Arylazo-glycenosides. Part I. Synthesis and Reactions of Some 2- and 3-Arylazo-derivatives of Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-D-hex-2-enopyranosides

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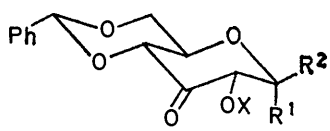
Preparations of the α- and β-anomers of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-D-*ribo*-hexopyranosid-3-ulose [(2) and (1)] and of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-D-*ribo*-hexopyranosidulose [(6) and (5)] are described. The phenylhydrazones [(12) and (28)] derivable from the α- and β-anomers of the 2-benzoate [(2) and (1)] have been converted by a base-catalysed elimination of benzoic acid into, respectively, the α- and β-anomers of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-D-*erythro*-hex-2-enopyranoside [(14) and (29)]. The phenylhydrazone (37) of the α-anomer of the corresponding 3-benzoate has likewise afforded the α-D-2-phenylazo-derivative (39).

The 3-phenylazo-derivatives (14) and (29) have been shown to be useful synthetic intermediates: they undergo 1,4-addition reactions in a highly stereoselective fashion with a wide range of nucleophiles. For example, methoxide and azide ions, amines, acetic acid, and metal hydrides have each been added to the β-anomer (29), and 2-methoxyethoxide, methylmagnesium iodide, and the enolate derived from acetylacetone, as well as the aforementioned reagents, have been added to the α-form (14). Both these anomers gave 3-phenylhydrazones with the D-*arabino*- and D-*ribo*-structures: with the α-anomer a majority of the reagents afforded compounds with the D-*arabino*-configuration, whereas additions to the β-anomer usually afforded a product with the D-*ribo*-structure.

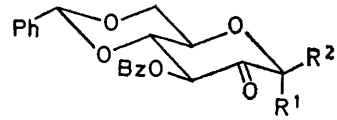
The α-D-2-phenylazo-derivative (39) underwent addition reactions less readily: sodium borohydride was the only reagent found to add smoothly, to afford the phenylhydrazone (42) of a 3-deoxyhexoside in high yield. On the other hand use of sodium azide gave a poor yield of a 3-azido-product with the D-*arabino*-configuration. Sodium methoxide, however, did not add to the unsaturated system in compound (39): instead it induced rearrangement to yield methyl 4,6-*O*-benzylidene-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosid-2-ulose phenylhydrazone (41).

Explanation of the differences in reactivity of these compounds and a rationalisation of the stereochemistry of the addition reactions are attempted.

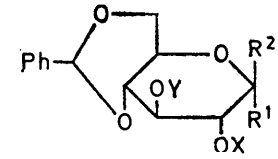
THE value of glycopyranosidulose derivatives as synthetic intermediates in carbohydrate chemistry is well known.[1] Recently, we have been engaged in extending the versatility of these compounds by studying the reactions of the products obtained when another unsaturated function is introduced in a position conjugated to that of the carbonyl group.



(1) R^1 = H, R^2 = OMe, X = Bz
(2) R^1 = OMe, R^2 = H, X = Bz
(3) R^1 = OMe, R^2 = H, X = Ts
(4) R^1 = OMe, R^2 = H, X = Me



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



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

Some years ago we reported[2] the ready conversion of glycopyranosidulose derivatives into glycenopyranosiduloses having a conjugated enone structure. Such derivatives are important intermediates since they undergo ready nucleophilic additions to the carbon–carbon double bond[3] and they serve as useful precursors for photochemical syntheses.[4] Now we report the preparation of conjugated arylazo-glycenoside derivatives and their reactions with nucleophilic reagents.[5]

The formation, by a 1,4-elimination process, of an azoalkene from a hydrazone possessing a leaving group in the position α to the anil carbon atom has long been known. Arylhydrazones derived from α-halogeno-[6,7] and α-acetoxy-[8-11] ketones, for example, have been employed. The carbohydrate examples that have been reported[10,11] are phenylhydrazones derived from aldose acetates.

The glycopyranosidulose derivatives selected for our study were the four isomeric benzoates (1), (2), (5), and

[1] W. G. Overend, *Chem. and Ind.*, 1963, 342.
[2] P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc.* (*C*), 1966, 1131.
[3] J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms and Structures,' McGraw-Hill, New York, 1968, p. 567; and unpublished observations made in our laboratory by E. Dimant.
[4] P. M. Collins and B. Whitton, *Carbohydrate Res.*, 1972, **21**, 487.
[5] Preliminary report, P. M. Collins, D. Gardiner, Mrs. S. Kumar, and W. G. Overend, *Chem. Comm.*, 1970, 1433.
[6] F. D. Chatterway and L. H. Farinholt, *J. Chem. Soc.*, 1930, 94.
[7] J. Buckingham and R. D. Guthrie, *J. Chem. Soc.* (*C*), 1967, 1700.
[8] L. Caglioti, G. Rosini, and F. Rossi, *J. Amer. Chem. Soc.*, 1966, **88**, 3865.
[9] A. J. Fatiadi, *Carbohydrate Res.*, 1968, **7**, 89.
[10] M. L. Wolfrom and M. G. Blair, *J. Amer. Chem. Soc.*, 1946, **68**, 2110.
[11] M. L. Wolfrom, G. Fraenkel, D. R. Linebach, and F. Komitsky, jun., *J. Org. Chem.*, 1964, **29**, 457.

(6), and the tosylate (3) which had been prepared by Baker and Buss.[12] Compounds (2) and (6) were readily obtained *via* mono-*O*-benzoylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. The 2-*O*-benzoyl derivative (7) forms preferentially with benzoyl chloride as the acylating reagent,[13] whereas with benzoic anhydride the 3-benzoate (8) is produced in sufficient amount to permit isolation by fractional crystallisation.[13] On the other hand the β-isomers (1) and (5) are less easy to prepare, since the secondary hydroxy-groups in methyl 4,6-*O*-benzylidene-β-D-glucopyranoside appear to have similar reactivities towards both acylation [14] and sulphonation.[15] Consequently, the positional isomers formed upon benzoylation of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside with benzoyl chloride (0·9 mol. equiv.) had to be separated chromatographically from a mixture of the 2,3-dibenzoate (9), the 2-benzoate (10) and the 3-benzoate (11) (1 : 2 : 2, respectively).

The structures of the 2- and 3-benzoates (10) and (11) were established from their n.m.r. spectra and by their conversion respectively into glycopyranosid-3- and -2-uloses (1) and (5). The signal for the anomeric proton in the 2-*O*-benzoyl derivative (10) appeared, as expected, as a doublet with a splitting of 8 Hz. The other significant low-field proton signal arose from the proton attached to the ester-bearing carbon atom; it was a triplet with 8 Hz splitting. This indicated that it was at position 2. The signal due to the anomeric proton of the 3-benzoate (11) was split by 7·5 Hz into a doublet, whereas the other relevant low-field signal, from the proton on the ester-bearing carbon atom, was a triplet split twice by 9 Hz. Consequently the ester group in this compound was not situated at position 2.

The four isomeric monobenzoates were oxidised with the Pfitzner–Moffatt reagent [16] as described by Baker and Buss,[12] and afforded the four corresponding glycopyranosiduloses (1), (2), (5), and (6) in high yield. In its i.r. spectrum each glycopyranosidulose showed two carbonyl absorptions about 10 cm^{-1} apart, centred approximately at 1745 cm^{-1}, indicating a keto-group and a benzoate ester group. The n.m.r. spectra indicated that each compound contained 20 protons, distributed as indicated in Table 1. The axial anomeric proton in the β-D-glycopyranosidulose (5) resonates 0·1 p.p.m. to lower field than the equatorial proton in the α-D-glycopyranosidulose (6). This is the reverse of normal findings for protons attached to a pyranoid ring.[17] The reversal, which we have observed in other pyranosiduloses,[18,19] arises from the anisotropy of the carbonyl group.[20]

In three of the glycopyranosiduloses [(1), (2), and (5)] long-range coupling of *ca.* 0·75—1·25 Hz was observed through the four bonds between the hydrogen atoms adjacent to the carbonyl group (see Table 1). However, such a coupling was not found with the glycopyranosidulose (6). Thus coupling is significant when

TABLE 1

N.m.r. parameters [τ and *J* (Hz) values] for methyl 2-(or 3-)*O*-benzoyl-D-hexopyranosid-3-(or 2-)uloses in $CDCl_3$ measured at 60 MHz

Compound	H-1	H-2 or -3	H-4, -5, -6, and -6′ *	OMe
α-Anomers				
(6)	5·2(s)	4·0(d) $J_{3,4}$ 10	5·4—6·2	6·5(s)
(2)	4·68(d) $J_{1,2}$ 4·5	4·68(q) $J_{2,4}$ 1·0	5·4—6·2	6·53(s)
β-Anomers				
(5)	5·1(d) $J_{1,3}$ 0·75	4·25(q) $J_{3,4}$ 10	5·5—6·2	6·4(s)
(1)	5·2(d) $J_{1,2}$ 7·5	4·55(q) $J_{2,4}$ 1·25	5·3—6·3	6·4(s)

* Complex multiplet. For each compound the proton attached to the acetal carbon atom gave a singlet in the region τ 4·42—4·45 and the aromatic protons formed a complex multiplet in the region τ 1·7—2·8.

the atoms H–C–C(O)–C–H have a symmetrical **U** relationship (*i.e.* both protons axial) but when these atoms do not form a symmetric array (*i.e.* an axial and an equatorial proton) then the coupling is very weak (<0·3 Hz). Examples of this type of coupling between two axial protons are less well documented than that which occurs between two equatorial protons where the system possesses the so-called **W** arrangement. The coupling mechanisms that have been proposed [21] predict coupling *via* the **U** and **W** pathways but not between axial and equatorial protons. This supports our observation.

Treatment of the 3-*O*-benzoyl-2-ulose (6) and the 2-*O*-benzoyl-3-ulose (2) (α-anomers) with phenylhydrazine or *p*-nitrophenylhydrazine afforded the phenylhydrazones (37) and (12) in 83 and 87% yields and the *p*-nitrophenylhydrazones (38) and (13) in 78 and 96% yields, respectively. The 2-*O*-benzoyl-3-ulose (1) (β-anomer) afforded a phenylhydrazone (28) in 60% yield. This yield was poor because the basic phenylhydrazine eliminated benzoic acid from the hydrazone

[12] B. R. Baker and D. H. Buss, *J. Org. Chem.*, 1965, **30**, (*a*) 2304, (*b*) 2308.
[13] R. W. Jeanloz and D. A. Jeanloz, *J. Amer. Chem. Soc.*, 1957, **79**, 2579.
[14] J. J. Willard, J. S. Brimacombe, and R. P. Brueton, *Canad. J. Chem.*, 1964, **42**, 2560; J. J. Willard, J. Sadowski, and W. Vitate, *ibid.*, 1963, **41**, 1223; A. C. Richardson, *Carbohydrate Res.*, 1967, **4**, 415.
[15] R. D. Guthrie, A. M. Prior, and S. E. Creasey, *J. Chem. Soc.* (*C*), 1970, 1961.
[16] K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, 1965, **87**, 5661, 5670.
[17] R. U. Lemieux, R. K. Kullig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.
[18] P. J. Beynon, P. M. Collins, and W. G. Overend, *J. Chem. Soc.* (*C*), 1969, 2770.
[19] R. F. Butterworth, P. M. Collins, and W. G. Overend, *Chem. Comm.*, 1969, 378.
[20] J. A. Elvidge in ' Nuclear Magnetic Resonance for Organic Chemists,' ed. D. W. Mathieson, Academic Press, London, 1967, p. 31.
[21] L. M. Jackman and S. Sternhell, ' Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 338.

with ease (see later). Upon similar treatment the 3-*O*-benzoyl-β-D-glycopyranosidulose derivative (**5**) gave a red oily mass which was a complex mixture of products whose structures have not yet been determined.

The spectra of these phenylhydrazones [(**37**), (**12**), and (**28**)] are consistent with their proposed structures. They all exhibited an intense u.v. absorption at *ca.* 280 nm, close to that observed for phenylhydrazone

TABLE 2

N.m.r. parameters [τ and *J* (Hz) values] for derivatives of methyl 4,6-*O*-benzylidene-D-hexopyranosidulose phenylhydrazones in $CDCl_3$ at 60 MHz

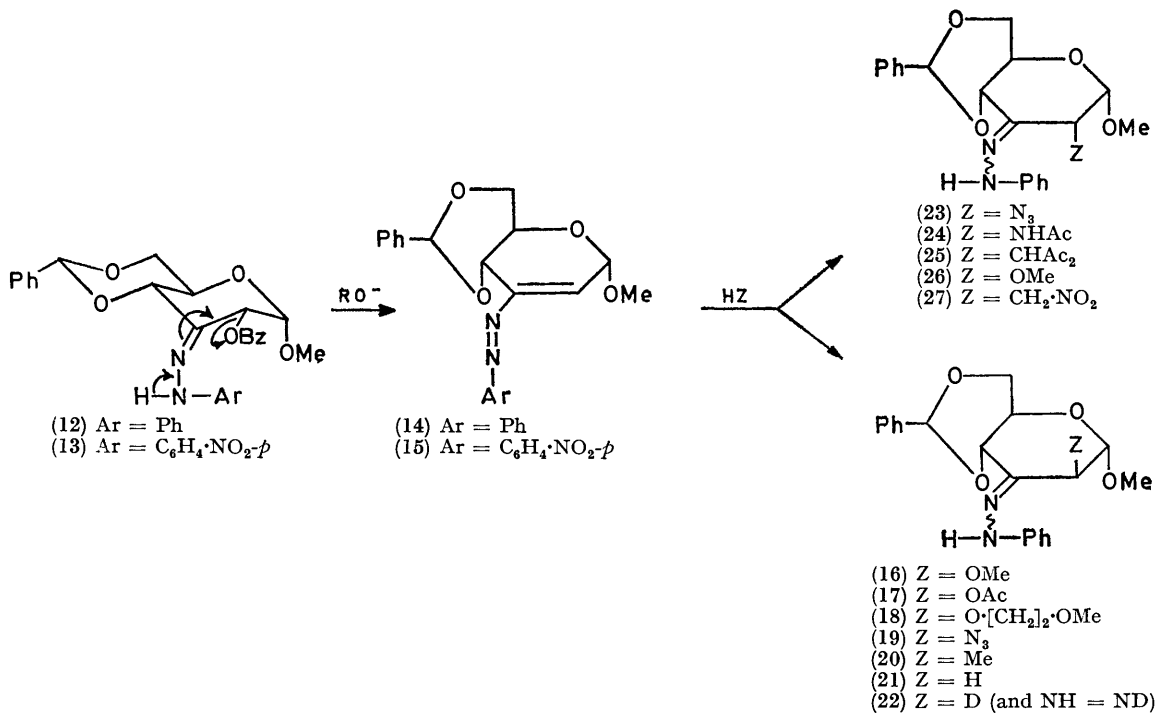
Entry	Compound	H-1	H-2	H-4	H-5	H-6	H-6′	NH	PhC*H*	OMe	Substituent at C-2
α-Anomers of 2-substituted-3-uloses											
1	(12)	5·23(d) $J_{1.2}$ 3·5	4·25(d)		5·8—6·7(cm)			−0·2(s)	4·88(s)	6·92(s)	In region 2·4—3·4(cm, OBz)
2	(16)	5·16(s)	5·0—6·2 region		5·0—6·2(cm)			0·09(s)	4·38(s)	6·55(s)	6·54(s, OMe)
3	(26)	5·06(d) $J_{1.2}$ 3·5	5·4—6·3 region		5·4—6·3(cm)			0·2(s)	4·38(s)	6·50(s)	6·33(s, OMe)
4	(17)	5·18(d) $J_{1.2}$ 1·0	4·58(d)		4·9—6·2(cm)			0·05(s)	4·32(s)	6·55(s)	7·06(s, OAc)
5	(18) *	5·18(d) $J_{1.2}$ 1·0	5·0—6·6 region		5·0—6·6(cm)			0·14(s)	4·40(s)	6·60(s)	6·60(s, Me) 5·8—6·6(cm, O·[CH_2]$_2$·O]
6	(19)	5·34(d) $J_{1.2}$ 1·0	5·0—6·3 region		5·0—6·3(cm)			0·22(s)	4·40(s)	6·64(s)	
7	(24)	4·94(d) $J_{1.2}$ 3·5	5·0—6·3 region		5·1—6·3(cm)			0·1(s)	4·39(s)	6·60(s)	7·86(s, Ac) 8·30(s, NH)
8	(20) *	5·39(s)	6·84(q) J 7·5		5·3—6·4(cm)			2·75(s)	4·30(s)	6·65(s)	8·70(d, Me)
9	(25) *	5·42(d) $J_{1.2}$ 3·0	4·31(q) J 10		5·4—6·3(cm)			0·70(s)	4·36(s)	6·70(s)	7·80(s, Me_2) 5·4—6·33 [*H*C(COR)$_2$]
10	(45) † *anti*-isomer	5·50(q) $J_{1.2ax}$ 4 $J_{1.2eq}$ 2	7·27(q)		5·8—6·7(cm)			−0·1(s)	4·38(s)	6·98(s)	7·76(q, H_{ax}) $J_{2ax.2eq}$ 14·5
11	(21) *syn*-isomer	5·03(q) $J_{1.2ax}$ 4·2 $J_{1.2eq}$ 1·5	7·00(q)		5·4—6·4(cm)			2·77(s)	4·32(s)	6·69(s)	7·60(q, H_{ax}) $J_{2ax.2eq}$ 15·0
12	(45) *anti*-isomer	5·12(t) $J_{1.2ax}$ 3·0†† $J_{1.2eq}$ 3·0††	7·35br(s)		5·2—6·3(cm)			0·25(s)	4·42(s)	6·65(s)	7·35br(s, H_{ax})
13	(22) *anti*-isomer	5·12(d) $J_{1.2}$ 2	7·30(d)		5·2—6·3(cm)				4·38(s)	6·65(s)	
13A	(23)	5·12(d) $J_{1.2}$ 3·5	5·5—6·4 region		5·5—6·4			0·2(s)	4·57	6·53	
13B	(27) §	5·51(d) $J_{1.2}$ 4·2	5·55—6·9 region		5·55—6·9			0·90(s)	6·78(s)	6·69(s)	In region 5·55—6·9
β-Anomers of 2-substituted-3-uloses											
14	(28) †	5·2(d) $J_{1.2}$ 5·5	4·14(d)		5·6—6·6(cm)			0·2(s)	4·8(s)	6·72(s)	1·7—3·2(cm, OBz)
15	(30) *†‡	5·12(d) $J_{1.2}$ 2·5	6·05(d)		5·4—5·9(cm)			0·48(s)	4·72(s)	6·75(s)	6·84(s, OMe)
16	(32) ‡	5·35(q) $J_{1.2ax}$ 8 $J_{1.2eq}$ 3	7·55(q)	5·42(d) $J_{4.5}$ 8·5	6·2—6·4(cm)	5·6(q) $J_{6.5}$ 3·5 $J_{6.6'}$ 9·5	6·16(t) $J_{6',5}$ 9·5	0·32(s)	4·42(s)	6·5(s)	7·17(q, H_{eq}) $J_{2eq.2ax}$ 14
17	(33) ‡	5·36(d) $J_{1.2}$ 8	7·55(d)	5·42(d) $J_{4.5}$ 8·5	6·2—6·4(cm)	5·6(q) $J_{6.5}$ 3·5 $J_{6.6'}$ 9·5	6·16(t) $J_{6',5}$ 9·5		4·42(s)	6·5(s)	
18	(34) *‡	5·46(d) $J_{1.2}$ 8·5	7·55(oct) $J_{2,Me}$ 6		5·5—6·4(cm)			0·06(s)	4·45(s)	6·48(s)	8·75(d, Me) $J_{Me.2}$ 6·0
19	(35) ‡	5·30(d) $J_{1.2}$ 5·5	4·62(d)	5·30(d) $J_{4.5}$ 9	5·8—6·1(cm)	5·6(q) $J_{6.5}$ 4 $J_{6.6'}$ 9	6·22(t) $J_{6',5}$ 9	0·36(s)	4·36(s)	6·57(s)	7·86(s, OAc)
20	(36) *†‡	5·85(d) $J_{1.2}$ 6	6·11(d)	6·00(d) $J_{4.5}$ 9·5	6·45(sex)	6·72(t) $J_{6.5}$ 9·5 $J_{6.6'}$ 2·5	6·00(q) $J_{6',5}$ 4·0	0·12(s)	4·96(s)	6·84(s)	
21	(31) *	5·07(d) $J_{1.2}$ 3·5	6·93(d)		5·2—6·4(cm)			−0·3(s)	4·28(s)	6·53(s)	7·53(s, NMe_2)

TABLE 2 (*Continued*)

Entry	Compound	H-1	H-2	H-4	H-5	H-6	H-6′	NH	PhC*H*	OMe	Substituent at C-2
α-Anomers of the 3-substituted-2-uloses											
22	(37) †	4·68(s)	3·50(d) ¶ $J_{3,4}$ 9·0		5·6—6·5(cm)			1·6—3·5 region	4·58(s)	6·97(s)	1·6—3·5 (OBz) ** region
23	(42)	4·97(s)	6·95(q) ¶ $J_{3eq,4}$ 5		5·8—6·5(cm)			2·3—3·3 region	4·46(s)	6·58(s)	7·6(q, H-3_{ax}) ** $J_{3ax,3eq}$ 14 $J_{3ax,4}$ *ca.* 10
24	(43) ‡	4·99(s)	6·95(d) ¶ $J_{3eq,4}$ 5		5·6—6·5(cm)			2·3—3·3 region	4·46(s)	6·56(s)	
25	(44) ‡	5·01(s)	5·35(d) ¶ $J_{3,4}$ 10		5·7—6·6(cm)			0·01(s)	4·63(s)	6·8(s)	

All spectra showed aromatic signals within the region τ 2·2—3·6. cm = Complex multiplet.

* Stereochemical assignment at C-2 rests entirely on the $J_{1,2}$ value obtained with one stereoisomer; † in C_6D_6; ‡ at 100 MHz; § in C_6D_6 containing *ca.* 10% $CDCl_3$; ¶ H-3; ** at C-3; †† average of 2 and 4 Hz.



(12) Ar = Ph
(13) Ar = $C_6H_4{\cdot}NO_2$-*p*

(14) Ar = Ph
(15) Ar = $C_6H_4{\cdot}NO_2$-*p*

(23) Z = N_3
(24) Z = NHAc
(25) Z = $CHAc_2$
(26) Z = OMe
(27) Z = $CH_2{\cdot}NO_2$

(16) Z = OMe
(17) Z = OAc
(18) Z = $O{\cdot}[CH_2]_2{\cdot}OMe$
(19) Z = N_3
(20) Z = Me
(21) Z = H
(22) Z = D (and NH = ND)

SCHEME 1

derivatives of similar ketones [9,11] and similar to that reported generally for phenylhydrazones of ketones.[22,23] They all exhibited very strong i.r. absorptions at 1600 and 1500 cm^{-1} due to the >C=N–NPh group,[22,24] and in addition showed a diagnostic sharp absorption close to 3200 cm^{-1} due to the >N–H group. Their n.m.r. spectra each showed 26 protons which were assigned as indicated in Table 2 (entries 1, 14, and 22).

It is known that hydrazones [25] and phenylhydrazones [26] of glycopyranosiduloses can exist as geometric isomerides similar to those that we have found for oximes.[18,27] The three phenylhydrazones (37), (12), and (28) each appear to be obtained in one geometric form but, as yet, the *syn*- or *anti*-configuration [26,27] has not been assigned to them. Chittenden and Guthrie [26] isolated *syn*- and *anti*-isomers of methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose phenylhydrazone but they were able to obtain only one form, of unassigned configuration, of its 2-*O*-acetyl derivative. Our benzoylated derivative (12) probably has the same geometrical configuration as their acetate.

Treatment of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose phenylhydrazone (12) with sodium methoxide (1·1 mol. equiv.) in hot methanol led to 1,4-elimination of benzoic acid as shown in Scheme

[22] D. C. Iffland, M. P. McAvery, and D. J. Weber, *J. Chem. Soc.* (*C*), 1969, 1703.
[23] Y. P. Kitaev, B. I. Buzykin, and T. V. Troepol'skaya, *Russ. Chem. Rev.*, 1970, **39**, 441.
[24] M. L. Wolfrom and C. C. Christman, *J. Amer. Chem. Soc.*, 1931, **53**, 3413; H. El Khadem, Z. M. El Shafei, and M. M. Mohammed-Ali, *J. Org. Chem.*, 1964, **29**, 1564; H. S. Blair and G. A. F. Roberts, *J. Chem. Soc.* (*C*), 1967, 2425.
[25] H. Paulsen and D. Stoye, *Chem. Ber.*, 1969, **102**, 834.
[26] G. J. F. Chittenden and R. D. Guthrie, *J. Chem. Soc.* (*C*), 1966, 695.
[27] P. M. Collins, *Chem. Comm.*, 1966, 164.

1 and the formation of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-*erythro*-hex-2-enopyranoside (14), which was precipitated as orange needles in 93% yield. The same compound was formed by treating the tosylated ulose (3) with phenylhydrazine but in this case the intermediate hydrazone could not be isolated, presumably owing to the propensity of the tosyloxy-residue to behave as a leaving group. This phenylazoalkene could also be prepared by a different route, are consistent with the proposed eliminative loss of benzoic acid from the benzoylated phenylhydrazone (12).

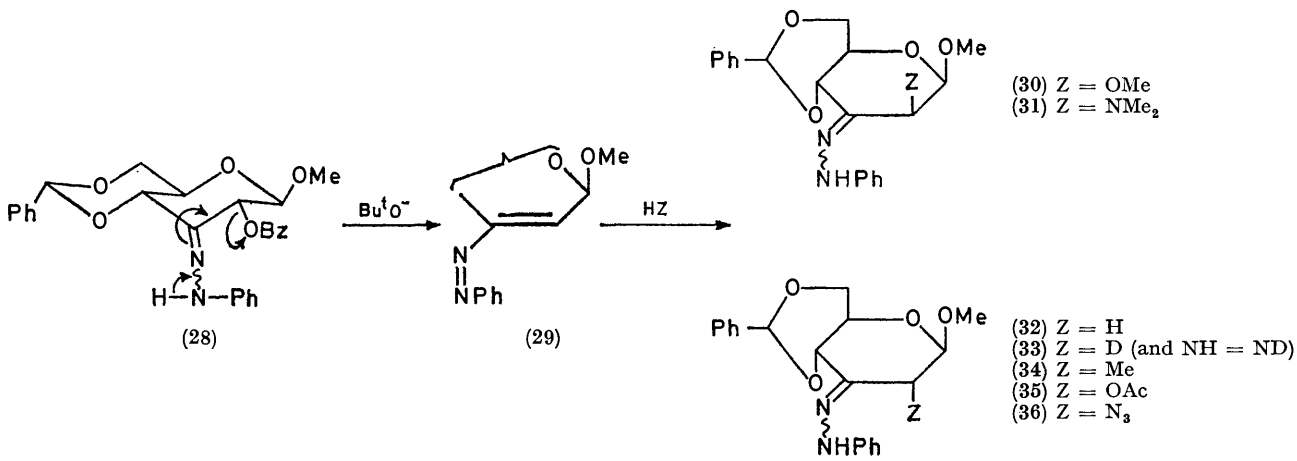
The isomeric phenylazoalkene (39) with the phenylazo-substituent at position 2 was prepared by a base-catalysed 1,4-elimination of benzoic acid from the phenylhydrazone (37) (see Scheme 3). However, compared with compound (14), this azoalkene was more susceptible to nucleophilic attack of the type described later, and so milder preparative conditions were em-

TABLE 3

Spectral parameters for methyl 2-(or 3-)arylazo-4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides

	N.m.r. (60 MHz; τ values; *J* in Hz) in $CDCl_3$ [a,b]				U.v. in EtOH	Relative abundances of mass spectral ions				
Compd.	H-1	HC=C<	H-5, -6, -6′	H-4	$\lambda_{max.}$/nm (ε)	*m/e* 149	*m/e* 203	*m/e* 248	*m/e* 352	*m/e* 397
(14) [c]	4·83(q) $J_{1.2}$ 3 $J_{1.4}$ 1	3·64(q) $J_{2.4}$ 2	5·4—6·1(cm)	5·19(cm)	302 (18,860)	20	5	0	34 [d]	0 [e]
(15) [f]	4·8(q) $J_{1.2}$ 3 $J_{1.4}$ 1	3·45(q) $J_{2.4}$ 2	5·1–6·1(cm)	5·1—6·1	311 (19,130)	68	8	46	0	64 [d,g]
(39) [c]	4·57(s)	2·99(d) $J_{3.4}$ 2	5·4—6·2(cm)	5·4—6·2	307 (21,600)	50	25	0	3 [d]	0 [e]
(40) [f]	4·51(s)	In region 1·5—2·85	5·2—6·2(cm)	5·2—6·2		99	0	30	0	10 [d,g]
(29) [c]	4·45(q) $J_{1.2}$ 1·5 $J_{1.4}$ 2·5	3·7(q) $J_{2.4}$ 2	5·5—6·3(cm)	5·0(oct) $J_{4.5}$ 8	301 (15,840)	14	3	0	33 [d]	0 [e]

[a] A three-proton sharp singlet from the aglycone OMe occurs in the range τ 6·4—6·5. [b] A one-proton sharp singlet from PhC*H* occurs in the range τ 4·28—4·36. [c] A ten-proton complex multiplet arising from the aromatic protons occurs in the range τ 2·1—2·8. [d] Molecular ion. [e] Base peak $C_6H_5^+$, *m/e* 77. [f] A nine-proton complex multiplet arising from the aromatic rings occurs in the range τ 1·3—2·9. [g] Base peak $C_7H_7^+$, *m/e* 91.



SCHEME 2

from the 2-*O*-tosyl derivative of methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucopyranoside, prepared by the method of Guthrie and Johnson.[28]

The structure of the 3-phenylazoalkene (14) follows from its methods of preparation, its empirical formula based on elemental analysis and mass spectral measurements (see Table 3), the characteristically intense u.v. absorption at 302 nm, and its orange-yellow colour. The n.m.r. spectrum (see Table 3) supports the structural assignment. In particular it shows only two phenyl groups, and a vinylic proton but no N–H signal (a feature confirmed by the i.r. spectrum). These observations ployed. Sodium methoxide in methanol at 25° for 5 min was found to produce the azoalkene in 65% yield. The structure was established spectroscopically and the relevant parameters are recorded in Table 3.

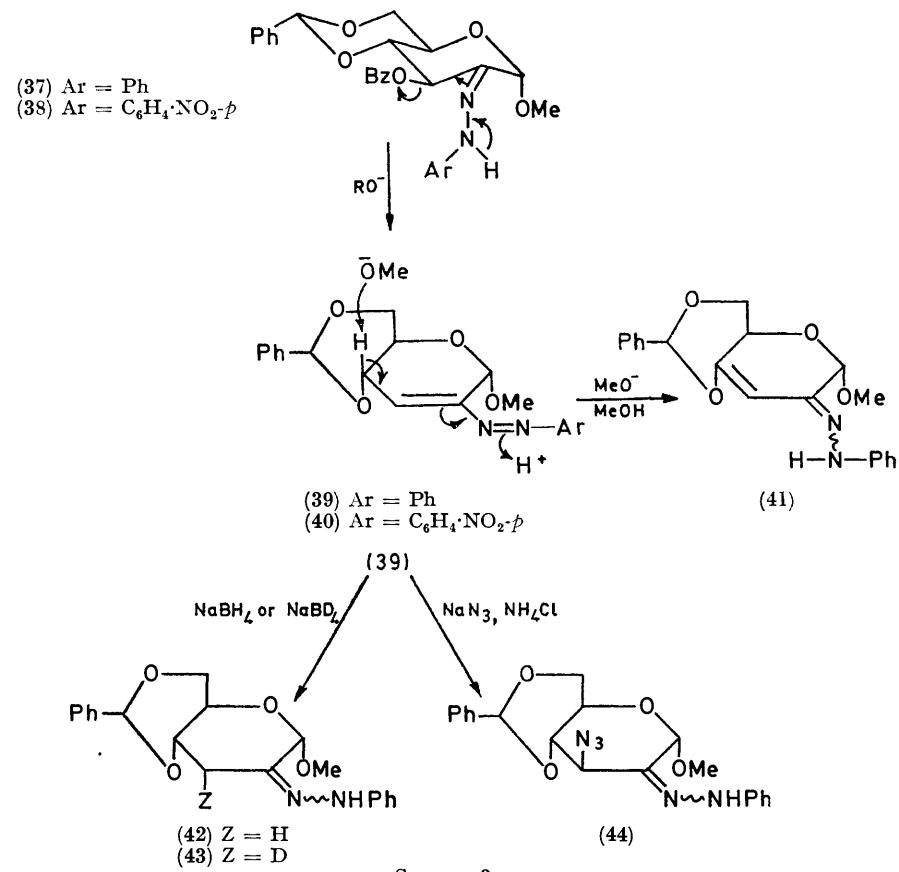
The 3-phenylazo-β-D-*erythro*-hex-2-enopyranoside (29) could not be prepared from the phenylhydrazone (28) by treatment with sodium methoxide in methanol because rapid addition of reagent to the first-formed azoalkene occurred, even at 0°. However, it could be prepared by using sodium t-butoxide in t-butyl alcohol (see Scheme 2) since, although a strong base, this bulky

[28] R. D. Guthrie and L. F. Johnson, *J. Chem. Soc.*, 1961, 4166.

alkoxide is a relatively poor nucleophile. The structure of the orange product was verified by its spectral characteristics (Table 3).

The 2- and 3-*p*-nitrophenylazoalkenes (40) and (15) (deep orange and violet crystals, respectively) were formed by treating the 2- and 3-*p*-nitrophenylhydrazones (38) and (13) with sodium t-butoxide. The spectral properties, from which the structures of these compounds were established, are given in Table 3.

The most abundant peaks in the mass spectra of the arylazoalkenes appear at *m/e* 77, 91, and 105. These



SCHEME 3

are due to the $C_6H_5^+$, $C_7H_7^+$, and $C_6H_5CO^+$ ions respectively.[29] The first of these is the base peak in the spectra of the phenylazoalkene derivatives. Presumably this peak is made up of contributions from both phenyl residues present in these molecules. The tropylium cation is the base peak in the case of the *p*-nitrophenyl-derivatives. This difference arises because fragmentation between the nitrogen atom and an aryl group in the *p*-substituted cases gives rise to nitrophenyl cations and this is manifested in the spectra, not only by a weaker phenyl cation peak, but also by the appearance of a strong peak at *m/e* 122 due to the $C_6H_4NO_2^+$ ion. Both the unsubstituted and the nitro-derivatives show strong peaks at *m/e* 149 and these could arise from the $PhCH=\overset{+}{O}\cdot CH_2\cdot CHO$ ion formed by the 'h-fragmentation' pathway that benzylidene derivatives have been shown to undergo by Chizhov and co-workers.[30] The peak at *m/e* 248 which is present in the spectra of the nitro-analogues could be the complementary ion that can be formed in an 'h-fragmentation', and similarly the ion at *m/e* 203 could be formed by the same mechanism from the unsubstituted compounds.

Addition Reactions to Azoalkenes.—When methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-*erythro*-hex-2-enopyranoside (14) was treated with sodium methoxide (1 mol. equiv.) in methanol, its orange colour was discharged and a new crystalline product, homogeneous by t.l.c., was isolated in 87% yield. It was shown to be a phenylhydrazone by its i.r. and u.v. spectra. Its n.m.r. spectrum (Table 2, entry 2) indicated that it was the phenylhydrazone (16) of methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-*arabino*-hexopyranosid-3-ulose. Thus the hydrazone was formed by 1,4-addition of methanol across the azoalkene system, with hydrogen attachment occurring on the nitrogen atom and oxygen at the carbon atom as shown in Scheme 1. This addition reaction takes place with great ease. Furthermore, the 2-*O*-methyl phenylhydrazone (16)

[29] N. K. Kochetkov and O. S. Chizhov, *Adv. Carbohydrate Chem.*, 1966, **21**, 39.

[30] O. S. Chizhov, L. S. Golovkina, and N. S. Wulfson, *Carbohydrate Res.*, 1968, **6**, 138.

could be formed directly from methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose phenylhydrazone (12) by treatment with 2 mol. equiv. of sodium methoxide. Under these conditions there was consecutive elimination of benzoic acid and addition of methanol to the first-formed product, and the 2-*O*-methyl derivative was obtained in one reaction stage.

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 product was shown to possess the D-*arabino*-configuration (16) by comparison with authentic samples of the phenylhydrazones prepared from independently synthesised methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-*arabino*-hexopyranosid-3-ulose and its *ribo*-epimer (4). The mother liquor of the phenylhydrazone formed in the addition product from the phenylazoalkene (14) was found to contain a substance with the same t.l.c. mobility as the authentic *ribo*-epimer (26) but it constituted at most 6% of the reaction product. Consequently, the addition of methanol must have occurred in a highly stereoselective fashion.

Nucleophilic additions to arylazoalkenes are not common. However, Guthrie [7,31] and Hassner [32] have reported the addition of phenylhydrazine to some steroidal azoalkenes, and methanol-addition by-products were found when reactions with these derivatives were conducted in methanol.[33] In view of this ready nucleophilic addition to a carbohydrate azoalkene the extent of this reaction with other nucleophiles was studied. In some of the following examples the stereochemistry of the addition products was established by unequivocal synthesis, as was carried out for the methanol addition product already discussed. With other products this was not done; recourse was made to the correlation [34] that exists between vicinal coupling constants and stereochemistry. The generalisation usually made [35] is that $J_{ax,ax} > 8$ Hz and $J_{ax,eq}$ and $J_{eq,eq} < 6$ Hz. This has been further refined by Coxon [36] who found that the values for $J_{1,2}$ in several methyl α-D-glycopyranosides were 4 Hz $> J_{eq,ax} > 2$ Hz $< J_{eq,eq}$. This empiricism is supported by observations made [15,37] with several β-glycopyranosides. Hence, usually, it is a simple matter to verify an axial–axial relationship between two vicinal protons (see later however), but to decide between an axial–equatorial and an equatorial–equatorial relationship is more difficult, particularly as the electronegativity of the substituents attached to the carbon atoms bearing the coupled hydrogen atoms can effect the degree of coupling.[38] Therefore, in order to evaluate the applicability of this method to the compounds at present under investigation some relevant J_{vic} values for a number of glycopyranosiduloses and their phenylhydrazones of proven structures are included in Tables 1 and 2. None of the values listed refute these empirical rules.

Further reactions with reagents that possess a nucleophilic oxygen atom have been found. Acetic acid added rapidly to the azoalkene (14) at 50° and the crystalline product, which separated from the solution on cooling, was shown to be methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-3-ulose phenylhydrazone (17). The configuration at position 2 was established from the small value for $J_{1,2}$ (1 Hz). This is well within the limit for an *eq,eq* coupling constant and this interpretation is substantiated by the $J_{1,2}$ value exhibited by the *ribo*-isomer, which is reported [26] to be 3·9 Hz. Therefore, the only reasonable alternative structure for the product is excluded.

In the presence of aqueous sodium hydroxide, 2-methoxyethanol behaved similarly to methanol, affording the phenylhydrazone (18). The D-*arabino*-configuration was assigned to the product because $J_{1,2}$ was found to be only 1·0 Hz. This assignment is reasonable in view of the similarity to the product obtained with methanol.

Attempts to effect the base-catalysed addition of water to this azoalkene failed. Neither of the known glycopyranosid-3-ulose phenylhydrazones unsubstituted at position 2 and with the D-*ribo*- or D-*arabino*-configuration could be obtained in this way.

Nitrogen nucleophiles also add readily to the α-D-3-azoalkene (14). With sodium azide in aqueous ethanol containing ammonium chloride 1,4-addition of hydrazoic acid across the conjugated system occurred in 2 h at 80° to afford the 2-azido-phenylhydrazone (19) with the D-*arabino*-configuration. The presence of the azido-residue was revealed by the i.r. spectrum, and the configuration at C-2 was established from the value (1·0 Hz) of $J_{1,2}$. This assignment is reasonable since the known [39] *ribo*-isomer of this azide exhibits a $J_{1,2}$ value of 3·3 Hz.

Although water has not yet been added successfully to these carbohydrate azoalkenes, addition of ammonia has been achieved. Saturation of a solution of the azoalkene (14) in ethanolic dioxan with ammonia caused the yellow colour to be discharged during 4 days at room temperature. Evaporation of the solution gave the 2-amino-2-deoxy-compound as a waxy solid. This was *N*-acetylated to produce the 2-acetamidophenylhydrazone (24), which exhibited i.r. absorptions expected for an amide group. The presence of this group was substantiated by the acetyl methyl signal in the n.m.r. spectrum. The coupling between the proton at C-2 and that at C-1 was 3·5 Hz, which indicates that this phenylhydrazone had the *ribo*-configuration; this was

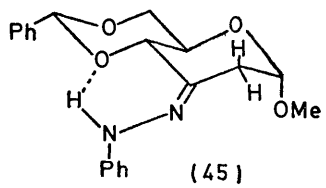
[31] J. Buckingham and R. D. Guthrie, *J. Chem. Soc.* (*C*), 1968, 3079.
[32] A. Hassner and P. Catsoulacos, *Chem. Comm.*, 1957, 121.
[33] V. R. Mattox and E. C. Kendal, *J. Amer. Chem. Soc.*, 1950, **72**, 2290.
[34] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
[35] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.
[36] B. Coxon, *Tetrahedron*, 1965, **21**, 3481.
[37] R. U. Lemieux and S. Levine, *Canad. J. Chem.*, 1964, **42**, 1473; K. Igatashi and T. Honma, *J. Org. Chem.*, 1967, **32**, 2521.
[38] Ref. 21, p. 276.
[39] Y. Ali and A. C. Richardson, *Carbohydrate Res.*, 1967, **5**, 441.

corroborated by comparison with the phenylhydrazone prepared from authentic methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosid-3-ulose.[12]

Reagents which generate nucleophilic carbon add to the phenylazoalkene (14) giving rise to branched-chain products. For example, methylmagnesium iodide in ether gave crystalline methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-α-D-*arabino*-hexopyranosid-3-ulose phenylhydrazone (20). The assignment of configuration at C-2 rests solely on the value of $J_{1,2}$ (1 Hz). Other features of the n.m.r. spectrum consistent with the proposed structure are the high-field three-proton doublet from the C-2 methyl substituent, and a one-proton broadened quartet to which the methyl group is coupled.

Another branched-chain derivative (25) was produced by the addition to the azoalkene (14) of the enolate formed from pentane-2,4-dione. This product showed a ketonic carbonyl i.r. absorption and n.m.r. signals for the two methyl groups in the branch. Because the anomeric proton signal appeared as a doublet split by 3·0 Hz the D-*ribo*-structure has been assigned tentatively to this compound.

Another reaction which can be considered as a 1,4-nucleophilic addition, is the reduction at room temperature of the phenylazoalkene (14) in tetrahydrofuran and methanol with sodium borohydride. This rapidly formed the compound (21/45) in 73% yield as a pure crystalline geometric isomer. The n.m.r. spectrum of this compound in $CDCl_3$ (Table 2, entry 12) showed the C-2 methylene protons as a rather broad singlet centred at τ 7·35. This occurred because both the axial and equatorial protons had similar chemical shifts in this solvent. Measurements of the spectrum in C_6D_6 [18,19,40] (Table 2, entry 10) caused the signal of the axial proton at C-2 to shift upfield. It then appeared as a quartet at τ 7·76 and the equatorial proton as another quartet at τ 7·27. This phenylhydrazone tentatively has been assigned [27] the *anti*-structure (45) because the appearance of the N–H



(45)

signal at very low field indicates that it is in an environment where intramolecular hydrogen bonding can occur. Furthermore, the similarity of the chemical shifts of the axial and equatorial protons at C-2 in $CDCl_3$ solution indicates that the NHPh group is not in a position where it will interact with the equatorial proton at C-2, as would be the case for the *syn*-isomer.[18]

When reduction of the azoalkene (14) with sodium borohydride was carried out in dimethylformamide and methanol the phenylhydrazone derivative was isolated in very high yield as a mixture in almost equal amounts of *syn*- and *anti*-forms. Fractional crystallisation gave two samples. One was an almost pure form of the isomer reported above, whereas the other sample was only about 65% pure. The n.m.r. signals from the major component in the latter sample showed it to be the same as the isomer which preponderated in the mixture of isomers formed by direct condensation of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose with phenylhydrazine. A sample of high isomeric purity could be obtained by this condensation and this material has been tentatively assigned the *syn*-structure by comparison of its n.m.r. spectrum (in $CDCl_3$) with that of the other isomer (Table 2, entry 11). The N–H signal appeared at relatively high field (τ 2·77), indicating that this proton was not strongly hydrogen bonded in this isomer. Furthermore the methylene protons appeared as two clearly resolved quartets because the H-2*eq* signal appeared at lower field than that due to H-2*ax*. This shift to lower field probably originates from the interaction between H-2*eq* and the NHPh group that is possible in this isomer.

In order to ascertain the stereochemistry of this hydride addition, the reduction was repeated under identical conditions with sodium borodeuteride and methan[^{2}H]ol. This yielded a compound with a simpler n.m.r. spectrum. In $CDCl_3$ solution the anomeric proton appeared as a doublet split by only 2 Hz by the high-field methylene proton. This also gave rise to a doublet, whereas the low-field methylene signal was absent, as was the N–H resonance. Consequently the methyl 4,6-*O*-benzylidene-2-deoxy-2-deuterio-α-D-hexopyranosid-3-ulose had the *arabino*-configuration (22).

Additions to the 3-phenylazoalkene (29) with the β-D-configuration were even more easily accomplished than with the α-anomer (Scheme 2). As already mentioned, attempts to form the azoalkene (29) from the 2-*O*-benzoyl phenylhydrazone (28) by methoxide-induced elimination of benzoic acid resulted only in a transient production of the azoalkene, as estimated by a temporary orange colouration. This colour rapidly disappeared and the product, isolated in 73% yield, was another phenylhydrazone which possessed a methoxy-group at position 2 instead of the benzoyl group present in the starting material. This was clearly indicated by the n.m.r. spectrum (Table 2, entry 15) (appearance of a second methoxy-group) and by the intensity of the signals in the aromatic region which were equivalent to ten protons, indicating that only two phenyl groups remained in the product. The absence of a benzoyl group was confirmed by the i.r. spectrum. The product, therefore, was methyl 4,6-*O*-benzylidene-2-*O*-methyl-β-D-*arabino*-hexopyranosid-3-ulose phenylhydrazone (30). The assignment of the *arabino*-configuration was deduced from the small coupling (2·5 Hz) between H-1 and H-2.

Sodium borohydride reduction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-β-D-*erythro*-hex-2-enopyranoside (29) afforded a phenylhydrazone (32)

[40] R. F. Butterworth, M. H. Freemantle, and W. G. Overend, *Chem. and Ind.*, 1968, 1485.

of a 2-deoxyglycoside in 80% yield. As only one isomer was isolated no assignment of configuration about the carbon–nitrogen double bond could be made.

The stereochemistry of the hydride addition was ascertained by carrying out the experiment with deuteriated reagents. The n.m.r. spectrum (Table 2, entry 17) of the deuteriated phenylhydrazone showed significant differences from that of its protonated analogue (Table 2, entry 16). The NH signal was greatly diminished, and the anomeric proton gave a doublet instead of a quartet. Only one of the methylene protons remained and its signal appeared as a doublet coupled only with the anomeric proton (8 Hz). The other methylene proton was originally coupled to H-1 by 3 Hz: therefore the product could be assigned the *ribo*-structure depicted in (33).

Addition of methylmagnesium iodide to compound (29) gave a product with the same stereochemistry as for the hydride addition. The 2-*C*-methyl branched-chain glycopyranosidulose phenylhydrazone so obtained showed a three-proton doublet at high field in the n.m.r. spectrum (Table 2, entry 18) and a large coupling (8·5 Hz) between H-1 and H-2. Consequently the D-*ribo*-structure (34) was assigned to this compound.

Acetic acid added smoothly to the phenylazoalkene (29) and the phenylhydrazone so formed in 60% yield was shown to possess an acetoxy-group at C-2 by a combination of i.r. and n.m.r. spectral measurements (Table 2, entry 19). The stereochemical assignment in this case was more difficult since the coupling between H-1 and H-2 was found to be 5·5 Hz. This value is the same as that in the closely related methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-*ribo*-hexopyranosid-3-ulose phenylhydrazone (28). Consequently, the 2-*O*-acetyl phenylhydrazone (35) was assigned the D-*ribo*-structure. The coupling between H-1 and H-2 was unexpectedly small in these derivatives especially since the $J_{1,2}$ value in the parent ulose (1) was 7·5 Hz (although even this value is slightly smaller than that expected for a vicinal coupling between two axial protons). The possibility that a more deep-seated transformation had occurred during the condensation of the ulose with phenylhydrazine was excluded by regenerating * the parent ulose from the phenylhydrazone (28).

Since phenylhydrazones (32) and (34) exhibited couplings of 8 Hz between H-1 and H-2 it appeared that conformational changes had occurred in the acetate (35) and the benzoate (28) so that the protons at C-1 and C-2 were no longer *trans*-diaxial to each other. This could be accommodated by a change from a $^4C_1$ conformation to a $^4B^1$ conformation. This is a transformation easily achieved with β-D-anomers since the aglycone group is thus placed in a quasi-axial position.

By treatment of the phenylazoalkene (29) with sodium azide in the presence of ammonium chloride a 2-azido-3-phenylhydrazone (36) was rapidly obtained in 80% yield. The stereochemistry of this product was not proved, but the 6·0 Hz coupling between H-1 and H-2 suggests that it has the *ribo*-configuration.

Dimethylamine is another nucleophilic reagent which readily adds to the phenylazoalkene (29). The 2-dimethylamino-3-phenylhydrazone (31) so formed exhibits a small $J_{1,2}$ value (3·5 Hz) which probably indicates that the compound possesses the D-*arabino*-structure, but the D-*ribo*-isomer cannot be excluded since this isomer is not available for comparison.

When treated with sodium methoxide in methanol, methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-*erythro*-hex-2-enopyranoside (39) underwent a different reaction from those already reported. Although a phenylhydrazone was obtained it did not have the expected structure, but one derived from an αβ-unsaturated ketone. Instead of addition of methanol to the azoalkene system, a base-catalysed rearrangement of a type encountered in steroid chemistry [33] occurred, as shown by arrows on (39) in Scheme 3. The product was identified as methyl 4,6-*O*-benzylidene-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosidulose phenylhydrazone (41) from its molecular formula [elemental analysis and mass spectral molecular weight (352·1423)], spectral characteristics [$\nu_{max.}$ 3300 (NH), 1650, 1600, 1570, and 1510 (C=C–C=N–N–Ph) cm^{-1}; $\lambda_{max.}$ 330 nm (ε 60,470) [41]], and n.m.r. signals indicating the presence of an aglycone methoxy-group, a benzylidene residue, and a N–H proton. Even more important to the structural assignment were the remaining n.m.r. signals, which were all very well resolved: the anomeric proton gave a singlet at τ 4·63, and the C-3 vinylic proton a doublet (2 Hz) at τ 4·06 coupled to the allylic C-5 proton. The proton at C-5 appeared, as expected, as an octet (*J* 10, 6·5, and 2 Hz) at τ 5·33 and one of the C-6 protons resonated at τ 6·2 as a triplet (10 and 10 Hz) whereas the other appeared as a quartet at τ 5·55 (10 and 6·5 Hz).

However, it was found that sodium borohydride added in a 1,4-fashion to the phenylazoalkene (39) to yield the 3-deoxyglycopyranosid-2-ulose phenylhydrazone (42) in 70% yield. Repetition of the experiment with deuteriated reagents afforded the 3-deuterio-analogue (43) which was shown to have the D-*ribo*-configuration. This was deduced from the simplification of the C-3 methylene signals observed in the n.m.r. spectrum [*cf.* compounds (42) and (43) in Table 2]. In the protonated compound they appeared as two quartets, H-3*eq* at τ 6·95 (5 and 14 Hz) and H-3*ax* at τ 7·6 (10 and 14 Hz). The deuteriated compound on the other hand exhibited only one methylene signal and this appeared as a doublet at τ 6·95 (5 Hz).

The phenylazoalkene (39) reacted with sodium azide in aqueous ethanol only slowly: after 2 h at 80° complete reaction was still not achieved. Prolonged heating, however, gave rise only to decomposition products. From the incompletely reacted mixture methyl 3-azido-3-deoxy-4,6-*O*-benzylidene-α-D-*arabino*-

* We thank Mrs. V. M. Racz for performing this experiment.

[41] 'Organic Electronic Spectral Data,' vol. II, ed. H. E. Ungnade, Interscience, London, 1960, p. 220.

hexopyranosidulose phenylhydrazone (44) was isolated in low yield. The presence of the azido-group in the product was clearly shown by the i.r. spectrum, and the D-*arabino*-configuration was determined from the large coupling (10 Hz) observed in the clearly resolved doublet of the C-3 proton (entry 25, Table 2). Reaction of the phenylazoalkene (39) occurred only slowly with other reagents such as acetic acid and methylmagnesium iodide, and resulted mainly in decomposition.

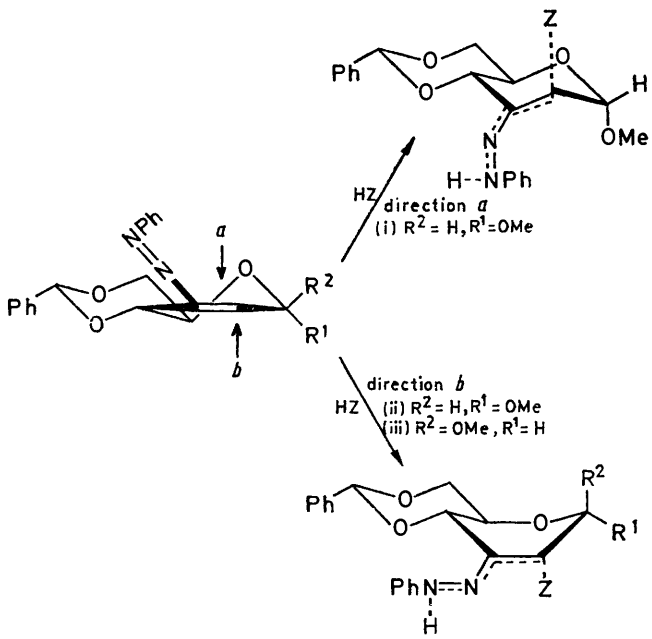


FIGURE 1

Stereochemistry.—Additions to these azoalkene systems might be expected to have some similarities to nucleophilic additions to cyclohexenones. The information available concerning the latter class of compounds suggests that, for stereoelectronic reasons, the incoming nucleophiles should be collinear with the *p*-orbital of the carbon atom that is attacked.[42] During the process of bond formation this carbon atom becomes tetrahedral and the six-membered ring is changed from its original half-chair conformation. The preferred direction of attack would be expected to be the one which places the attached substituent in an axial orientation on a chair form of the six-membered ring, rather than the alternative quasi-axial position on the ring in a boat conformation.

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-*erythro*-hex-2-enopyranoside (14) was attacked by most nucleophiles with a high degree of stereoselectivity: direction *a* in Figure 1(i) usually being preferred as shown by the preponderance of products with the D-*arabino*-structure. The formation of this stereoisomer is probably favoured for two reasons, (i) that it is produced *via* a chair-like transition state [Figure 1(i)] and (ii) that attack by a nucleophile at C-2 would favour an approach *trans* to the methoxy-substituent at C-1. An examination of the stereochemical course of additions to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-hex-2-enopyranosides, which have been extensively studied by Baer and his co-workers,[43] reveals that the substituent at C-2 has also entered *trans* to the aglycone methoxy-group. Although these reactions result in a net 1,2-addition of the reagent, similarities between the two modes of addition might be expected.

In a few cases the D-*ribo*-isomer was formed from the phenylazoalkene (14). These reactions probably involved a 'boat-like' transition state in which the incoming nucleophile approached from the stereoelectronically acceptable, axial direction as shown in Figure 1(ii). The reason why ammonia and carbanionic reagents prefer this direction of attack, which is *cis* to the methoxy-group at C-1, is not understood.

With the phenylazoalkene (29) most nucleophiles again react with a high degree of stereoselectivity: phenylhydrazones with the D-*ribo*-structure were formed most often. This supports the view [35] that one of the factors influencing the direction of nucleophilic attack is the preference of the group entering at C-2 to approach *trans* to the substituent at C-1, as shown in Figure 1(iii). The required 'boat-like' transition can easily be achieved with the β-D-anomer (29) because of the favourable anomeric effect such an arrangement affords.

The behaviour of the 2-phenylazoalkene (39), with an α-glycosidic substituent, is interesting. Attack at C-3 from direction *a* (Figure 2) will be rather unfavourable in this compound, because the 'boat-like' transition state required for the nucleophile to enter axially will be

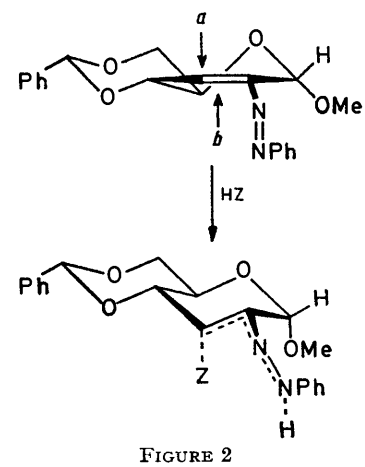


FIGURE 2

difficult to achieve, owing to the inflexibility imposed at C-3 in the pyranoid ring by the close proximity of the *trans*-fused dioxolan ring. On the other hand, attack

[42] D. N. Kirk and M. P. Hartshorn, 'Steroid Reaction Mechanisms,' ed. C. Eaborn and N. B. Chapman, Elsevier, Amsterdam, 1968, p. 195.

[43] H. H. Baer, *Adv. Carbohydrate Chem.*, 1969, **24**, 67, and references therein.

from direction *b* would be stereoelectronically favourable because a chair-like transition state would be involved. However, this direction of attack is unfavourable with bulky nucleophiles because they would then have to enter *cis* to the substituent at C-4. Consequently when this compound was treated with methoxide in methanol nucleophilic attack at a carbon atom did not occur. Instead, the methoxide behaved as a base and abstracted the proton at C-4 to afford the phenylhydrazone (41).

With nucleophiles that are only weakly basic, such as deuteride and azide ions, the tendency towards proton attack is reduced. Therefore, with sodium borodeuteride, reaction occurs at C-3, with the small deuteride ion approaching from the sterically crowded but electronically favoured direction *b*, whereas, with the somewhat more bulky azide ion, C-3 is attacked from direction *a*. This is achieved only with difficulty and the conditions required to bring about the addition cause decomposition. Similarly prolonged treatment was required to induce the azoalkene to react with methylmagnesium iodide or acetic acid, and decomposition was extensive.

Closely related to these elimination–addition reactions is the transformation of methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulphonyl-α-D-*ribo*-hexopyranosid-3-ulose oxime into the corresponding 2-deoxy-2-pyridinium tosylate, which Jones and his co-workers have reported.[44] These workers also found that the latter compound could be converted, with sodium benzoate, into the 2-*O*-benzoyl-*arabino*-derivative in what they described as a nucleophilic displacement reaction. As we have shown that elimination–addition reactions occur with great ease in this type of compound, it is possible that the ready displacement reaction at C-2 which the Canadian workers described could also proceed *via* such a route.

EXPERIMENTAL

Unless stated otherwise i.r. spectra were measured for solid samples dispersed in potassium bromide with a Perkin-Elmer Infracord model 137; u.v. spectra were obtained for ethanolic solutions with a Unicam SP 700 spectrophotometer; mass spectra were measured with an A.E.I. MS 902 instrument operated with an ionising potential of 70 eV and a probe inlet temperature of 150°; optical rotations were measured for solutions in chloroform 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.

Preparation of Partially Protected Methyl Glycopyranosides

Methyl 3-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-*glucopyranoside* (8).[13]—A solution of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (20 g) in dry pyridine (100 ml) containing benzoic anhydride (21 g) was kept at room temperature for 48 h, after which the usual work-up afforded compound (8) as fine needles (3·5 g), m.p. 217—219°, $[\alpha]_D$ +34·5° (*c* 1), $\nu_{max.}$ 3400 (OH) and 1730 and 1600 (PhCO) cm^{-1} (lit.,[13] m.p. 219—220°, $[\alpha]_D$ +34°).

Methyl 2-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-*glucopyranoside* (7).[13]—Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (28 g) in dry pyridine (50 ml) was treated with benzoyl chloride (14 ml) in pyridine (25 ml) at 0° for 20 h and then at 20° for 2 days. Work-up afforded the 2-benzoate (7) as needles (15 g), m.p. 169—170°, $[\alpha]_D$ +108° (*c* 1), $\nu_{max.}$ 3400 (OH) and 1730 and 1600 (PhCO) cm^{-1} (lit,[13] m.p. 167—169°, $[\alpha]_D$ +111°).

Alternatively *N*-benzoylimidazole [prepared from imidazole (27·2 g) in pure chloroform (300 ml) and benzoyl chloride (25 ml)] could be used to benzoylate methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (57·4 g) in chloroform (300 ml) by heating the substances together under reflux for 8 h. After washing the cooled solution with water, drying, concentration to a residue, and recrystallisation from methylene chloride–light petroleum (b.p. 40—60°), the 2-benzoate (34 g) was obtained with m.p. 168—170°.

Methyl 4,6-O-*Benzylidene*-β-D-*glucopyranoside* 2-*Benzoate* (10) *and* 3-*Benzoate* (11).—Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (16 g) in dry pyridine (15 ml) was mixed with benzoyl chloride (8 ml) in pyridine (15 ml) at 0° and kept at 20° for 2 days. The solution was poured into ice–water (*ca.* 300 ml) and the crude solid which separated was collected and fractionally crystallised from ethanol to give methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9) (8 g), m.p. 182—183°, $[\alpha]_D$ +17° (*c* 1), (lit.,[45] m.p. 185°, $[\alpha]_D$ +15·8°).

The mother liquors were fractionated on a silica gel column. The first component in the eluate was *methyl* 2-O-*benzoyl*-4,6-O-*benzylidene*-β-D-*glucopyranoside* (10), isolated as white needles (4 g, 18%), m.p. 195—196°, $[\alpha]_D$ −34° (*c* 0·5), $\nu_{max.}$ 3500 (OH) and 1730 and 1600 (PhCO) cm^{-1}, τ ($CDCl_3$) 1·8—2·8 (complex m, 10H, 2Ph), 4·4 (s, 1H, PhC*H*), 4·9 (t, 1H, H-2, $J_{2.1} = J_{2.3} = 8$ Hz), 5·45 (d, 1H, H-1), 5·5—6·5 (complex m, 5H), 6·52 (s, 3H, OMe), and 7·25br (d, 1H, OH) (Found: C, 65·3; H, 5·6. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%).

The second component eluted from the column was the corresponding 3-*benzoate* (11) (6·7 g, 31%), m.p. 177—178°, $[\alpha]_D$ −107° (*c* 0·5), $\nu_{max.}$ 3500 (OH) and 1720 and 1600 (PhCO) cm^{-1}, τ ($CDCl_3$) 1·9—2·8 (complex m, 10H, 2Ph), 4·5 (s, 1H, PhC*H*), 4·55 (t, 1H, H-3, $J_{3.2} = J_{3.4} = 9$ Hz), 5·56 (d, 1H, H-1, $J_{1.2}$ 7·5 Hz), 5·6 (complex m, 1H), 6·1—6·4 (complex m, 4H), 6·42 (s, 3H, OMe), and 7·1 (d, 1H, OH, *J* 3 Hz) (Found: C, 65·6; H, 5·8. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%).

Oxidation of Partially Protected Methyl Glycopyranosides

Methyl 3-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-arabino-*hexopyranosidulose* (6).—Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (8) (7·7 g) was oxidised with dimethyl sulphoxide (80 ml) containing dicyclohexylcarbodi-imide (9 g) and anhydrous phosphoric acid (0·6 ml) according to the method of Baker and Buss.[12] The isolated *pyranosidulose* (6) was recrystallised from methylene chloride–ether–pentane to afford white needles (6·7 g, 88%), m.p. 51—52°, $[\alpha]_D$ −18° (*c* 0·5 in EtOH), $\nu_{max.}$ 1750 (CO) and 1730 and 1600 (PhCO) cm^{-1} (Found: C, 65·3; H, 5·2. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%); n.m.r. spectrum Table 1.

[44] W. A. Szarek, B. T. Lawton, and J. K. N. Jones, *Tetrahedron Letters*, 1969, 4867.
[45] H. Ohle and K. Spencker, *Ber.*, 1928, **61**, 2387.

Methyl 3-O-*Benzoyl*-4,6-O-*benzylidene*-β-D-arabino-*hexopyranosidulose* (5).—Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (11) (3 g) was oxidised similarly to the α-anomer and afforded the β-D-*glycopyranosidulose* (5) (2·7 g, 90%) as needles, m.p. 166—168°, $[\alpha]_D$ −126° (*c* 0·6), $\nu_{max.}$ 1750 (CO) and 1730 and 1600 (PhCO) cm^{-1} (Found: C, 65·7; H, 5·1. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%); n.m.r. spectrum Table 1.

Methyl 2-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-ribo-*hexopyranosid*-3-*ulose* (2).—The 2-benzoate (7) (56 g) was oxidised by the method used for the oxidation of the isomeric 3-benzoate (8). This gave compound (2) (51 g, 88%), m.p. 198—199°, $[\alpha]_D$ +94° (*c* 0·5); n.m.r. spectrum Table 1 (Found: C, 65·7; H, 5·4. Calc. for $C_{21}H_{20}O_7$: C, 65·6; H, 5·2%) (lit.,[46] m.p. 211—213°).

Methyl 2-O-*Benzoyl*-4,6-O-*benzylidene*-β-D-ribo-*hexopyranosid*-3-*ulose* (1).—Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (10) (4 g) was oxidised by the same method as used for the other isomers. This yielded the β-D-ribo-*hexopyranosid*-3-*ulose* (1) (3·6 g, 90%), m.p. 198—199° (decomp.), $[\alpha]_D$ −12° (*c* 0·5), $\nu_{max.}$ 1740 (CO) and 1730 and 1600 (PhCO) cm^{-1}; see Table 1 for n.m.r. spectrum (Found: C, 65·8; H, 5·4. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%).

Methyl 4,6-O-*Benzylidene*-2-O-*methyl*-α-D-arabino-*hexopyranosid*-3-*ulose*.—Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-altropyranoside [47] (9·8 g) in freshly distilled dichloromethane (100 ml) was treated with ruthenium tetroxide [from ruthenium dioxide hydrate (5·1 g)] in carbon tetrachloride (200 ml). Isolation of the oxidation product in the usual way [2,48] afforded the title compound as a chromatographically homogeneous syrup (7·6 g, 78%), $\nu_{max.}$ 1740 cm^{-1} (CO), τ 4·96br (s, 1H, H-1), 6·32br (s, 1H, H-2), 5·1—6·5 (complex m, 4H, H-4, -5, -6, and -6′), 4·37 (s, 1H, PhC*H*), 2·3—2·7 (complex m, 5H, Ph), and 6·58br (s, 6H, 2OMe).

Preparation of Methyl Glycopyranosidulose Arylhydrazones

Methyl 3-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-arabino-*hexopyranosidulose Phenylhydrazone* (37).—A solution of compound (6) (4·7 g) in pyridine (15 ml) was treated with phenylhydrazine hydrochloride (2 g) at 20° for 6 h. Then water was added and the oil which formed was separated from the aqueous supernatant liquor. The oily product was washed with water and then dissolved in ethanol, from which the *pyranosidulose phenylhydrazone* (37) crystallised as cream-coloured needles (4·0 g), m.p. 135—137°, $[\alpha]_D$ +87° (*c* 0·5 in EtOH), $\lambda_{max.}$ 278 nm (ε 34,500), $\nu_{max.}$ 3300 (NH), 1730 (PhCO), and 1600 and 1500 (C=N−N−Ph) cm^{-1}; n.m.r. spectrum Table 2 (entry 22) (Found: C, 68·4; H, 5·8; N, 5·8. $C_{27}H_{26}N_2O_6$ requires C, 68·3; H, 5·5; N, 5·9%).

Methyl 2-O-*Benzyol*-4,6-O-*benzylidene*-α-D-ribo-*hexopyranosid*-3-*ulose Phenylhydrazone* (12).—The 2-*O*-benzoyl-α-D-pyranosid-3-ulose (2) (16·7 g) was treated with phenylhydrazine hydrochloride (6·6 g) in pyridine (100 ml). The procedure just described afforded the *phenylhydrazone* (12) (18 g, 87%), m.p. 118—120°, $[\alpha]_D$ +97° (*c* 2), $\lambda_{max.}$ 280 nm (ε 22,000), $\nu_{max.}$ 3300 (NH), 1725 (PhCO), and 1600 and 1500 (C=N−NPh) cm^{-1}; n.m.r. signals Table 2 (entry 1) (Found: C, 68·2; H, 5·6; N, 6·0. $C_{27}H_{26}N_2O_6$ requires C, 68·3; H, 5·5; N, 5·9%).

Methyl 2-O-*Benzoyl*-4,6-O-*benzylidene*-β-D-ribo-*hexopyranosid*-3-*ulose Phenylhydrazone* (28).—The 2-*O*-benzoyl-β-D-pyranosid-3-ulose (1) (2·8 g) in pyridine (15 ml) was treated with phenylhydrazine hydrochloride (1·2 g) as described in the preparation of compound (12). This produced the *pyranosid*-3-*ulose phenylhydrazone* (28) as fine cream-coloured needles (2·0 g, 58%), m.p. 123—125°, $[\alpha]_D$ −65° (*c* 0·75), $\lambda_{max.}$ 280 nm (ε 18,820), $\nu_{max.}$ 3320 (NH), 1730 (PhCO), and 1600 and 1500 (C=N−NPh) cm^{-1}; n.m.r. spectrum Table 2 (entry 14) (Found: C, 68·4; H, 5·5; N, 6·0. $C_{27}H_{26}N_2O_6$ requires C, 68·3; H, 5·5; N, 5·9%).

Methyl 2-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-ribo-*hexopyranosid*-3-*ulose* p-*Nitrophenylhydrazone* (13).—*p*-Nitrophenylhydrazine (0·44 g) in glacial acetic acid (4 ml) was added to a solution of the 2-*O*-benzoyl-α-D-hexopyranosid-3-ulose (2) (1 g) in ethanol (20 ml) and the mixture was heated under reflux for 0·5 h. During the reaction the *pyranosid*-3-*ulose* p-*nitrophenylhydrazone* (13) was deposited as yellow needles (1·3 g, 96%), m.p. 218—219° (decomp.), $[\alpha]_D$ +110° (*c* 0·4), $\lambda_{max.}$ 380 nm (ε 21,050), $\nu_{max.}$ 3300 (NH), 1725 (PhCO), and 1630 and 1510 (C=N−NPh) cm^{-1}, τ −0·5 (s, 1H, NH), 1·7—3·6 (complex m, 14H, aryl groups), 4·37 (d, 1H, H-2, $J_{2,1}$ 3·5 Hz), 4·38 (s, 1H, PhC*H*), 4·9 (d, 1H, H-1), 5·2—6·2 (complex m, 4H), and 6·48 (s, 3H, OMe) (Found: C, 62·4; H, 4·8; N, 8·0. $C_{27}H_{25}N_3O_8$ requires C, 62·4; H, 4·9; N, 8·1%).

Methyl 3-O-*Benzoyl*-4,6-O-*benzylidene*-α-D-arabino-*hexopyranosidulose* p-*Nitrophenylhydrazone* (38).—To a solution of the 3-*O*-benzoyl-α-D-glycopyranosidulose (6) (0·6 g) in ethanol (4 ml), *p*-nitrophenylhydrazine (0·24 g) and acetic acid (0·6 ml) were added. The mixture was heated on a steam-bath for 15 min and then cooled; the 3-O-*benzoyl*-α-D-*glycopyranosidulose* p-*nitrophenylhydrazone* (38) separated as yellow needles (0·63 g, 78%), m.p. 196—198° (decomp.), $[\alpha]_D$ +171° (*c* 0·5), $\lambda_{max.}$ 371 nm (ε 23,160), $\nu_{max.}$ 3300 (NH), 1735 (PhCO), and 1600 and 1500 (C=N−NPh) cm^{-1} (Found: C, 62·4; H, 4·9; N, 8·3. $C_{27}H_{25}N_3O_8$ requires C, 62·4; H, 4·9; N, 8·1%).

Methyl 4,6-O-*Benzylidene*-2-O-*methyl*-α-D-arabino-*hexopyranosid*-3-*ulose Phenylhydrazone* (16).—The 2-*O*-methyl, *arabino*-hexopyranosid-3-ulose (1 g) was treated with phenylhydrazine hydrochloride (0·4 g) in pyridine (6 ml) for 6 h. The usual work-up afforded the phenylhydrazone (16) (0·8 g) which, after recrystallisation from methanol, had m.p. 136—138°, $[\alpha]_D$ +50° (*c* 1), $\nu_{max.}$ 3400 (NH) and 1620 and 1520 (C=N−NPh) cm^{-1}; n.m.r. data identical to those for the phenylhydrazone prepared by the addition of methanol to the azoalkene derivative (14) (Table 2, entry 2).

Methyl 4,6-O-*Benzylidene*-2-O-*methyl*-α-D-ribo-*hexopyranosid*-3-*ulose Phenylhydrazone* (26) (*with* V. M. Racz).—The 2-*O*-methyl-*ribo*-hexopyranosid-3-ulose (0·14 g) was treated as just described to afford compound (26) (0·12 g, 63% m.p. 161—162°, $\lambda_{max.}$ 282 nm (ε 17,000), $\nu_{max.}$ 3320 (NH) and 1595 and 1510 (C=N−NPh) cm^{-1}; n.m.r. data Table 2, entry 3.

Methyl 2-*Azido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-ribo-*hexopyranosid*-3-*ulose Phenylhydrazone* (23).—The 2-azido-α-D-*ribo*-hexopyranosid-3-ulose [39] (3·1 g) was converted in the usual way into its *phenylhydrazone* (23) (1·9 g, 47%), m.p. 162—164°, $[\alpha]_D$ +425° (*c* 2); n.m.r. data Table 2

[46] F. A. Carey and K. A. Hodgson, *Carbohydrate Res.*, 1970, **12**, 463.

[47] G. A. Grob and D. A. Prins, *Helv. Chim. Acta*, 1945, **28**, 840.

[48] P. J. Beynon, P. M. Collins, D. Gardiner, and W. G. Overend, *Carbohydrate Res.*, 1968, **6**, 431.

(entry 13A) (Found: C, 60·9; H, 5·4; N, 18·0. $C_{20}H_{21}N_5O_4$ requires C, 60·8; H, 5·4; N, 17·7%).

Methyl 2-*Acetamido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-ribo-*hexopyranosid*-3-*ulose Phenylhydrazone* (24).—The 2-acetamido-α-D-*ribo*-glycopyranosid-3-ulose derivative [12] (0·5 g) was converted into its phenylhydrazone in the usual way. The crystalline product had m.p. 260° (decomp.) and its n.m.r. spectral parameters were identical with those obtained for this derivative when prepared *via* an addition reaction to the azoalkene (14) (Table 2, entry 7).

Preparation of Arylazo-enopyranosides

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-3-*phenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (14).—(*a*) Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose phenylhydrazone (12) (40 g) was dissolved in hot methanol (1·5 l), and sodium methoxide [prepared by mixing sodium hydride (2·0 g) with methanol (20 ml)] was added. The mixture was heated under reflux for 5 min and separation of the deep orange needles, which began during the reaction, was completed by cooling. Filtration afforded the 3-*phenylazo*-α-D-*hex*-2-*enopyranoside* (14) (23 g, 77%), m.p. 175—176°, $[\alpha]_D$ +1019° (*c* 0·2); u.v., n.m.r., and mass spectral data in Table 3 (Found: C, 68·2; H, 5·7; N, 7·7. $C_{20}H_{20}N_2O_4$ requires C, 68·2; H, 5·7; N, 8·0%).

(*b*) Methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulphonyl-α-D-*ribo*-hexopyranosid-3-ulose (3) [12a] (4·35 g) was treated with phenylhydrazine hydrochloride (1·6 g) in pyridine (20 ml) at 20°. An orange colour rapidly developed, indicating that the first-formed phenylhydrazone had undergone a subsequent elimination reaction. This was taken to completion by adding triethylamine (3·1 ml) and keeping the mixture at 2° for 18 h. The mixture was then poured into water (150 ml) and the solid that separated was filtered off, washed with water, and recrystallised from aqueous acetone to give the azoalkene (14) (3·1 g, 88%), m.p. 168—171°.

(*c*) Methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucopyranoside [28] (9·25 g) was treated with toluene-*p*-sulphonyl chloride (5·25 g) in pyridine (25 ml) for 3 days at room temperature. Water was added and the crystalline 2-*O*-*p*-tolylsulphonyl derivative was filtered off. It was dissolved in 1,4-dioxan (100 ml), triethylamine (20 ml) was added, and the solution was heated at 100° for 4 h. Water (100 ml) was added to the hot solution to induce crystallisation, and after 18 h at 0° the 3-phenylazo-α-D-hex-2-enopyranoside (14) (5·94 g, 68%) was collected.

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2-*phenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (39).—Treatment of the 3-*O*-benzoyl-α-D-glycopyranosidulose phenylhydrazone (37) (2 g) with methanol (100 ml) containing sodium hydride (0·1 g) at 25° brought about an immediate darkening of the solution, from which the 2-*phenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (39) separated as deep orange crystals (1·2 g), m.p. 143—144° (from ethanol), $[\alpha]_D$ −1054° (*c* 0·2); u.v., n.m.r., and mass spectral data in Table 3 (Found: C, 68·2; H, 6·0; N, 8·2. $C_{20}H_{20}N_2O_4$ requires C, 68·2; H, 5·7; N, 8·0%).

This compound was also prepared by treating methyl 4,6-*O*-benzylidene-3-*O*-tosyl-α-D-*arabino*-hexopyranosidulose hydrate (4·52 g) with phenylhydrazine hydrochloride (1·6 g) in pyridine (20 ml). After recrystallisation (twice) from ethanol the product (1 g) had m.p. 142—143°.

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-3-*phenylazo*-β-D-erythro-*hex*-2-*enopyranoside* (29).—The 2-*O*-benzoyl-β-D-hexopyranosid-3-ulose phenylhydrazone (28) (2 g) in t-butyl alcohol (20 ml) was treated at 60° with t-butyl alcohol (10 ml) in which sodium hydride (0·15 g) had been dissolved. An immediate reaction ensued which afforded *methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-3-*phenylazo*-β-D-erythro-*hex*-2-*enopyranoside* (29) (1 g, 67%) as orange needles, m.p. 136—137° (from ethanol), $[\alpha]_D$ +1000° (*c* 0·1); u.v., n.m.r., and mass spectral data in Table 3 (Found: C, 68·4; H, 5·7; N, 8·2. $C_{20}H_{20}N_2O_4$ requires C, 68·2; H, 5·7; N, 8·0%).

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-3-p-*nitrophenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (15).—The 2-*O*-benzoyl-α-D-hexopyranosid-3-ulose *p*-nitrophenylhydrazone (13) (0·8 g) was dissolved in t-butyl alcohol (5 ml) and sodium t-butoxide was added [from sodium hydride (0·05 g) in t-butyl alcohol]. The solution was heated under reflux for 10 min and then diluted with 40% aqueous t-butyl alcohol; the 3-p-*nitrophenylazo*-α-D-*hex*-2-*enopyranoside* (15) separated as deep violet crystals (0·55 g, 90%), m.p. 200—201°, $[\alpha]_D$ +1046°; u.v., n.m.r., and mass spectral data in Table 3 (Found: C, 60·7; H, 5·0; N, 10·3. $C_{20}H_{19}N_3O_6$ requires C, 60·5; H, 4·8; N, 10·6%).

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2-p-*nitrophenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (40).—The 3-*O*-benzoyl-α-D-glycopyranosidulose *p*-nitrophenylhydrazone (38) (0·4 g) was treated in the same way as the analogous 2-*O*-benzoyl-3-ulose. The 2-p-*nitrophenylazo*-α-D-*hex*-2-*enopyranoside* (40) was formed as deep orange needles (0·2 g, 67%), m.p. 193—195°, $[\alpha]_D$ +1558° (*c* 0·1); see Table 3 for n.m.r. and mass spectral characteristics (Found: C, 60·0; H, 5·0; N, 10·5. $C_{20}H_{19}N_3O_6$ requires C, 60·5; H, 4·8; N, 10·6%).

1,4-*Addition Reactions with Methyl* 4,6-O-*Benzylidene*-2,3-*dideoxy*-3-*phenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (14).—(a) *Methanol.* The 3-phenylazo-derivative (14) was prepared *in situ* from the 2-*O*-benzoyl-α-D-glycopyranosid-3-ulose phenylhydrazone (12) (0·59 g, 1·25 mmol) by treatment in methanol (40 ml) with sodium methoxide [from sodium hydride (0·06 g, 2·5 mmol)]. The 3-phenylazo-derivative was precipitated initially but redissolved during heating at 65°. After 1 h the orange colour had faded almost completely. Water (10 ml) was added and, after 1 h at 0°, *methyl* 4,6-*O*-*benzylidene*-2-*O*-*methyl*-α-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (16) (0·42 g, 87%) was obtained as colourless crystals, m.p. 136—138° (from methanol) (not depressed on admixture with authentic compound), $[\alpha]_D^{24}$ +50° (*c* 1); n.m.r. data in Table 2 (entry 2) (Found: C, 65·4; H, 6·3; N, 7·6. $C_{21}H_{24}N_2O_5$ requires C, 65·6; H, 6·3; N, 7·3%).

(b) *Acetic acid.* The 3-phenylazo-derivative (14) (0·35 g) was warmed to 50° in glacial acetic acid (5 ml) containing acetic anhydride (0·5 ml) for 10 min. During this period the colour was discharged and, on cooling, *methyl* 2-O-*acetyl*-4,6-O-*benzylidene*-α-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (17) (0·28 g, 69%) was deposited as white needles, m.p. 170—174° (decomp.) (from ethanol), $[\alpha]_D$ +57° (*c* 2), $\nu_{max.}$ 3350 (NH), 1745 (MeCO), and 1610 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 4) (Found: C, 64·1; H, 5·9; N, 7·0. $C_{22}H_{24}N_2O_6$ requires C, 64·1; H, 5·9; N, 6·8%).

(c) 2-*Methoxyethanol.* The 3-phenylazo-derivative (14) (1·1 g) was treated with warm aqueous M-sodium hydroxide (1 ml) in 2-methoxyethanol (50 ml) for 3 min in an en-

deavour to add the elements of water to the azoalkene system. The mixture was worked-up by adding water (150 ml) and extracting the product into methylene chloride. Evaporation afforded *methyl* 4,6-O-*benzylidene*-2-O-(2-*methoxyethyl*)-α-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (18) (0·53 g) as needles, $\nu_{max.}$ 3370 (NH) and 1610 and 1510 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 5).

(d) *Elements of Hydrazoic Acid.* The 3-phenylazo-derivative (14) (1 g) in 25% aqueous ethanol (20 ml) containing sodium azide (1 g) and ammonium chloride (0·2 g) was heated on a steam-bath for 2 h. Water (5 ml) was added and the mixture kept at 0° for 2 h. *Methyl* 2-*azido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (19) crystallised from the solution (0·97 g, 87%), m.p. 147—148°, $[\alpha]_D$ −157° (*c* 1·3), $\nu_{max.}$ 3330 (NH), 2100 (N_3), and 1605 and 1510 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 6) (Found: C, 60·8; H, 5·1; N, 17·7. $C_{20}H_{21}N_5O_4$ requires C, 60·8; H, 5·4; N, 17·7%).

(e) *Ammonia.* A solution of the 3-phenylazo-derivative (14) (1·72 g) in ethanol (150 ml) was saturated with ammonia gas. 1,4-Dioxan (50 ml) was then added and the orange solution was stored at room temperature for 4 days. Evaporation of the then pale yellow solution yielded a semi-solid, which was acetylated with acetic anhydride (5 ml) in methanol (200 ml). White crystals which rapidly separated were essentially pure *methyl* 2-*acetamido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-ribo-*hexopyranosid*-3-*ulose phenylhydrazone* (24) (1·3 g, 64%), m.p. *ca.* 260° (decomp.), $[\alpha]_D$ +54° (*c* 2), $\nu_{max.}$ 3380 and 3300 (NH), 1660 and 1555 (HNCO), and 1610 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 7) (Found: C, 64·2; H, 5·9; N, 10·0. $C_{22}H_{25}N_3O_5$ requires C, 64·2; H, 6·1; N, 10·2%).

(f) *Methylmagnesium iodide.* The 3-phenylazo-derivative (14) (1·3 g) in boiling ether (150 ml) was treated with methylmagnesium iodide [magnesium (0·5 g) and methyl iodide (0·65 ml) in ether (50 ml)] and the mixture was heated for 10 min. The usual work-up afforded a syrup which gave crystalline *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-C-*methyl*-α-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (20) (0·47 g, 35%) [from ethanol (25 ml)], m.p. 168—172° (decomp.), $[\alpha]_D$ −22° (*c* 1), $\nu_{max.}$ 3360 (NH) and 1610 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 8) (Found: C, 68·3; H, 6·4; N, 7·3. $C_{21}H_{24}N_2O_4$ requires C, 68·5; H, 6·6; N, 7·6%).

(g) *Pentane*-2,4-*dione.* To pentane-2,4-dione (25 g) containing sodium hydride (0·1 g) the 3-phenylazo-derivative (14) (0·35 g) was added; the mixture was heated on a steam-bath for 1 h, then poured into water (250 ml), and the crude product separated as a sticky solid. This was recrystallised twice from ethanol to give pure *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-C-*diacetylmethyl*-α-D-ribo-*hexopyranosid*-3-*ulose phenylhydrazone* (25) (0·16 g, 40%), m.p. 185—190° (decomp.), $[\alpha]_D$ −28° (*c* 2), $\nu_{max.}$ 3360 (NH), 1700 (CO), and 1610 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 9) (Found: C, 66·4; H, 6·3; N, 6·1. $C_{25}H_{28}N_2O_6$ requires C, 66·4; H, 6·2; N, 6·2%).

(h) *Nitromethane.* A suspension of the 3-phenylazo-derivative (14) (1·72 g) in nitromethane (50 ml) and triethylamine (10 ml) was heated at 100° for 2·5 h. Concentration of the product gave a solid, which was recrystallised twice from ethanol to give *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-*nitromethyl*-α-D-ribo-*hexopyranosid*-3-*ulose phenylhydrazone* (27) (0·65 g, 34%), m.p. 148—152° (decomp.), $[\alpha]_D$ −177° (*c* 2), $\nu_{max.}$ 3360, 1610 and 1530—1510 (C=N–NPh), and 1560 and 1380 (C–NO_2) cm^{-1} (Found: C, 61·1; H, 5·9; N, 9·9. $C_{21}H_{23}N_3O_6$ requires C, 61·0; H, 5·6; N, 10·2%); n.m.r. data Table 2 (entry 13B).

(i) *Sodium borohydride.* The 3-phenylazo-derivative (14) (0·35 g) was dissolved in a mixture of methanol (3 ml) and tetrahydrofuran (5 ml). Sodium borohydride (0·1 g) was then added and the mixture was stirred until the orange colour had been discharged (*ca.* 0·5 h). Water (0·5 ml) was added and the solution cooled. The crystals which separated afforded *methyl* 4,6-O-*benzylidene*-2-*deoxy*-α-D-erythro-*hexopyranosid*-3-*ulose* anti-*phenylhydrazone* (45) (0·28 g, 75%), m.p. 172—174° (from ethanol), $[\alpha]_D$ +77° (in EtOH), $\nu_{max.}$ 3320 (NH) and 1600 and 1500 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entries 10 and 12) (Found: C, 67·4; H, 5·8; N, 7·8. $C_{20}H_{22}N_2O_4$ requires C, 67·8; H, 6·3; N, 7·9%).

When this reduction was carried out with sodium borodeuteride in methan[^{2}H]ol, methyl 4,6-*O*-benzylidene-2-deoxy-2-deuterio-α-D-*arabino*-hexopyranosid-3-ulose [*N*-^{2}H]phenylhydrazone (22) was obtained (73%), m.p. 178—179°, $[\alpha]_D$ +70°; n.m.r. data in Table 2 (entry 13) (Found: C, 67·5; H and D, 6·3; N, 7·8. $C_{20}H_{20}D_2N_2O_4$ requires C, 67·4; H and D, 6·8; N, 7·9%).

Reduction of the 3-phenylazo-derivative (14) (1·1 g) in a mixture of *NN*-dimethylformamide (15 ml) and methanol (5 ml) with sodium borohydride (0·08 g) afforded, after 15 min at room temperature, a crude mixture (1·06 g) composed of approximately equal amounts of the 2-deoxy-α-D-glycopyranosid-3-ulose *syn*- and *anti*-phenylhydrazones. The more mobile component on t.l.c. [SiO_2; C_6H_6–EtOAc (4 : 1 v/v)] was isolated in 90% purity after five recrystallisations from ethanol and found to be the *anti*-isomer by comparison of its n.m.r. spectrum with the material prepared before.

The less mobile component was not so easy to obtain from this experiment. However, it was found to preponderate in the isomeric mixture obtained by condensing methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose with phenylhydrazine. After two recrystallisations of the crude product so obtained, a sample which was 90% pure syn-*isomer* (10% *anti*-isomer contaminant) was obtained. Its i.r. spectrum and analytical figures were identical with those of the *anti*-isomer but its n.m.r. spectrum was different (Table 2, entry 11).

Reduction of compound (14) (1·27 g) in boiling ether (50 ml) with lithium aluminium hydride (0·57 g) for 5 min also afforded compound (21) (*syn*-isomer) but in poor yield (20%). However, increase in the reaction time resulted in over-reduction, apparently at the >C=N– group of the phenylhydrazone, to give a 2,3-dideoxy-3-phenylhydrazino-derivative which is being studied further.

1,4-*Addition Reactions with Methyl* 4,6-O-*Benzylidene*-2,3-*dideoxy*-3-*phenylazo*-β-D-erythro-*hex*-2-*enopyranoside* (29).—(a) *Methanol.* The 3-phenylazo-derivative (29) (0·14 g) was dissolved in warm methanol (5 ml) and then heated under reflux for 5 min with methanol (2 ml) in which sodium hydride (0·24 g) had been dissolved. The orange colour of the solution faded during the period of reflux to a pale yellow, and upon cooling *methyl* 4,6-O-*benzylidene*-2-O-*methyl*-β-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (30) separated as fine needles (0·11 g, 73%), m.p. 151—153°, $[\alpha]_D$ −274° (in EtOH) (*c* 0·1), $\lambda_{max.}$ 284 nm (ε 31,510), $\nu_{max.}$ 3300 (NH) and 1600 and 1500 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 15) (Found: C, 65·6; H,

6·1; N, 7·2. $C_{21}H_{24}N_2O_5$ requires C, 65·6; H, 6·3; N, 7·3%).

(b) *Acetic acid.* The 3-phenylazo-derivative (29) (0·1 g) was treated as in (b) for the α-anomer. Recrystallisation of the crude product from ethanol afforded pure *methyl* 2-O-*acetyl*-4,6-O-*benzylidene*-β-D-ribo-*hexopyranosid*-3-*ulose phenylhydrazone* (35) (0·07 g, 60%), m.p. 169—170°, $[\alpha]_D$ −340° (*c* 0·5), $\lambda_{max.}$ 281 nm (ε 53,350), $\nu_{max.}$ 3300 (NH), 1745 (Ac), and 1600 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 19) (Found: C, 64·0; H, 6·0; N, 6·9. $C_{22}H_{24}N_2O_6$ requires C, 64·1; H, 5·9; N, 6·8%).

(c) *Elements of hydrazoic acid.* The 3-phenylazo-derivative (29) (0·1 g) was treated as described in (d) for the α-anomer except that the period of heating was reduced to 5 min. The white needles deposited were recrystallised from ethanol to afford *methyl* 2-*azido*-4,6-O-*benzylidene*-2-*deoxy*-β-D-ribo-*hexopyranosid*-3-*ulose phenylhydrazone* (36) (0·95 g, 81%), m.p. 173—174°, $[\alpha]_D$ +21° (*c* 0·5), $\lambda_{max.}$ 282 nm (ε 32,670), $\nu_{max.}$ 3300 (NH), 2160 (N_3), and 1600 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 20) (Found: C, 60·6; H, 5·2; N, 17·6. $C_{20}H_{21}N_5O_4$ requires C, 60·8; H, 5·4; N, 17·7%).

(d) *Dimethylamine.* The 3-phenylazo-derivative (29) (0·15 g) was dissolved in anhydrous dimethylamine and maintained at 0·5° for 10 min. The colourless solution was evaporated to afford a solid which crystallised from ethanol–light petroleum (b.p. 40—60°) to give *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-*dimethylamino*-β-D-arabino-*hexopyranosid*-3-*ulose phenylhydrazone* (31) (0·1 g, 59%), m.p. 172—174° (decomp.), $[\alpha]_D$ −356° (*c* 0·4), $\lambda_{max.}$ 280 nm (ε 12,380), $\nu_{max.}$ 3300 (NH) and 1600 and 1500 (C=N–NPh) cm^{-1}; see Table 2 (entry 21) for n.m.r. data (Found: C, 66·3; H, 7·0; N, 10·4. $C_{22}H_{27}N_3O_4$ requires C, 66·5; H, 6·8; N, 10·6%).

(e) *Methylmagnesium iodide.* The 3-phenylazo-derivative (29) (0·2 g) was treated as described in (f) for the α-anomer to give *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-C-*methyl*-β-D-ribo-*hexopyranosid*-3-*ulose phenylhydrazone* (34) (0·04 g, 19%), m.p. 209—210°, $[\alpha]_D$ −40° (EtOH) (*c* 0·1), $\lambda_{max.}$ 278 nm (ε 21,950), $\nu_{max.}$ 3310 (NH) and 1600 and 1520 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 18) (Found: C, 68·3; H, 6·6; N, 7·6. $C_{21}H_{24}N_2O_4$ requires C, 68·5; H, 6·6; N, 7·6%). A second product, shown by t.l.c. to form about half the crude reaction mixture, was not isolated.

(f) *Sodium borohydride.* The 3-phenylazo-derivative (29) (0·2 g) was reduced with sodium borohydride, as described in (i) for the α-anomer, to give *methyl* 4,6-O-*benzylidene*-2-*deoxy*-β-D-erythro-*hexopyranosid*-3-*ulose phenylhydrazone* (32) (0·16 g, 80%), m.p. 188—189°, $\nu_{max.}$ 3300 (NH) and 1600 and 1500 (C=N–NPh) cm^{-1}; n.m.r. data in Table 2 (entry 16) (Found: C, 67·5; H, 6·2; N, 7·9. $C_{20}H_{22}N_2O_4$ requires C, 67·8; H, 6·3; N, 7·9%).

Repetition of this experiment with sodium borodeuteride and methan[^{2}H]ol afforded *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-*deuterio*-β-D-ribo-*hexopyranosid*-3-*ulose* [N-^{2}H]*phenylhydrazone* (33) (67%), m.p. 186—188°; see Table 2 (entry 17) for n.m.r. data (Found: C, 67·4; H and D, 6·3; N, 7·7. $C_{20}H_{20}D_2N_2O_4$ requires C, 67·4; H and D, 6·8; N, 7·9%).

Reactions of Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2-*phenylazo*-α-D-erythro-*hex*-2-*enopyranoside* (39).—(a) *Sodium methoxide.* The 2-phenylazo-derivative (39) (0·5 g) was treated with sodium methoxide in methanol as described for the β-anomer of the 3-phenylazo-derivative (29) to give the rearrangement product, *methyl* 4,6-O-*benzylidene*-3,4-*dideoxy*-α-D-glycero-*hex*-3-*enopyranosidulose phenylhydrazone* (41) (0·4 g, 75%) which formed white needles, m.p. 119—121° (from ethanol), $[\alpha]_D$ +558° (*c* 0·4 in EtOH), $\lambda_{max.}$ 330 nm (ε 60,470), $\nu_{max.}$ 3330 (NH), 1650, 1600, 1570, and 1500 (C=C–C=N–NPh) cm^{-1}; τ($CDCl_3$) 2·3—3·2 (complex m, 11H, NH and 2Ph), 4·05 (d, 1H, H-3, $J_{3,5}$ 2 Hz), 4·32 (s, 1H, PhC*H*), 4·62 (s, 1H, H-1), 5·31 (octet, 1H, H-5, $J_{5,6eq}$ 6·5, $J_{5,6ax}$ 10·0 Hz), 5·55 (q, 1H, H-6*eq*, $J_{6eq,6ax}$ 10·0 Hz), 6·2 (t, 1H, H-6*ax*), and 6·42 (s, 3H, OMe), *m/e* 352 (M^+, 45%), 321 (29), 214 (20), 203 (37), 106 (40), 105 (72), and 77 (100) (Found: C, 68·0; H, 5·8; N, 8·1. $C_{20}H_{20}N_2O_4$ requires C, 68·2; H, 5·7; N, 8·0%).

(b) *Elements of hydrazoic acid.* The 2-phenylazo-derivative (39) (0·2 g) was treated as described in (*d*) for the 3-phenylazo-α-isomer (14). Although after heating for 2 h some starting material remained, this reaction period gave an optimum yield of product (further heating resulted in decomposition). *Methyl* 3-*azido*-4,6-O-*benzylidene*-3-*deoxy*-α-D-arabino-*hexopyranosid*-*ulose phenylhydrazone* (44) (0·04 g, 18%) had m.p. 165—166°, $\nu_{max.}$ 3300 (NH), 2100 (N_3), and 1600 and 1500 (C=N–NPh) cm^{-1}; see Table 2 (entry 25) for n.m.r. data (Found: C, 60·6; H, 5·3; N, 17·1. $C_{20}H_{21}N_5O_4$ requires C, 60·8; H, 5·4; N, 17·7%).

(c) *Sodium borohydride.* The 2-phenylazo-derivative (39) (0·35 g) was reduced as described in (i) for the 3-phenylazo-derivative (14) to give *methyl* 4,6-O-*benzylidene*-3-*deoxy*-α-D-erythro-*hexopyranosidulose phenylhydrazone* (42) (0·25 g, 70%), m.p. 177—179°, $\lambda_{max.}$ 275 nm (ε 27,760), $\nu_{max.}$ 3300 (NH) and 1600 and 1500 (C=N–NPh) cm^{-1}; n.m.r. spectrum in Table 2 (entry 23) (Found: C, 67·8; H, 6·4; N, 7·7. $C_{20}H_{22}N_2O_4$ requires C, 67·8; H, 6·3; N, 7·9%).

Repetition of this experiment with deuteriated reagents afforded *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*deuterio*-α-D-ribo-*hexopyranosidulose* [N-^{2}H]*phenylhydrazone* (43), m.p. 177—179°, $\lambda_{max.}$ 277 nm (ε 23,080), $\nu_{max.}$ 1600 and 1500 cm^{-1} (C=N–NPh); n.m.r. data in Table 2 (entry 24) (Found: C, 67·3; H and D, 6·2; N, 7·9. $C_{20}H_{20}D_2N_2O_4$ requires C, 67·4; H and D, 6·8; N, 7·9%).

Removal of a Phenylhydrazone Group

Methyl 2-O-*Benzoyl*-4,6-O-*benzylidene*-β-D-ribo-*hexopyranosid*-3-*ulose from its Phenylhydrazone* (*with* V. M. Racz).—Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-*ribo*-hexopyranosid-3-ulose phenylhydrazone (28) (0·11 g) was heated under reflux with benzaldehyde (0·12 ml) in 25% aqueous ethanol (5 ml) containing acetic acid (0·02 ml). The glycopyranosidulose was isolated by preparative t.l.c. (SiO_2; benzene). In order to achieve good separation, the plate was redeveloped after it had dried from the first development. The methyl glycopyranosid-3-ulose derivative obtained (0·037 g, 42%) had m.p. 188—190° (decomp.) and its n.m.r. spectral parameters were identical with those for the product (1) obtained by oxidation of the partially protected glycopyranoside (10).

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