quintet. Doubt concerning the n.m.r. spectral assignment was allayed by examination of the simplified spectrum of the C-3 deuterio-derivative (6), prepared, as described later, by photolysis of the deuterated erythro-pentopyranosidulose (5).[15] In this spectrum only a weak broad signal appeared from the protons which remained at C-3 and the H-4 signal was simplified to a triplet.

The 4,6-O-ethylidenepyranosid-3-ulose derivatives (16)—(19) were prepared in the same way as their known 4,6-O-benzylidene analogues. Their structures were confirmed spectroscopically and by comparison of spectral properties with those of the benzylidene derivatives.

Photolyses of Pyranosiduloses.—Isopropyl 3,4-O-isopropylidene-α-L-erythro-pentopyranosidulose (1) was irradiated in t-butyl alcohol (1·4% w/v) under nitrogen, with a 450 W medium-pressure mercury arc lamp through quartz or Pyrex according to method (a) (see Experimental section). The reaction was monitored by g.l.c., which showed that the volatile product formed reached an optimum yield of 50% when three-quarters of the pyranosidulose (1) had reacted. The reaction was ca. five times faster when the full spectrum of the lamp was used, but the products were the same as those obtained with a Pyrex filter. The product was separated from the residue remaining after solvent removal by isobaric distillation. It was shown to be the 1,5-anhydro-pent-2-ulose (3) by comparison with an authentic sample. Acetone, also produced in the reaction, was detected in the solvent distilled from the photolysis as its 2,4-dinitrophenylhydrazone. These products are formed by a type II elimination as shown in Scheme 2.

It was of interest to see if the orientation of the group eliminated from the pyranoid ring was important in this reaction. For such a study an anomeric pair of glycosiduloses was required, and the methyl erythro-pentopyranosiduloses (2) and (4), synthesised from the anomers of methyl arabinopyranoside, were chosen for study. Both these anomers were more readily available than the isopropyl analogues and thus were expected to be of greater use in synthetic sequences.

The methyl β-L-pyranosidulose [13] (4) in t-butyl alcohol (5% w/v) was irradiated through quartz according to method (b). The effluent nitrogen gas (used to agitate the solution) was found to contain formaldehyde, which was characterised as its 2,4-dinitrophenylhydrazone. G.l.c. analysis of the photolysate showed that one other volatile product was formed and this increased in concentration during the irradiation. After 1·5 h it reached an optimum yield of 40%, when half the

[14] S. J. Angyal, *Angew. Chem. Internat. Edn.*, 1969, **8**, 157.
[15] R. F. Butterworth, Ph.D. Thesis, University of London, 1969.

pyranosidulose (4) had reacted. The photoproduct was unstable in this photolysate, however this was not because of the mild acidity of the medium, since although addition of solid calcium carbonate removed the acid present, it did not preserve the compound. Preparative g.l.c. was the most satisfactory method of obtaining the photoproduct, which was identified as the 1,5-anhydro-pent-2-ulose (3), identical with that obtained from the isopropyl analogue.

The same products were formed by a similar irradiation of the α-L-anomer (2) of this pentopyranosidulose derivative. They were accompanied by another compound (10%) with an R_f value identical to that of the

facility with which a tertiary γ-hydrogen atom is abstracted by the excited carbonyl group either in its triplet [12] or in its singlet [8,16] state. Since both the α- and β-methyl anomers undergo type II cleavage it might appear that the stereochemical requirement for this cleavage is not stringent. However, as we have already discussed, the conformation of the α-L-anomer is not known with certainty. Furthermore, both the α- or β-anomers have conformations that are mobile; consequently deductions from this experiment might be misleading.

In order to examine this aspect of the reaction further, pyranosiduloses which possessed structures that were
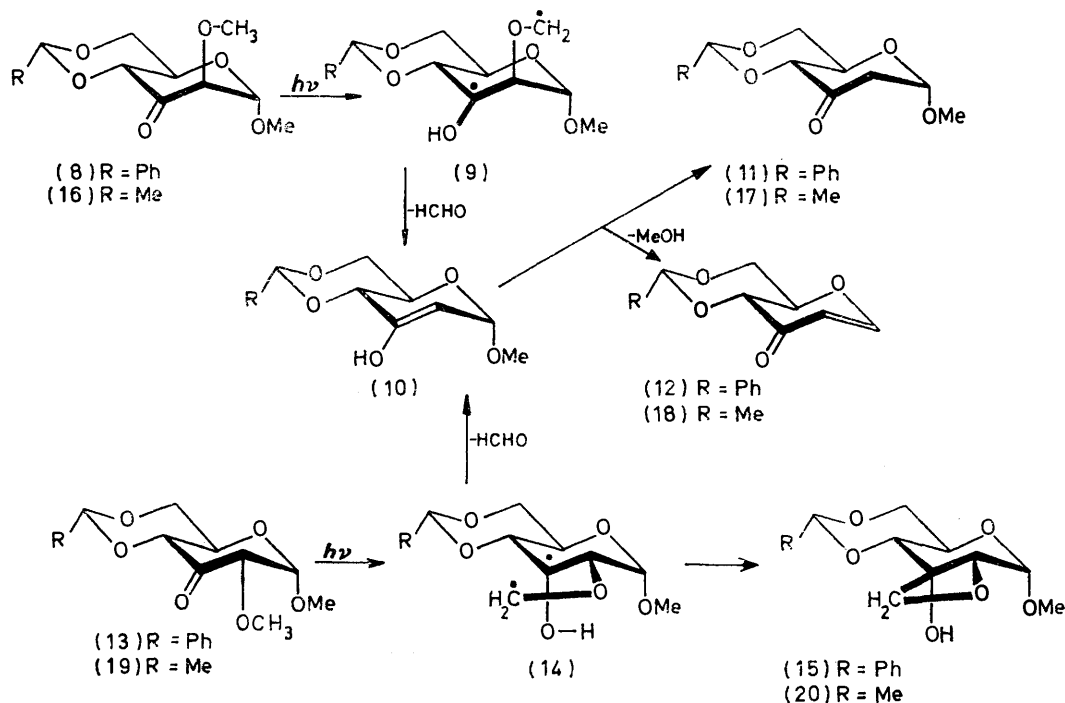
SCHEME 3

β-L-pyranosidulose anomer (4). These pyrano-products were isolated in small quantities by g.l.c. and their structures were confirmed by comparison with authentic materials.

The formation of the derivative (3) from the pyranosiduloses (1), (2), and (4) is consistent with a type II cleavage occurring in the reaction of each compound as shown in Scheme 2. Isomerisation of the methyl α-L-anomer (2) to its more thermodynamically stable β-L-anomer (4) presumably arises from concomitant type I cleavage during the photolysis. We have shown [2] that type I cleavage occurs with glycosiduloses that do not possess a γ-hydrogen atom in their aglycon residues (e.g. t-butyl glycosiduloses). Anomerisation of the isopropyl glycosidulose (1) did not occur, indicating that type I cleavage played an insignificant part in this photolysis. This is probably because of the greater
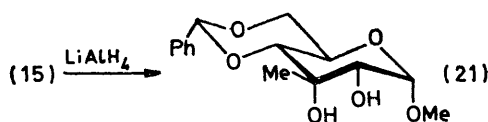
more conformationally rigid were studied. The compounds selected were the methyl 4,6-O-benzylidene-2-O-methyl-α-D-hexopyranosiduloses with the arabino- (8) [17] and ribo- (13) configurations. These have a pyranoid ring locked in the $^4C_1$ conformation with a methoxy-group at C-2 adjacent to the carbonyl group; in the former the methoxy-group is axially orientated and in the latter equatorially disposed. Solutions of these compounds in benzene (0·5% w/v) were irradiated for 12·5 h through Pyrex or for 2·5 h through quartz by method (a). The photolysate from the arabino-isomer (8) was fractionated by column chromatography. A sample of the starting material was isolated and it was estimated (see Experimental section) that 40% of it had not been photolysed. Three products were detected: the ribo-isomer (13) (3%), characterised by its n.m.r. spectrum, the enone (12) (46%), and the 2-deoxy-3-ulose

[16] J. C. Dalton and N. J. Turro, J. Amer. Chem. Soc., 1971, **93**, 3569.

[17] P. M. Collins, D. Gardiner, Mrs. S. Kumar, and W. G. Overend, J.C.S. Perkin I, in the press.

(11) (5%). The last two products could not be separated chromatographically; the mixture was therefore characterised by comparison of its n.m.r. and i.r. spectra with those of a 9 : 1 mixture of authentic (12)[18] and (11) [13]. A small amount of enone (12) was eventually obtained pure from the mixture after several fractional crystallisations.

The *ribo*-isomer (13) underwent photolysis more rapidly than the *arabino*-compound (8), as revealed by the preparative t.l.c. separation of the photolysate. This showed that only 6% of the starting material remained unchanged. Two product fractions were isolated: one was a 9 : 1 mixture of the enone (12) and the 2-deoxypyranosidulose (11), present as a minor component (4%), and the other was obtained as an unstable oil in substantial amounts (65%). It was an alcohol (i.r. spectrum), homogeneous on t.l.c., which still possessed the benzylidene residue and the anomeric methoxy-group as shown by its n.m.r. spectrum. The n.m.r. spectrum also showed that there was not a methoxy-group at position 2 and that a hydroxy-proton was present that could be exchanged with D_2O. Apart from the n.m.r. signals referred to, signals for another eight protons were present as a complex multiplet which could not be analysed by first-order methods. From this evidence the compound was assigned the oxetanol structure (15 or its C-3 epimer), a product not unexpected in an α-alkoxy-ketone photolysis.[10,12,19] Although attempts to acylate and trimethylsilylate the hydroxy-group in the oxetanol failed, probably because it was a tertiary alcohol, its structure was proved conclusively by reducing it with lithium aluminium hydride to the known [20] branched-chain sugar derivative, methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside (21).* This reaction involved [21] cleavage of the oxetanol ring by hydride attack at the least hindered methylene carbon atom. Thus the four-membered ring in structure (15) is *trans*-diequatorially fused at C-2 and C-3 of the pyranoid ring. However this compound may not have been formed stereospecifically since the presence of trace

$$(15) \xrightarrow{\text{LiAlH}_4} (21)$$

amounts of the C-3 epimer of (21) in the reduction product was not excluded.

In order to examine this photochemical reaction more quantitatively, derivatives which could be analysed by

g.l.c. were sought. The 4,6-*O*-ethylidene derivatives (16) and (19) were prepared and photolysed. Types of products similar to those obtained from the benzylidene derivatives were formed. The structures of the enone (18) and the 2-deoxypyranosidulose (17) were ascertained by comparison with authentic materials prepared by conventional means. The identification of the oxetanol (20), however, rested solely upon spectroscopic evidence, since it too proved to be an unstable oil, from which we could not obtain a stable derivative. In the event neither this compound nor (17) would tolerate the conditions necessary for g.l.c. analysis; thus further progress could not be made by this approach.

The formation of these products from the 4,6-*O*-benzylidene and the ethylidene derivatives can be rationalised as shown in Scheme 3. Diradicals formed from either the *arabino*- or the *ribo*-derivatives may either ring close to oxetanols or fragment to give formaldehyde and an enol, which readily ketonises. The enone (12) probably arises by a 1,4-elimination of methanol from the enol (10; R = Ph). A mechanism similar to this has been postulated [22] for the formation of enones by acid-catalysed dehydration of β-hydroxyketones, and this type of elimination product has also been observed [23] in the photolysis of 4-methyl-4-methoxypentan-2-one. The possibility that the enone (12) was formed from the methoxy-ketone (11), a conversion known [13] to occur in the presence of acid, was excluded in the present case by experiment, and it has also been shown that thermal and photochemical breakdown of the oxetanol (15) does not yield any enone (12), although such a transformation is possible in principle.[2,19]

The results, although of a non-quantitative nature, clearly indicate a difference in the type II photochemistry of the pyranosid-3-uloses that possess axial and equatorial methoxy-groups at position 2. The *ribo*-isomer (13), which has an equatorial C-2 methoxy-group, undergoes photolysis more rapidly than the *arabino*-derivative (8). In this connection it is noteworthy that 2-alkylcyclohexanones show an increase in reactivity when the alkyl group is bulky; Barltrop and Coyle [24] attributed this, at least in part, to an increase in the population of the conformer in which the alkyl group is equatorial. A more striking dependence of reactivity upon alkyl group orientation has been reported by Turro and Weiss.[25] These authors found that *cis*-2-propyl-4-t-butylcyclohexanone (equatorial propyl group in the preponderant chair conformation), upon photolysis in cyclohexane, underwent type II cleavage, whereas the *trans*-isomer did not; instead it slowly isomerised to the equatorial isomer *via* a type I process. The lability of

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* *Note added in proof:* The assignment of the *allo*-configuration to compound (21) has been verified by method of S. T. K. Bukari, R. D. Guthrie, A. I. Scott, and A. D. Wrixon, *Tetrahedron*, 1970, **26**, 3653. Its cuprammonium complex shows a c.d. curve which is positive in the 300 nm region and negative in the 600 nm region. This indicates an *allo*- or *marine*-structure. Only the former configuration is reasonable in the present case.

[18] P. M. Collins, *Carbohydrate Res.*, 1969, **11**, 125.

[19] W. M. Horspool, in ' Photochemistry,' Chem. Soc. Specialist Periodical Reports, vol. 1, 1970, p. 144.

[20] G. B. Howarth, W. A. Szarek, and J. K. N. Jones, *Canad. J. Chem.*, 1968, **46**, 3575.

[21] S. Searles, jun., in ' Heterocyclic Compounds with Three and Four Membered Rings,' ed. A. Weissberger, Interscience, New York, 1964, p. 1009.

[22] D. S. Noyce, P. A. King, C. A. Lane, and W. L. Reed, *J. Amer. Chem. Soc.*, 1962, **84**, 1638.

[23] D. J. Coyle, R. V. Peterson, and J. Heicklen, *J. Amer. Chem. Soc.*, 1964, **86**, 3850.

[24] J. A. Barltrop and J. D. Coyle, *Chem. Comm.*, 1970, 390.

[25] N. J. Turro and D. S. Weiss, *J. Amer. Chem. Soc.*, 1968, **90**, 2185.

the *arabino*-compound (8) towards type II fragmentation, which we report, probably arises from the activating [12,26] influence of the oxygen atom in the methoxy-group at position 2.

Although isomerisation of the *arabino*-isomer (8) to the thermodynamically more stable *ribo*-isomer (13) did occur to a small extent, it could not have been responsible for the type II fragmentation observed since, as we describe, the *ribo*-compound (13) yields mainly a cyclisation product.

The most striking difference between the results of photolysis of the C-2 epimeric pyranosiduloses (8) and (13) is that they yield different proportions of cyclisation and fragmentation products. This is probably explicable in terms of the structure of the two intermediate diradicals involved. The elimination of formaldehyde from intermediate (9; R = Ph) would be expected to be favourable on stereoelectronic grounds [26-29] (*cf.* the ready ground state β-elimination that occurs with *trans*-diaxially arranged substituents), since in this configuration continuous orbital overlap is possible during the fragmentation process and for this reason the *arabino*-isomer (8) affords compounds (11) and (12) in preference to an oxetanol. However, with intermediate (14; R = Ph) formed from (13), elimination would not be particularly favourable; thus ring closure would be expected to become important. In keeping with this result is the recent report [28] that some cyclisation products are formed during the photolysis of *cis*-2-propyl-4-t-butylcyclohexanone in t-butyl alcohol, particularly from the triplet state. A high proportion of cyclisation with the carbohydrate derivative would be anticipated, since the methoxy-group oxygen atom would favour a ring closure.[12] Furthermore the pyranosidulose can be considered as an alkoxy-ketone with a substituent at the α-position (*i.e.* C-1 of the pyranoid ring). Lewis and Hilliard [29] have shown that aliphatic non-cyclic ketones with α-substituents yield a greater proportion of cyclobutanols in their photoproducts.

The preference for ring closure to give the *trans*-diequatorially fused oxetanol might possibly arise because the hydroxy-group in the intermediate diradical (14) adopts the axial orientation, so that it can hydrogen bond to the anomeric methoxy-group. Intramolecular hydrogen bonding between these groups would be possible in an intermediate with this structure.[30] Furthermore, Wagner [7] has shown that hydrogen bonding between diradical intermediates and solvent molecules plays an important role in type II photochemistry, and recently others [12] have cited intramolecular hydrogen bonding as being significant.

[26] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1968, **90**, 5896.

[27] D. S. Weiss, N. J. Turro, and J. C. Dalton, *Mol. Photochem.*, 1970, **2**, 91; R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 4752; F. D. Lewis and R. A. Ruden, *Tetrahedron Letters*, 1971, 715; A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, 1969, **91**, 456.

[28] I. Fleming, A. V. Kemp-Jones, and E. J. Thomas, *Chem. Comm.*, 1971, 1158.

EXPERIMENTAL

Unless stated otherwise optical rotations were measured for 1% w/v solutions in chloroform with a Bellingham and Stanley polarimeter; u.v. spectra were measured for ethanolic solutions with a Perkin-Elmer spectrophotometer model 402; i.r. spectra were measured for solids dispersed in potassium bromide with a Perkin-Elmer Infracord model 137; n.m.r. spectra (τ values; J in Hz) were measured with a Varian Associates instrument (model A-60D or HA-100D; use of the latter will be mentioned in the text) and mass spectra were measured with an A.E.I. MS 902 instrument operating at 70 eV. N.m.r. (100 MHz) and mass spectra were obtained by the P.C.M.U. at Harwell.

T.l.c. employed silica gel G, and column chromatography silica gel (0·05—0·2 mm). One of the following solvent systems was used (i) CH_2Cl_2–EtOAc (1 : 1 v/v), (ii) C_6H_6–EtOAc (3 : 2 v/v), (iii) EtOAc. For g.l.c. a Varian Aerograph model 202 fitted with either column A [10 ft × ¼ in, SE 52 (20%) on 60—80 mesh Chromosorb W] or column B [10 ft × ¼ in, SE30 (20%) on 60—80 mesh Chromosorb W] was used with hydrogen as carrier gas and a thermal conductivity detector.

Preparation of Materials

Methyl 4,6-O-Benzylidene-2-O-methyl-ribo-hexopyranosid-3-ulose (13).—The *arabino*-pyranosidulose [17] (8) (7 g) was heated under reflux for 30 min in ethanol 96% (150 ml) containing triethylamine (1·5 ml). The cooled solution was diluted with methylene chloride (50 ml), decolourised with charcoal, filtered through kieselguhr, and evaporated under reduced pressure to give a solid. Recrystallisation from ethanol–pentane gave, in two crops, the ribo-*pyranosidulose derivative* (13), as fine white needles (5·1 g, 75%), m.p. 198—200°, $[\alpha]_D$ +45°, $\nu_{max.}$ 1740 cm⁻¹ (C=O), $\lambda_{max.}$ 284 nm (ε 361), τ (CDCl₃) 6·52 (s, OMe), 6·42 (s, OMe), 4·71 (d, $J_{1,2}$ 4·3), 4·34 (s, PhCHO₂), 5·1—6·2 (m, H-2, -4, -5, -6, and -6′), and 2·32—2·7 (m, aromatic) (Found: C, 61·3; H, 6·4. $C_{18}H_{18}O_6$ requires C, 61·2; H, 6·2%).

Methyl 4,6-O-Ethylidene-2-O-methyl-α-D-altropyranoside.—Methyl 4,6-O-ethylidene-2,3-bis-O-p-tolylsulphonyl-α-D-glucopyranoside [31] (1·0 g) in dichloromethane (20 ml) was heated under reflux with sodium methoxide [from methanol (20 ml) and sodium (1 g)] for 6 h. Normal work-up gave the 2-O-methylaltroside (0·44 g, 90%), m.p. 104—105°, τ (CCl₄) 6·6 (s, OMe), 6·65 (s, OMe), 8·73 (d, J 5·0, CMe), 5·3 (q, $J_{H.Me}$ 5·0, MeCHO₂), 5·45 (d, $J_{1,2}$ 1·0), 5·80—6·6 (m, H-2, -3, -4, -5, and -6′), and 7·5 (d, OH, exchangeable with D₂O).

Methyl 4,6-O-Ethylidene-2-O-methyl-α-D-arabino-hexopyranosid-3-ulose (16).—The 2-O-methylaltroside (20 g) in carbon tetrachloride (200 ml) was oxidised with ruthenium tetroxide [from the dioxide (20 g)] during 30 min at room temperature. The excess of oxidant was destroyed with isopropyl alcohol (1 ml); the solution was filtered and then evaporated to give the 3-*ulose* (16). Recrystallisation from light petroleum (b.p. 60—80°) gave crystals (15·7 g, 78%), m.p. 82°, $[\alpha]_D$ +126°, $\nu_{max.}$ 1745 cm⁻¹ (C=O), τ (CDCl₃) 6·61br (s, 2 × OMe), 8·59 (d, $J_{Me.H}$ 5·0, CMe), 5·03 (d, $J_{1,2}$ 1·3),

[29] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 1970, **92**, 6672.

[30] R. J. Ferrier, W. G. Overend, G. A. Rafferty, H. M. Wall, and N. R. Williams, *Proc. Chem. Soc.*, 1963, 133; B. Flaherty, W. G. Overend, and N. R. Williams, *J. Chem. Soc.* (C), 1966, 398.

[31] A. G. Ansell and J. Honeyman, *J. Chem. Soc.*, 1952, 2778.

5·19 (q, J 5·0, MeCHO$_2$), and 5·25—6·5 (m, H-2, -4, -5, -6, and -6′) (Found: C, 51·8; H, 7·0. $C_{10}H_{16}O_6$ requires C, 51·7; H, 6·9%).

Methyl 4,6-O-*Ethylidene*-2-O-*methyl*-α-D-*ribo*-*hexopyranosid*-3-*ulose* (19).—Crude *arabino*-hexopyranosidulose (16) (10 g) was dissolved in ethanol (250 ml) containing triethylamine (3 ml) and heated under reflux for 30 min. T.l.c. [system (i)] showed that the two epimeric uloses were present in approximately equal amounts. The solvent was evaporated off and the gum so formed treated with diethyl ether (300 ml), which produced a solid (4·5 g). Treatment of the mother liquors again gave more solid (0·8 g). Recrystallisation from light petroleum (b.p. 60—80°) gave the pure *ribo*-*hexosidulose* (19) (4·2 g), m.p. 134—135°, $[\alpha]_D$ +61°, $\nu_{max.}$ 1750 cm^{-1} (C=O), τ (CDCl$_3$) 6·39 (s, OMe), 6·49 (s, OMe), 8·55 (d, $J_{Me.H}$ 5·0, CMe), 4·69 (d, $J_{1.2}$ 4·0), 5·26 (q, J 5·0, MeCHO$_2$), and 5·7—6·4 (H-2, -4, -5, -6, and -6′) (Found: C, 52·0; H, 6·8. $C_{10}H_{16}O_6$ requires C, 51·7; H, 6·9%).

Methyl 2-*Deoxy*-4,6-O-*ethylidene*-α-D-*erythro*-*hexopyranosid*-3-*ulose* (17).—Methyl 2-deoxy-4,6-O-ethylidene-α-D-*ribo*-hexopyranoside (2·3 g) (prepared by lithium aluminium hydride cleavage of the oxiran ring in the corresponding allopyranoside 2,3-anhydride derivative) was oxidised in carbon tetrachloride (100 ml) with ruthenium tetroxide [from the dioxide (1·6 g)]. The usual work-up gave a solid which crystallised from ethanol to yield the *deoxypyranosidulose* (17) (0·6 g, 26%), m.p. 104—105°, $[\alpha]_D$ +150°, $\nu_{max.}$ 1740 cm^{-1} (C=O), τ (CDCl$_3$) 6·66 (s, OMe), 8·60 (d, $J_{Me.H}$ 5·0), 4·90 (q, $J_{1.2ax}$ 4·0, $J_{1.2eq}$ 2·0), 5·2 (q, J 5·0, MeCHO$_2$), 7·22 (q, $J_{2ax.2eq}$ 15), 7·38 (q, H-2eq), and 5·6—6·5 (H-4, -5, -6, and -6′) (Found: C, 53·5; H, 6·7. $C_9H_{14}O_5$ requires C, 53·5; H, 7·0%).

1,2-*Dideoxy*-4,6-O-*ethylidene*-D-*erythro*-*hex*-1-*enopyranosid*-3-*ulose* (18).—1,2-Dideoxy-4,6-O-ethylidene-D-*ribo*-hex-1-enopyranose (1·5 g) (prepared in two steps from the 2,3-anhydroallopyranoside derivative) was oxidised in an identical way to that used for the benzylidene analogue.[18] This produced a crude product (0·9 g) which crystallised from diethyl ether–light petroleum (b.p. 40—60°) to give the pure *enone* (18) (0·38 g), m.p. 121—123°, $[\alpha]_D$ +245°, $\nu_{max.}$ 1690 and 1590 cm^{-1} (C=C–C=O), $\lambda_{max.}$ 260 nm (ε 7000), τ (CCl$_4$) 8·61 (d, $J_{Me.H}$ 5·0, CMe), 2·87 (d, $J_{1.2}$ 6·0), 4·72 (d, $J_{2.1}$ 6·0), 5·31 (q, MeCHO$_2$), and 5·6—6·5 (m, H-4, -5, -6, and -6′) (Found: C, 56·5; H, 6·0. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9%).

Isopropyl α-L-*Arabinopyranoside*.—2,3,4-Tri-O-acetyl-β-L-arabinosyl bromide (40 g) was treated with anhydrous propan-2-ol (700 ml) and freshly prepared silver carbonate (40 g) according to the method of Koenigs and Knorr.[32] Deacetylation[33] of the product afforded the *arabinoside* (8 g, 51%), m.p. 115—116°, $[\alpha]_D$ +15° (c 1·0 in H$_2$O), $\nu_{max.}$ 3300 cm^{-1} (OH) (Found: C, 49·7; H, 8·2. $C_8H_{16}O_5$ requires C, 50·0; H, 8·4%).

Isopropyl 3,4-O-*Isopropylidene*-α-L-*arabinopyranoside*.—The isopropyl arabinoside (10 g) was dissolved in anhydrous acetone (500 ml) and phosphorus pentoxide (ca. 0·1 g) was added.[34] The mixture was stirred vigorously and after 15 min t.l.c. [system (iii)] indicated the reaction was complete. The acetone solution was filtered, neutralised with sodium hydrogen carbonate, and evaporated to give a solid which crystallised from acetone–diethyl ether to give the *iso*-

propylidenearabinoside as needles (5·6 g, 46%), m.p. 118—120°, $[\alpha]_D$ +26° (c 0·88), $\nu_{max.}$ 3400 cm^{-1} (OH), m/e 217 (M^+ − 15), τ (C$_6$D$_6$) 8·9 (d, J 6·0) and 8·76 (d, J 6·0) (Me$_2$CHO), 8·73 (s) and 8·5 (s) (Me$_2$CO$_2$), 5·75 (d, $J_{1.2}$ 7·0), and 5·85—7·0 (m, H-2 to -5′, Me$_2$CH, and OH) (Found: C, 56·5; H, 8·7. $C_{11}H_{20}O_5$ requires C, 56·9; H, 8·7%).

Isopropyl 3,4-O-*Isopropylidene*-α-L-*erythro*-*pentopyranosid*-2-*ulose* (1).—Isopropyl 3,4-O-isopropylidene-α-L-arabinoside (4·0 g) in carbon tetrachloride (250 ml) was oxidised[13] with ruthenium tetroxide [from ruthenium dioxide (2·4 g)]. After 4 h, g.l.c. of the mixture on column A at 160° showed that about 95% of the starting material (R_t 8·75 min) had reacted and one volatile product, the pyranosidulose (1) (R_t 8·25 min), had been formed. The usual work-up gave a solid which crystallised from light petroleum (b.p. 60—80°) to give the *ketone* (1) as plates (1·7 g, 42%), m.p. 103—105°, $[\alpha]_D$ −12° (c 0·8), $\nu_{max.}$ 1760 cm^{-1} (C=O), $\lambda_{max.}$ 306 nm (ε 24), m/e 215 (M^+ − 15), τ (100 MHz; CDCl$_3$) 8·78 (d, J 6·5) and 8·72 (d, J 6·5) (Me$_2$CHO), 8·61 (s) and 8·52 (s) (Me$_2$CO$_2$), 5·05 (d, $J_{1.3}$ 0·8), 5·23 (sex, $J_{4.5}$ 6·0, $J_{4.5'}$ 6·0, 5·43 (q, $J_{3.4}$ 7·5), and 5·95—6·1 (m, H-5, H-5′, and CHMe$_2$) (Found: C, 57·2; H, 7·8. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·9%).

Reduction of Isopropyl 3,4-O-*Isopropylidene*-α-L-*erythro*-*pentopyranosid*-2-*ulose* (1).—The ulose (1) (0·11 g) was reduced with lithium aluminium hydride (0·03 g) in diethyl ether (5 ml) by heating under reflux for 18 h. G.l.c. analysis at 145° on column A showed the product (R_t 22 min) and a little starting material (R_t 18 min) (isopropyl 3,4-O-isopropylidene-α-L-arabinoside possessed R_t 25·5 min). The usual work-up yielded a solid which crystallised from light petroleum (b.p. 40—60°) to give pure *isopropyl* 3,4-O-*isopropylidene*-α-L-*ribopyranoside* (0·9 g, 83%), m.p. 103—104°, $[\alpha]_D$ −128° (c 0·9), $\nu_{max.}$ 3600 cm^{-1} (OH), m/e 217 (M^+ − 15), τ (C$_6$D$_6$) 9·04 (d, J 6·0) and 8·88 (d, J 6·0) (Me$_2$CHO), 8·75 (s) and 8·51 (s) (Me$_2$CO$_2$), 7·58br (d, OH, exchangeable with D$_2$O), 5·29 (d, $J_{1.2}$ 4·5), and 5·6—6·8 (5H, m) (Found: C, 56·95; H, 8·7. $C_{11}H_{20}O_5$ requires C, 56·9; H, 8·7%).

Hydrolysis of the reduction product in aqueous 2м-hydrochloric acid gave a sugar with a paper chromatographic R_F value identical to that of an authentic sample of ribose.

Methyl 3,4-O-*Isopropylidene*-α-L-*arabinopyranoside*.—Methyl α-L-arabinopyranoside (10 g) in dry acetone (600 ml) was heated under reflux with toluene-*p*-sulphonic acid (0·1 g) in an apparatus fitted with a Soxhlet head containing molecular sieve (type 3A).[35] The solution was kept acidic during the 7 h reaction period by the addition of extra portions (0·1 g) of the sulphonic acid. The solution was neutralised with sodium hydrogen carbonate and evaporated to yield methyl isopropylidenearabinoside, which crystallised from di-isopropyl ether as prisms (9·4 g, 75%), m.p. 69—70° (lit.[36] for the enantiomer, m.p. 73—74°), $[\alpha]_D$ +29°, $\nu_{max.}$ 3400 cm^{-1} (OH), m/e 189 (M^+ − 15), τ (CDCl$_3$) 8·64 (s) and 8·48 (s) (CMe$_2$), 6·9br (s, exchangeable with D$_2$O, OH), 6·48 (s, OMe), and 5·6—6·4 (m, H-1 to H-5′) (Found: C, 52·6; H, 7·8. Calc. for $C_9H_{16}O_5$: C, 52·9; H, 7·9%).

Methyl 3,4-O-*Isopropylidene*-α-L-*erythro*-*pentopyranosid*-2-*ulose* (2).—Methyl 3,4-O-isopropylidene-α-L-arabinoside (5 g) was oxidised with ruthenium tetroxide [from the

[32] W. Koenigs and E. Knorr, *Ber.*, 1901, **34**, 957.
[33] G. Zemplén, *Ber.*, 1936, **69**, 1827.
[34] J. Honeyman, *J. Chem. Soc.*, 1946, 990.
[35] E. J. Hedgley and H. G. Fletcher, jun., *J. Org. Chem.*, 1965, **30**, 1282.
[36] H. B. Wood and H. G. Fletcher, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 5242.

dioxide (3·0 g)] in carbon tetrachloride (300 ml) solution in the usual way. After 15 h, g.l.c. analysis (column A) at 160° indicated that the reaction was almost complete [starting material R_t 13 min, ulose (2) R_t 12·5 min]. The usual work-up [13] gave a solid product (4·2 g, 72%), which was a mixture of the ulose (2) and its *gem*-diol, $\nu_{max.}$ 3350 (OH) and 1760 cm^{-1} (C=O); the n.m.r. spectrum (CDCl₃) showed singlets of almost equal intensity at τ 8·42, 8·55, 8·60, and 8·70 due to the Me_2CO_2 residues in the ulose and diol forms and at τ 6·18 and 6·15 from the OMe groups of each modification [Found: C, 50·9; H, 6·9. $C_9H_{14}O_5$(ulose) requires C, 53·5; H, 7·0%. $C_9H_{16}O_6$ (diol) requires C, 49·1; H, 7·3%].

The *gem*-diol form of the ulose was dehydrated by g.l.c. and the effluent appearing after 12·5 min was collected in anhydrous carbon tetrachloride contained in traps protected from atmospheric moisture. This procedure gave a sample which exhibited an intense i.r. carbonyl absorption but no hydroxy-absorption.

1,5-*Anhydro*-3,4-O-*isopropylidene*-L-erythro-*pent*-2-*ulose* (3).—1,5-Anhydro-3,4-O-isopropylidene-L-arabinitol (5 g) (prepared by standard procedures [35] from acetobromo-arabinose) was oxidised in carbon tetrachloride (150 ml) with ruthenium tetroxide in the usual way. The solid obtained upon work-up crystallised from methylene chloride–pentane to give a pure sample of the *anhydro-pentulose* (3) (3·5 g, 70%), m.p. 81—82°, $[\alpha]_D$ +63°, $\nu_{max.}$ 1725 cm^{-1} (C=O), $\lambda_{max.}$ 300 nm (ε 75), m/e 172 (M^+) and 157 (M^+ − 15). The 100 MHz n.m.r. spectrum (CCl₄) exhibited signals at τ 8·70 (s) and 8·60 (s) due to the isopropylidene residue and the signals for the ring protons shown in Table 2 (note that the chemical shifts of H-5 and -5' are fortuitously the same) (Found: C, 55·95; H, 6·7. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%).

TABLE 2

N.m.r. parameters (τ values; J in Hz) and double-resonance studies on compounds (3) and (6)

Com- pound	H-1	H-1'	H-3	H-4	H-5	H-5'
(3)	6·13(d)	5·9(d)	5·73(d)	5·50 (quint)	6·25(d)	
	$J_{1,1'}$ 16·5 *	$J_{1',1}$ 16·5	$J_{3,4}$ 6·8	$J_{4,5}$ 3·4	$J_{5,4}$ 3·4	
	(d)	(d)	(d)	(d) $J_{4,3}$ 6·8	Irrad.	
	(d)	(d)	(s)	Irrad.	(s)	
	(d)	(d)	Irrad.	(quint)	(d)	
(6)	(d)	(d)	Weak signal	(t)	(d)	

* Ref. 37.

Photolyses

General Procedure.—A Hanovia medium-pressure mercury arc 450 W lamp was used either in conjunction with a Pyrex filter (when mainly wavelengths longer than 290 nm were transmitted) or with no filter (when the full spectrum of the lamp was used).

The pyranosiduloses were dissolved in solvent and the solutions agitated by bubbling dry nitrogen gas through them. The solutions were photolysed either (a) in the annular space formed between a water-cooled quartz immersion well and an outer Pyrex vessel, whose diameter was such that when the cavity was filled with solution the full length of the lamp was utilised or, (b) in quartz or

[37] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, 1966, Suppl. 7, p. 355.

Pyrex test tubes attached to the surface of the quartz water-cooled immersion well so that were 25 nm from the centre of the lamp.

All solvents used were distilled under dry nitrogen gas.

Methyl 3,4-O-*Isopropylidene*-β-L-erythro-*pentopyranosid*-2-*ulose* (4).—The pyranosidulose (4) [38] in t-butyl alcohol (10 ml) was irradiated through quartz according to method (b). The reaction was monitored by g.l.c. analysis on column B at 150°; this showed that after 1·5 h half the starting material (4) (R_t 13 min) had reacted, producing one detectable product (ca. 40% equivalent to 80% conversion), R_t 4·5 min. This compound was unstable in the photolysate, which had become mildly acidic. However neutralisation of the acid with calcium carbonate did not improve the product's stability. Immediate separation by preparative g.l.c. was the most satisfactory method for its isolation. In this way a pure sample of 1,5-anhydro-3,4-O-isopropylidene-*L-erythro*-pent-2-ulose (3) was obtained; m.p. 81—82°, $[\alpha]_D$ +63°. The other physical constants were identical with those already reported.

That the effluent nitrogen contained formaldehyde was confirmed by extracting the latter from the gas into water and converting it into its 2,4-dinitrophenylhydrazone derivative, m.p. 166° (lit.,[39] 167°).

Irradiation of the ulose (4) with light filtered through Pyrex, but otherwise under the same conditions, converted only 10% of the starting material into the anhydro-pentulose (3) during 1·5 h.

Methyl 3-C-*Deuterio*-3,4-O-*isopropylidene*-β-L-erythro-*pentopyranosidulose* (5).—Irradiation of the deuteriated ulose (5) (75% ²H) (prepared according to the method of Butterworth [15]) under conditions identical to those used for the unlabelled ulose (4), gave 1,5-anhydro-3-C-deuterio-3,4-O-isopropylidene-L-*erythro*-pent-2-ulose (6). The n.m.r. spectrum showed the same signals as those of the unlabelled derivative, except that the H-3 signal at τ 5·73 was reduced to 0·25H intensity and the H-4 signal had collapsed to a broad triplet (see Table 2).

Isopropyl 3,4-O-*Isopropylidene*-α-L-erythro-*pentopyranosid*-2-*ulose* (1).—The pyranosidulose (1) (2·0 g) in t-butyl alcohol (150 ml) was irradiated through Pyrex according to method (b). G.l.c. analysis (with column B at 150°) of the photolysate showed that after 2·5 h an optimum yield of product, R_t 4·5 min (50%), had been formed, and 30% of the pyranosidulose (1), R_t 13 min, remained unchanged. The same result was obtained after 30 min irradiation through quartz. The solvent was cautiously distilled off and treated with 2,4-dinitrophenylhydrazine to give acetone 2,4-dinitrophenylhydrazone, m.p. 128°.[39] The oily photolysate residue was distilled during 18 h at 35° (0·05 × 133 Nm^{-2}), the distillate being collected at −50°. This gave the anhydropentulose (3) (0·53 g, 35%) (50% conversion), m.p. and mixed m.p. 80—81°, $[\alpha]_D$ +56°, mass n.m.r., and i.r. spectra identical with those of authentic material.

The residue remaining in the distillation flask was triturated with diethyl ether; the solid was filtered off and crystallised from light petroleum (b.p. 60—80° to give the pentopyranosidulose (1) (0·25 g, 13%).

Methyl 3,4-O-*Isopropylidene*-α-L-erythro-*pentopyranosid*-2-*ulose* (2).—The pyranosidulose (2) (25 mg) was freed from

[38] J. S. Burton, W. G. Overend, and N. R. Williams, *J. Chem. Soc.*, 1965, 3443.
[39] 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

its diol by dehydration (g.l.c. on column B at 180°). It was collected directly in anhydrous t-butyl alcohol (2 ml) contained in a quartz photolysis tube and irradiated by method (b). The solution was monitored by g.l.c. (column B, 150°) which showed that after 30 min most of the ulose (2) (R_t 11·5 min) had reacted. The two products formed were obtained by g.l.c. The major one was the anhydropentulose (3) (R_t 4·5 min) (physical constants identical with those of an authentic specimen). The minor product (R_t 13 min), obtained initially as an oil, was the β-L-arabinoside derivative (4). It crystallised upon seeding and the crystals gave only one peak on g.l.c. Its mass spectrum was identical with that of the pyranosidulose (4) prepared by conventional means.

Methyl 4,6-O-Benzylidene-2-O-methyl-α-D-arabino-hexopyranosid-3-ulose (8).—The pyranosidulose (8) (1 g) in benzene (200 ml) was irradiated for 2·5 h through quartz, or for 12·5 h through Pyrex, by method (a). T.l.c. [system (ii)] showed that the starting material (8), R_F 0·51, which remained, was accompanied by products with R_F 0·43 (intense) and 0·29 (very weak). Evaporation of the solvent left a solid mixture which was fractionated chromatographically [system (ii)] giving unchanged pyranosidulose (8) (0·2 g), material with R_F 0·43 (0·25 g), a mixture estimated by n.m.r. and u.v. spectroscopy to be composed of equal parts of these two fractions (0·4 g), and a small amount of material of R_F 0·29 (0·03 g).

The material with R_F 0·43 was made up of two compounds which had the same chromatographic mobility in all solvent systems employed. The mixture was shown to be composed of nine parts of 4,6-O-benzylidene-1,2-dideoxy-D-erythro-hex-1-enopyran-3-ulose (12) and one part of methyl 4,6-O-benzylidene-2-deoxy-α-D-erythro-hexopyranosid-3-ulose (11) by comparing the i.r. and n.m.r. spectra of an authentic 9 : 1 mixture of compounds (12) and (11) synthesised by independent routes. Recrystallisation of this two-component mixture from isopropyl alcohol gave the pure enone (12), m.p. 125—126°, $\nu_{max.}$ 1700 and 1600 cm^{-1}, $\lambda_{max.}$ 264 nm (C=C–C=O) (lit.,[18] m.p. 128—129°). The material with R_F 0·29 was shown to be the isomeric riboulose (13) by comparison of n.m.r. spectra.

Methyl 4,6-O-Benzylidene-2-O-methyl-α-D-ribo-hexopyranosid-3-ulose (13).—The pyranosidulose (13) was irradiated for 2·5 h according to method (a). T.l.c. of the photolysate [system (ii)] on 20 cm plates showed that most of the starting material (13), R_F 0·20, had reacted, forming products which appeared as an intense spot at R_F 0·30 and a weak spot at R_F 0·43 (20 cm plates were necessary since the materials with R_F 0·20 and 0·30 were difficult to distinguish on microscope slide plates).

P.l.c. gave a 9 : 1 mixture (0·04 g) of enone (12) and the 2-deoxy-3-ulose derivative (11); unchanged starting material (13) (0·06 g); and a thermally unstable syrup, R_F 0·30 (0·65 g), $\nu_{max.}$ 3500s cm^{-1} (OH), τ (CDCl₃) 2·3—2·7 (m, Ph), 4·42 (s, PhCHO₂), 4·79 (s, OH, exchangeable with D₂O), 6·45 (s, OMe), and 4·9—6·4 (8H, m).

Methyl 4,6-O-Benzylidene-3-C-methyl-α-D-allopyranoside (21).—Methyl 4,6-O-benzylidene-2-O-methyl-α-D-ribo-hexopyranosid-3-ulose (13) (0·6 g) in benzene (100 ml) was irradiated for 45 min according to method (a). The photolysate was then heated under reflux with lithium aluminium hydride (1·0 g) for 15 h, and water (2 ml) was added to the cooled mixture. The flocculent precipitate was filtered off and washed thoroughly with warm benzene and methylene chloride. The filtrate and washings were combined and evaporated to a syrup, which was redissolved in the same solvent. The solution was filtered and evaporated to a gum (0·4 g). T.l.c. on 20 cm plates [EtOAc–C₆H₆–MeOH (30 : 30 : 20)] showed five minor products, R_F 1·7, 2·5, 4·6, 5·2, and 6·5 and a major one, R_F 3·4. The n.m.r. spectrum of this crude material (CCl₄) exhibited signals for a benzylidene residue and for OMe and CMe groupings. The OMe signal was 0·6 times as intense as the phenyl signal and the CMe signal ca. 0·4 times as intense.

The carbon tetrachloride solution slowly deposited compound (21) as a solid (0·13 g) (no effort was made to maximise this yield), m.p. 195—196°, τ (CDCl₃) 8·61 (s, CMe), 6·5 (s, OMe), 5·22 (d, $J_{1.2}$ 4·0), 4·42 (s, PhCHO₂), and 2·4—2·8 (m, Ph). A further recrystallisation from propan-2-ol gave crystals of m.p. 200—205°, $[\alpha]_D$ +94°, $\nu_{max.}$ (0·1% in CCl₄) 3572 and 3545 cm^{-1} (lit.,[20] m.p. 210—212°, $[\alpha]_D$ +95°, and n.m.r. parameters identical to those reported here).

Methyl 4,6-O-Ethylidene-2-O-methyl-α-D-arabino-hexopyranosid-3-ulose (16).—The pyranosidulose (16) (2 g) in benzene (100 ml) was irradiated according to method (a) for 1 h with unfiltered light. T.l.c. [system (i)] of the reaction mixture showed two product spots, R_F 0·25 and 0·47. Separation by column chromatography of a portion of the photolysate gave small amounts of unchanged ulose (16), R_F 0·65, the enone (18), and 2-deoxy-3-ulose (17), R_F 0·47, characterised by their n.m.r. and i.r. spectra; and the 2-O-methyl-ribo-hexopyranosid-3-ulose (19), R_F 0·25, characterised by its n.m.r. spectrum.

Methyl 4,6-O-Ethylidene-2-O-methyl-α-D-ribo-hexopyranosid-3-ulose (19).—The pyranosidulose (19) (1 g) in benzene (200 ml) was irradiated [method (a)] for 45 min. Evaporation of the solvent and separation of a part of the crude product by column chromatography [system (i)] gave the following fractions: the enone (18) and 2-deoxy-3-ulose derivative (17) as a mixture, and an oil thought to be the oxetanol derivative (20), R_F 0·25, $\nu_{max.}$ 3450 cm^{-1} (OH), τ (CDCl₃) 5·31 (q, MeCHO₂), 4·85br (s, OH, exchangeable with D₂O), 6·57 (s, OMe), 8·73 (d, MeCHO₂), and 5·0—6·7 (8H, complex m).