Arylazo-glycenosides. Part IV.[1] Synthesis and Reactions of Some 2- and 3-Arylazo-derivatives of Methyl 2,3-Dideoxy-D-pent-2-enofuranoside

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A method for the modification of some methyl D-pentofuranosidulose derivatives at the position α to the carbonyl group has been studied. Preparations are described of some new 2- and 3-phenylazo- and *p*-nitrophenylazo-derivatives of methyl 2,3-dideoxy-D-pent-2-enofuranoside using D-xylose as the initial material. The procedures adopted for the syntheses are essentially those developed in our laboratories for the preparation of phenylazo-derivatives of sugars and described in Part I.

The new arylazo-derivatives have been shown to be useful synthetic intermediates: they undergo 1,4-addition reactions in a highly stereoselective way with a wide range of nucleophiles. For example, the following have been used in addition reactions, ammonia and dimethylamine, water, acetic acid, methoxide and azide ions, hydride and deuteride ions, and a range of sulphur nucleophiles. Structures of the products have been established by analysis of their n.m.r. spectra.

A brief examination is reported of the formation of methyl D-pentofuranosiduloses carrying a substituent at position α to the carbonyl group from their arylhydrazones, which are the initial products of the addition reactions.

As part of a study of the value of glycosidulose derivatives as synthetic intermediates in carbohydrate chemistry, we have investigated the preparation of conjugated arylazo-glycenosides and examined their reactions with nucleophilic reagents. Initially, we worked with arylazoglycenosides derived from methyl glycopyranosides *via* the glycopyranosiduloses and already we have described the synthesis and 1,4-nucleophilic addition reactions of some 2- and 3-arylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides [2] and the additions of dienes and dimethyloxosulphonium methylide to these arylazo-derivatives.[3] Now the investigation has been extended to include five-membered furanoid derivatives and a study has been completed of the preparation and reactions of some 2- and 3-arylazo-derivatives of methyl 2,3-dideoxy-D-pent-2-enofuranosides derived from methyl pentofuranosiduloses.

The methyl pentofuranosiduloses used for this investigation were the isomeric *O*-benzoyl derivatives (1), (2), (4), and (5) and the 5-*O*-trityl derivative (3), all of which were prepared from D-xylose.

The immediate precursors of the furanosiduloses were synthesised as follows: an anomeric mixture of methyl 3,5-*O*-isopropylidene-D-xylofuranoside (which could be prepared readily in quantity) was separated by distillation into the α- and β-D-forms,[4] each of which was benzoylated at position 2.[5] Hydrolysis of the 3,5-*O*-isopropylidene group followed by benzoylation at low

[1] Part III, P. M. Collins, S. Kumar, and W. G. Overend, *Carbohydrate Res.*, 1972, **22**, 187.

[2] P. M. Collins, D. Gardiner, S. Kumar, and W. G. Overend, *J.C.S. Perkin I*, 1972, 2596.

[3] P. M. Collins, D. Gardiner, S. Kumar, and W. G. Overend, *J.C.S. Perkin I*, 1972, 2611.

[4] B. R. Baker, R. E. Shaub, and J. H. Williams, *J. Amer. Chem. Soc.*, 1955, **77**, 7.

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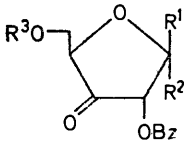
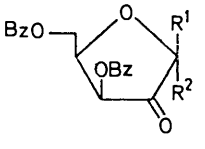
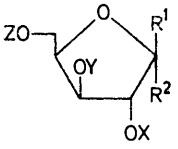
temperature [6] selectively at the primary hydroxy-group, afforded methyl 2,5-di-*O*-benzoyl-α-D-xylofuranoside (6) and its β-D-anomer (7). Monotritylation of methyl



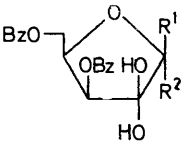
(1) R^1 = H, R^2 = OMe, R^3 = Bz
(2) R^1 = OMe, R^2 = H, R^3 = Bz
(3) R^1 = H, R^2 = OMe, R^3 = Ph_3C



(4) R^1 = H, R^2 = OMe
(5) R^1 = OMe, R^2 = H



(6) R^1 = Y = H, R^2 = OMe, X = Z = Bz
(7) R^1 = OMe, R^2 = Y = H, X = Z = Bz
(8) R^1 = Y = H, R^2 = OMe, X = Bz, Z = Ph_3C
(9) R^1 = X = H, R^2 = OMe, Y = Z = Bz
(10) R^1 = OMe, R^2 = X = H, Y = Z = Bz



(11) R^1 = H, R^2 = OMe
(12) R^1 = OMe, R^2 = H

2-*O*-benzoyl-α-D-xylofuranoside gave the 5-*O*-trityl derivative (8). Partially benzoylated methyl D-xylofuranosides unprotected at position 2 were obtained by converting D-xylose into first 1,2-*O*-isopropylidene-α-D-xylofuranose [7] and then 3,5-di-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-xylofuranose, which upon treatment with methanolic hydrogen chloride underwent deacetonation and glycosidation. Chromatographic separation of the glycosides afforded methyl 3,5-di-*O*-benzoyl-α-D-xylofuranoside (9) (2 parts) and its β-D-anomer (10) (3 parts). The structures of these monohydroxy-dibenzoates [(6), (7), (9), and (10)] follow from the route used for their synthesis, their i.r. spectra, and in some cases their n.m.r. spectral parameters. Thus the $J_{1,2}$ values for compounds (7), (9), and (10) were consistent with their assigned anomeric configurations.[8,9] In the spectrum of compound (9) the H-1 signal was a doublet, $J_{1,2}$ 4.8 Hz, whereas for its anomer (10) $J_{1,2}$ was only 1.0 Hz indicating the *trans*-relationship for H-1 and H-2 and consequently the β-D-configuration. The n.m.r. spectrum of compound (7) showed the H-1 signal as a singlet ($J_{1,2}$ <0.3 Hz) indicating, therefore, that this methyl 2,5-di-*O*-benzoyl-xylofuranoside had the β-D-configuration. This implies that compound (6) is the α-D-isomer. Since compounds (6) and (8) were both prepared from the same precursor it follows that they have the same anomeric configuration. The optical rotations of the glycosides (6), (7), (9), and (10) were consistent with these anomeric assignments.

Oxidation of compounds (6)—(8) with ruthenium tetraoxide [10,11] gave, respectively, methyl 2,5-di-*O*-benzoyl-α-D-*erythro*-pentofuranosid-3-ulose (1), its β-D-anomer (2), and methyl 2-*O*-benzoyl-5-*O*-trityl-α-D-*erythro*-pentofuranosid-3-ulose (3), all crystalline and in good yields. On the other hand, the hydrates (11) and (12) of the 2-ulosides (4) and (5) were obtained in highest yields by oxidising compounds (9) and (10) respectively with semi-catalytic amounts of ruthenium tetraoxide [12-15] and buffering of the solution of sodium periodate to pH 7.5 with potassium hydroxide. Williams,[16] working in our laboratory, has shown that these conditions result in a minimum of over-oxidation [10,17,18] or decomposition. The hydrates (11) and (12) could be dehydrated to give the oxo-forms (4) and (5) by azeotropic removal of water.

Elemental analyses and i.r. and n.m.r. spectral characteristics were in accord with the structures assigned to compounds (1)—(5). The characteristic

TABLE 1

N.m.r. spectral parameters (τ and *J*/Hz values) for methyl pentofuranosiduloses at 60 MHz

Compd.	Solvent	H-1	H-2	H-3	H-4	H-5, -5′	MeO	Aromatic
(1)	C_6D_6	4.70 (d), $J_{1,2}$ 5.0	4.41 (q), $J_{2,4}$ 1.0		6.03 (t), $J_{4,5}$ 3.5	5.28 (q), $J_{5,5'}$ 12.0; 5.73 (q), $J_{5',4}$ 3.0	6.94 (s)	1.7—2.9
(2)	$CDCl_3$	4.62 (d), $J_{1,2}$ 3.5	4.90 (q), $J_{2,4}$ 0.5		← 5.0—5.7 →		6.50 (s)	1.7—2.8
(3)	$CDCl_3$	4.35 (d), $J_{1,2}$ 5.0	4.21 (q), $J_{2,4}$ 0.8		5.83br (t)	6.3—6.8	6.55 (s)	1.7—3.1
(4)	CCl_4	5.17 (d), $J_{1,3}$ *ca.* 0.5		4.09 (q), $J_{3,4}$ 8.0	← 4.8—5.8 →		6.53 (s)	1.8—3.0
(5)	CCl_4	5.12 (d), $J_{1,3}$ *ca.* 1.0		4.15 (q), $J_{3,4}$ 8.0	← 4.8—5.7 →		6.60 (s)	1.7—3.0

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[13] V. M. Parikh and J. K. N. Jones, *Canad. J. Chem.*, 1965, **43**, 3452.
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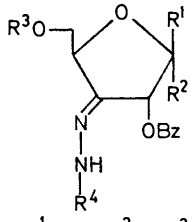
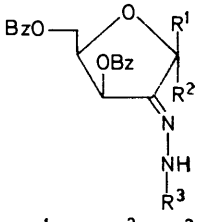
ketone carbonyl i.r. absorptions [10,19-21] at *ca.* 1 780 cm^{-1} for the 2-ulosides (4) and (5) and 3-ulosides (1)—(3) occur at a higher wavenumber than those observed for the carbonyl group in pyranoid ulosides, which are usually at *ca.* 1 740 cm^{-1}.[10,11,13]

The n.m.r. signals of most protons in these compounds, apart from those at C-4 and -5 which usually had similar chemical shifts, could be analysed by first-order methods (see Table 1). The furanosid-2-uloses (4) and (5) exhibited a high $J_{3,4}$ value of 8 Hz which suggested that H-3 and H-4 in both compounds had retained the same *cis*-stereochemistry as in their precursors. Consequently, since compounds (4) and (5) were isomers, the anomeric configurations of their respective precursors (9) and (10) were unaltered during the oxidation. The α-D-furanosid-3-uloses (1) and (3) possessed a coupling constant between H-1 and H-2 of 5 Hz which was satisfactory for protons that are *cis*-disposed, whereas the β-D-furanosid-3-ulose (2) exhibited a smaller coupling of 3.5 Hz between these protons suggesting that these were *trans*-related [9] (a conclusion confirmed by the n.m.r. spectrum of its arylhydrazone). There appears, therefore, to be no change in configuration at C-2 during oxidation and, judging from observations [22] with a related compound, no change at C-4 either. These results extend a previous conclusion [23-25] that oxidations with ruthenium tetraoxide do not induce isomerisation at carbon atoms adjacent to the carbonyl group in pyranosiduloses.

In most cases the conversion of the ulosides into their arylhydrazone derivatives was readily achieved and compounds (13)—(19) were prepared. The compounds differed significantly in their stability and whereas crystalline materials [(13), (14), (16), (18), and (19)] could be stored, gummy products [(15), (17), and (18A)] could not be kept for long periods. The spectra of the arylhydrazones are consistent with their proposed structures. Phenylhydrazones exhibited intense u.v. absorption at *ca.* 280 nm, close to that reported generally for phenylhydrazones of ketones,[26,27] whereas the *p*-nitrophenylhydrazones showed intense u.v. absorption at *ca.* 370 nm. All the hydrazones exhibited strong i.r. absorptions at 1 600 cm^{-1} due to the >C=N-NAr



(13) R^1 = OMe, R^2 = H, R^3 = Bz, R^4 = Ph
(14) R^1 = OMe, R^2 = H, R^3 = Bz, R^4 = $C_6H_4NO_2$-*p*
(15) R^1 = H, R^2 = OMe, R^3 = Bz, R^4 = Ph
(16) R^1 = H, R^2 = OMe, R^3 = Bz, R^4 = $C_6H_4NO_2$-*p*
(17) R^1 = H, R^2 = OMe, R^3 = Ph_3C, R^4 = Ph



(18A) R^1 = OMe, R^2 = H, R^3 = Ph
(18) R^1 = OMe, R^2 = H, R^3 = $C_6H_4NO_2$-*p*
(19) R^1 = H, R^2 = OMe, R^3 = $C_6H_4NO_2$-*p*

TABLE 2

N.m.r. spectral parameters (τ and *J*/Hz values) for methyl pentofuranosidulose arylhydrazones at 60 MHz

Entry	Compd.	Solvent	H-1	H-2	H-3	H-4	H-5′	H-5	MeO	Ph	NH
1	(13)	C_6D_6	4.90 (s)	3.95 (d), $J_{2,4}$ 1.5		5.05 (m), $J_{4,5}$ 6.5	5.2 (q), $J_{5',4}$ 1.5	5.98 (q), $J_{5,4}$ 6.5, $J_{5,5'}$ 13.0	6.81 (s)	1.7—3.4 (m)	0.73 (s)
2	(13)	$CDCl_3$	4.8 (s)	4.24 (d), $J_{2,4}$ 1.5		4.8 (m)	4.95 (q), $J_{5',4}$ 1.5	5.76 (q), $J_{5,4}$ 6.5, $J_{5,5'}$ 13.0	6.45 (s)	1.7—3.4 (m)	0.96 (s)
3	(14)	$CDCl_3$	4.6 (s)	4.24 (d), $J_{2,4}$ 2		← 4.6—6.0 →			6.38 (s)	1.6—3.3 (m)	0.02(s)
4	(15a)	C_6D_6	← 3.8—5.4 (m) →			← 3.8—5.4 →			6.86 (s)	← 1.5—3.5 (m) →	
5	(15b)	C_6D_6	4.66 (d), $J_{1,2}$ 4.8	4.07 (q), $J_{2,4}$ 2		5.08 (m)	5.2 (q), $J_{5',4}$ 1.5	5.95 (q), $J_{5,5'}$ 12.5 $J_{5,4}$ 6.0	6.85 (s)	1.5—3.4 (m)	1.11 (s)
6	(15b)	$CDCl_3$	4.45 (d), $J_{1,2}$ 5	4.22 (q), $J_{2,4}$ 2		← 4.8—5.8 →			6.58 (s)	1.7—3.3 (m)	1.53 (s)
7	(16)	$CDCl_3$	4.46 (d), $J_{1,2}$ 4.5	4.20 (q), $J_{2,4}$ 2		← 4.8—5.6 →			6.55 (s)	1.8—3.3 (m)	0.94 (s)
8	(17)	C_6D_6	4.80 (d), $J_{1,2}$ 5	4.17 (q), $J_{2,4}$ 2		5.0—5.5	← 6.2—6.7 →		6.87 (s)	1.3—3.7 (m)	1.21 (s)
9	(18)	$CDCl_3$	4.7—5.7 (m)		4.51 (d) $J_{3,4}$ 6		← 4.7—5.7 →		6.52 (s)	1.7—3.3 (m)	3.55 (s)
10	(19)	$CDCl_3$	4.0—6.0 (m)			← 4.0—6.0 →			6.38 (s) 6.50 (s)	1.6—3.1 (m)	−0.15 (s) 0.01 (s)

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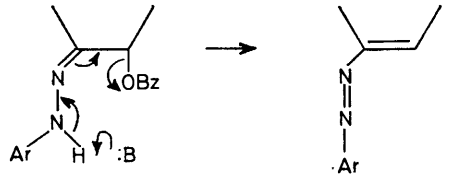
group [26,28] and in addition showed a diagnostic sharp absorption close to 3 250 cm^{-1} due to >N–H. The *p*-nitrophenylhydrazones had a further absorption at *ca.* 1 490 cm^{-1} arising from the nitro-group. The assignments of protons in the n.m.r. spectra are listed in Table 2. Signals for the anomeric protons in the α-D-compounds (15)—(17) appeared as doublets, $J_{1,2}$ *ca.* 5 Hz, similar to that found in the parent pentofuranosidulose and satisfactory for a *cis*-1,2-coupling.

The β-D-compounds (13) and (14) on the other hand had values for $J_{1,2}$ <0.5 Hz. This is smaller than the value exhibited by the parent ulose (2) and it affords, therefore, evidence which corroborates the β-configuration already assigned to compound (2).

It is known that phenylhydrazones of glycopyranosiduloses can exist as geometric isomerides.[2,29] Thus two forms of the phenylhydrazone of methyl 2,5-di-*O*-benzoyl-α-D-*erythro*-pentofuranosid-3-ulose (5a and 15b) were isolated but the configurations could not be assigned unequivocally by application of the method adopted by Karabatsos and his co-workers,[30] because only one isomer afforded resolvable n.m.r. spectra and in these only the H-2 signal could be seen. The form of the phenylhydrazone (13) isolated was assigned, however, the *anti* *-structure by this method because the H-2 signal suffered a downfield shift (−0.29 p.p.m.) and that of H-4 an upfield shift (+0.25 p.p.m.) in [$^2H_6$]-benzene relative to their chemical shifts in $CDCl_3$ and hence the PhNH group was nearer to H-4 than to H-2.

From treatment of the arylhydrazones with either sodium methoxide in methanol, or potassium t-butoxide, or triethylamine, or 1,8-bis(dimethylamino)naphthalene it was not possible to isolate arylazo-derivatives. This was unexpected in view of previous experience with arylhydrazones derived from glycopyranosiduloses.[2] Since in the treatment with sodium methoxide in methanol the colours of the orange or deep red solutions first formed were immediately discharged with final production of colourless or pale yellow solutions it appeared that arylazo-derivatives were transiently produced but underwent an addition reaction. Potassium t-butoxide gave mixtures of products with the pentofuranosidulose arylhydrazones, but the other two bases mentioned induced no reaction. However, 1,4-elimination of



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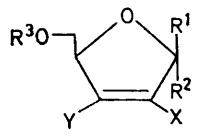
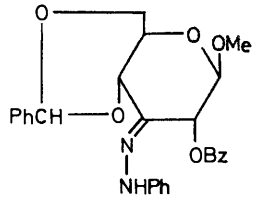
benzoic acid from these arylhydrazones leading to arylazo-derivatives (see Scheme) could be induced cleanly by use of the heterocyclic base 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) [32] in benzene, which under the conditions employed functioned as a strong base but a poor nucleophile. In this way the arylazo-derivatives (20)—(24) were prepared. It was necessary to adopt milder conditions (*e.g.* lower temperature and shorter





(25)

(20) R^1 = X = H, R^2 = OMe, Y = N_2Ph, R^3 = Bz
(21) R^1 = OMe, R^2 = X = H, Y = N_2Ph, R^3 = Bz
(22) R^1 = OMe, R^2 = Y = H, X = N_2Ph, R^3 = Bz
(23) R^1 = OMe, R^2 = Y = H, X = $N_2C_6H_4NO_2$-*p*, R^3 = Bz
(24) R^1 = X = H, R^2 = OMe, Y = N_2Ph, R^3 = Ph_3C

reaction times) than those found to be necessary to prepare 2- and 3-arylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides.[2]

In making both five-membered and six-membered cyclic azoalkenes from the arylhydrazones of methyl glycosid-3-uloses it was noted that, under identical conditions, compounds in the β-D-series were formed much more rapidly than the isomeric α-D-compounds. The higher rate at which the phenylhydrazone of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-*ribo*-hexopyranosid-3-ulose (25) reacts with base compared with its α-D-anomer can be explained by considering the non-bonded interactions between the leaving group at C-2 and the substituent at C-1. In the α-D-compound there is an unfavourable dipolar interaction [33] between the departing benzoate group at C-2 and the aglycone which is not so marked in the β-D-isomer. This explanation is also applicable to the difference in reaction times noted for the α- and β-D-pentofuranosid-3-ulose phenylhydrazones (15) and (13).

The furanoid arylazo-derivatives were orange-coloured and exhibited u.v. absorption in the region 300—315 nm. Apart from the carbonyl band of the benzoate ester at *ca.* 1 710 cm^{-1}, the azoalkenes had no distinguishing features in the i.r. region. The n.m.r., u.v., and i.r. spectral parameters of the methyl 2- (or 3-) arylazo-2,3-dideoxy-D-pent-2-enofuranosides are given in Table 3. The n.m.r. spectra of compounds (20), (21), and (24) could be completely analysed by first-order means and they showed long range allylic ^4J and homoallylic ^5J couplings.

Evidence drawn from other branches of organic chemistry indicated that arylazoalkenes incorporating an

* In this paper the *syn*-form is regarded as the isomer in which the arylimino-group is directed towards the ring carbon atom with lowest number: the other isomer is the *anti* form.[29,31]

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[31] P. M. Collins, *Chem. Comm.*, 1966, 164.

[32] H. Oediger and F. R. Moller, *Angew. Chem. Internat. Edn.*, 1967, **6**, 76.

[33] A. C. Richardson, *Carbohydrate Res.*, 1969, **10**, 395.

unsaturated pentofuranoid ring would be more reactive than the analogous derivatives incorporating an unsaturated hexopyranoid ring. This is as found, but even so they have been shown to be useful intermediates in carbohydrate syntheses, although some were more valuable than others. Their reactivity was demonstrated by the formation of a dimer in the preparation. Thus, in the preparation of compound (21) a dimer was also obtained. Spectral evidence indicated that it was produced by 1,2-addition of one molecule of the phenylazo-derivative (21) across positions 1 and 4 of another molecule. Compound (22) also tended to dimerise and so had to be purified as required for further reactions.

$J_{3,4}$ combined with knowledge of the configuration at C-4.

Nitrogen nucleophiles added readily. When compound (20) was treated with sodium azide in acetone and water containing ammonium chloride, methyl 2-azido-5-*O*-benzoyl-2-deoxy-α-D-*threo*-pentofuranosidulose phenylhydrazone was produced. Initially (10 min at ambient temperature) one isomer (26) (tentatively assigned the *anti*-structure) was formed, but during 24 h in solution it isomerised [presumably to the *syn*-isomer (27)]. The *syn*- or *anti*-structures were assigned from an analysis of the ^{1}H n.m.r. spectra in terms of the solvent shift method of Karabatsos *et al.*[30] (see Table 4). For

TABLE 3

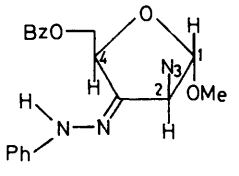
Spectral parameters for methyl 2- (or 3-)arylazo-2,3-dideoxy-D-pent-2-enofuranosides

Compd.	τ (60 MHz; $CDCl_3$; J in Hz) [a,b] H-1	HC=C	H-4	H-5, -5′	(EtOH) $\lambda_{max.}$/nm (ε)	$\nu_{C:O}$/cm^{-1}
(20)	3.91 (q), $J_{1,2}$ 1.5, $J_{1,4}$ 4.0	3.10 (t), $J_{2,4}$ 1.5	4.42 (m) $J_{4,5}$ 3.8, $J_{4,5'}$ 2.5	5.13 (q) 5.43 (q), $J_{5,5'}$ 12.2	313 (22 600)	1 710
(21)	4.14 (q), $J_{1,2}$ 1.5, $J_{1,4}$ 1.0	3.12 (t), $J_{2,4}$ 1.5	4.64 (m) $J_{4,5}$ 4.8, $J_{4,5'}$ 2.5	5.10 (q) 5.44 (q), $J_{5,5'}$ 12	311 (21 800)	1 710
(22)	3.93 (s)	2.91 (d), $J_{3,4}$ 2	4.72 (sx), $J_{4,5}$ 5 $J_{4,5'}$ 5	5.1—5.7 (m)	307	1 720
(24)	3.71 (q), $J_{1,2}$ 1.2, $J_{1,4}$ 4.4	3.07 (t), $J_{2,4}$ 1.8	4.7 (m), $J_{4,5'}$ 2.6 $J_{4,5}$ 12.1	6.2—6.7 (m)		

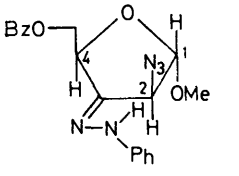
[a] A three-proton sharp singlet from the aglycone MeO occurs in the range τ 6.51—6.55. [b] A complex multiplet arising from the aromatic protons occurs in the range τ 1.7—3.3.

The new phenylazoalkenes were found to undergo ready 1,4-additions when treated with nucleophiles. The most studied reactions were those carried out with compounds (20) and (21). The additions occurred in a manner analogous to those observed with 2- and 3-arylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides,[2] to give products that were established as α-substituted hydrazones from elemental analyses and spectral measurements. Like the pentofuranosidulose phenylhydrazones (13), (15), and (17) the products had u.v. and i.r. absorption maxima at, respectively, *ca.* 280 nm, and *ca.* 3 200 (NH) and 1 600 cm^{-1} (C=N–NPh). They all displayed an imino-proton singlet (in the region τ 0.2—2.4), an aglycone methoxy-singlet (τ 6.5—7.0 depending on the solvent), and aromatic proton signals in the region τ 1.6—3.5. Signals for the two protons at C-5 appeared as unresolved multiplets in the spectra of all hydrazones except (32) and (47). Seven hydrazones showed three clearly resolved ring proton signals, but most exhibited only two, since the H-4 signal was often obscured by that of H-5.

Additions to the 3-azoalkenes gave 2-substituted derivatives of a pentofuranosid-3-ulose arylhydrazone. The addition reaction converts position 2 in the sugar ring from the sp^2 to the sp^3 state of hybridisation, and so a pair of epimers may be produced from such a reaction. The stereochemistry at C-2 was deduced from the value of $J_{1,2}$ (see Table 4) and a knowledge of the anomeric configuration. 3-Substituted derivatives of a pentofuranosid-2-ulose arylhydrazone resulted from the additions to the 2-azoalkenes. For these cases the configuration at C-3 was obtained from the value of the compound assigned the *anti*-structure, the H-2 signal moved upfield by 0.04 p.p.m. (see Table 4) in the aromatic solvent whereas that of H-2 in the compound assigned the *syn* structure (27) moved upfield (shielding)



(26)



(27)

by 0.73 p.p.m. in C_6D_6 compared to $(CD_3)_2CO$. The method of assigning *syn*- or *anti*-structures to ketoximes,[31,34] which depends upon *cis*-protons in the *syn*-isomers being deshielded relative to the *anti*-isomer, was found to be inapplicable to the phenylhydrazones (26) and (27). For compounds prepared in this work, it appears that the solvent shift technique provides the most satisfactory method of evaluating arylhydrazone isomerism, other than *X*-ray crystallography.

The presence of the azido-residue in compounds (26) and (27) was revealed by the i.r. spectrum and the configuration at C-2 was established by a $J_{1,2}$ value of less than 0.5 Hz indicating a *trans*-relationship for H-1 and H-2.[8,9] Since the glycosides have the α-D-configuration, both derivatives have the D-*threo*-structure.

A 2-azido-derivative was also prepared from the tritylated azoalkene (24).

[34] P. J. Beynon, P. M. Collins, and W. G. Overend, *J. Chem. Soc.* (*C*), 1969, 272.

TABLE 4

N.m.r. spectral parameters (τ and J/Hz values) for derivatives of methyl D-pentofuranosid-3-ulose phenylhydrazones at 60 MHz

Entry	Compd.	Solvent	H-1	H-2	H-4	H-5′	H-5	MeO	Others	Ph	NH
1	(26)	C_6D_6	5.27 (s)	5.73 (s)	← 5.1—5.5 →		5.98 (q), $J_{5,5'}$ 13, $J_{5,4}$ 6	6.96 (s)		1.8—3.4 (m)	0.84 (s)
2	(26)	$CDCl_3$	5.1 (s)	5.69 (s)	← 4.8—5.3 →		5.76 (q), $J_{5,5'}$ 13, $J_{5,4}$ 6.5	6.68 (s)		1.7—3.4 (m)	0.94 (s)
3	(27)	C_6D_6	4.9—5.5	6.03 (s)	← 4.9—5.5 →			6.94 (s)		1.6—3.3 (m)	2.35 (s)
4	(27)	$(CD_3)_2CO$	4.73 (s)	5.3 (s)	← 4.7—5.9 →			6.59 (s)		1.7—3.4 (m)	0.83 (s)
5 *	(28)	$CDCl_3$	5.12 (s)	← 5.2—5.4 →			5.60 (q), $J_{5,5'}$ 12, $J_{5,4}$ 5	6.63 (s)	8.20 (s, Ac); 4.20 (d, AcNH), J 8.0	1.7—3.4	0.89 (s)
6	(29)	$CDCl_3$	4.93 (s)	6.88 (s)	← 4.9—5.2 →		5.72 (q), $J_{5,5'}$ 13, $J_{5,4}$ 7.0	6.65 (s)	7.64(s, NMe_2)	1.7—3.4 (m)	1.11 (s)
7	(30)	C_6D_6	5.0 (s)	4.60 (s)	← 5.0—5.5 →			6.91 (s)	8.55 (s, OAc)	1.7—3.4 (m)	0.55 (s)
8	(31)	C_6D_6	5.05 (s)	5.87 (s)	5.32 (q), $J_{4,5}$ 8.5, $J_{4,5'}$ 4.5	← 6.0—6.5 →		6.77 (s) 6.83 (s)	7.1 (m)	2.6—3.3 (m)	0.72 (s)
9	(33)	$CDCl_3$	4.69 (s)	5.93 (d), $J_{2,4}$ 1	5.14 (m)	5.45 (q), $J_{5,4}$ 2.5	6.1 (q), $J_{5,5'}$ 12, $J_{5,4}$ 7	6.62 (s)		1.8—3.3 (m)	2.0 (s)
10	(34)	$CDCl_3$	4.84 (s)	5.5 (s)	← 4.9—5.6 →			6.59 (s)	7.63 (s, SAc)	1.7—3.3 (m)	2.04 (s)
11	(35)	C_6D_6	4.88 (s)	4.53 (d), $J_{2,4}$ 1	← 4.9—5.6 →			6.85 (s)		1.7—3.5 (m)	2.4 (s)
12	(36)	$(CD_3)_2CO$	4.77 (q), $J_{1,2'}$ 5, $J_{1,2}$ 0.5	7.42 (q), $J_{2,4}$ 2 [H-2′ 6.98 (oct), $J_{2',2}$ 16]	4.9 (m)	5.40 (q), $J_{5',4}$ 3	5.20 (q), $J_{5,5'}$ 12, $J_{5,4}$ 5	6.68 (s)		1.7—3.4 (m)	1.43 (s)
13	(37)	$(CD_3)_2CO$	4.79 (s)	7.41br (s)	4.85 (q), $J_{4,5}$ 3, $J_{4,5'}$ 4	← 5.0—5.6 →		6.68 (s)		1.7—3.4 (m)	1.43 (s)
14	(38)	$CDCl_3$	5.1 (s)	5.6 (d), $J_{2,4}$ 2				6.50 (s)		1.7—3.3 (m)	0.92 (s)
15	(39)	$(CD_3)_2SO$	4.8 (s)	← 4.8—5.9 →				6.64 (s)	8.02 (s, Ac); 1.20 (d, AcNH)	1.8—3.4 (m)	0.25 (s)
16	(40)	$CDCl_3$	5.1 (s)	5.95 (d), $J_{2,4}$ 1	5.20 (oct), $J_{4,5}$ 7.5, $J_{4,5'}$ 4.5	← 6.0—6.4 →		6.50 (s) 6.68 (s)	6.95(t, OH) J 5	2.5—3.4 (m)	0.94 (s)
17	(41)	$CDCl_3$	4.77 (d), $J_{1,2}$ 0.5	6.20 (q), $J_{2,4}$ 1	← 4.8—5.6 →			6.61 (s)	7.39 (q), 8.73 (t) (Et)	1.7—3.4 (m)	1.8—2.0 (s)
18	(42)	$CDCl_3$	4.69 (s)	5.88 (s) $J_{2,4}$ *ca.* 1	← 5.1—5.7 →			6.65 (s)		1.7—3.4 (m)	2.07 (s)
19	(43)	$(CD_3)_2CO$	4.89 (s)	5.4 (s)	← 4.9—5.7 →			6.60 (s)	7.55 (s, SAc)	1.7—3.4 (m)	1.53 (s)
20	(44)	C_6D_6	4.6—6.2 (m)	4.50 (d), $J_{2,4}$ 2	← 4.6—6.2 →			6.70 (s) 6.81 (s)		1.7—3.5 (m)	1.57 (s)
21	(45)	$(CD_3)_2CO$	4.76 (q), $J_{1,2'}$ 5	(+H-2′) 6.7—7.5 (m), $J_{1,2}$ 2	4.9 (m)	5.15 (q), $J_{5',5}$ 12 $J_{5',4}$ 3	5.58 (q), $J_{5,5'}$ 12 $J_{5,4}$ 7	6.60 (s)		1.7—3.5 (m)	1.45 (s)
22	(46)	$(CD_3)_2CO$	4.76 (d), $J_{1,2}$ 2	7.28br (s)	4.9 (m)	5.15 (q), $J_{5',5}$ 12, $J_{5',4}$ 3	5.58 (q), $J_{5,5'}$ 12 $J_{5,4}$ 7	6.61 (s)		1.7—3.4 (m)	
23	(32)	C_6D_6	5.07 (s)	5.87 (s)	5.25 (q), $J_{4,5}$ 9, $J_{4,5'}$ 4	← 6.0—6.5 →		6.82 (s) 6.87 (s)		2.2—3.4 (m)	0.97 (s)
24	(47)	C_6D_6	5.42 (s)	5.73 (s)	5.37 (m)	← 6.0—6.7 →		6.99 (s)		2.3—3.4 (m)	0.78 (s)

* Measured at 100 MHz.

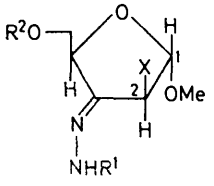
Treatment of compound (20) with ammonia and acetylation of the product afforded a crystalline 2-acetamido-derivative (28). The n.m.r. spectrum (see Table 4, entry 5) showed that H-2 was deshielded by the amido-group and only the H-1 signal was resolved. It was a singlet and consequently H-1 and H-2 are *trans*-related.

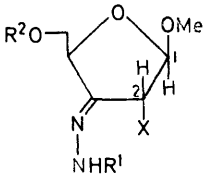
The azoalkene (20) with dimethylamine underwent very rapid reaction, even at 0 °C, and gave the 2-dimethylamino-derivative (29) as a glass which required storage under nitrogen. I.r. maxima at 3 200 and 1 600 cm^{-1} were consistent with the proposed structure. In the n.m.r. spectrum the dimethylamino group at C-2 gave rise to a six-proton singlet. The H-2 signal was at relatively high field (τ 6.88), as expected for a 2-amino-2-deoxy-sugar. Since it was a singlet, H-2 must be *trans* to the anomeric proton, which also gave a singlet. This evidence supports structure (29) for the dimethylamino-compound.

Reagents possessing a nucleophilic oxygen atom underwent reaction with the azoalkene (20). Acetic acid added readily at ambient temperature to give crystalline methyl 2-*O*-acetyl-5-*O*-benzoyl-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (30). The configuration at position 2 was established from the n.m.r. spectrum (see Table 4, entry 7): the H-1 and H-2 signals (τ 5.0 and 4.6 respectively) were both singlets, and the presence of the 2-acetate function was indicated by a three proton singlet at τ 8.55.

When methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-α-D-*glycero*-pentenofuranoside (20) was heated briefly with methanol containing a small amount of sodium methoxide the orange colour was discharged and a new glassy product was obtained. Besides the addition reaction, debenzoylation had occurred and the product was found by spectral analysis (see Table 4, entry 8 and Experimental section) to be methyl 2-*O*-methyl-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (31). The same compound could be obtained directly from methyl 2,5-di-*O*-benzoyl-α-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (15) by treatment with sodium methoxide in methanol. Its trityl derivative (32) was formed when methyl 2,3-dideoxy-3-phenylazo-5-*O*-trityl-α-D-*glycero*-pent-2-enofuranoside (24) was treated likewise with methanol containing a small amount of sodium methoxide. The 2-methoxy-substituent was shown to be *trans* to the aglycone in these products since the anomeric proton and H-2 gave rise to singlets in the n.m.r. spectrum.

Several sulphur-containing nucleophiles were added to the azoalkene (20). With benzenethiol it gave methyl 5-*O*-benzoyl-2-*S*-phenyl-2-thio-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (33). With thioacetic acid diluted with acetone the analogous 2-*S*-acetyl compound (34) was formed rapidly and if potassium dithiobenzoate was used then the 2-*S*-thiobenzoyl derivative (35) was obtained. All these compounds were isolated in crystalline form. The structures followed from the n.m.r. spectra, particularly the small $J_{1,2}$ values observed (see Table 4, entries 9—11). Hedgley and Leon [35] have demonstrated that protons attached to carbon, bonded to bivalent sulphur, resonate upfield from those bonded to alkoxy-substituents: Horton *et al.*[36] have noted that *S*-acetyl methyl signals resonate about 0.35 p.p.m. downfield from those of their *O*-acetyl analogues. Consequently, the ambident nucleophile MeCOS reacted through sulphur to give the 2-thiolacetate phenylhydrazone (34), as might be expected from the work with potassium thioacetate [37-40] which always displaces leaving groups in its thiolacetate form.





(28) X = NHAc, R^1 = Ph, R^2 = Bz
(29) X = NMe_2, R^1 = Ph, R^2 = Bz
(30) X = OAc, R^1 = Ph, R^2 = Bz
(31) X = OMe, R^1 = Ph, R^2 = H
(32) X = OMe, R^1 = Ph, R^2 = Ph_3C
(33) X = SPh, R^1 = Ph, R^2 = Bz
(34) X = SAc, R^1 = Ph, R^2 = Bz
(35) X = S·SCPh, R^1 = Ph, R^2 = Bz
(36) X = H, R^1 = Ph, R^2 = Bz
(37) X = D, R^1 = Ph, R^2 = Bz
(47) X = N_3, R^1 = Ph, R^2 = Ph_3C

(38) X = N_3, R^1 = Ph, R^2 = Bz
(39) X = NHAc, R^1 = Ph, R^2 = Bz
(40) X = OMe, R^1 = Ph, R^2 = H
(41) X = SEt, R^1 = Ph, R^2 = Bz
(42) X = SPh, R^1 = Ph, R^2 = Bz
(43) X = SAc, R^1 = Ph, R^2 = Bz
(44) X = S·SCPh, R^1 = Ph, R^2 = Bz
(45) X = H, R^1 = Ph, R^2 = Bz
(46) X = D, R^1 = Ph, R^2 = Bz

The α-D-3-phenylazoalkene (20) in methanolic solution was reduced readily with an excess of sodium borohydride and it gave in high yield the 2-deoxy-α-D-furanosidulose phenylhydrazone (36) as indicated by the signals from a methylene group and the splitting of the H-1 signal into a quartet (5.0 and 0.5 Hz). The methylene proton gave rise to two separate resonances with a geminal coupling of 16 Hz. The proton at C-2, which was *cis* to H-4, was long-range coupled to it by 2 Hz. If the azoalkene (20) in methan[^{2}H]ol was reduced with sodium borodeuteride it yielded the 2-deuterio-product (37), which exhibited a signal for the methylene group with an intensity of only one proton. The H-1 signal appeared as a singlet; thus $J_{1,2} < 0.5$ Hz, indicating that the deuterium had entered *trans* to the aglycone. A singlet at τ 1.43 could be attributed to the imino-proton, which had replaced deuterium during purification.

[35] E. J. Hedgley and N. H. Leon, *J. Chem. Soc.* (*C*), 1970, 466.
[36] D. H. Horton and W. N. Turner, *Carbohydrate Res.*, 1966, **1**, 444.
[37] M. J. Cox and L. N. Owen, *J. Chem. Soc.* (*C*), 1967, 1121.
[38] T. J. Adley and L. N. Owen, *J. Chem. Soc.* (*C*), 1966, 1287.
[39] L. N. Owen and P. L. Ragg, *J. Chem. Soc.* (*C*), 1966, 1291.
[40] C. J. Clayton and N. A. Hughes, *Carbohydrate Res.*, 1967, **4**, 32.

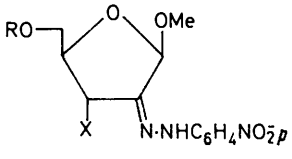
Additions with methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-β-D-*glycero*-pent-2-enofuranoside (21) were also carried out. Thus the 2-azido-phenylhydrazone (38) was prepared and it showed i.r. and u.v. absorption maxima similar to those of the analogous α-D-isomers (26) and (27). In its n.m.r. spectrum the anomeric proton signal appeared as a singlet indicating that H-1 and H-2 were *trans* related, whereas that of H-2 was a doublet long-range coupled with H-4 by 2 Hz. Addition of ammonia to compound (21), followed by acetylation of the product, yielded the 2-acetamido-phenylhydrazone (39). The structure of this solid followed from the i.r. and n.m.r. spectral evidence (see Table 4). Treatment of either the azoalkene (21) or methyl 2,5-di-*O*-benzoyl-β-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone with sodium methoxide in methanol gave good yields of methyl 2-*O*-methyl-β-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (40). This product had absorptions at 3 300, 3 200, and 1 590 cm^{-1} but the absorption of the benzoate group was absent. Its structure was deduced from the mode of preparation, and its n.m.r. spectrum in which the H-1 signal appeared as a singlet and that of H-2 as a doublet long-range coupled with H-4 by 1 Hz. It was inferred from the small $J_{1,2}$ value that the aglycone and 2-methoxy-groups were *trans*. A triplet at τ 6.95 showing equal coupling to H-5 and H-5′ by 5 Hz, and exchangeable with D_2O, was assigned to the hydroxy-proton at position 5.

Several sulphur nucleophiles were added to the β-D-3-phenylazoalkene (21). In this way the 2-*S*-ethyl (41), 2-*S*-phenyl (42), 2-*S*-acetyl (43), and 2-*S*-thiobenzoyl (44) derivatives of methyl 5-*O*-benzoyl-2-thio-β-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone were prepared by addition, respectively, of ethanethiol, benzenethiol, thioacetic acid, and potassium dithiobenzoate. Structures were assigned on the basis of the n.m.r. spectral characteristics of the compounds (see Table 4, entries 17—20) and their i.r. spectra. The structural assignment for compound (44) is only tentative. Although signals for two phenyl groups and an imino-proton could be seen in the n.m.r. spectrum there were anomalies. Thus two methoxy-signals of equal intensity were noted at τ 6.70 and 6.81 which were thought to indicate a mixture of *syn*- and *anti*-hydrazones. Only one other signal could be analysed and this was a doublet at τ 4.50 which was assigned to H-2. It showed long-range coupling with H-4 of 2 Hz.

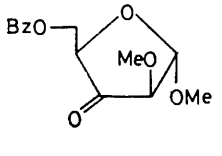
The azoalkene (21) could be reduced with either sodium borohydride or sodium borodeuteride to give, respectively, compounds (45) and (46). In the n.m.r. spectrum of compound (45) (see Table 4, entry 21), the H-1 signal appeared as a quartet with couplings of 2 and 5 Hz to the protons at C-2, but unfortunately these had similar chemical shifts in the region τ 6.7—7.5 and the signals could not be analysed. The n.m.r. spectrum (see Table 4, entry 22) of the 2-deuterio-analogue (46) was as expected for substitution of a proton by deuterium at C-2. The broad singlet which remained at τ 7.28 integrated for only one proton and the multiplicity of the H-1 resonance was reduced to a doublet, $J_{1,2}$ 2 Hz. Hence it seems that the deuteride anion had undergone addition *trans* to the aglycone in compounds (20) and (21) with a high degree of stereoselectivity. A singlet at τ 1.45 which was present in compound (45) and could be attributed to the imino-proton, was absent in (46).

The feasibility of additions to an azoalkene with the phenylazo-substituent at position 2 of the unsaturated furanoid ring was tested with methyl 5-*O*-benzoyl-2,3-dideoxy-2-(*p*-nitrophenylazo)-β-D-*glycero*-pent-2-enofuranoside (23). This substance underwent ready addition of water under acidic conditions and in this respect was unique amongst all the sugar-azoalkenes studied in our laboratory.[1-3] As the analogous phenylazoalkene (22) did not add water, it seems probable that the inductive properties of the *p*-nitro-group on the phenyl ring exert an influence which favours the addition of water in the presence of acid.

The major product (90% by t.l.c.) of the addition reaction with compound (23) was isolated in crystalline form and shown to be methyl 5-*O*-benzoyl-β-D-pentofuranosid-2-ulose *p*-nitrophenylhydrazone (48). It was readily converted into a 3-*O*-benzoyl derivative (49) indicating the presence of one hydroxy-group. The balance of evidence leads to the conclusion that compounds (48) and (49) have the D-*erythro*-configuration. The n.m.r. spectrum of compound (48) was not clearly resolved, particularly the important H-3 resonance. The anomeric proton and the methoxy-group resonances were singlets as was the imino-proton resonance at τ 1.14. This singlet and the hydroxy-proton doublet at τ 7.01, which showed coupling with H-3 of 5 Hz, were both removed by D_2O. The spectrum of the dibenzoate (49) was different from that of methyl 3,5-di-*O*-benzoyl-β-D-*threo*-pentofuranosid-2-ulose *p*-nitrophenylhydrazone (18). For compound (49), the H-3 signal appeared as a doublet at τ 3.67 ($J_{3,4}$ 6 Hz), whereas that of H-1 was a singlet at τ 4.33 as anticipated. However, for compound (18), H-3 was also coupled with H-4 (6.0 Hz) which makes it difficult to make any valid conclusion on n.m.r. spectral evidence concerning the configuration at C-3 in compounds (48) and (49). However, compound (49) had different physical properties from compound (18),



(48) X = OH, R = Bz
(49) X = OBz, R = Bz
(50) X = OMe, R = Bz
(51) X = R = H



(52)

and as the latter substance has the D-*threo*-configuration, it seems likely that (49) [and hence (48)] has the D-*erythro* configuration and that addition has occurred in compound (23) to give a *trans*-disposition to the hydroxy-group at C-3 and the bulky substituent at C-4. This evidence

has not precluded the rather unlikely possibility that compounds (18) and (49) have the same *threo*-configuration but are *syn*- and *anti*-forms of the *p*-nitrophenylhydrazone.

When the β-D-2-*p*-nitrophenylazoalkene (23) was treated with azide ion in aqueous 1,2-dimethoxyethane, a competitive addition of azide and hydroxide ions occurred as shown by t.l.c. and the i.r. spectrum of the crude reaction mixture. However, it was possible to isolate only the hydroxy-compound (48). The azide adduct appeared to undergo decomposition and in this respect its behaviour resembled that noted when the analogous phenylazoalkene (22) was treated with sodium azide. On addition of sodium azide to compound (22) reaction occurred within a few minutes as shown by loss of colour of the solution and t.l.c. analysis, which indicated that one major product had been formed. (51b) are given in Table 5 [entries 4 and 5 (different) solvents were used owing to solubility problems encountered with these substances].

From the work described with the methyl 2,3-dideoxy-3-phenylazo-D-pent-2-enofuranosides (20), (21), and (24), it seems that attack of a nucleophile at C-2 is usually in a direction *trans* to the aglycone. Too few examples of addition at C-3 to methyl 2-arylazo-2,3-dideoxy-D-pent-2-enofuranosides have been examined to permit generalisations concerning the direction of addition, but for compound (23) the entering nucleophile was located *trans* to both the aglycone and the bulky substituent at C-4 in all the reactions studied.

To complete the method as an approach to the synthesis of a furanosulose modified in the position α to the carbonyl group, it is necessary to regenerate the carbonyl group from the arylhydrazone produced in the

TABLE 5

N.m.r. spectral parameters (τ and *J*/Hz values) for derivatives of methyl D-pentofuranosid-2-ulose arylhydrazones at 60 MHz

Entry	Compd.	Solvent	H-1	H-3	H-4	H-5, H-5′	MeO	Others	Ph	NH
1	(48)	$CDCl_3$	4.46 (s)	←	4.8—5.8	→	6.50 (s)	7.01 (d), $J_{OH.3}$ 5	1.7—3.1 (m)	1.14 (s)
2	(49)	$CDCl_3$	4.33 (s)	3.67 (d), $J_{3.4}$ 6	←	4.8—5.5 →	6.45 (s)		1.7—3.1 (m)	1.11 (s)
3	(50)	$CDCl_3$	4.35 (t), $J_{1.3}$ 1	5.73 (t), $J_{3.4}$ 1	←	5.0—5.6 →	6.46 (s) 6.50 (s)		1.7—3.0 (m)	1.02 (s)
4	(51a)	$(CD_3)_2CO$	4.72 (s)	(+H-3′) 6.8—7.4 (m)	5.3—5.7 (m)	6.1—6.5 (m)	6.56 (s)	6.7br (s) OH	1.7—2.9 (m)	0.7br (s)
5	(51b)	$CDCl_3$	4.49 (s)	6.8—7.4 (m)	5.2—5.7 (m)	6.1—6.6 (m)	6.44 (s)	7.3br (s)	1.7—3.1 (m)	1.51 (s)

However, on attempting to isolate the product the colourless solution became orange again and chromatographic analysis indicated that the azoalkene (22) had been re-formed, so obviously a reversible reaction was involved.

The arylazoalkene (23) when treated with methoxide ion afforded the 5-hydroxy-3-methoxy-*p*-nitrophenylhydrazone which could be rebenzoylated to give gummy methyl 5-*O*-benzoyl-3-*O*-methyl-β-D-*erythro*-pentofuranosid-2-ulose *p*-nitrophenylhydrazone (50). The same compound could be obtained directly from methyl 3,5-di-*O*-benzoyl-β-D-*threo*-pentofuranosidulose *p*-nitrophenylhydrazone (18) by sequential treatment with sodium methoxide and benzoyl chloride. In the n.m.r. spectrum (see Table 5, entry 3), the H-1 signal appeared as a doublet at τ 4.35, long-range coupled with H-3 by *ca.* 1 Hz. The signal for the latter proton was a triplet at τ 5.73 coupled to H-4 by less than 1 Hz, thereby indicating that H-3 and H-4 were *trans*-related.

Reduction of compound (23) with sodium borohydride in 1,2-dimethoxyethane gave two products, isolated by layer chromatography, which are believed to be the *syn*- and *anti*-isomers of methyl 3-deoxy-β-D-*glycero*-pentofuranosid-2-ulose *p*-nitrophenylhydrazone (51). The reduction is accompanied by debenzoylation at C-5 of the sugar ring. An analogous debenzoylation has been noted [41] in the borohydride reduction of methyl 4,6-*O*-benzylidene-2-*O*-benzoyl-α-D-*arabino*-hexopyranosid-3-ulose in methanol. Details of the n.m.r. spectra of the major product (51a) and of the other isolated isomer

addition reaction with the arylazoalkene. Initially, this was attempted with methyl 2-*O*-methyl-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (31). Treatment of the substance in methyl cyanide with pyruvic acid gave methyl 2-*O*-methyl-α-D-*threo*-pentofuranosid-3-ulose, which was isolated after benzoylation of the hydroxy-group at C-5. The 3-ulose gave a n.m.r. spectrum with the H-1 signal as a narrow doublet at τ 4.84 showing coupling to H-2 (at τ 5.6) by 1.3 Hz. This coupling confirmed that H-1 and H-2 were still *trans* and that anomerisation had not occurred during the acidic hydrolysis.

The same procedure was successful for the conversion of phenylhydrazone (40) back into a furanosidulose. The products from compounds (31) and (40) showed $\nu_{max.}$ 1 780 and 1 720 cm^{-1}, indicative of a carbonyl group in a five-membered ring and a benzoate carbonyl group, respectively. No absorption was observed for the C=N–NPh group. In our experience, however, phenylhydrazone hydrolysis has been achieved only when a primary hydroxy-group is present in the pentofuranosidulose phenylhydrazone. Thus, although compounds (31) and (40) could be hydrolysed to the parent uloses, their 5-*O*-benzoyl derivatives were unchanged after similar treatment. In this connection, whereas 4,6-*O*-benzylidene-3-deoxy-D-*erythro*-hexosulose 2-phenylhydrazone could not be hydrolysed to the parent ulose, the 4,6-*O*-benzylidene-3-deoxy-D-*erythro*-hexulose phenylhydrazone obtainable from the hexosulose by

[41] N. Oparaeche, personal communication.

reduction, could be hydrolysed by acetic acid containing pentane-2,4-dione to give 4,6-*O*-benzylidene-3-deoxy-D-*erythro*-hexulose.[1] The presence of the primary hydroxy-group in the hexulose phenylhydrazone was determinative in promoting the hydrolysis. The problems raised by the hydrolysis of arylhydrazones to regenerate the carbonyl group of the parent uloses are being investigated further and this project will form the subject of a further publication, together with an account of the application of the methods described in this paper to the modification of naturally occurring nucleosides.[42]

EXPERIMENTAL

Materials and Methods.—Unless stated otherwise u.v. spectra were measured on ethanolic solutions with a Perkin–Elmer 402 spectrophotometer; i.r. spectra of solid samples dispersed in potassium bromide were determined with a Perkin–Elmer Infracord model 137: gums were measured as smears on potassium bromide discs; optical rotations were measured for solutions in chloroform (unless stated otherwise) with a Bellingham and Stanley polarimeter; 60 and 100 MHz n.m.r. spectra were determined respectively with Varian A-60D and HA-100D instruments (tetramethylsilane as internal standard).

Reactions were monitored by t.l.c. on glass slides coated with either Kieselgel G (Stahl) or G_{254} (fluorescent type) (Stahl) (Merck, Darmstadt) as stationary phase, and air-dried. The following solvent systems (v/v) were used: A, methylene chloride; B, methylene chloride–ethyl acetate (10 : 1); C, diethyl ether; and D, diethyl ether–petroleum (b.p. 40—60°) (1 : 1). Spots were detected either by spraying with 0.1% anisaldehyde in ethanol–sulphuric acid (20 : 1 v/v) followed by heating to 150 °C or, for compounds on fluorescent silica gel, with a u.v. lamp (UVSL-25 supplied by UV Products Inc.). Preparative layer chromatography (p.l.c.) was carried out on plates (20 × 100 cm) evenly coated to a depth of 0.1 mm with Keiselgel GF_{254}. Compounds (0.4—0.6 g) were applied in a volatile solvent and plates were developed by vertical ascent of the solvent. Components were located by means of a u.v. lamp and were retrieved by washing from the silica gel with either acetone–ethanol (10 : 1 v/v) or ethyl acetate. Column chromatography was carried out on Kieselgel columns which had been wet-packed. Benzene and 1,2-dimethoxyethane were dried over molecular sieves, type 3A or 4A (B.D.H.).

Preparation and Oxidation of Partially Protected Furanoid Derivatives.—Methyl 3,5-O-*isopropylidene-α- and -β-*D-*xylofuranoside.* These compounds were prepared by the method of Baker and his co-workers [4] from methyl D-xylofuranoside (120 g), dry acetone (1.25 l), anhydrous copper sulphate (250 g), and toluene-*p*-sulphonic acid (0.5 g). Fractional distillation of the crude product gave as syrups, the α-D-anomer (45 g, 30%) [b.p. 85—88° at 0.1 mmHg, $[\alpha]_D$ +16° (*c* 2 in H_2O) (lit.,[4] b.p. 85—88° at 0.1 mmHg, $[\alpha]_D$ +17.6° (*c* 2 in H_2O)] and the β-D-anomer (30 g, 20%) [b.p. 107—110° at 0.1 mmHg, $[\alpha]_D$ −62° (*c* 1.8 in H_2O) (lit.,[4] b.p. 108—110° at 0.1 mmHg, $[\alpha]_D$ −64° (*c* 2 in H_2O)].

Both acetonated glycosides were readily benzoylated by treatment with benzoyl chloride in dry pyridine. Methyl 2-*O*-benzoyl-3,5-*O*-isopropylidene-α-D-xylofuranoside (73%) had m.p. 89—90° [from diethyl ether–light petroleum (b.p. 40—60°)], $[\alpha]_D$ +128° (*c* 2.8) {lit.,[5] m.p. 92—93°, $[\alpha]_D$ +127° (*c* 2)}. The analogous 2-benzoate in the β-D-series (97%) was a glass, $[\alpha]_D$ −4° (*c* 2), $\nu_{max.}$ 1 720 cm^{-1}.

Methyl 2,5-*di*-O-*benzoyl*-α-D-*xylofuranoside* (6). Methyl 2-*O*-benzoyl-α-D-xylofuranoside (36 g, 94%), m.p. 89° (from ether–pentane), $[\alpha]_D$ +136° (*c* 2.7) {lit.,[5] m.p. 89—90°, $[\alpha]_D$ +142° (*c* 2)}, was prepared by deacetonation of the 3,5-*O*-isopropylidene derivative (44 g) by heating at 50—60 °C for 2 h with 30% aqueous acetic acid (135 ml) and isolation of the product in conventional fashion. To a vigorously stirred solution of this 2-benzoate (36 g) in dry pyridine (200 ml) at −5 °C, benzoyl chloride (15.6 ml) was added dropwise during 1 h. After storage overnight at 0 °C the product was isolated and methyl 2,5-di-*O*-benzoyl-α-D-xylofuranoside (49 g, 98%) was obtained as a gum, $[\alpha]_D$ +97° (*c* 1.7), $\nu_{max.}$ 3 400(OH) and 1 710 cm^{-1} (C=O), τ ($CDCl_3$) 4.5—5.0 (complex m, H-1, H-2), 5.0—5.7 (complex m, H-3, -4, -5, -5′), 6.2 (s, OH exchangeable with D_2O), 6.60 (s, OMe), and 1.7—2.9 (complex m, 2Ph).

Methyl 2,5-*di*-O-*benzoyl*-β-D-*xylofuranoside* (7). This compound was prepared similarly to the α-D-anomer from methyl 2-*O*-benzoyl-3,5-*O*-isopropylidene-β-D-xylofuranoside (44 g). The glassy deacetonated product (36 g, 94%) {$[\alpha]_D$ −5.4° (*c* 3), $\nu_{max.}$ 3 400(OH) and 1 710 cm^{-1} (C=O)} was selectively benzoylated to give the title compound (49 g, 98%) as a gum {$[\alpha]_D$ +6.4° (*c* 2.6), $\nu_{max.}$ 3 400 (OH), 1 710 cm^{-1} (C=O), τ ($CDCl_3$) 4.82 (s, H-1), 4.26 (d, $J_{2,3}$ 1 Hz), 5.0—5.7 (complex m, H-3, -4, -5, -5′), 6.75 (complex m, OH exchangeable with D_2O), 6.51 (s, OMe), and 1.6—2.8 (complex m, 2Ph)}.

Methyl 2-O-*benzoyl*-5-O-*trityl*-α-D-*xylofuranoside* (8). Methyl 2-*O*-benzoyl-α-D-xylofuranoside (10 g) in dry pyridine (50 ml) was heated on a steam-bath for 1 h with trityl chloride (10.4 g). Then most of the pyridine was evaporated off and the residue was dissolved in chloroform (250 ml). The solution was worked up conventionally to afford the glassy 5-*O*-trityl derivative, $[\alpha]_D$ +103° (*c* 0.6), $\nu_{max.}$ 3 400(OH) and 1 720 cm^{-1} (C=O), τ ($CDCl_3$) 4.5—4.9 (complex m, H-1, -2), 5.3 (t, H-3), 5.64 (quintet, H-4), 6.2—6.9 (complex m, H-5, -5′), 7.0 (complex m, OH exchangeable with D_2O), 6.61 (s, OMe), and 1.7—3.1 (complex m, 4Ph).

3,5-*Di*-O-*benzoyl*-1,2-O-*isopropylidene*-α-D-*xylofuranose.* 1,2-*O*-Isopropylidene-α-D-xylofuranose [7] (32 g) in pyridine (150 ml) was dibenzoylated with benzoyl chloride (50 ml) which was added in portions at 20 °C. After 0.5 h at ambient temperature and 5 min at 50 °C, the product was isolated as a gum (65 g, 97%), $[\alpha]_D$ −44° (*c* 1.7), $\nu_{max.}$ 1 720 cm^{-1} (C=O), τ (C_6D_6) 4.14 (d, $J_{1,2}$ 4.0 Hz), 5.62 (d, H-2), 4.33 (d, $J_{3,4}$ 2.5 Hz), 5.1—5.5 (complex m, H-4, -5, -5′), 8.58 and 8.90 (2s, CMe_2), and 1.7—3.3 (complex m, 2Ph).

Methyl 3,5-*di*-O-*benzoyl*-α- *and* -β-D-*xylofuranoside* [(9) *and* (10)]. 3,5-Di-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-xylofuranose (52 g) was heated under reflux in methanolic 1% hydrogen chloride (500 ml) for 40 min and then was treated with ice-cold saturated aqueous sodium hydrogen carbonate (1 l). The mixture was extracted with chloroform (3 × 150 ml) and the extract was worked up by a standard procedure to afford a gum (46 g). This was separated on a column of silica gel (700 g) with solvent B for elution to afford first glassy methyl 3,5-di-*O*-benzoyl-α-D-xylofuranoside (7.1 g, 15%) {$[\alpha]_D$ +117° (*c* 1.6), $\nu_{max.}$ 3 400(OH) and 1 720 cm^{-1} (C=O), τ($CDCl_3$) 4.92 (d, $J_{1,2}$ 4.8 Hz), 5.5 (complex

[42] P. M. Collins, J. R. Hurford, and W. G. Overend, unpublished results.

m, H-2, $J_{2,3}$ 5 Hz), 4.39 (t, $J_{3,4}$ 6.0 Hz), 5.0—5.8 (3 H, complex m, H-4, -5, -5'), 6.48 (s, OMe), 6.85 (d, OH exchangeable with D_2O, $J_{2,OH}$ 7.5 Hz), and 1.8—3.0 (complex m, 2Ph)}, and then *methyl* 3,5-*di*-O-*benzoyl*-β-D-*xylofuranoside* (10) (11.3 g, 24%) as white needles, m.p. 82.5—83.5° (from methylene chloride–pentane), $[\alpha]_D$ −62° (*c* 1.3), $\nu_{max.}$ 3 400(OH) and 1 720 cm^{-1} (C=O), τ ($CDCl_3$), 4.99 (d, $J_{1,2}$ 1.0 Hz), 5.59 (complex m, $J_{3,2}$ 2.2 Hz), 4.50 (q, $J_{3,4}$ 5.6 Hz), 5.0—5.5 (complex m, H-4, -5, -5'), 6.14 (d, OH exchangeable with D_2O, $J_{2,OH}$ 3.8 Hz), 6.57 (s, OMe), and 1.8—2.9 (complex m, 2Ph) (Found: C, 64.1; H, 5.4. $C_{20}H_{20}O_7$ requires C, 64.5; H, 5.4%).

Methyl 2,5-*di*-O-*benzoyl*-α-D-erythro-*pentofuranosid*-3-*ulose* (1). Methyl 2,5-di-*O*-benzoyl-α-D-xylofuranoside (25 g) in purified carbon tetrachloride (200 ml) was oxidised with ruthenium tetraoxide [from ruthenium dioxide hydrate (8 g)] at ambient temperature for 15 min. Excess of oxidant was eliminated by addition of propan-2-ol and the oxidation product was isolated in the usual way.[10,11] The α-D-erythro-*pentofuranosid*-3-*ulose* (1) (17 g, 68%) was recrystallised from diethyl ether; m.p. 98.5°, $[\alpha]_D$ +259° (*c* 1.4), $\nu_{max.}$ 1 780 and 1 720 cm^{-1} (C=O), τ values in Table 1 (Found: C, 64.7; H, 4.9. $C_{20}H_{18}O_7$ requires C, 64.9; H, 4.9%).

Methyl 2,5-*di*-O-*benzoyl*-β-D-erythro-*pentofuranosid*-3-*ulose* (2). Methyl 2,5-di-*O*-benzoyl-β-D-xylofuranoside (7) (25 g) was oxidised by the method used for the α-D-isomer. This yielded *methyl* 2,5-*di*-O-*benzoyl*-β-D-erythro-*pentofuranosid*-3-*ulose* (2) (15.5 g, 63%) which after recrystallisation from diethyl ether–pentane had m.p. 102°, $[\alpha]_D$ +7.7° (*c* 1.4), $\nu_{max.}$ 1 780 and 1 720 cm^{-1} (C=O); see Table 1 for τ values (Found: C, 64.7; H, 4.9. $C_{20}H_{18}O_7$ requires C, 64.9; H, 4.9%).

Methyl 2-O-*benzoyl*-5-O-*trityl*-α-D-erythro-*pentofuranosid*-3-*ulose* (3). By the usual procedure methyl 2-*O*-benzoyl-5-*O*-trityl-α-D-xylofuranoside (8) (18 g) was oxidised with ruthenium tetraoxide [from 6 g of ruthenium dioxide dihydrate] and the product was crystallised from diethyl ether–pentane. After recrystallisation from ethanol *methyl* 2-O-*benzoyl*-5-O-*trityl*-α-D-erythro-*pentofuranosid*-3-*ulose* (3) (9.1 g, 51%) was obtained as fine needles, m.p. 134—135°, $[\alpha]_D$ +180° (*c* 2.4), $\nu_{max.}$ 1 780 and 1 720 cm^{-1}; τ values in Table 1 (Found: C, 75.7; H, 5.4. $C_{32}H_{28}O_6$ requires C, 75.6; H, 5.55%).

Methyl 3,5-*di*-O-*benzoyl*-β-D-threo-*pentofuranosid*-2-*ulose hydrate* (12). To methyl 3,5-di-*O*-benzoyl-β-D-xylofuranoside (10) (3 g) in purified methylene chloride (75 ml) containing a suspension of ruthenium dioxide dihydrate (0.2 g), sodium periodate (7.5 g) in water (75 ml) and potassium hydroxide (1.5 g) in water (15 ml) were added and the mixture was shaken vigorously for 2.5 h at room temperature. Propan-2-ol (1 ml) was added and the organic phase was separated, washed with water, dried ($MgSO_4$), and decolourised with charcoal. Filtration through kieselguhr and evaporation gave a chromatographically homogeneous solid which was recrystallised from ether. *Methyl* 3,5-*di*-O-*benzoyl*-β-D-threo-*pentofuranosid*-2-*ulose hydrate* (12) (2.3 g, 74%) was obtained as white needles, m.p. 102—104°, $[\alpha]_D$ −92° (*c* 0.5), $\nu_{max.}$ 3 400, 3 300(OH, diol), and 1 720 cm^{-1} (C=O), τ ($CDCl_3$) 1.8—2.9 (complex m, 2Ph), 4.45 (q, $J_{3,1}$ 2, $J_{3,4}$ 5.5 Hz), 4.7—5.7 (complex m, H-1, H-4, H-5, -5', OH), 5.97br (s, OH, exchangeable with D_2O), and 6.57 (s, OMe) (Found: C, 61.5; H, 5.2. $C_{20}H_{20}O_8$ requires C, 61.8; H, 5.2%). This *gem*-diol (2.3 g) could be dehydrated by azeotropic distillation of a solution in benzene. The procedure was repeated as necessary until the $\nu_{max.}$ intensity ratio 3 400(OH) : 1 780(C=O) of the product was constant and the 3 400 cm^{-1} band was very weak. Essentially pure 2-ulose (5) was obtained as a very hygroscopic gum; τ values in Table 1.

Methyl 3,5-*di*-O-*benzoyl*-α-D-threo-*pentofuranosid*-2-*ulose* (4). Methyl 3,5-di-*O*-benzoyl-α-D-xylofuranoside (9) (3 g) in purified methylene chloride (75 ml) was oxidised for 4 h by essentially the method used for the β-D-isomer. A colourless but impure gum (1.7 g, 57%) was obtained which was essentially the hydrate (11) of the ulose (4); $\nu_{max.}$ 3 400(OH) and 1 780w cm^{-1} (C=O). Chromatographic separation of the gum failed owing to its instability on silica gel or alumina.

The crude *gem*-diol (1.7 g) in toluene (30 ml) was subjected to distillation, final traces of solvent being removed under reduced pressure. This procedure was carried out three times to give a gum in which the intensity ratio $\nu_{max.}$ 3 400(OH) : 1 780(C=O) had reached a constant value and which contained about 70% of the 2-ulose (4) (for τ values see Table 1) and 30% of its hydrate (11).

Preparation of Methyl Glycofuranosidulose Arylhydrazones.—Methyl 2,5-*di*-O-*benzoyl*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (13). A stirred solution of compound (2) (10 g) in warm ethanol (200 ml) was treated under nitrogen with phenylhydrazine hydrochloride (4 g) in the absence of light for 0.5 h. Pyridine (2 ml) was added and reaction was allowed to proceed for 1 h at 45 °C. After storage at 0 °C for 4 h the *furanosidulose phenylhydrazone* (13) crystallised as fine white needles (6.2 g, 51%), m.p. 146—147° (from ethanol), $[\alpha]_D$ −72° (*c* 1.5), $\lambda_{max.}$ (EtOH) 282 nm (ε 17 400), $\nu_{max.}$ 3 270(NH), 1 730 and 1 700(PhCO), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum in Table 2 (entries 1 and 2) (Found: C, 67.9; H, 5.2; N, 6.0. $C_{26}H_{24}N_2O_6$ requires C, 67.8; H, 5.3; N, 6.1%).

Methyl 2,5-*di*-O-*benzoyl*-β-D-erythro-*pentofuranosid*-3-*ulose* p-*nitrophenylhydrazone* (14). The 3-ulose (2) (1 g), ethanol (20 ml), acetic acid (1 ml), and *p*-nitrophenylhydrazine (0.41 g) were heated together under reflux for 10 min. On cooling a pale yellow solid separated. This was collected and recrystallised twice from ethanol–ethyl acetate to yield the 3-*ulose* p-*nitrophenylhydrazone* (14) (0.36 g, 26%) as pale yellow crystals, m.p. 184—185°, $[\alpha]_D$ −61° (*c* 1), $\lambda_{max.}$ (EtOH) 369 nm (ε 20 400), $\nu_{max.}$ 3 200 (NH), 1 720 and 1 690(PhCO), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum in Table 2 (entry 3) (Found: C, 61.9; H, 4.6; N, 8.1. $C_{26}H_{23}N_3O_8$ requires C, 61.8; H, 4.6; N, 8.3%).

Methyl 2,5-*di*-O-*benzoyl*-α-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (15). Phenylhydrazine hydrochloride (4.7 g) was added during 40 min to a stirred solution of the 3-ulose (1) (12 g) in dry pyridine (100 ml) under nitrogen in the absence of light at ambient temperature. T.l.c. showed that the ulose (R_F 0.50) had been converted into two new products (R_F 0.45 and 0.55) which were obtained as a yellow oil on trituration with water. The oil was extracted with ether (3 × 100 ml) and the extract was worked up by standard methods to give the *phenylhydrazone* (15) as a pale yellow powder (14.6 g, 98%), $[\alpha]_D$ +174° (*c* 2), $\lambda_{max.}$ (EtOH) 284 nm (ε 16 900), $\nu_{max.}$ 3 300(NH), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh). The n.m.r. spectrum showed that two isomers, presumably *syn*- and *anti*-forms, were present in the ratio 1 : 3.7. P.l.c. of the powder (0.5 g) gave a minor component (R_F 0.55) as a pale yellow gum (0.09 g, 18%) (15a) [$\nu_{max.}$ 3 260, 1 710, and 1 600 cm^{-1}, n.m.r. spectrum Table 2 (entry 4)] and a major component (R_F 0.45) as a colourless glass (15b) (0.33 g,

66%), $\nu_{max.}$ 3 260 (sharp), 1 710, and 1 600 cm^{-1}; n.m.r. spectrum Table 1 (entries 5 and 6).

Methyl 2,5-*di*-O-*benzoyl*-α-D-erythro-*pentofuranosid*-3-*ulose* p-*nitrophenylhydrazone* (16). The glycofuranosidulose (1) (1 g) in ethanol (20 ml) containing acetic acid (3 ml) and *p*-nitrophenylhydrazine (0.41 g) was heated under reflux for 10 min and then was poured into cold water (100 ml). The orange crystals that precipitated were collected and recrystallised (thrice) from ethanol to give *compound* (16) as pale yellow crystals (0.34 g, 25%), m.p. 147—148°, $[\alpha]_D$ +650° (*c* 1.1), $\lambda_{max.}$ (EtOH) 375 nm (ε 23 600), $\nu_{max.}$ 3 200 (NH), 1 720(C=O) and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum Table 2 (entry 7) (Found: C, 62.1; H, 4.7; N, 8.2. $C_{26}H_{23}N_3O_8$ requires C, 61.8; H, 4.6; N, 8.3%).

Methyl 3,5-*di*-O-*benzoyl*-β-D-threo-*pentofuranosidulose* p-*nitrophenylhydrazone* (18). Dried glycofuranosidulose (5) (2.4 g) in absolute ethanol (25 ml) containing *p*-nitrophenylhydrazine (0.99 g) and acetic acid (0.2 ml) was warmed at 60 °C and then cooled. Recrystallisation of the solid which separated afforded the 2-*ulose* p-*nitrophenylhydrazone* (18) (2.3 g, 71%) as pale yellow needles, m.p. 146°, $[\alpha]_D$ −20° (*c* 0.2), $\lambda_{max.}$ (EtOH) 375 nm (ε 14 600), $\nu_{max.}$ 3 300(NH), 1 720(C=O), 1 600(C=N–NPh), and 1 490 cm^{-1} (NO_2); n.m.r. spectrum Table 2 (entry 9) (Found: C, 60.7; H, 4.7; N, 8.0. $C_{26}H_{23}N_3O_8$ requires C, 61.8; H, 4.6; N, 8.3%). The phenylhydrazone (18A) was also prepared from methyl 3,5-di-*O*-benzoyl-β-D-*threo*-pentopyranosidulose but was obtained only as an unstable yellow gum, $\nu_{max.}$ 3 300(NH), 1 720(C=O), and 1 600 cm^{-1} (C=N–NPh).

Methyl 2-O-*benzoyl*-5-O-*trityl*-α-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (17). Methyl 2-*O*-benzoyl-5-*O*-trityl-α-D-*erythro*-pentofuranosid-3-ulose (3 g) was treated with phenylhydrazine hydrochloride (0.85 g) in pyridine (20 ml) under nitrogen in the absence of light at ambient temperature. Work-up gave the 3-ulose phenylhydrazone (*syn–anti*-mixture) as a pale yellow powder (3.5 g, 98%), $\nu_{max.}$ 3 300(NH), 1 720(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum Table 2 (entry 8).

Methyl 3,5-*di*-O-*benzoyl*-α-D-threo-*pentofuranosidulose* p-*nitrophenylhydrazone* (19). Impure dried glycosidulose (4) (2.7 g) in absolute ethanol (25 ml) was treated with *p*-nitrophenylhydrazine (1 g) and acetic acid (0.2 ml) for 10 min at 50 °C, and then at room temperature for 0.5 h. The solution was poured into cold water and the red gum that separated was extracted into methylene chloride. Work-up and concentration of the extract gave a residue that was crystallised thrice from ethyl acetate after successive purification *via* column chromatography and p.l.c. The p-*nitrophenylhydrazone* (0.015 g) was obtained as yellow crystals, m.p. 173—177°, $[\alpha]_D$ −8° (*c* 0.7), $\lambda_{max.}$ (EtOH), 368 nm, $\nu_{max.}$ 3 300(NH), 1 720, 1 690(C=O), 1 600(C=N–NPh) and 1 500 cm^{-1} (NO_2); n.m.r. spectrum Table 2 (entry 10) (Found: C, 61.7; H, 4.7; N, 7.9. $C_{26}H_{23}N_3O_8$ requires C, 61.8; H, 4.6; N, 8.3%).

Preparation of Arylazo-enofuranosides.—*Methyl* 5-O-*benzoyl*-2,3-*dideoxy*-3-*phenylazo*-α-D-glycero-*pent*-2-*enofuranoside* (20). Methyl 2,5-di-*O*-benzoyl-α-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (15) (14 g) in dry benzene (100 ml) was treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (6 ml) with stirring at room temperature for 0.5 h. Diethyl ether (300 ml) was added to the cooled stirred solution to precipitate DBU hydrobenzoate, which dissolved upon addition of water (100 ml). Standard work-up yielded an orange gum (10.1 g) which crystallised on addition of methanol (50 ml) to give orange needles (7.6 g, 70%). Recrystallisation from methanol gave the 3-*phenylazo*-α-D-*pent*-2-*enofuranoside*, m.p. 81—82°, $[\alpha]_D$ −41° (*c* 0.4), u.v., i.r., and n.m.r. spectral data in Table 3 (Found: C, 67.8; H, 5.4; N, 7.9. $C_{19}H_{18}N_2O_4$ requires C, 67.4; H, 5.4; N, 8.3%).

Methyl 5-O-*benzoyl*-2,3-*dideoxy*-3-*phenylazo*-β-D-glycero-*pent*-2-*enofuranoside* (21).—Methyl 2,5-di-*O*-benzoyl-β-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (13) (6 g) and DBU (2.5 ml) in dry benzene (50 ml) were kept together for 1 min and the product was worked up as described for the α-D-anomer. The orange gum obtained was crystallised from methanol (15 ml) and recrystallised from the same solvent to give the 3-*phenylazo*-β-D-*pent*-2-*enofuranoside* (2.7 g, 62%) as fine orange needles, m.p. 72.5°, $[\alpha]_D$ −145° (*c* 0.4); u.v., i.r., and n.m.r. spectral data in Table 3 (Found: C, 67.5; H, 5.3; N, 8.1. $C_{19}H_{18}N_2O_4$ requires C, 67.4; H, 5.4; N, 8.3%).

A side-product concentrated in the mother liquors was isolated by p.l.c. as an unstable pale yellow gum, $\lambda_{max.}$ (EtOH) 275 nm (ε 15 800), $\nu_{max.}$ 1 720 cm^{-1} (C=O), n.m.r. proton count 36 H, τ($CDCl_3$) 1.8—3.3 (20 H, complex m, Ph), 4.5—4.7 (8 H, complex m, ring protons), 6.47 (3 H, s, OMe), 6.55 (3 H, s, OMe), 6.6 (1 H, complex m, ring proton), and 7.3 (1 H, complex m, ring proton). No signals appeared in the low-field, vinylic proton region. This compound is possibly a Diels–Alder-type dimer.

Methyl 5-O-*benzoyl*-2,3-*dideoxy*-2-*phenylazo*-β-D-glycero-*pent*-2-*enofuranoside* (22). Crude methyl 3,5-di-*O*-benzoyl-β-D-*threo*-pentofuranosidulose phenylhydrazone (18A) (2.5 g) in dry benzene (15 ml) was stirred with DBU (1 ml) for 1 min at room temperature (t.l.c. revealed that the reaction was then complete). Conventional work-up afforded the title compound as an orange gum (1.7 g, 87%) which was difficult to store owing to its tendency to dimerise. A portion of the gum (0.5 g) was purified by p.l.c. and was obtained as an orange coloured glass (95% purity); u.v., i.r., and n.m.r. spectral data in Table 3.

A dimeric compound was also isolated by p.l.c. as a pale yellow unstable gum, $\lambda_{max.}$ (EtOH) 274 nm (ε 12 200), $\nu_{max.}$ 3 400br, s, 1 720(C=O), and 1 600 cm^{-1} (C=N–NPh), n.m.r. proton count 36 H, τ($CDCl_3$) 4.40 (1 H, s, ring proton), 4.81 (1 H, s, ring proton), 4.9—6.5 (6 H, complex m, ring protons), 7.0—7.4 (2 H, complex m, ring protons), 6.64 (3 H, s, OMe), 6.73 (3 H, s, OMe), and 1.7—3.2 (20 H, complex m, Ph).

Methyl 5-O-*benzoyl*-2,3-*dideoxy*-2-(p-*nitrophenylazo*)-β-D-glycero-*pent*-2-*enofuranoside* (23). Methyl 3,5-di-*O*-benzoyl-β-D-*threo*-pentofuranosidulose *p*-nitrophenylhydrazone (18) (0.2 g) in dry 1,2-dimethoxyethane (5 ml) was treated with DBU (0.08 ml). The solution rapidly became dark red ($\lambda_{max.}$ 371 nm) indicating formation of the azoalkene. Owing to its high reactivity this azoalkene was not isolated but was employed *in situ* for nucleophilic addition reactions.

Methyl 2,3-*dideoxy*-3-*phenylazo*-5-O-*trityl*-α-D-glycero-*pent*-2-*enofuranoside* (24). Methyl 2-*O*-benzoyl-5-*O*-trityl-α-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (17) (3 g) was treated with DBU (1 ml) in benzene (15 ml). An orange gum was isolated and purified by column chromatography. The azoalkene (1.5 g, 62%) was obtained as an orange glass; n.m.r. spectral data in Table 3.

1,4-*Addition Reactions with Methyl* 5-O-*Benzoyl*-2,3-*dideoxy*-3-*phenylazo*-α-D-glycero-*pent*-2-*enofuranoside* (20).—(a) *Elements of hydrazoic acid.* (i) The 3-phenylazoalkene derivative (20) (0.4 g) was added to a solution of sodium

azide (0.2 g) in acetone (20 ml) and water (6 ml) containing ammonium chloride (0.1 g). After 10 min at room temperature t.l.c. revealed one major product (R_F 0.5) and one minor component (R_F 0.4) and the solution was diluted with water. The oil which separated was extracted with ether and from the extract a gum was isolated and crystallised from ethanol. Recrystallisation afforded *methyl 2-azido-5-O-benzoyl-2-deoxy-α-D-threo-pentofuranosidulose anti-phenylhydrazone* (26) (0.23 g, 51%) as white needles, m.p. 103°, $[\alpha]_D$ −274° (*c* 1.1), $\lambda_{max.}$ (EtOH) 283 nm (ε 13 900), $\nu_{max.}$ 3 300(NH), 2 100(N_3), 1 700(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. data in Table 4 (entries 1 and 2) (Found: C, 60.1; H, 5.0; N, 18.3. $C_{19}H_{19}N_5O_4$ requires C, 59.8; H, 5.0; N, 18.4%).

(ii) When the reaction was repeated and the mixture set aside for 24 h, t.l.c. showed that the component with R_F 0.4 had increased in concentration at the expense of the product with R_F 0.5. Isolation of the product yielded a yellow gum which was separated into its constituents by p.l.c. The component with R_F 0.4 was obtained as a glass (0.21 g, 47%) [$\lambda_{max.}$ (EtOH) 283 nm (ε 16 000), $\nu_{max.}$ 3 300 (NH), 2 100(N_3), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh)] that decomposed slowly. N.m.r. spectral measurements (data in Table 4, entries 3 and 4) indicated that this substance was the *syn*-phenylhydrazone (27). The other component (0.08 g) had m.p. 103° and was identical with the *anti*-hydrazone isolated in (i).

(b) *Ammonia.* To a solution of the 3-phenylazo-derivative (20) (0.18 g) in acetone (5 ml), ammonia (*d* 0.880; 1 ml) was added. After 6 h at room temperature the solvent was removed under diminished pressure to leave a gum which was dissolved in methanol (3 ml) and acetic anhydride (0.5 ml). After 10 min water was added. Evaporation left a gum which was purified by p.l.c. The glass (0.14 g) obtained was crystallised from methanol (2 ml) and after recrystallisation the *methyl 2-acetamido-5-O-benzoyl-2-deoxy-α-D-threo-pentofuranosid-3-ulose phenylhydrazone* (28) (0.11g, 53%), had m.p. 178.5—179.5°, $[\alpha]_D$ +291° (*c* 1.2), $\lambda_{max.}$ (EtOH) 282 nm (ε 22 400), $\nu_{max.}$ 3 200(NH), 1 720(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 5) (Found: C, 63.6; H, 5.9; N, 10.6. $C_{21}H_{23}N_3O_5$ requires C, 63.5; H, 5.8; N, 10.6%).

(c) *Dimethylamine.* The 3-phenylazoalkene derivative (20) (0.2 g) was dissolved in dimethylamine (1 ml) at 0 °C and after 1 min the amine was removed by evaporation. This procedure afforded *methyl 5-O-benzoyl-2-deoxy-2-NN-dimethylamino-α-D-threo-pentofuranosid-3-ulose phenylhydrazone* (29) (0.2 g) as a glass {$[\alpha]_D$ −93° (*c* 2.3), $\lambda_{max.}$ (EtOH) 281 nm (ε 15 800), $\nu_{max.}$ 3 200(NH), 1 700(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. data Table 4 (entry 6)} which slowly turned yellow even when stored under nitrogen at 0 °C.

(d) *Acetic acid.* The 3-phenylazo-derivative (20) (0.2 g) was dissolved in acetic acid (2.5 ml) and acetic anhydride (0.5 ml) and stored at ambient temperature for 1 day. Water was added and the solution was concentrated under diminished pressure to a yellow gum which crystallised on trituration with ethanol. Recrystallisation gave crystals of *methyl 2-O-acetyl-5-O-benzoyl-α-D-threo-pentofuranosid-3-ulose phenylhydrazone* (30) (0.12 g, 50%), m.p. 113—113.5°, $\lambda_{max.}$ (EtOH) 284 nm (ε 14 600), $\nu_{max.}$ 3 250(NH), 1 720, 1 680(C=O), and 1 590 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 7) (Found: C, 62.8; H, 5.7; N, 7.2. $C_{21}H_{22}N_2O_6$ requires C, 63.2; H, 5.6; N, 7.0%).

(e) *Methanol.* A solution of the 3-phenylazo-derivative (20) (0.3 g) in methanol (6 ml) containing sodium methoxide (5 mg) was heated under reflux briefly and then kept at room temperature for 0.5 h. Solid carbon dioxide and water were added and the solution was concentrated under reduced pressure to a gum. P.l.c. yielded methyl 2-*O*-methyl-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (31) (0.17 g, 70%) as a colourless glass, $[\alpha]_D$ +349° (*c* 1.7), $\lambda_{max.}$ (EtOH) 282 nm (ε 18 900), $\nu_{max.}$ 3 400(OH), 3 200(NH), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum Table 4 (entry 8).

The same compound could be obtained directly from methyl 2,5-di-*O*-benzoyl-α-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (15) (1 g) by treatment in methanol (50 ml) with sodium methoxide (100 mg). After heating for 2 min the solution was cooled, and water and solid carbon dioxide were added. The solution was concentrated to a gum which was redissolved in water (15 ml) and extracted with ether (4 × 15 ml). From the extract the 2-*O*-methyl derivative (0.52 g) was obtained and purified by conventional methods.

(f) *Benzenethiol.* The 3-phenylazoalkene (20) (0.2 g) was treated with benzenethiol (1 ml) for 20 min at room temperature. Evaporation of the excess of benzenethiol under reduced pressure left a yellow gum (0.21 g) which was purified by p.l.c. to give a glass. This was crystallised and recrystallised from ethanol to afford *methyl 5-O-benzoyl-2-S-phenyl-2-thio-α-D-threo-pentofuranosid-3-ulose phenylhydrazone* (33) (0.15 g, 60%), as cubic crystals, m.p. 89°, $[\alpha]_D$ −235° (*c* 0.7), $\lambda_{max.}$ (EtOH) 286 nm (ε 15 000), $\nu_{max.}$ 3 260 (NH), 1 700(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum Table 4 (entry 9) (Found: C, 67.1; H, 5.2; N, 6.3; S, 7.6. $C_{25}H_{24}N_2O_4S$ requires C, 67.0; H, 5.4; N, 6.3; S, 7.1%).

(g) *Thioacetic acid.* The 3-phenylazoalkene (20) (0.14 g) in acetone (1 ml) was treated at ambient temperature with thioacetic acid (0.2 ml). The solution became colourless within a few seconds. Trituration with water induced white crystals to precipitate. These were collected, washed, dried, and recrystallised from ethanol to give *methyl 2-S-acetyl-5-O-benzoyl-2-thio-α-D-threo-pentofuranosidulose phenylhydrazone* (34) (0.15 g, 84%) as needles, m.p. 164.5—165°, $[\alpha]_D$ +253° (*c* 0.5), $\lambda_{max.}$ (EtOH) 284 nm (ε 15 300), $\nu_{max.}$ 3 200(NH), 1 680(C=O), and 1 590 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 10) (Found: C, 61.0; H, 5.5; N, 7.2; S, 8.2. $C_{21}H_{22}N_2O_5S$ requires C, 60.9; H, 5.4; N, 6.8; S, 7.7%).

(h) *Potassium dithiobenzoate.* The phenylazoalkene (20) (0.15 g) was added to a solution of potassium dithiobenzoate (0.09 g) and ammonium chloride (0.04 g) dissolved in acetone (7 ml) and water (2 ml). The colour of the solution changed from dark red to pink within 1 s. Water was added to faint turbidity and the solution was cooled to 0 °C. The red crystals which formed were collected by filtration, dried, and recrystallised from ethanol to give *methyl 5-O-benzoyl-2-thio-2-S-thiobenzoyl-α-D-threo-pentofuranosid-3-ulose phenylhydrazone* (35) (0.2 g, 91%) as fine pink needles, m.p. 139—139.5°, $[\alpha]_D$ +778° (*c* 0.5), $\lambda_{max.}$ (EtOH) 309 nm (ε 23 400), $\nu_{max.}$ 3 250(NH), 1 720(C=O), 1 590(C=N–NPh), and 1 280 cm^{-1} (C=S); n.m.r. spectral data Table 4 (entry 11) (Found: C, 63.2; H, 4.9; N, 5.7; S, 13.1. $C_{26}N_{24}N_2O_4S_2$ requires C, 63.4; H, 4.9; N, 5.7; S, 13.0%).

(i) *Reduction with sodium borohydride.* A solution of the alkene (20) (0.25 g) and sodium borohydride (0.1 g) in methanol (6 ml) was stirred vigorously for 10 min at room temperature. On addition of water a yellow oil formed and

this was collected and purified by p.l.c. Methyl 5-*O*-benzoyl-2-deoxy-α-D-*glycero*-pentofuranosid-3-ulose (36) (0.18 g, 72%) was isolated as a glass, $[\alpha]_D$ +106° (*c* 1 in C_6H_6), $\lambda_{max.}$ (EtOH) 276 nm (ε 22 600), $\nu_{max.}$ 3 250(NH), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 12).

When the 3-phenylazo-derivative (20) (0.25 g) in MeOD (6 ml) was reduced with sodium borodeuteride (0.1 g) an oil was deposited on addition of deuterium oxide. This was purified as described above and methyl 5-*O*-benzoyl-2-deoxy-2-deuterio-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (37) (0.19 g, 76%) was obtained as a colourless glass, $\lambda_{max.}$ (EtOH) 275 nm (ε 19 300), $\nu_{max.}$ 3 250(NH), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectrum Table 4 (entry 13).

1,4-*Addition Reactions with Methyl* 5-O-*Benzoyl*-2,3-*dideoxy*-3-*phenylazo*-β-D-glycero-*pent*-2-*enofuranoside* (21).—(a) *Elements of hydrazoic acid.* The 3-phenylazo-β-D-*glycero*-pent-2-enofuranoside (21) (0.16 g) was added to a solution of sodium azide (0.1 g) and ammonium chloride (0.05 g) in acetone (5 ml)–water(2 ml). After 10 min white crystals began to precipitate and at 1 h the reaction was terminated by addition of water. The crystals were collected by filtration, washed with cold ethanol, and dried. Recrystallisation from ethanol gave *methyl* 2-*azido*-5-O-*benzoyl*-2-*deoxy*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (38) (0.14 g, 80%), m.p. 165—166°, $[\alpha]_D$ −126° (*c* 0.9), $\lambda_{max.}$ (EtOH) 284 nm (ε 13 100), $\nu_{max.}$ 3 300(NH), 2 100(N_3), 1 700(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 14) (Found: C, 60.3; H, 4.9; N, 18.9. $C_{19}H_{19}N_5O_4$ requires C, 59.8; H, 5.0; N, 18.4%).

(b) *Ammonia.* The β-D-3-phenylazoalkene (21) (0.16 g) was treated with ammonia and subsequently acetic anhydride as described for the α-D-analogue (20). After addition of water the solution was cooled to 0 °C and pale yellow crystals formed. These were collected and recrystallised twice from ethanol to afford *methyl* 2-*acetamido*-5-O-*benzoyl*-2-*deoxy*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (39) (0.13 g, 70%), m.p. 182.5—183°, $[\alpha]_D$ +0.9° (*c* 0.5), $\lambda_{max.}$ (EtOH) 282 nm (ε 17 900), $\nu_{max.}$ 3 200(NH), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 15) (Found: C, 63.8; H, 5.8; N, 10.6. $C_{21}H_{23}N_3O_5$ requires C, 63.5; H, 5.8; N, 10.6%).

(c) *Methanol.* The β-D-3-phenylazoalkene (21) (0.2 g) was treated in like manner to the α-D-anomer with methanol (6 ml) and sodium methoxide (5 mg). The solid obtained was recrystallised from benzene to give *methyl* 2-O-*methyl*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (40) (0.12 g, 75%) as fine white needles, m.p. 136—137°, $[\alpha]_D$ +117° (*c* 1.1), $\lambda_{max.}$ (EtOH) 284 nm (ε 19 300), $\nu_{max.}$ 3 300(OH), 3 200(NH), and 1 590 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 16) (Found: C, 59.0; H, 6.8; N, 10.6. $C_{18}H_{18}N_2O_4$ requires C, 58.6; H, 6.8; N, 10.5%).

This compound could also be obtained directly from methyl 2,5-di-*O*-benzoyl-β-D-*erythro*-pentofuranosidulose phenylhydrazone (13) (1 g) according to the method used for the α-D-anomer (15). The yield of product (40) was 0.51 g (88%).

(d) *Ethanethiol.* The 3-phenylazo-derivative (21) (0.16 g) and ethanethiol (1 ml) were mixed and stored at ambient temperature for 2 days. Evaporation gave a yellow gummy residue which was crystallised from ethanol (0.2 ml) after 1 day at −10 °C. Recrystallisation from the same solvent yielded *methyl* 5-O-*benzoyl*-2-S-*ethyl*-2-*thio*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (41) (0.13 g, 68%), m.p. 67°, $[\alpha]_D$ +431° (*c* 1.7), $\lambda_{max.}$ (EtOH) 284 nm (ε 16 200), $\nu_{max.}$ 3 250(NH), 1 720(C=O), and 1 610 cm^{-1} (C=N–NPh); n.m.r. data Table 4 (entry 17) (Found: C, 62.7; H, 6.0; N, 7.1; S, 8.3. $C_{21}H_{24}N_2O_4S$ requires C, 63.0; H, 6.0; N, 7.0; S, 8.0%).

When ethanethiol was replaced with benzenethiol, glassy methyl 5-*O*-benzoyl-2-*S*-phenyl-2-thio-β-D-*erythro*-pentofuranosid-3-ulose phenylhydrazone (42) (66%) was obtained with $[\alpha]_D$ +447° (*c* 2.1), $\lambda_{max.}$ (EtOH) 290 nm (ε 12 000), $\nu_{max.}$ 3 300(NH), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 18).

(e) *Thioacetic acid.* The 3-phenylazo-derivative (21) (0.2 g) was treated with thioacetic acid according to the method described for the α-D-analogue. On addition of water an oil was deposited which, after purification by p.l.c., afforded a gum. Crystallisation and recrystallisation from ethanol gave *methyl* 2-S-*acetyl*-5-O-*benzoyl*-2-*thio*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (43) as plates (0.15 g, 63%), m.p. 98°, $[\alpha]_D$ +137° (*c* 0.8), $\lambda_{max.}$ (EtOH) 286 nm (ε 15 100), $\nu_{max.}$ 3 300(NH), 1 710, 1 660 (C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 19) (Found: C, 60.6; H, 5.4; N, 7.2; S, 8.3. $C_{21}H_{22}N_2O_5S$ requires C, 60.9; H, 5.4; N, 6.8; S, 7.7%).

(f) *Potassium dithiobenzoate.* The 3-phenylazoalkene (21) (0.15 g) when treated as described under the 1,4-additions to the α-D-3-phenylazo-analogue (20) afforded a product which was recrystallised from ethyl acetate to give *methyl* 5-O-*benzoyl*-2-*thio*-2-S-*thiobenzoyl*-β-D-*erythro*-*pentofuranosid*-3-*ulose phenylhydrazone* (44) (0.2 g, 91%) as long pink needles, m.p. 118—120°, $\lambda_{max.}$ (EtOH) 308 nm (ε 26 100), $\nu_{max.}$ 3 200(NH), 1 700(C=O), 1 600(C=N–NPh), and 1 280 cm^{-1} (C=S); n.m.r. spectral data Table 4 (entry 20) indicated *syn*- and *anti*-isomers (Found: C, 62.8; H, 4.8; N, 5.7; S, 13.1. $C_{28}H_{24}N_2O_4S_2$ requires C, 63.4; H, 4.9; N, 5.7; S, 13.0%).

(g) *Sodium borohydride.* Methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-β-D-*glycero*-pent-2-enofuranoside (21) (0.15 g) and sodium borohydride (0.07 g) in methanol (5 ml) were stirred vigorously for 10 min at room temperature and then cooled to 0 °C. After 2 h the white crystals which had precipitated were collected, dried, and crystallised from methanol to afford *methyl* 5-*O*-*benzoyl*-2-*deoxy*-β-D-glycero-*pentofuranosid*-3-*ulose phenylhydrazone* (45) (0.1 g, 66%), m.p. 110—111°, $[\alpha]_D$ −292° (*c* 0.8 in C_6H_6), $\lambda_{max.}$ (EtOH) 278 nm (ε 22 400), $\nu_{max.}$ 3 250 (NH), 1 700(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 21) (Found: C, 66.9; H, 5.8; N, 8.1. $C_{19}H_{20}N_2O_4$ requires C, 67.0; H, 5.9; N, 8.2%).

The 3-phenylazoalkene (21) (0.15 g) was also reduced with sodium borodeuteride to give white needles of *methyl* 5-O-*benzoyl*-2-*deoxy*-2-*deuterio*-β-D-erythro-*pentofuranosid*-3-*ulose phenylhydrazone* (46) (0.1 g, 66%), m.p. 114—115°, $[\alpha]_D$ −339° (*c* 0.8 in C_6H_6), $\lambda_{max.}$ (EtOH) 278 nm (ε 20 600), $\nu_{max.}$ 3 250(NH), 1 700(C=O), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 22) (Found: C, 66.9; H, 6.03; N, 8.3. $C_{19}H_{19}D_1N_2O_4$ requires C, 66.9; H + D, 6.2; N, 8.2%).

1,4-*Addition Reactions with Methyl* 2,3-*Dideoxy*-3-*phenylazo*-5-O-*trityl*-α-D-glycero-*pent*-2-*enofuranoside* (24).—(a) *Methanol.* The 5-*O*-trityl-3-phenylazo-derivative (24) (0.27 g) was treated with methanol (5 ml) and sodium methoxide (5 mg) according to the procedures already outlined. Methyl 2-*O*-methyl-5-*O*-trityl-α-D-*threo*-pentofuranosid-3-

ulose phenylhydrazone (32) (0.22 g, 71%) was obtained as a colourless gum, $\nu_{max.}$ 3 300(NH) and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 23).

(b) *Elements of hydrazoic acid.* The tritylated 3-phenylazoalkene (24) (0.41 g) was added to a solution of sodium azide (0.2 g) and ammonium chloride (0.1 g) in acetone (20 ml) and water (6 ml). After 1 h the product was isolated by p.l.c. as an unstable yellow gum (0.16 g) which is considered to be methyl 2-azido-2-deoxy-5-*O*-trityl-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (47), $\nu_{max.}$ 3 300 (NH), 2 100(N_3), and 1 600 cm^{-1} (C=N–NPh); n.m.r. spectral data Table 4 (entry 24).

1,4-*Addition Reactions with Methyl* 5-O-*Benzoyl*-2,3-*dideoxy*-2-(p-*nitrophenylazo*)-β-D-glycero-*pent*-2-*enofuranoside* (23).—(a) *Water.* The *p*-nitrophenylazoalkene (23) (0.17 g) generated *in situ* in 1,2-dimethoxyethane (5 ml) was treated with aqueous 0.2M-sulphuric acid (0.5 ml) with stirring at ambient temperature. The colour of the solution changed immediately from dark red to orange. The solution was neutralised with an aqueous solution of sodium hydrogen carbonate and evaporated to a gum, which was purified by standard procedures. Crystallisation from methanol followed by recrystallisation gave *methyl* 5-O-*benzoyl*-β-D-erythro-*pentofuranosid*-2-*ulose* p-*nitrophenylhydrazone* (48) (0.13 g, 72%) as orange needles, m.p. 150°, $[\alpha]_D$ −2° (*c* 2.2), $\lambda_{max.}$ (EtOH) 275 nm (ε 24 800)(OH),3 300, $\nu_{max.}$ 3 400(NH), 1 720(C=O), 1 600(C=N–NPh), and 1 490 cm^{-1} (NO_2); n.m.r. spectral data Table 5 (entry 1) (Found: C, 56.4; H, 4.8; N, 10.2. $C_{19}H_{19}N_3O_7$ requires C, 56.9; H, 4.8; N, 10.5%).

This compound was converted into its 3-*O*-benzoyl derivative (49) by treatment with benzoyl chloride in pyridine. It was isolated as a yellow glass, $[\alpha]_D$ +56° (*c* 1), $\lambda_{max.}$ (EtOH) 373 nm (ε 22 800), $\nu_{max.}$ 3 300(NH), 1 720(C=O), 1 600(C=N–NPh), and 1 490 cm^{-1} (NO_2); n.m.r. spectral data Table 5 (entry 2).

When the 2-*p*-nitrophenylazoalkene (23) (0.17 g) in 1,2-dimethoxyethane (5 ml) was treated with a solution of ammonium chloride (0.5 g) and sodium azide (0.1 g) in 1,2-dimethoxyethane (5 ml), and water (4 ml) was added with stirring at ambient temperature, there was an immediate colour change from dark red to orange. Standard work-up procedures provided an orange gum (0.13 g) shown by t.l.c. to contain two components. The i.r. spectrum [$\nu_{max.}$ 3 400(OH), 3 200(NH), 2 120(N_3), 1 710(C=O), and 1 600 cm^{-1} (C=N–NPh)] indicated that the elements of water and of hydrazoic acid had added competitively to the azoalkene (23). Crystallisation of the gum from methanol afforded orange needles of methyl 5-*O*-benzoyl-β-D-*erythro*-pentofuranosid-2-ulose *p*-nitrophenylhydrazone. Because the product of azide addition in the mother liquors appeared to be decomposing it was not isolated.

(b) *Methanol.* Methyl 3,5-di-*O*-benzoyl-β-D-*threo*-pentofuranosidulose *p*-nitrophenylhydrazone (18) (0.35 g) in methanol (20 ml) was treated with sodium methoxide (40 mg) under reflux for 2 min and then at ambient temperature for 0.5 h. Water and solid carbon dioxide were added and the solution was concentrated to a gum which was redissolved in water and extracted with ether. From the extract a red gum was obtained which was benzoylated and purified by p.l.c. Methyl 5-*O*-benzoyl-3-*O*-methyl-β-D-*erythro*-pentofuranosid-2-ulose *p*-nitrophenylhydrazone (50) (0.1 g, 35% overall) was isolated as a yellow glass, $\lambda_{max.}$ (EtOH) 383 nm (ε 22 600), $\nu_{max.}$ 3 300(NH), 1 720(C=O), 1 600 (C=N–NPh), and 1 490 cm^{-1} (NO_2); n.m.r. spectral data Table 5 (entry 3).

(c) *Sodium borohydride.* The 2-*p*-nitrophenylazoalkene (23) (0.27 g) in 1,2-dimethoxyethane (15 ml) was stirred vigorously with sodium borohydride (0.2 g) at room temperature for 20 min. T.l.c. indicated the presence of two new substances in the mixture. Water was added and the solution was worked up by standard procedures. The two products were isolated by p.l.c. and had the following characteristics: major product (51a) (0.09 g): yellow glass, R_F 0.1, $[\alpha]_D$ −265° (*c* 1.4), $\lambda_{max.}$ (EtOH) 382 nm (ε 18 000), $\nu_{max.}$ 3 400(OH), 3 300(NH), 1 600(C=N–NPh), and 1 490 cm^{-1} (NO_2); n.m.r. spectral data Table 5 (entry 4); minor product (51b) (0.05 g): yellow glass, R_F 0.2, $[\alpha]_D$ +9° (*c* 0.8), $\lambda_{max.}$ (EtOH) 380 nm (ε 21 200), $\nu_{max.}$ 3 400(OH), 3 300(NH), 1 600(C=N–NPh), and 1 490 cm^{-1} (NO_2); n.m.r. spectral data Table 5 (entry 5).

The components are considered to be the *syn*- and *anti*-forms of methyl 3-deoxy-β-D-*glycero*-pentofuranosid-2-ulose *p*-nitrophenylhydrazone (51).

Removal of a Phenylhydrazone Group.—Methyl 2-*O*-methyl-α-D-*threo*-pentofuranosid-3-ulose phenylhydrazone (31) (0.8 g) was dissolved in methyl cyanide (15 ml), water (5 ml), and pyruvic acid (0.9 ml). The solution was stirred at 50—60 °C for 10 h. Ethyl acetate (25 ml) and lead carbonate (6 g) were added with stirring and the neutralised solution was filtered. The filtrate was concentrated to a red gum (0.2 g) of *ca.* 90% purity (t.l.c.). The gum was benzoylated [benzoyl chloride (0.2 ml)] in pyridine (2 ml) to afford a syrup which was purified by column chromatography. Methyl 5-*O*-benzoyl-2-*O*-methyl-α-D-*threo*-pentofuranosid-3-ulose (52) (0.3 g) was obtained as a colourless gum, $\nu_{max.}$ 1 780 and 1 720 cm^{-1} (C=O), τ($CDCl_3$) 4.84 (d, $J_{1,2}$ 1.3 Hz), 5.6(d, H-2), 5.1—5.9(complex m, H-4, -5, -5′), 6.52(6 H, s, 2 OMe), and 1.7—3.1(complex m, aromatic).

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