Arylazo-glycenosides. Part V.[1] Cycloadditions with Methyl 5-*O*-Benzoyl-2,3-dideoxy-3-phenylazo-α- and -β-D-*glycero*-pent-2-enofuranoside

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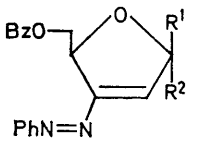
Methods for the formation of fused bicyclic systems in which one of the rings is furanoid have been examined by studying the addition of acrylonitrile to methyl 5-*O*-benzoyl-2.3-dideoxy-3-phenylazo-α- or -β-D-*glycero*-pent-2-enofuranoside. 1,4-Cycloaddition occurs across these azoalkenes. Diazomethane and dimethyloxosulphonium methylide undergo 1.2-*cis*-addition across the carbon–carbon double bond of the α-D-azoalkene. The stereochemistry of the products has been studied by n.m.r. spectral methods. The adduct from the diazomethane reaction extrudes nitrogen when heated. and the product undergoes cyclisation to give a 4'.5'-dihydro-1'-phenyl-(methyl 5-*O*-benzoyl-2.3-dideoxy-α-D-pentofuranosido)[3.2-*c*]-Δ$^{2'}$-pyrazole and methyl 5-*O*-benzoyl-2.3-dideoxy-2.3-*C*-methylene-3-phenylazo-α-D-lyxofuranoside. Comment is made on the mechanisms of some of the reactions studied.

In Part II [2] we reported on the cycloaddition reactions of the 2- and 3-phenylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides with dimethyloxosulphonium methylide and with dienophiles. Whereas methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-*erythro*-hex-2-enopyranoside reacted with dimethyloxosulphonium methylide by addition of a methylene group to the carbon–carbon double bond of the azoalkene system to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*C*-methylene-2-phenylazo-α-D-allopyranoside, the 3-phenylazo-isomer with this ylide gave a mixture of 1'-phenyl(methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*arabino*- and *ribo*-hexopyranosido)[3,2-*c*]-Δ$^{2'}$-pyrazolines. The β-anomer, methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-β-D-*erythro*-hex-2-enopyranoside, behaved similarly but only one of the isomeric Δ$^{2'}$-pyrazolines was isolated.

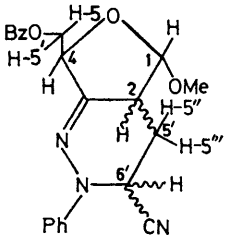
In other experiments [2] it was shown that the α-anomers of the 2- and 3-phenylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides undergo cycloadditions with acrylonitrile or methyl acrylate to give novel heterocyclic structures with a pyranoid ring fused to a tetrahydropyridazine ring. Consequently, by these reactions it is possible to obtain new heterocyclic derivatives which have a six-membered pyranoid ring fused to another cyclic structure which is either a five-membered or a six-membered 1,2-diazine.

The preparation and addition reactions of some 2- and 3-arylazo-derivatives of methyl 2,3-dideoxy-D-pent-2-enofuranosides are described in the preceding paper.[1] We considered it of interest to examine whether such compounds could be used to prepare heterocyclic structures analogous to those described above, but with the pyranoid ring replaced by a five-membered furanoid ring. From experiments with methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-α- and -β-D-*glycero*-pent-2-enofuranoside [(1) and (2)] it is concluded that such substances can be obtained.

The phenylazoalkene (1) [1] undergoes a slow reaction over 3 weeks with acrylonitrile to give a mixture of two products (A and B) in equal amounts which was separated into its crystalline components. Compound A crystallised from the product and compound B was obtained from the mother liquors. Both displayed characteristic i.r. absorption at 1710 cm^{-1} for the benzoate carbonyl and at 1600 cm^{-1} for the C=N–NPh grouping, but no N–H



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



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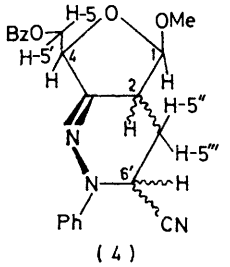

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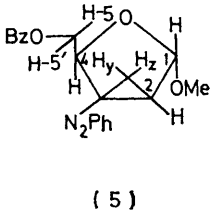

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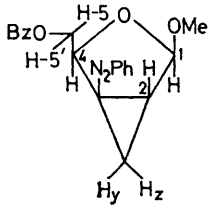


(6)

stretching band at *ca.* 3200 cm^{-1}. The compounds seemed to be isomeric tetrahydropyridazine derivatives (3) formed by Diels–Alder-type additions and elemental analyses were in accord with this conclusion, as were the 100 MHz n.m.r. spectra. In the spectra of both compounds A and B there were signals for two phenyl

[1] Part IV, P. M. Collins, J. R. Hurford, and W. G. Overend, preceding paper.

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

groups, a methoxy-group, and eight other protons none of which were vinylic.

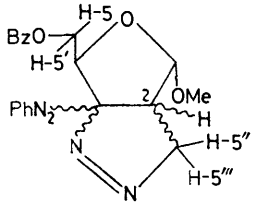
In the spectrum of adduct A signals of five of these eight other protons were well resolved and could be analysed. There were two high-field resonances, which could be assigned to the C-5′ methylene group, an octet at τ 8.16 and a sextet at τ 9.10 which were coupled by 3 and 5 Hz respectively with a quartet at τ 6.09 which had been assigned to H-6′ from its chemical shift and by analogy with results obtained with acrylonitrile adducts already reported.[2] The methine proton (H-6′) clearly was not coupled to H-2 but the H-2 quintet at τ 7.60 showed coupling to the methylene protons by 6 and 13 Hz. Therefore, H-2 must be adjacent to the protons of C-5′ and compound A must have general structure (3). H-2 was coupled to the anomeric proton (τ 5.32) by 5.0 Hz. Thus assignment of stereochemistry at C-2 was not possible with the Karplus equation.

In the n.m.r. spectrum of compound B, signals for four of the eight protons so far not assigned could be analysed by first-order methods. There were three high field signals, two octets arising from H-5″ and -5‴ and one sextet from H-2. The C-5′ methylene group octets at τ 7.72 and 6.98 showed coupling to H-2 (τ 7.32) by 7.5 and 8.5 Hz. H-2 was also coupled to the anomeric proton at τ 4.84 by 5.0 Hz. Therefore, since compound B is not a positional isomer of A it must be a stereoisomer of general structure (3). Isomerism can occur at C-2 and C-6′, but although all the relevant vicinal couplings amongst the protons at C-1, -2, -5′, -6′ have been extracted from both spectra, definitive structures cannot be assigned to these compounds.

Methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-β-D-*glycero*-pent-2-enofuranoside (2) also reacted with acrylonitrile, but in this case only one crystalline adduct (C) was isolated, together with a small amount of a Diels–Alder dimer of compound (2). In the adduct there was no N–H group but a C=N–NPh grouping was present (i.r. spectrum). In the n.m.r. spectrum there was a well resolved triplet at τ 6.30 assigned to H-6′. This ruled out the possibility that the proton at C-6′ was vicinal to that at C-2 because a more complex signal than a triplet would then have been expected. No further evidence was obtained and so the partial structure (4) has been assigned to the adduct C.

Both compounds (1) and (2) reacted with dimethyloxosulphonium methylide to give in low yield products (5) and (6) respectively which were shown spectroscopically to be similar to the cyclopropane derivatives formed from the 2-phenylazo-hexenopyranosides with this reagent. The presence in compounds (5) and (6) of phenylazo- and benzoyl residues was indicated by the u.v. and i.r. absorptions, and was confirmed by the n.m.r. spectra. In each case the n.m.r. spectrum further showed signals for H-4, -5, and -5′ and an anomeric proton. But the most informative features of these spectra were the high field three-spin systems (for analysis see Experimental section) which were characteristic of three interacting cyclopropane protons. Since the α-D-compound (5) exhibited a $J_{1,2}$ value of less than 0.5 Hz it was assigned the 2,3-dideoxy-2,3-*C*-methylene-3-phenylazo-α-D-*arabino*-structure.* The β-D-compound (6) also exhibited a weak coupling between H-1 and -2 and consequently it was assigned the β-D-*xylo*-structure.*

The reaction of compound (1) with diazomethane in ether was also investigated; in 0.5 h one product was formed in good yield as yellow crystals. Elemental analysis indicated that the entire molecule of diazomethane had added to the phenylazoalkene. Spectral measurements indicated that the benzoate group had been retained and that a phenylazo-group was present. This suggested that a 1,3-dipolar addition had occurred between the diazomethane and the olefinic double bond of the azoalkene to give a dihydropyrazole with either structure (7) or (8), depending upon the orientation of the two reactants. Evidence to distinguish between these



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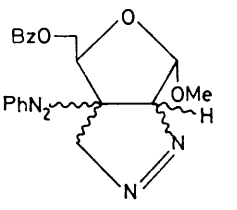


(8)

structures was obtained from the chemical shift and multiplicity of the H-2 signal in the n.m.r. spectrum. A quartet (8 and 4.5 Hz) at high field (τ 7.21) was assigned to H-2. Since the anomeric proton signal at τ 5.70 was a singlet it follows that H-2 must be adjacent to the methylene group of the dihydropyrazole ring, as in structure (7), rather than as in the alternative structure (8) where the H-2 signal would be a doublet or singlet. Therefore, in this addition the diazo-carbon atom has bonded to the carbon β to the phenylazo-substituent in compound (1). Analogous directing influences have been observed with αβ-unsaturated esters,[3-5] sulphones,[6] and nitro-compounds.[3,4]

In a double-resonance experiment when the H-2 quartet was irradiated, the two quartets at τ 5.72 (18.5 and 8 Hz) and 5.85 (18.5 and 4.5 Hz) were simplified. Consequently, these signals were assigned to the methylene protons (H-5″ and H-5‴) of the dihydropyrazole ring. Hence, the other pair of quartets at τ 4.52 and 5.10 arise from the C-5 protons (H-5 and -5′). These

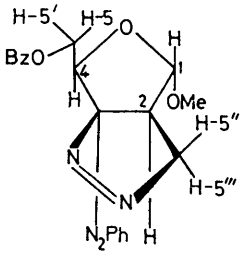
* The configuration is defined at C-2 and -3 by application of the sequence rule in accordance with a tentative recommendation for naming geminally disubstituted sugars proposed by the British Carbohydrate Nomenclature Committee (*i.e.* the group with higher sequence rule priority is considered equivalent to OH).

[3] W. E. Parham, H. G. Braxton, and P. R. O'Connor, *J. Org. Chem.*, 1961, **26**, 1805.
[4] W. E. Parham, C. Serres, and P. R. O'Connor, *J. Amer. Chem. Soc.*, 1958, **80**, 588.
[5] S. D. Andrews, A. C. Day, and A. W. McDonald, *J. Chem. Soc.* (*C*), 1969, 787.
[6] W. E. Parham, F. D. Blake, and D. R. Theissen, *J. Org. Chem.*, 1962, **27**, 2415.

showed coupling to the quartet at τ 4.65 which was attributed to H-4. The zero value for the $J_{1,2}$ coupling implies that the methylene end of diazomethane has added at C-2 *trans* to the aglycone. If diazomethane had added *trans* across the 2,3-double bond of compound (1), then a product would be formed with the furanoid ring in a $^3T_2$ conformation in which the H-1, H-2 dihedral angle would be 170°. Since the $J_{1,2}$ spacing is less than 0.5 Hz an H-1,H-2 dihedral angle of 80—100° is to be expected and this would be consistent with the product being formed by *cis*-addition across the double bond, giving rise to structure (9) in a $^2T_3$ conformation. Consideration of the orbital symmetries [7] of the reactants leads to the prediction that *cis*-annulation would occur since 1,3-dipolar additions of diazomethane to olefinic double bonds are classified as $[_\sigma 4_s + _\pi 2_s]$ cycloadditions.

Several workers,[5,8,9] have reported on the addition reactions of diazoalkenes to multiple bonds and have shown that diazomethane adds in an all-*cis* sense to some $\alpha\beta$-unsaturated compounds.

Δ^1-Dihydropyrazoles are thermally unstable,[5,8-11] undergoing tautomeric change or extrusion of nitrogen.



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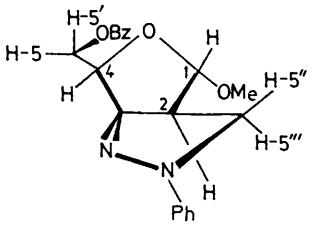

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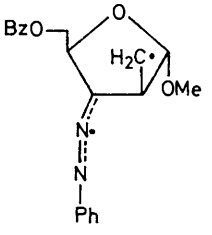

(11)

The adduct assigned structure (9) was found to be thermally unstable and evolved nitrogen on pyrolysis. The yellow residue could be separated into two components. The minor component was identical with the cyclopropyl adduct (5).

The major product gave a positive Knorr test for dihydropyrazoles and its u.v., i.r., and n.m.r. spectral characteristics were consistent with it being 4',5'-dihydro-1'-phenyl(methyl 5-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-pentofuranosido)[3,2-*c*]-$\Delta^{2'}$-pyrazole (10) or its α-D-*erythro*-isomer. All the proton signals in the n.m.r. spectrum could be analysed by first-order methods. A distinction between the signals for the methylene protons at C-5 and C-5' was established in a double-resonance experiment. Irradiation of the H-4 octet at τ 4.85 caused the quartets at τ 5.18 and 5.50 to simplify and the H-2 multiplet of twelve peaks at τ 6.21 to collapse to a sextet. Thus the benzoyloxymethylene protons (H-5 and -5') were attributed to the two quartets coupled to H-4 by 6.0 and 3.2 Hz, respectively. H-4 was also long-range coupled with H-2 by 1.4 Hz. The C-5' methylene signals were readily identified from their couplings to H-2. The $J_{1,2}$ value was 4.5 Hz and this does not permit an assignment of configuration at C-2. However, from mechanistic considerations outlined below the α-D-*threo*-structure (10) may be assigned tentatively to this compound.

The formation of the pyrolysis products (5) and (10) can be most economically explained by a mechanism in which the loss of nitrogen from compound (9) affords a diradical intermediate (11) from which both products can arise. Cyclisation through nitrogen gives the dihydropyrazole (10), whereas cyclisation through carbon gives the cyclopropane derivative (5). It is significant that compound (9) affords (5) with retention of configuration at C-2, and so presumably the diradical has the configuration at C-2 as depicted in (11). It is probable also that the diradical (11) gives rise to the pyrazole (10) with retention of configuration at C-2. It is noteworthy that the 3-phenylazo-derivatives (1) and (2) of these pentenofuranosides gave, with dimethyloxosulphonium methylide, the *C*-methylene derivatives rather than the dihydropyrazoles which were obtained with the analogous hexenopyranosides. It was only the 2-phenylazohexenopyranosides that yielded cyclopropane derivatives with dimethyloxosulphonium methylide. Experiment has shown that thermal instability of pyrazole derivatives is not responsible for the cyclopropane derivatives being formed. A mechanistic interpretation of the differences between the pyrolysis reactions of the furano- and pyrano-derivatives must await quantitative experiment.

EXPERIMENTAL

Methods.—I.r. spectra were measured with a Perkin-Elmer Infracord model 137. Solid samples were dispersed in potassium bromide, and gums were smeared on KBr discs; u.v. spectra were obtained for 96% ethanolic solutions with a Perkin-Elmer spectrometer model 402; optical rotations were measured on solutions in chloroform with a Bellingham and Stanley polarimeter; most of the n.m.r. spectra were determined with a Varian A-60D instrument although a few were carried out with a Varian HA-100D spectrometer: in both cases Me_4Si was used as internal standard; t.l.c. was carried out on Kieselgel G or G_{254} (Stahl) (Merck, Darmstadt) with one of the solvent systems: A, dichloromethane; B, diethyl ether–petroleum (b.p. 40—60°) (1 : 1): compounds were located with anisaldehyde–sulphuric acid or with a u.v. lamp; p.l.c. was effected on glass plates (100 × 20 cm) coated to a depth of 0.1 mm with Kieselgel GF_{254} (Stahl): the compound in a volatile solvent was applied by means of a Burkard t.l.c. applicator (type

[7] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1970, **8**, 781.
[8] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565, 633.
[9] D. E. McGreer, R. S. McDaniel, and M. C. Vinje, *Canad. J. Chem.*, 1965, **43**, 139.
[10] E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968.
[11] F. D. Green, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, 1970, **92**, 867.

SA 100), the plate was developed by vertical ascent of the solvent, and components were located with a u.v. lamp. Fractions were retrieved by washing them from the silica gel with either acetone–ethanol (10 : 1 v/v) or ethyl acetate.

1′,4′,5′,6′-Tetrahydro-1′-phenyl(methyl 5-O-benzoyl-2,3-dideoxy-α-D-pentofuranosido)[3,2-c]pyridazine-6′-carbonitrile (3).— Methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-α-D-*glycero*-pent-2-enofuranoside (1) (0.2 g) in acrylonitrile (2 ml) was stored at ambient temperature in the absence of light. T.l.c. (solvent A) indicated that after three weeks less than 5% of the phenylazo-derivative remained and two new products (A and B) had been formed. The solution was concentrated to a gum (0.24 g) which was crystallised. The crystalline product A was recrystallised from ethanol. *1′,4′,5′,6′-Tetrahydro-1′-phenyl(methyl 5-O-benzoyl-2,3-dideoxy-α-D-pentofuranosido)[3,2-c]pyridazine-6′-carbonitrile* (3) (0.11 g) was obtained with m.p. 143°, $[\alpha]_D$ −80° (*c* 1.6), $\lambda_{max.}$ (EtOH) 274 nm, $\nu_{max.}$ 1710 (C=O) and 1600 cm^{-1} (C=N–NPh), τ (100 MHz; C_6D_6) 5.32 (d, $J_{1.2}$ 5.0 Hz), 7.60 (quintet, $J_{2.5''}$ 13.0 Hz), 5.04—5.44 (m, H-4, -5, -5′), 9.10 (sex, $J_{5''.5'''}$ 13.0 Hz), 8.16 (oct, $J_{5'''.2}$ 6.0 Hz), 6.09 (q, $J_{6'.5''}$ 5.0, $J_{6'.5'''}$ 3.0 Hz), 6.70 (s, OMe), and 2.5—3.1 and 1.5—1.7 (8 H and 2 H, aromatic) (Found: C, 67.4; H, 5.4; N, 10.7. $C_{22}H_{21}N_3O_4$ requires C, 67.5; H, 5.4; N, 10.7%).

From the mother liquors two further crops of crystals (total yield 0.1 g) were obtained. After recrystallisation they afforded a *stereoisomer* B of the title compound as white needles with m.p. 96°, $[\alpha]_D$ −171° (*c* 1.3), $\lambda_{max.}$ (EtOH) 274 nm, $\nu_{max.}$ 1710 (C=O) and 1600 cm^{-1} (C=N–NPh), τ (100 MHz; $CDCl_3$) 4.84 (d, $J_{1.2}$ 5.0 Hz), 7.32 (sex, $J_{2.5''}$ 7.5, $J_{2.5'''}$ 8.5 Hz), 4.6—5.5 (H-4, -5,-5′, and -6′), 7.72 (oct, $J_{5''.5'''}$ 13.0, $J_{5''.6'}$ 6.0 Hz), 6.98 (oct, $J_{5'''.6'}$ 7.5 Hz), 6.40 (s, OMe), and 2.2—2.8 and 1.6—1.9 (8 H and 2 H, aromatic) (Found: C, 67.4; H, 5.5; N, 10.9%).

1′,4′,5′,6′-Tetrahydro-1′-phenyl(methyl 5-O-benzoyl-2,3-dideoxy-β-D-pentofuranosido)[3,2-c]pyridazine-6′-carbonitrile (4).—Methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-β-D-*glycero*-pent-2-enofuranoside (2) (0.18 g) was treated with acrylonitrile (2 ml) as described for the α-D-isomer (1). T.l.c. (solvent B) of the crude product (0.2 g) showed it was comprised of a major component, a trace of the azoalkene (2), and a small amount of a pale yellow material. Crystallisation from ethanol gave solid C (0.05 g), which was recrystallised to afford the title *compound* as fine white needles, m.p. 149°, $[\alpha]_D$ +371° (*c* 1.4), $\lambda_{max.}$ (EtOH) 274 nm, $\nu_{max.}$ 1710 (C=O) and 1600 cm^{-1} (C=N–NPh), τ (60 MHz; C_6D_6) 1.7—3.4 (complex m, 2 Ph), 5.0—5.8 (complex m, H-1, -4, -5, -5′), 6.30 (t, H-6′), 6.77 (s, OMe), and 7.5—8.7 (complex m, H-2, -5″, -5‴) (Found : C, 67.5; H, 5.4; N, 10.8. $C_{22}H_{21}N_3O_4$ requires C, 67.5; H, 5.4; N, 10.7%).

Further crops of this material could not be obtained from the mother liquors and from a preparative layer chromatogram only a small amount of a dimer of the phenylazo-derivative could be isolated.

Methyl 5-O-Benzoyl-2,3-dideoxy-2,3-C-methylene-3-phenylazo-α-D-arabinofuranoside (5).—Dimethyloxosulphonium methylide was prepared *in situ* from trimethyloxosulphonium iodide (0.3 g) in dry dimethyl sulphoxide (8 ml) by stirring with sodium hydride (0.033 g) under nitrogen until hydrogen evolution ceased. Methyl 5-*O*-benzoyl 2,3-dideoxy-3-phenylazo-α-D-*glycero*-pent-2-enofuranoside (1) (0.35 g) in dry dimethyl sulphoxide (5 ml) was mixed with the colourless ylide solution, and after 5 min water (50 ml) was added to the resulting red solution. The amorphous orange precipitate which formed was filtered off and washed repeatedly with water. The major component was separated by p.l.c. (solvent A) as a homogeneous yellow gum (0.12 g), $[\alpha]_D$ +300° (*c* 0.8), $\lambda_{max.}$ (EtOH) 280 nm (ε 15,400), $\nu_{max.}$ 1720 cm^{-1} (C=O). This substance was *methyl* 5-O-*benzoyl*-2,3-*dideoxy*-2,3-C-*methylene*-3-*phenylazo*-α-D-*arabinofuranoside* (5), τ (60 MHz; $CDCl_3$) 5.10 (s, $J_{1.2} < 0.3$ Hz), 8.40 (t, $J_{2.y}$ 5.5, $J_{2.z}$ 5.0 Hz), 4.73 (q, $J_{4.5}$ 4.0, $J_{4.5'}$ 6.0 Hz), 5.1—5.5 (m, H-5, H-5′), 7.45 and 7.95 (2q, H_y and H_z, $J_{y.z}$ 9.0 Hz), 6.58 (s, OMe), and 1.8—2.9 (m, 2Ph) (Found: C, 67.9; H, 6.0; N, 7.9. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 8.0%).

Methyl 5-O-Benzoyl-2,3-dideoxy-2,3-C-methylene-3-phenylazo-β-D-xylofuranoside(6).—Methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-β-D-*glycero*-pent-2-enofuranoside (2) (1.0 g) was treated as described for the α-D-anomer. This gave, after p.l.c. (solvent A), a homogeneous gum (0.1 g), $[\alpha]_D$ −141° (*c* 1.0), $\lambda_{max.}$ (EtOH) 284 nm (ε 11,700), $\nu_{max.}$ 1720 cm^{-1} (C=O), characterised as compound (6), τ (100 MHz; C_6D_6) 5.4 (s, H-1), 9.10 (t, $J_{2.y}$ 6.0, $J_{2.z}$ 4.5 Hz), 4.9—5.3 (m) and 4.6 (q, 2.5 and 11.5 Hz, H-4, -5, and -5′), 7.52 and 8.12 (2 × q, H_y and H_z, $J_{y.z}$ 9.0 Hz), 6.81 (s, OMe), and 1.7—2.9 (m, 2 × Ph).

4′,5′-Dihydro-(methyl 5-O-benzoyl-2,3-dideoxy-3-phenylazo-α-D-lyxofuranosido)[3,2-c]-Δ¹′-pyrazole (9).—Methyl 5-*O*-benzoyl-2,3-dideoxy-3-phenylazo-α-D-*glycero*-pent-2-enofuranoside (1) (0.48 g) was dissolved in ethereal diazomethane (20 ml; *ca.* 0.2 g CH_2N_2). After storage in the dark for 30 min at ambient temperature the yellow solution was concentrated under diminished pressure to a solid (0.54 g) which was recrystallised from diethyl ether–n-pentane. The title *compound* (0.4 g) was obtained as bright yellow needles with m.p. 102.5—103.5°, $[\alpha]_D$ +61° (*c* 2.1), $\lambda_{max.}$ (EtOH) 283 nm (ε 14,500), $\nu_{max.}$ 1720 cm^{-1} (C=O), τ (100 MHz; C_6D_6) 5.70 (s, H-1), 7.21 (q, $J_{2.5''}$ 8.0, $J_{2.5'''}$ 4.5 Hz), 4.65 (q, $J_{4.5}$ 4.0, $J_{4.5'}$ 6.5 Hz), 4.52 and 5.10 (2 × q, H-5 and H-5′, $J_{5.5'}$ 10.5 Hz), 5.72 and 5.85 (2 × q, H-5″ and H-5‴, $J_{5''.5'''}$ 18.5 Hz), 6.95 (s, OMe), and 1.8—3.1 (m, 2Ph) (irradiation of the H-2 quartet caused the H-5″ and H-5‴ signals to simplify) (Found: C, 63.1; H, 5.4; N, 14.7. $C_{20}H_{20}N_4O_4$ requires C, 63.1; H, 5.3; N, 14.7%).

The dihydropyrazole (9) (0.3 g) was heated at 111 °C and 20 mmHg for 0.3 h after which evolution of nitrogen had ceased. T.l.c. of the residual pale yellow glass (0.25 g) revealed that it was comprised of two new components and no initial material. These substances were separated by p.l.c. (solvent B). One product (R_F 0.65) (a gum stored under nitrogen at 0 °C) (0.15 g, 60%) gave a deep purple colour in the Knorr test for dihydropyrazoles and was *4′,5′-dihydro-1′-phenyl(methyl 5-O-benzoyl-2,3-dideoxy-α-D-threo-pentofuranosido)[3.2-c]-Δ²′-pyrazole* (10), $\lambda_{max.}$ 283 nm (ε 8900), $\nu_{max.}$ 1720 (C=O) and 1600 and 1490 cm^{-1} (C=N–NPh), τ (100 MHz; $CDCl_3$) 5.02 (d, $J_{1.2}$ 4.5 Hz), 6.21 (t of q, $J_{2.5''}$ 11.4, $J_{2.5'''}$ 10.0, $J_{2.4}$ 1.4 Hz), 4.85 (oct., $J_{4.5}$ 3.2, $J_{4.5'}$ 6.0 Hz), 5.18 and 5.50 (2 × q, H-5 and H-5′, $J_{5.5'}$ 11.8 Hz), 5.73 and 6.4—6.8 (q and m, H-5‴ and H-5″, $J_{5''.5}$ 8.5 Hz), 6.5 (s, OMe), and 1.8—3.2 (m, 2Ph) [irradiation of the H-4 octet caused the H-2 signal to collapse to a sextet (11.5, 10, and 4.6 Hz) and that of H-5′ to collapse to a doublet (11.8 Hz)].

The other gummy product (0.06 g, 24%) (R_F 0.70) had spectral characteristics identical with those of the 2,3-*C*-methylene derivative.

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