Photo-bromination of Carbohydrate Derivatives. Part 2.[1] Penta-*O*-acetyl-β-D-glucopyranose; the 5-Bromo-derivative and Products of Further Bromination

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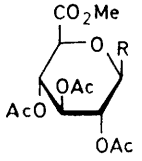
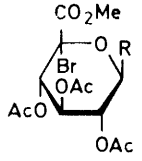
Photo-bromination of penta-*O*-acetyl-β-D-glucopyranose with *N*-bromosuccinimide in carbon tetrachloride causes specific replacement of H-5, and the 5-bromo-derivative can be isolated crystalline in high yield. By-products of the reaction contain monobromoacetyl and dibromoacetyl groups. When bromine was used as reagent the 5-substituted compound was again formed as initial product, but, ultimately, tetra-*O*-acetyl-α-D-glucopyranosyl bromide and dibromides with halogen substituents at C-1 and C-5, and with both bromine atoms at C-1, were also produced. A two-step route from glucose penta-acetate to 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enose is defined. Since the C-5 epimer of the penta-acetate affords the same products, it is proposed that the initial bromination proceeds by way of a discrete radical at the tertiary site.

IN the course of work with D-glucopyranuronic acid derivatives,[1] it was observed in this laboratory that bromination occurred at C-5 when these compounds were treated with *N*-bromosuccinimide in refluxing carbon tetrachloride and under bright light to give a new class of compounds, one member of which has been employed in a new synthetic route to L-ascorbic acid.[1,2] When the reaction was applied to *S*-phenyl 1-thiohexoside [3] and 1-thiohexuronoside [1] ester, competitive reaction occurred at C-1 and led to hex-1-enopyranosid-3-ulose derivatives, but in the absence of a sulphur substituent at C-1 (envisaged as stabilising free radicals at that position) bromination at C-5, with retention of configuration, was the dominant reaction. Methyl tetra-*O*-acetyl-β-D-glucopyranuronate (1) thus gave the crystalline 5-bromo-product (2) in 68% yield, and methyl tri-*O*-acetyl-2,6-anhydro-L-gulonate (3) afforded the crystalline analogue (4) in 47% yield, this latter product offering new access to vitamin C.[1,2] Although *N*-bromosuccinimide remains the reagent of choice for some brominations, we have found that, for others, bromine is more effective allowing, for example, the yield of compound (2) to be increased to 90%.[4]



(1) R = OAc
(3) R = H



(2) R = OAc
(4) R = H

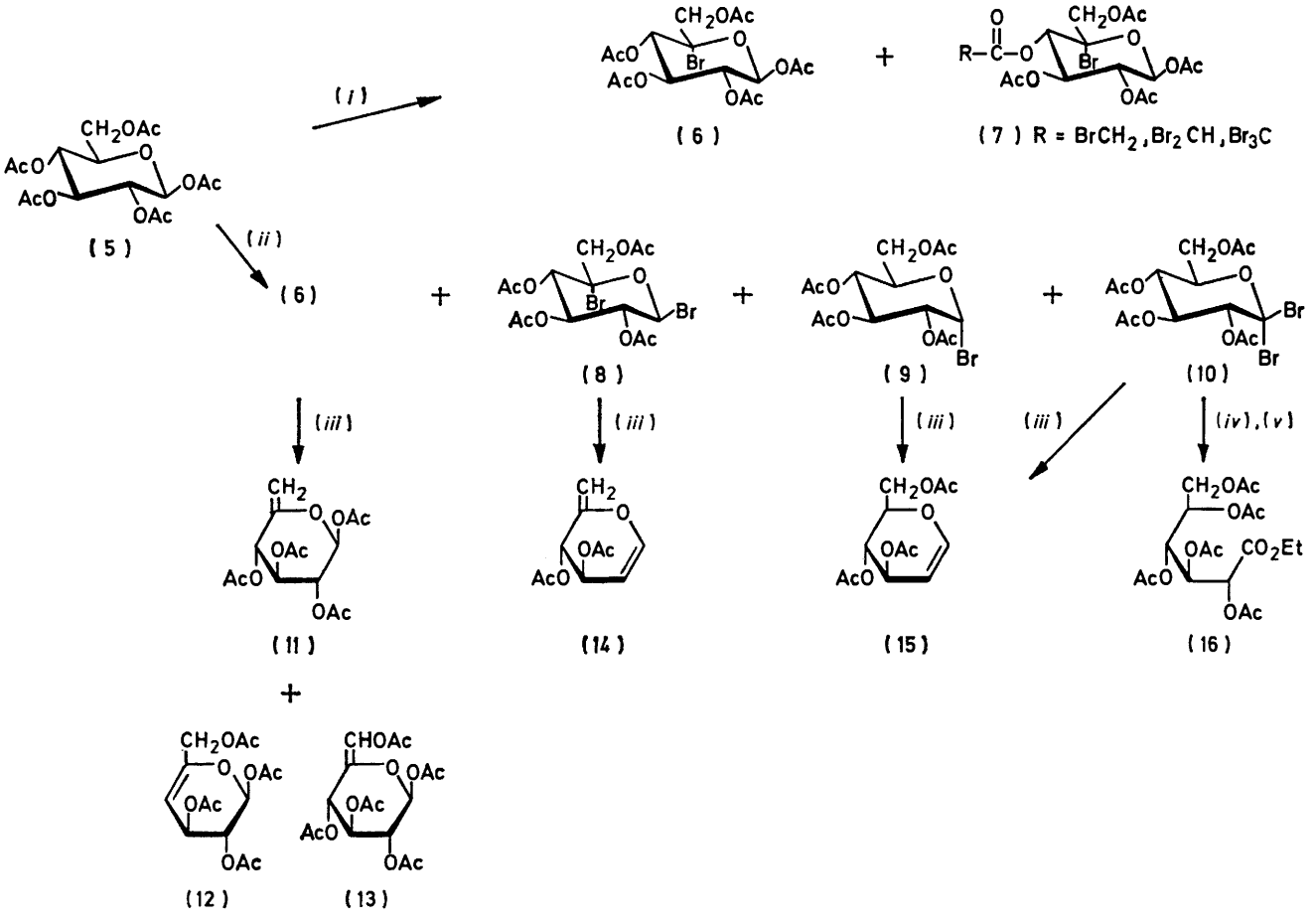
We have reported briefly on the photo-bromination of peracylaldopyranoses,[4] some of which react smoothly, and now describe a comparative study of the processes undergone by penta-*O*-acetyl-β-D-glucopyranose (5) when treated separately with *N*-bromosuccinimide and with bromine in refluxing carbon tetrachloride under bright artificial light.

RESULTS AND DISCUSSION

Experiments carried out on a small scale (0.2 g acetate) indicated that both reagents caused the conversion of the ester into a chromatographically more mobile product (6) which, in the case of the experiment with *N*-bromosuccinimide, was obtained by direct crystallisation in *ca.* 50% yield and in 82% yield by column chromatographic separation. Reaction with bromine was appreciably faster than with *N*-bromosuccinimide, as expected from the likelihood that both processes involve hydrogen abstraction by bromine atoms produced from molecular bromine.[5] In the ^{1}H n.m.r. spectrum of the product (6) no resonance for H-5 was observed, H-6 and H-6′ resonated as an AB pair of doublets, and H-4 as a broad doublet indicating the replacement of H-5, and $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ values of 9 Hz showed that the ring conformation and the anomeric configuration were unaltered by the reaction. In the spectrum of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (9),[6] H-3 and H-5, which have the *syn*-diaxial relationship with the bromine atom, are deshielded by *ca.* 0.4 p.p.m. with respect to these protons in penta-*O*-acetyl-β-D-glucopyranose,[7] and in the product (6) the axial H-3 and H-1 were similarly deshielded, which is therefore consistent with the presence of an axial bromine atom at C-5. That is, the *S*-configuration is indicated at this site, and this is confirmed by the optical rotation of the compound which is appreciably more negative than that of the starting material (5).[1] On treatment with zinc–acetic acid the bromide (6) underwent reduction to give the known alkene (11) [8] and its endocyclic isomer (12) in the ratio 3.5 : 1, together with a trace of a product (13), from loss of hydrogen bromide. Such conditions are traditionally used to remove the elements of acyl hypobromite from acylated glycopyranosyl bromides to give glycal esters,[9] and have also been employed to obtain the 4-*C*-vinylfuranose derivative from tetra-*O*-benzoyl-6-bromo-6-deoxy-β-D-galactofuranose and in related cases.[10] In the inositol series they afforded means of obtaining an exocyclic

methylene derivative from a *gem*-substituted acetoxy-iodomethyl compound.[11]

Reaction of the penta-acetate with *N*-bromosuccinimide on a larger scale (5 g) took appreciably longer and again gave the 5-bromo-derivative (6) as main product (65% isolated by column chromatography), but a minor product (7) (14% isolated) was also formed, which gave a ^{1}H n.m.r. spectrum consistent with its being a mixture of



SCHEME (*i*) *N*-Bromosuccinimide, CCl_4, *hν*; (*ii*) Br_2, CCl_4, *hν*; (*iii*) Zn–AcOH; (*iv*) $AgNO_3$–H_2O–EtOH; (*v*) Ac_2O–pyridine

two monobromoacetyl and two dibromoacetyl analogues of the main product. Sharp singlets at δ 3.82 and 3.96 are consistent with the presence of the former,[3,12] and at δ 5.80 and 5.90 with the presence of the latter.[12] The bromine content of the material indicated the presence of approximately five bromine atoms per molecule (only one being ionisable) and it is believed that the material comprises a mixture of mono-, di-, and possibly tri-bromoacetyl analogues of compound (6), which may have arisen by successive brominations of 4,5- and 5,6-acetoxonium ions or radicals. This is in keeping with the presence of 2-monobromoacetates in the products of photo-bromination with *N*-bromosuccinimide of phenyl 1-thiohexoside tetra-acetates.[3] Reduction of the mixed bromoacetates (7) with zinc–acetic acid gave the two alkenes (11) and (12) and a small proportion of the third (13) indicating the presence of bromine at C-5 and that reductive substitution had occurred within the ester groups. The major alkene (11) could be isolated by direct crystallisation in 47% yield (total after chromatography 59%), and this represents a new practical synthesis of the compound (and of others of this class) which are of interest as sources of deoxyinososes.[13]

When the reaction with bromine was carried out with 10 g of the acetate (5), the time for complete reaction increased from 0.75 h to 3 h, and under these conditions, two products, both more mobile than the 5-bromide (6), which remained the main product, were detected on t.l.c. plates. Resolution of the mixture by column chromatography afforded pure samples of the initial bromide (6) (19%), and the by-products, which were identified as the 1,5-dibromide (8) (13%) and the 1,1-dibromide (10) (17%), as well as small amounts of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (9). The n.m.r. spectrum of the unresolved mixture indicated that all four products were present in appreciable proportions. Although liable to decompose at room temperature, the new bromo-compounds (6), (8), and (10) could be stored at 4 °C for considerable times, and the first, once crystallised, was the most stable. Each, on treatment with zinc–acetic acid, was converted into alkenes as indicated in the Scheme.

The 1,5-dibromide (8) had (apart from the expected

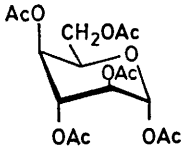
changes) a similar ^{1}H n.m.r. spectrum to that of the ma in bromide (6), but the resonances for H-2, H-3, and H-4 were not as well resolved. Whatever the cause of this effect, it does not appear to result from ring inversion since a $J_{1,2}$ value of 8 Hz is consistent with retention of the $^4C_1$ chair conformation, and with the β-configuration. Reduction gave the known diene (14).[14] ^{1}H N.m.r. spectroscopy of the second dibromide (10) showed that H-1 had been replaced and the signals for H-3 and H-5 were deshielded by *ca.* 0.2 and 0.4 p.p.m. with respect to those for compound (5), indicating the presence of an axial bromine atom at C-1. However, the resonances for H-2, H-3, and H-4 were again not well resolved, establishing that the second, equatorial bromine atom bonded to C-1 was having a significant influence on these resonances, as was the case with compound (8). Reduction with zinc–acetic acid gave tri-*O*-acetyl-D-glucal, which confirms the ability of this reagent to reductively cleave carbon–bromine bonds as well as effect elimination reactions. Treated with silver nitrate in moist ethanol the 1,1-dibromide (10) gave a product with optical rotation and ^{1}H n.m.r. spectrum consistent with those of ethyl 2,3,4,6-tetra-*O*-acetyl-D-gluconate,[15] and on acetylation it gave the known penta-acetate (16).[16]

It is envisaged that, in its photochemical reaction with bromine, penta-*O*-acetyl-β-D-glucopyranose (5) underwent radical substitution at C-5 (it did not react in the dark under otherwise identical conditions), and that the hydrogen bromide formed concurrently then reacted with unused starting material to give the glycosyl bromide (9) (the acidic conditions permitting the equilibration of the anomers), and also with the product (6) to afford the 1,5-dibromide (8). This latter compound, under equilibrating conditions, would be expected to exist predominantly in the β-modification, as do related glycosides with axial substituents at C-5,[17] thus avoiding a destabilising 1,5-*syn*-axial,axial interaction. [In a control experiment the penta-acetate (5) did not react in carbon tetrachloride with hydrogen bromide at an appropriate rate to confirm the above point, but with added bromine, reaction to give the glycosyl bromide (9) occurred readily].

How the 1,1-dibromide (10) was produced is not certain; it does not appear to have arisen by way of the glycosyl bromide (9), because this did not react under comparable photo-bromination conditions. However, its β-anomer could have been a precursor or, alternatively, radical bromination at C-1 of the starting material could have given a *gem*-related acetoxybromide which could have undergone acid-catalysed nucleophilic displacement.

Substantial support was provided for the role of hydrogen bromide in the subsidiary reactions leading to compounds (8)—(10) by the finding that the product of bromination at C-5 (6) constituted *ca.* 90% of the compounds formed when the photo-bromination was repeated under the same conditions (10 g of penta-acetate) but in the presence of potassium carbonate. Direct reduction of the product of this reaction gave a mixture from which the alkene (11) crystallised directly (38% based on penta-acetate used; total 47%), and from which the expected alternative alkene (12) was also obtained in appropriate proportion (16%). The alkenes (14) and (15) derived from the by-products (8)—(10) were isolated in only small proportions (total 8%). Likewise, when the reaction was carried out on a 2-g scale, and without potassium carbonate, the penta-acetate reacted in 1.5 h (half the time required for 10 g of acetate to react), and the products, after reduction, afforded the crystalline, main alkene (11) directly in 37% yield.

In order to investigate aspects of the mechanism of the photo-bromination of penta-*O*-acetyl-β-D-glucopyranose (5) the reactions with *N*-bromosuccinimide and with bromine were repeated using penta-*O*-acetyl-α-D-idopyranose, the enantiomer of which is the C-5 epimer of the β-D-*gluco*-compound. With the former reagent, a product was obtained which was shown by t.l.c., and particularly ^{1}H n.m.r. spectroscopy, to be almost entirely penta-*O*-acetyl-5-bromo-β-glucopyranose and to be identical in all respects to the product from compound (5). However, the specific rotation was +70°, whereas that of the product derived in a parallel experiment with the *gluco*-compound (5) was −66°, and that of the pure 5-*C*-bromide (6) was −91°. Similar observations were made in small-scale experiments using bromine, although in this case the results were somewhat less clear-cut, and these observations are taken to establish that both the glucose penta-acetate (5) and its C-5 epimer react by way of a common tertiary radical which brominates from the axial direction. In the case of penta-*O*-acetyl-α-D-idopyranose, which exists in solution [18] and in the crystal [19] in the $^4C_1$ conformation (17), reaction involves abstraction of an axial hydrogen atom (as is the case with the β-*gluco*-compound which adopts the same chair form) and leads to a conformationally unstable radical which ring-inverts prior to its bromination to give the L-*gluco*-compounds (18), *i.e.* the enantiomer of compound (6).



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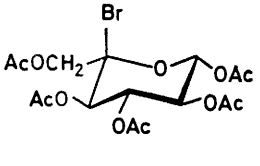

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As pointed out previously,[1] there seem to be few analogies to this photo-bromination process. Additional reactions which may involve points of similarity are the photochemical [20] and lead tetra-acetate [20,21] induce glycosidic cleavages of uronic acid derivatives.

EXPERIMENTAL

Unless otherwise stated, optical rotations were measured in chloroform solutions within the concentration range 0.5—2%. ^{1}H N.m.r. spectra were measured at 60 MHz in

deuteriochloroform on a Perkin-Elmer–Hitachi R-20 spectrometer.

Ionisable bromide was determined by addition of ethanolic silver nitrate solution (2%) to ethanol solutions of the bromo-compounds and weighing of the precipitated silver bromide. Total bromide was determined by heating the compounds with silver nitrate and fuming nitric acid in a sealed tube at 240 °C for 24 h.[22] After dilution of the products, the precipitated silver bromide was again collected and weighed.

Reductions with zinc–acetic acid were conducted by stirring the bromo-compounds (x g) in aqueous acetic acid ($30x$ ml, 1 : 2) containing sodium acetate ($4x$ g) and copper sulphate ($0.2x$ g) for 20 h in the presence of zinc dust ($3x$ g). The mixtures were filtered and the filtrates extracted with chloroform. The extracts were washed with water, aqueous sodium hydrogencarbonate solution, and again with water before drying and removal of the solvent.

Small-scale Photo-brominations.—(a) *With N-bromosuccinimide.* The penta-acetate (5) (0.20 g) was heated in carbon tetrachloride (20 ml) with *N*-bromosuccinimide (0.4 g, 4.4 mol equiv.) over a 275-W heat lamp for 2 h when the starting material (t.l.c.; R_F 0.35) had been replaced mainly by one product (R_F 0.52). The cooled solution was filtered, and the filtrate was washed with water, dried, and the solvent removed to leave a syrup which was purified on a column of silica gel to give 1,2,3,4,6-*penta*-O-*acetyl*-5-*bromo*-β-D-*glucopyranose* (6) (0.2 g, 82%), which on recrystallisation from dry ether at −10 °C had m.p. 119—120 °C, $[\alpha]_D$ −90° (Found: C, 41.1; H, 4.5; Br, 16.0. $C_{16}H_{21}BrO_{11}$ requires C, 41.0; H, 4.5; Br, 17.0%); δ 1.98, 2.04, 2.07, 2.09, and 2.11 (15 H, 5 s, OAc), 4.23 and 4.56 (2 H, 2 d, J 12.5 Hz, H-6 and -6'), 5.14 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 5.18 (1 H, t, $J_{2,3} = J_{1,2}$ = 9 Hz, H-2), 5.55 (1 H, t, H-3), and 6.17 (1 H, d, H-1). This product can be obtained crystalline in about 50% yield without column purification.

(b) *With bromine.* The penta-acetate (5) (0.20 g) was heated in refluxing carbon tetrachloride (20 ml) with bromine (0.20 g, 2.4 mol equiv.) over a 275-W heat lamp for 45 min. The cooled solution was evaporated to a syrup which was identical by t.l.c. and ^{1}H n.m.r. spectroscopy with the initial product obtained using *N*-bromosuccinimide.

Large-scale Photo-bromination with N-Bromosuccinimide.—The reaction was repeated using the penta-acetate (5) (5.0 g), *N*-bromosuccinimide (10.0 g, 4.4 mol equiv.), and carbon tetrachloride (200 ml), and required 16 h for completion. As well as the main product (R_F 0.52), a minor product (R_F 0.72) was observed. Processing as above gave a light brown syrup (6.0 g), a portion of which (2.0 g) was fractionated on a column of silica gel with light petroleum–ether (1 : 1) as eluting solvent. *Fraction* (i) (R_F 0.72) was a mixture (7) of derivatives of penta-*O*-acetyl-5-bromo-β-D-glucopyranose having approximately four bromine substituents in the acetyl groups (see Discussion section) (0.47 g, *ca.* 14%), $[\alpha]_D$ +1° (Found: ionisable Br 10.0; total 53.1. $C_{16}H_{17}Br_5O_{11}$ requires for one ionisable atom Br 10.2; total Br 50.9%). Treatment with zinc–acetic acid converted this material (0.24 g) into a mixture of 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enopyranose (11) and 1,2,3,6-tetra-*O*-acetyl-4-deoxy-α-L-*threo*-hex-4-enopyranose (12) (0.088 g, 87%), 4 : 1 by n.m.r. analysis; see below. Small amounts of 1,2,3,4,6-penta-*O*-acetyl-β-D-*xylo*-hex-5-enopyranose (13) (see below) were also detected in the spectrum.

Fraction (ii) (R_F 0.52) was 1,2,3,4,6-penta-*O*-acetyl-5-bromo-β-D-glucose (6) (1.30 g, 65%). Recrystallised from ether at −10 °C it had m.p. 119—120 °C, $[\alpha]_D$ −90° and i.r. and ^{1}H n.m.r. spectra identical to those of the above sample. Treatment of this bromo-compound (0.44 g) with zinc–acetic acid gave a mixture of the alkenes (11) and (12) (0.22 g, 71%), 3.5 : 1 by n.m.r. analysis (see below) with a small amount of 1,2,3,4,6-penta-*O*-acetyl-β-D-*xylo*-hex-5-enopyranose (13).

The remainder (4.0 g) of the initial bromination products was reduced with zinc–acetic acid and gave crystalline 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enopyranose (11) directly. Recrystallised (×3) from ethanol this product (1.32 g, 47%) had m.p. 115—117 °C, $[\alpha]_D$ −35°, and i.r. and ^{1}H n.m.r. data identical to those of the material described immediately below. A portion (0.7 g) of the non-crystalline product (1.03 g) was resolved on a column of silica gel to give: *fraction* (*a*) (from ethanol) 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enopyranose (11) (0.23 g, total 59%), m.p. 115—117 °C, $[\alpha]_D$ −35° (lit.,[8] m.p. 119 °C, $[\alpha]_D$ −35°); δ 2.05—2.1 (12 H, 4 Ac), 4.50 (1 H, t, $J_{6,6'} = J_{6,4}$ = 1.5 Hz, H-6), 4.76 (1 H, t, $J_{6',4}$ 1.5 Hz, H-6'), 4.93—5.20 (2 H, m, H-2 and -3), 5.52 (1 H, m, $W_{\frac{1}{2}}$ 12 Hz, H-4), and 5.91 (1 H, d with virtual coupling, $J_{1,2}$ 4 Hz, H-1). *Fraction* (*b*) (from ethanol) was 1,2,3,6-*tetra*-O-*acetyl*-4-*deoxy*-α-L-threo-*hex*-4-*enopyranose* (12) (0.29 g, 15%), m.p. 79—81 °C, $[\alpha]_D$ +20° (Found: C, 50.8; H, 5.5. $C_{14}H_{18}O_9$ requires C, 50.9; H, 5.5%); δ 2.05 (12 H, s, 4 Ac), 4.44 (2 H, s, H-6 and -6'), 4.9—5.15 (3 H, m, H-2, -3, and -4), 6.13 (1 H, d with virtual coupling, $J_{1,2}$ 3 Hz, H-1). *Fraction* (*c*) (from methanol) was 1,2,3,4,6-*penta*-O-*acetyl*-β-D-xylo-*hex*-5-*enopyranose* (13) (0.11 g, 5%), m.p. 138—139 °C, $[\alpha]_D$ −45° (Found: C, 49.1; H, 5.3. $C_{16}H_{20}O_{11}$ requires C, 49.5; H, 5.2%); δ 2.05—2.15 (15 H, 5 Ac), 4.8—5.2 (2 H, m, H-2 and -3), 5.40 (1 H, m, $W_{\frac{1}{2}}$ 9 Hz, H-4), 6.01 (1 H, d with virtual coupling, $J_{1,2}$ 5 Hz, H-1), 6.84 (1 H, s, H-6).

Large-scale Photo-bromination with Bromine in the Absence of Base.—The ester (5) (10.0 g) was heated in refluxing carbon tetrachloride (260 ml) with bromine (10.0 g, 2.5 mol equiv.) between two 275-W heat lamps for 3 h. T.l.c. indicated that all starting material (R_F 0.35; silica gel plates developed with light petroleum–ether, 1 : 2) had been replaced by a major product (R_F 0.52), and two minor compounds (R_F 0.55 and 0.75). The solvent and excess of bromine were removed under vacuum, and a portion (2.6 g) of the resulting syrup (13 g) was fractionated on a column of silica gel using light petroleum–ether (1 : 1) as eluting solvent to give four products. *Fraction* (i), R_F 0.75, was 2,3,4,6-*tetra*-O-*acetyl*-5-*bromo*-β-D-*glucopyranosyl bromide* (8) (0.3 g, 13%), $[\alpha]_D$ −90° (Found: ionisable Br, 31.2. $C_{14}H_{18}Br_2O_9$ requires Br, 32.6%); δ 1.98, 2.05, 2.08, and 2.11 (12 H, 4 s, 4 OAc), 4.34 and 4.64 (2 H, 2 d, J 12.5 Hz, H-6 and -6'), 5.05—5.55 (3 H, m, H-2, -3, and -4), and 5.86 (1 H, d, $J_{1,2}$ 8 Hz, H-1). Reduction of the dibromide (0.19 g) with zinc–acetic acid gave 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-D-*threo*-hexa-1,5-dienitol (14) as a light yellow oil (0.06 g, 73%), $[\alpha]_D$ −181° (lit.,[14] −198 and −177°). The i.r., n.m.r., and mass spectra were consistent with published data.[14a]

Fraction (ii) (R_F 0.55) was 2,3,4,6-*tetra*-O-*acetyl*-1-*bromo*-D-*glucopyranosyl bromide* (10) (0.4 g, 17%), $[\alpha]_D$ +98° (Found: ionisable Br, 29.5. $C_{14}H_{18}Br_2O_9$ requires Br, 32.6%); δ 1.95, 2.00, 2.10, and 2.15 (12 H, 4 s, 4 OAc), 4.0—4.4 (3 H, m, H-5, -6, and -6'), and 5.1—5.4 (3 H, m, H-2, -3, and -4). After the 1,1-dibromide (0.14 g) had been treated with ethanolic silver nitrate and the precipitated silver bromide removed, the filtrate was taken to dryness to leave a residue which was extracted (×3) with chloroform

The extracts were washed with water, dried, and taken to dryness to give ethyl 2,3,4,6-tetra-*O*-acetyl-D-gluconate (0.07 g, 62%), $[\alpha]_D$ +22° lit.,[15] $[\alpha]_D$ +19°). The n.m.r. spectrum was in good agreement with published data,[15] and acetylation (of 0.06 g) with acetic anhydride (1 ml) in pyridine (2 ml) gave ethyl 2,3,4,5,6-penta-*O*-acetyl-D-gluconate (16) (0.05 g, 75%) which crystallised from ethanol. Recrystallised from this solvent it had m.p. and mixed m.p. 103—104 °C, $[\alpha]_D$ +18° (lit.,[16] m.p. 103—104 °C, $[\alpha]_D$ +20.5°). The ^{1}H n.m.r. spectrum was consistent with published data [16] and identical to that of an authentic sample prepared from calcium D-gluconate by acetylation,[23] followed by treatment with phosphorus pentachloride, then ethanol.[16]

A further portion of the 1,1-dibromide (0.22 g) was reduced with zinc–acetic acid to give tri-*O*-acetyl-D-glucal (15) (0.08 g, 66%) which crystallised from ethanol. Recrystallised from light petroleum, it had m.p. and mixed m.p. 51—55 °C, $[\alpha]_D$ −13° (ethanol) [lit.,[24] m.p. 54—55 °C, $[\alpha]_D$ −15.5° (ethanol)]. The ^{1}H n.m.r. spectrum was identical to that of an authentic sample.

Fraction (iii) (0.56 g, *ca.* 23%) was re-fractionated on a column of silica gel to give the 1,1-dibromide (10) (0.04 g, t.l.c., n.m.r. identification) and tetra-*O*-acetyl-α-D-glucopyranosyl bromide (9) (0.06 g, R_F 0.55), m.p. and mixed m.p. (from ether) 83—87 °C, $[\alpha]_D$ +170° (lit.,[25] m.p. 87—88 °C, $[\alpha]_D$ +199°) (i.r. and n.m.r. spectra identical to those of an authentic sample.) The remaining fractions (0.39 g) comprised mixtures of these compounds and penta-*O*-acetyl-5-bromo-β-D-glucopyranose (6).

Fraction (iv) (R_F 0.52, 0.46 g, 19%) crystallised from dry ether. Recrystallised (×2) from this solvent at −10 °C, 1,2,3,4,6-penta-*O*-acetyl-5-bromo-β-D-glucose (6) had m.p. 119—121 °C, $[\alpha]_D$ −91° and gave an n.m.r. spectrum identical to that of the authentic material.

Photo-bromination with Bromine in the Presence of Potassium Carbonate.—The bromination was repeated under identical conditions but in the presence of potassium carbonate (5 g), and after reaction was complete, the solids and volatile components were removed to leave a syrup which was reduced with zinc–acetic acid to give a mixture of alkenes from which, on trituration with ethanol at 0 °C, 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enopyranose (11) (3.2 g, 38%) crystallised. Recrystallised from ethanol it had m.p. 115—117 °C, $[\alpha]_D$ −34° and gave a ^{1}H n.m.r. spectrum identical to that of the earlier sample.

A portion (0.7 g) of the non-crystalline product (2.65 g) was resolved on a column of silica gel with light petroleum–ether (1 : 1) as eluting solvent to give four fractions.

Fraction (i) (R_F 0.83) was 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-D-*threo*-hexa-1,5-dienitol (14) (0.02 g, 1.5%), $[\alpha]_D$ −188°, identical by t.l.c., ^{1}H n.m.r., i.r., and mass spectrometry to the previous sample.

Fraction (ii) (R_F 0.65) was tri-*O*-acetyl-D-glucal (15) (0.11 g, 6%), m.p. 53—54 °C, $[\alpha]_D$ −15° (ethanol), identical by t.l.c., ^{1}H n.m.r., and i.r. to the previous sample.

Fraction (iii) (R_F 0.48) was 1,2,3,4-tetra-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enopyranose (11) (0.2 g, 9%, total 47%), m.p., $[\alpha]_D$, i.r. and ^{1}H n.m.r. spectra identical to those of the main product.

Fraction (iv) (R_F 0.50) was 1,2,3,6-tetra-*O*-acetyl-4-deoxy-α-L-*threo*-hex-4-enopyranose (12) (0.35 g, 16%). Recrystallised from ethanol (×3) it had m.p. 81—82 °C, $[\alpha]_D$ +20.5°, and gave an n.m.r. spectra identical to that of the earlier sample.

Photo-bromination of Penta-O-acetyl-α-D-idopyranose.—The D-idose ester [26] (0.2 g) was heated with *N*-bromosuccinimide (0.4 g, 4.4 mol equiv.) for 2 h in refluxing carbon tetrachloride (15 ml) over a 275-W heat lamp. Removal of the volatile components left an unstable syrup, $[\alpha]_D$ +70°, with a ^{1}H n.m.r. spectrum identical to that derived from the products of photo-bromination of penta-*O*-acetyl-β-D-glucopyranose carried out in exactly parallel fashion ($[\alpha]$ −66°). The n.m.r. spectra further indicated that these products were almost entirely penta-*O*-acetyl-5-bromo-β-glucopyranose [compound (6) and its enantiomer].

This experiment was repeated using the idose ester (0.2 g) and bromine (0.2 g, 2.4 mol equiv.) in refluxing carbon tetrachloride for 1 h. The product (0.25 g, 103%) had $[\alpha]_D$ +47°, and the ^{1}H n.m.r. spectrum showed that it contained mainly the enantiomer of compound (6). The product derived under identical conditions from the *gluco*-ester (5) had $[\alpha]_D$ −24°.

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