Unsaturated Carbohydrates. Part 26.[1] Alkenes from 4-Bromohexofuranose Esters; Reactions of 5-Deoxyald-4-enofuranose Derivatives in the Presence of Mercury(II) Ions

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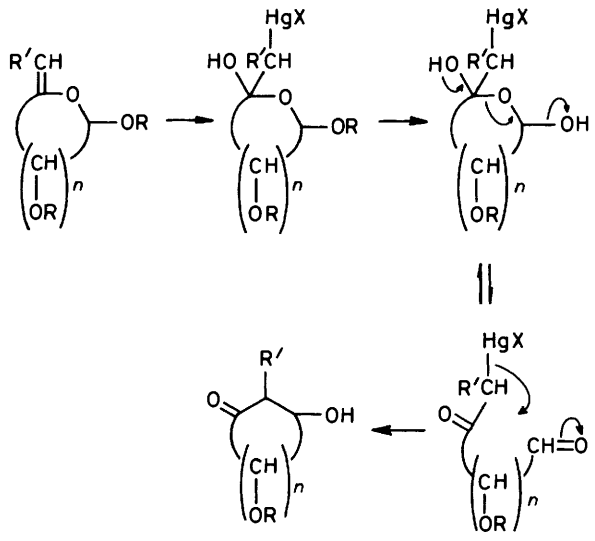
Removal of hydrogen bromide from mixed 1-*O*-acetyl-2,3,5,6-tetra-*O*-benzoyl-4-bromo-β-D-gluco- and galacto-furanose with 1,5-diazabicyclo[5.4.0]undec-5-ene gives the endocyclic 3-ene (**2**), whereas treatment with a zinc–copper couple in aqueous acetic acid affords a mixture of 1-*O*-acetyl-2,5,6-tri-*O*-benzoyl-3-deoxy-β-D-*erythro*-hex-3-enofuranose (**4**) and the exocyclic (*E*)- and (*Z*)-5-deoxyhex-4-enofuranose isomers (**3**). The latter compounds and methyl 2,3-di-*O*-benzoyl-5-deoxy-α-D-*threo*-pent-4-enofuranoside (**9**) in the presence of mercury(II) salts do not give cyclopentanone derivatives. Instead, the C-5-mercury intermediates undergo elimination or hydrolysis reactions. This resistance to ring closure under conditions in which 6-deoxyhex-5-enopyranose derivatives readily give cyclohexanones is consistent with Baldwin's rules for ring closure.

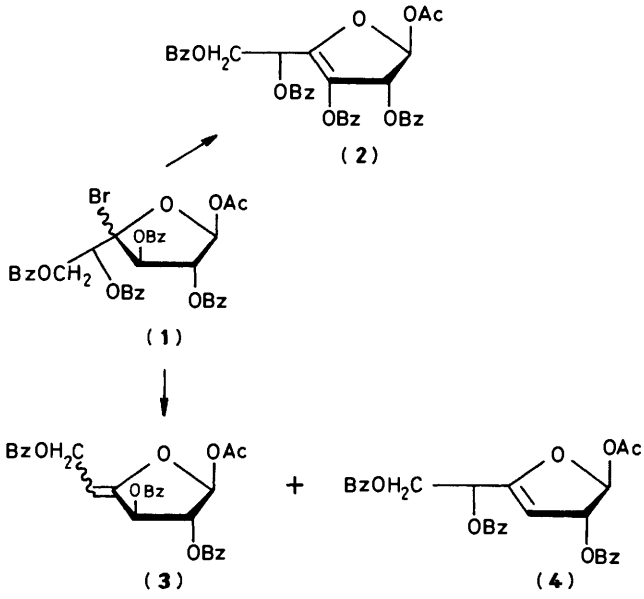
An important area of growth in carbohydrate chemistry in recent years has been the use of sugars for the synthesis of enantiomerically pure non-carbohydrate compounds—particularly natural products.[2] Many acyclic and heterocyclic substances have now been derived in this way, but sugars also provide means of access to functionalised carbocyclic derivatives although only a limited range of methods have so far been developed for producing compounds of this kind.[3] One of our recent objectives has been to find efficient routes from sugars to cyclopentanes,[3] and the present report describes one approach which, in failing, illustrates the significance of phenomena encompassed in Baldwin's rules of ring closure[4] in the synthesis of carbocyclic compounds from carbohydrates.

An efficient method for converting hexoses into cyclohexanone compounds depends upon treatment of 6-deoxyhex-5-enopyranose derivatives in aqueous media with mercury(II) salts which effects hydroxymercuriation to give intermediates (previously isolated but not as yet reported[5]) which react by an intramolecular aldol process to give β-hydroxycyclohexanones (Scheme 1; $n = 3$, R′ = H).[6] Although the starting alkenes are usually made by processes which involve elimination of 5-H and a leaving group at C-6 of pyranose compounds,[7] other access is provided by 5-bromohexose esters which can be prepared efficiently by the photobromination process.[8] With 4-bromofuranose esters now available[9] it became of interest to determine whether they could be made to undergo elimination in the *exo* sense and provide a suitable route to 5-deoxyald-4-enofuranoses, and whether these could then give access to β-hydroxycyclopentanones (Scheme 1; $n = 2$). A study was therefore undertaken of the elimination reactions undergone by 4-bromofuranose esters on treatment with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), and with zinc–acetic acid, with which alkenes have previously been produced from 5-bromohexopyranose esters.[8a]

Treatment of the mixed D-*gluco*- and D-*galacto*-bromide (**1**), produced from 1-*O*-acetyl-2,3,5,6-tetra-*O*-benzoyl-β-D-glucose, with DBU in *NN*-dimethylformamide (DMF) gave a single alkene isolated after chromatography in 66% yield in which both C-6 protons were strongly coupled to the same neighbouring proton and the 3-ene structure (**2**) can consequently be assigned to the product (Scheme 2). Homoallylic coupling[10] of 1 Hz was observed between 2-H and 5-H, and in the ^{13}C n.m.r. spectrum a resonance for C-5 at δ_C 66.4 p.p.m. is consistent only with this atom being in the acyclic part of the molecule.[9,11] A



Scheme 1.

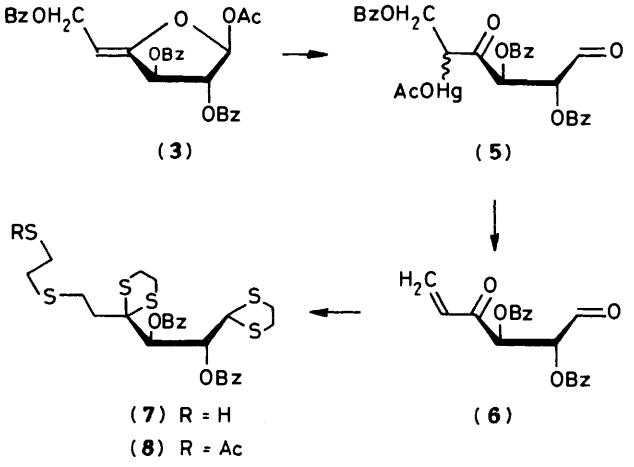


Scheme 2. Bz = benzoyl

resonance at δ_C 146.6 p.p.m. for C-4 agrees with expectations based on the chemical shift of C-5 of a 4-enopyranose analogue (δ_C 143.0 p.p.m.);[8a] no resonance for C-3 was observed, but this by the same analogy should be near δ_C 127 p.p.m., and it is assumed to have been obscured by the aromatic carbon resonances.

On treatment with a zinc–copper couple in aqueous acetic acid the mixed bromides (**1**) gave the two chromatographically different products (**3**) and (**4**) obtained pure in 45 and 6%, respectively, after column chromatography, the faster moving compound giving a ^{13}C n.m.r. spectrum which indicated that it was a mixture of isomers (6:1) of the *exo*-alkene (**3**); in particular, no resonance for an exocyclic sp^3-hybridised C-5 was present in the ^{13}C n.m.r. spectrum, and chemical evidence (see below) confirmed this assignment. In the hexopyranose series[8a] it was concluded that the zinc-induced elimination of bromine from C-5 and an ester group from C-6 may have involved a planar E_2 transition state, and if it is assumed in the present case that this is again the main mechanism for the formation of the *exo*-alkene the *Z*-structure (**3**) can be assigned to the major product if it is also assumed that it was derived from the main D-*galacto*-bromide. The chromatographically slower moving reaction product (**4**) showed coupling of 1.1 Hz between 2-H and 5-H, and an ester carbon resonance at δ_C 68.3 p.p.m. which are similar to the corresponding values for compound (**2**), and consistent with the assigned structure.

To test the *exo*-alkenes (**3**) as potential sources of cyclopentanes (Scheme 1; $n = 2$) they were heated in aqueous acetone with mercury(II) chloride—conditions in which 6-deoxyhex-5-enopyranose derivatives are efficiently converted into β-hydroxycyclohexanones[6]—but no reaction was detected (t.l.c.). Attention therefore was turned to the use of the more ionic, electrophilic, and reactive mercury(II) acetate,[12] and with this salt the alkenes (**3**) reacted in aqueous acetone at room temperature by the expected addition process. An impure product, isolated by solvent extraction and drying, gave ^1H and ^{13}C n.m.r. spectra consistent with those expected for the mercury-containing dicarbonyl compound (**5**). In particular, in

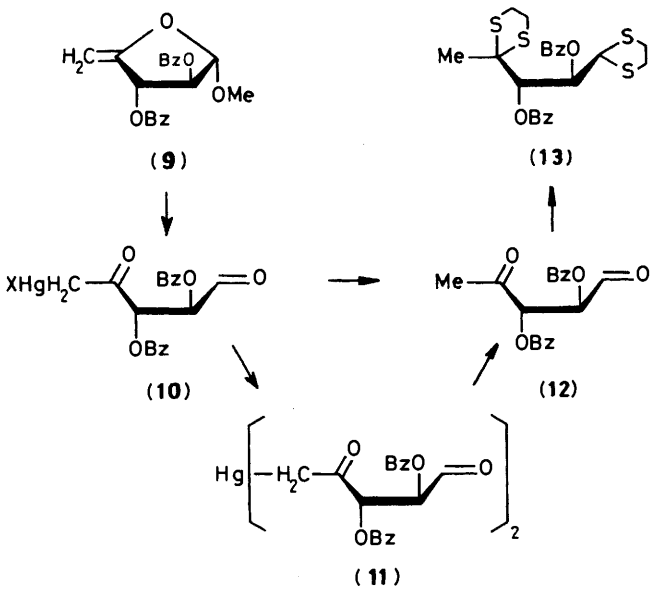


Scheme 3.

the ^1H n.m.r. spectrum resonances for formyl and acetyl groups as well as a mercuriated C-5 group were observed, and in the ^{13}C spectrum signals for an aldehyde and ketonic group as well as the other expected resonances were present.

When the mercuriation reaction was repeated at reflux temperature the mercurial adduct decomposed to give a chromatographically mobile product whose spectrum retained the formyl proton resonance and the two coupled resonances for 2-H and 3-H, but now showed three doublets of doublets with *J* values of 17.3, 10.2, and 1.9 Hz which are diagnostic of a vinyl group,[13] and the product can therefore be assigned structure (**6**). Treatment with ethane-1,2-dithiol and catalytic boron trifluoride gave a product, deduced from its ^1H and ^{13}C n.m.r. spectra, to be the hexathio-compound (**7**) which, on acetylation, gave the monoacetate (**8**) (Scheme 3). 1,4-Addition of the dithiol had therefore occurred to the conjugated enone prior to dithioacetalation—a process for which there is precedent in the literature.[14]

Although the strategy outlined in Scheme 1 ($n = 2$, R′ = CH_2OBz) had succeeded with (**3**) to the extent that a metallated, carbanionic centre was developed at C-5 together with an aldehydic group at C-1, it finally failed because of the elimination which occurred at C-5–C-6 which is analogous to that observed previously with 3-*O*-acyl-2-deoxy-2-mercurioaldoses.[15] Therefore, to test the strategy further it was necessary to use an alkene which could not react in this manner by having a leaving group at C-6. The pentose derivative (**9**) was selected, and it was prepared from a 5-deoxy-5-iodo-compound, although such alkenes are presumably obtainable from 4-bromopentofuranose esters.[9] When (**9**) was treated with



Scheme 4.

mercury(II) acetate in aqueous acetone at room temperature it gave an adduct which was isolated by solvent extraction and shown by ^1H and ^{13}C spectroscopy to be the expected mercurial (**10**; X = OAc)—in particular the appropriate carbonyl and acetyl resonances were present. Heating of this compound in dioxane caused complete conversion into a chromatographically more mobile, mercury-containing product which was believed to be the dialkylmercury compound (**11**) since, on treatment with hydrogen sulphide, it gave the 5-deoxyosulose ester (**12**) which was characterised as the bis-dithioacetal (**13**). These reactions are shown in Scheme 4. When the initial adduct (**10**; X = OAc) was itself treated with hydrogen sulphide the methyl ketone (**12**) was again observed amongst mixed products which did not contain any cyclopentanone derivative as judged by lack of an appropriate carbonyl carbon resonance in the ^{13}C n.m.r. spectrum. All other attempts to induce the adduct (**10**; X = OAc) to undergo ring-closure also resulted in the formation of the same product: these included heating in aqueous acetone with mercury(II) acetate and conversion into the corresponding chloromercurio-compound (**10**; X = Cl) by treatment with

sodium chloride and heating the product in aqueous acetone. In parallel with these experiments, methyl 3,4-di-*O*-benzoyl-6-deoxy-2-*O*-(*p*-tolylsulphonyl)-α-D-*xylo*-hex-5-enopyranoside was treated in analogous manner and its ready conversion into the corresponding β-hydroxycyclohexanone was confirmed.

If the assumption is made that the ring closure step in Scheme 1 is an (enol *endo*)-*exo-trig* process,[4b] the dramatic differences observed in reaction between 6-deoxyald-5-enopyranose and 5-deoxyald-4-enofuranose derivatives in aqueous media in the presence of mercury(II) ions can be accounted for by reference to Baldwin's rules for ring closure.[4] These state that such processes are favoured for cyclisations which give 3-hydroxycyclohexanones, and are disfavoured for 3-hydroxycyclopentanones, but for these generalisations to apply in the above cases it is necessary to assume that the nucleophilic centres acquire some enolate character during their reaction. This seems acceptable, because, even in a synchronous process, as the carbon–mercury bonds lengthen there will be simultaneous shortening of carbonyl–C bond and transfer of electron density in the direction of the oxygen atom. Consistent with this is the report that, dependent upon reaction conditions, some α-keto organomercurials may undergo alkylation at oxygen.[16]

In summary, experience to date indicates that whereas 6-deoxyald-5-enopyranose derivatives readily give β-hydroxycyclohexanones on treatment with mercury(II) salts in aqueous media, analogous exocyclic alkenes derived from furanoid compounds do not undergo ring-closure reactions under these conditions; instead, the mercury adducts which are formed undergo elimination or protonolysis reactions. The latter types of reaction of organomercurials are well known.[16]

Experimental

N.m.r. spectra were measured with a Varian FT80A instrument and in perdeuterioacetone unless otherwise stated. Optical rotations were measured on chloroform solutions within the concentration range 0.5—1.5%. Solutions were dried over $MgSO_4$.

1-O-*Acetyl*-2,3,5,6-*tetra*-O-*benzoyl*-β-D-erythro-*hex*-3-*enofuranose* (**2**).—A suspension of 1-*O*-acetyl-2,3,5,6-tetra-*O*-benzoyl-β-D-glucofuranose (1.00 g) and bromine (0.96 g) in 1,1,2-trichlorotrifluoroethane (100 ml) was heated under reflux over a 275 W heat-lamp for 40 min. The solvent was removed under reduced pressure and the microcrystalline residue was dissolved in DMF (7 ml). A solution of DBU (0.34 g, 1.4 mol equiv.) in this solvent (3 ml) was then added to the stirred solution of the crude bromides (**1**) and the mixture was left at room temperature for 22 h. Removal of the solvent under reduced pressure left a dark brown syrup which was purified by column chromatography [eluant light petroleum (b.p. 60—68 °C)–ethyl acetate] to yield the *hex*-3-*enofuranose* (**2**) (0.66 g, 66%), $[\alpha]_D$ −139° (Found: C, 68.0, H, 4.7. $C_{36}H_{28}O_{11}$ requires C, 67.9; H, 4.4%); δ_H 2.14 (3 H, s, Ac), 4.77 (1 H, dd, $J_{5,6}$ 5,6 $J_{6',6'}$ 11.5 Hz, 6-H), 4.93 (1 H, dd, $J_{5,6'}$ 4.9 Hz, 6'-H), 6.25 (1 H, m, 5-H), 6.32 (1 H, t, $J_{1,2} = J_{2,5}$ = 1.0 Hz, 2-H), and 6.67 (1 H, d, 1-H); δ_C 62.9 (C-6), 66.4 (C-5), 78.8 (C-2), 98.9 (C-1), *ca.* 130 (C-3), and 146.6 p.p.m. (C-4) + ester resonances.

(E,Z)-1-O-*Acetyl*-2,3,6-*tri*-O-*benzoyl*-5-*deoxy*-α-L-threo-*hex*-4-*enofuranose* (**3**) *and* 1-O-*Acetyl*-2,5,6-*tri*-O-*benzoyl*-3-*deoxy*-β-D-erythro-*hex*-3-*enofuranose* (**4**).—A suspension of 1-*O*-acetyl-2,3,5,6-tetra-*O*-benzoyl-β-D-glucofuranose (3.00 g) and bromine (1.0 ml) in 1,1,2-trichlorotrifluoroethane (300 ml) was heated under reflux over a 275 W heat-lamp for 45 min. After removal of the solvent under reduced pressure, the crude product mixture (**1**) was dissolved in acetone (50 ml) and the solution was cooled on an ice–water bath. A solution of sodium acetate (12 g) in water (40 ml) and glacial acetic acid (90 ml), together with zinc–copper couple (13 g), was added to the stirred mixture, the mixture was further stirred at room temperature for 44 h and, after filtration, the solvent was removed under reduced pressure. The syrupy residue was partitioned between water (200 ml) and chloroform (200 ml), and the aqueous layer was extracted with chloroform (50 ml). The combined extracts were washed in turn with water (250 ml), saturated aqueous sodium hydrogen carbonate (250 ml) and water, dried, and the solvent was removed under reduced pressure. Column chromatography of the syrupy residue resulted in partial separation of the isomeric products and gave the hex-4-enofuranose (**3**) (1.08 g, 45%) as a mixture of geometric isomers (ratio 6:1) in the first fraction (Found: C, 67.0; H, 5.0. $C_{29}H_{24}O_9$ requires C, 67.4; H, 4.7%); δ_H 2.20 (3 H, s, Ac), 4.75—5.2 (2 H, m, 6-H_2), 5.40 (1 H, t, $J_{5,6} = J_{5,6'}$ = 7.0 Hz, 5-H), 5.62 (1 H, t, $J_{1,2} = J_{2,3}$ = 0.5 Hz, 2-H), 6.11 (1 H, s, 3-H), 6.70 (1 H, s, 1-H), and 7.3—8.3 (15 H, ArH); some small additional resonances, particularly for 1-H at δ 6.61, were observed for the minor isomer; δ_C (major isomer) 59.7 (C-6), 74.5 (C-3), 79.0 (C-2), 99.6 (C-1), 101.7 (C-5), and 156.0 p.p.m. (C-4) + ester resonances; δ_C (minor isomer) 61.3 (C-6), 71.7 (C-3), 78.9 (C-2), 99.3 (C-1), 101.2 (C-5), and 159.3 p.p.m. (C-4). The second fraction (0.44 g) was a mixture of the hex-4-enofuranose (**3**) and the hex-3-enofuranose (**4**) in the ratio 1:1.3 (total yield of hex-4-enofuranose, 1.27 g, 52%). Pure *hex*-3-*enofuranose* (**4**) (0.13 g, 6%; total 0.38 g, 17%) was obtained from the third fraction; $[\alpha]_D$ −139° (Found: C, 67.3; H, 5.3%); δ_H 2.11 (3 H, s, Ac), 4.71 (1 H, dd, $J_{5,6}$ 5.3, $J_{6,6'}$ 12.0 Hz, 6-H), 4.92 (1 H, dd, $J_{5,6'}$ 3.8 Hz, 6'-H), 5.66 (1 H, dd, $J_{2,3}$ 2.6, $J_{3,5}$ 1.1 Hz, 3-H), 5.87 (1 H, ddd, $J_{1,2}$ 0.9, $J_{2,5}$ 1.1 Hz, 2-H), 6.13 (1 H, m, 5-H), 6.70 (1H, d, 1-H), and 7.2—8.1 (15 H, ArH); δ_C 63.5 (C-6), 68.3 (C-5), 81.7 (C-2), 99.2 (C-1), 100.9 (C-3), and 159.9 p.p.m. (C-4) + ester resonances.

Reaction of the Hex-4-*enofuranose Ester* (**3**) *with Mercury*(II) *Acetate.*— (a) *At room temperature.* The ester (**3**) (0.04 g) and mercury(II) acetate (0.05 g, 2 mol equiv.) were dissolved in aqueous acetone (3 ml; 1:4) containing 1% of acetic acid and after 1.5 h at 20 °C the acetone was removed and the products were partitioned between ethyl acetate (30 ml) and water (15 ml). The organic phase was washed with water (15 ml) and dried. The solvent was removed and the residue was dried azeotropically with benzene to give the mercurial ester (**5**), $\delta_H(CDCl_3)$ 1.95 (3 H, s, Ac), 4.22 (1 H, t, $J_{5,6} = J_{5,6'}$ = 7 Hz, 5-H), 4.85 (2 H, d, 6-H_2), 5.9—6.1 (2 H, m, 2- and 3-H), and 9.63 (1 H, d, $J_{1,2}$ 3 Hz, 1-H); $\delta_C(CDCl_3)$ 22.1 (CH_3), 51.4 (C-5), 61.9 (C-6), 76.2 and 76.7 (C-2 and -3), 177.1 (CH_3C=O), 194.8 (C-1), and 199.2 p.p.m. (C-4) + ester resonances.

(b) *At reflux temperature.* The ester (**3**) (0.18 g) and mercury(II) acetate (0.18 g) were heated under reflux in aqueous acetone (6 ml; 1:4) containing 1% of acetic acid for 4.75 h. The acetone was removed and the products were partitioned between chloroform (10 ml) and water (10 ml). The aqueous phase was extracted with chloroform and the organic solutions were washed with water and dried. Removal of the solvent gave the syrupy alkene (**6**), δ_H 5.96 (1 H, dd, $J_{5,6}$ 10.2, $J_{6,6'}$ 1.9 Hz, 6-H), 6.22 (1 H, d, $J_{2,3}$ 2.7 Hz, 2- or 3-H), 6.44 (1 H, d, 3- or 2-H), 6.46 (1 H, dd, $J_{5,6'}$ 17.4 Hz, 6'-H), 6.94 (1 H, dd, 5-H), 7.3—8.2 (ArH), and 9.85 (1 H, s, 1-H). The residue was dissolved in dichloromethane (6 ml), ethane-1,2-dithiol (0.5 ml), and boron trifluoride–diethyl ether (0.5 ml) were added, and after 0.75 h saturated aqueous sodium hydrogen carbonate (20 ml) was used to destroy the catalyst. The aqueous phase was extracted with chloroform (20 ml) and the organic solution, after being washed, was dried, and the solvent was removed to leave a syrup which was purified by preparative t.l.c. The n.m.r. spectra were consistent with those expected for the hexathio-compound (**7**); $\delta_H(CDCl_3)$ 2.2—2.9 (9 H, m, acyclic CH_2 and SH), 3.1—3.4 (8 H, m, cyclic CH_2), 4.64 (1 H, d, $J_{1,2}$ 9.5 Hz, 1-H), 5.75 (1 H, dd, $J_{2,3}$ 1.1 Hz, 2-H), 5.90 (1 H, d, 3-H), and 7.3—8.2 (10 H, m,

ArH); $\delta_C(CHCl_3)$ 24.7, 28.0, 35.8, 37.9, 38.4, 38.8, 39.9, and 40.0 (CH_2), 55.4 (C-1), 73.3 (C-4), and 73.8 and 76.7 p.p.m. (C-2 and -3). Acetylation (acetic anhydride, pyridine) of this thiol gave the monoacetate (**8**), $[\alpha]_D$ −34°; δ_H 2.31 (3 H, s, Ac), 2.3—3.0 (8 H, m, acyclic CH_2), 3.2—3.4 (8 H, m, cyclic CH_2), 4.72 (1 H, d, $J_{1,2}$ 9.4 Hz, 1-H), 5.77 (1 H, dd, $J_{2,3}$ 1.2 Hz, 2-H), 5.96 (1 H, d, 3-H), and 7.3—8.2 (10 H, m, ArH); δ_C 28.9, 29.9, 30.6, 32.2, 38.4, 38.7, 39.8, 40.4, and 40.6 (CH_3 and CH_2), 56.3 (C-1), 74.3 (C-4), and 74.5 and 77.6 p.p.m. (C-2 and -3).

Methyl 2,3-*Di*-O-*benzoyl*-5-O-(p-*tolylsulphonyl*)-α-D-*arabinofuranoside*.—D-Arabinose (3.5 g) was stirred in a solution of hydrogen chloride (0.86 g) in dry methanol (90 ml) at 35 °C for 3 h. After the addition of pyridine (10 ml) to the reaction mixture, the solvent was removed under reduced pressure and the resulting syrup was dissolved in pyridine (25 ml). A solution of toluene-*p*-sulphonyl chloride (4.44 g, 1.0 mol equiv.) in dichloromethane (30 ml) was added dropwise to the stirred mixture at 0 °C, and the mixture was left for 64 h at 4 °C and then at 20 °C for 7 h. Benzoyl chloride (9 ml) was added and the mixture was kept overnight at 20 °C, after which time it was diluted with chloroform (100 ml) and poured into water. After separation of the organic phase, the aqueous phase was extracted with chloroform (2 × 50 ml) and the combined extracts were washed in turn with dilute hydrochloric acid (2 × 200 ml) and saturated aqueous sodium hydrogen carbonate (200 ml), and then dried. Application of column chromatography [eluant light petroleum (b.p. 60—68 °C)–ethyl acetate) to the syrup obtained on removal of the solvent yielded the triester (7.73 g, 63%), which crystallised upon trituration with ethanol. Recrystallisation from acetone–ethanol gave crystals, m.p. 125—126 °C; $[\alpha]_D$ −21° (Found: C, 61.9; H, 5.4; S, 6.0. $C_{27}H_{26}O_9S$ requires C, 61.6; H, 5.0; S, 6.1%); $\delta_H(CDCl_3)$ 2.36 (3 H, s, $C_6H_4CH_3$), 3.41 (3 H, s, OMe), 4.3—4.5 (3 H, m, 4-and 5-H_2), 5.06 (1 H, s, 1-H), 5.27 (1 H, br d, $J_{3,4}$ 4.2 Hz, 3-H), 5.45 (1 H, d, $J_{2,3}$ 1.1 Hz, 2-H), and 7.1—8.1 (14 H, m, ArH); $\delta_C(CDCl_3)$ 21.6 ($C_6H_4CH_3$), 55.1 (OCH_3), 68.9 (C-5), 77.7 (C-3), 81.0 and 81.3 (C-2, and -4), and 107.1 p.p.m. (C-1) + ester resonances.

Methyl 2,3-*Di*-O-*benzoyl*-5-*deoxy*-5-*iodo*-α-D-*arabinofuranoside*.—The 5-tosylate (0.50 g) was dissolved in butanone (15 ml) and sodium iodide (1.00 g) was added. After being heated under reflux for 2.25 h, the mixture was filtered and the solvent was removed under reduced pressure. The residue was partitioned between chloroform (50 ml) and water (50 ml) and the organic phase was washed successively with aqueous sodium thiosulphate (50 ml) and water (50 ml), and dried. Evaporation of the solvent left the 5-*iodide* (0.45 g, 98%) as a syrup, which was homogeneous by t.l.c. A sample purified by preparative t.l.c. had $[\alpha]_D$ −15° (Found: C, 50.1; H, 4.2. $C_{20}H_{19}IO_6$ requires C, 49.8; H, 4.0%); $\delta_H(CDCl_3)$ 3.46 (3 H, s, OMe), 3.57 (1 H, dd, $J_{4,5}$ 5.0, $J_{5,5'}$ 10.0 Hz, 5-H), 3.71 (1 H, dd, $J_{4,5'}$ 5.0 Hz, 5'-H), 4.25 (1 H, ddd, $J_{3,4}$ 5.0 Hz, 4-H), 5.15 (1 H, s, 1-H), 5.31 (1 H, m, $J_{2,3}$ 1.4 Hz, 3-H), 5.52 (1 H, d, 2-H), and 7.3—8.1 p.p.m. (10 H, m, ArH); $\delta_C(CDCl_3)$ 5.8 (C-5), 55.1 (OCH_3), 81.1, 81.7, and 82.4 (C-2, -3, and -4), and 106.9 p.p.m. (C-1) + ester resonances.

Methyl 2,3-*Di*-O-*benzoyl*-5-*deoxy*-α-D-threo-*pent*-4-*enofuranoside* (**9**).—The 5-iodide (1.63 g) and DBU (0.57 g, 1.1 mol equiv.) were stirred in DMF (10 ml) at 65 °C for 18 h. After removal of the solvent under reduced pressure, the crude mixture was purified by column chromatography and yielded the *alkene* (**9**) (1.14 g, 95%) which crystallised upon trituration with ethanol. After recrystallisation from the same solvent it had m.p. 88.5—90 °C, $[\alpha]_D$ −95° (Found: C, 68.1; H, 5.1. $C_{20}H_{18}O_6$ requires C, 67.8; H, 5.1%); $\delta_H(CDCl_3)$ 3.55 (3 H, s, OMe), 4.54 (1 H, br s, 5-H), 4.73 (1 H, br s, 5'-H), 5.30 (1 H, s, 1-H), 5.45 (1 H, s, 2-H), 5.97 (1 H, s, 3-H), and 7.3—8.1 (10 H, m, ArH); $\delta_C(CDCl_3)$ 56.0 (OCH_3), 74.1 (C-3), 79.3 (C-2), 89.0 (C-5), 107.7 (C-1), and 158.7 p.p.m. (C-4) + ester resonances.

Reaction of the Pent-4-*enofuranoside Ester* (**9**) *with Mercury*(II) *Acetate*.—The alkene (**9**) (0.35 g) and mercury(II) acetate (0.53 g, 2 mol equiv.) were dissolved in aqueous acetone (35 ml; 1:4) containing 1% of acetic acid. After 3 h at 20 °C the acetone was removed and the products were partitioned between ethyl acetate (20 ml) and water (20 ml) and the mercurial intermediate (**10**; X = OAc) (0.60 g, 100%) was isolated in the same way as was compound (**5**), $\delta_H(CDCl_3)$ 1.92 (3 H, s, Ac), 3.04 (2 H, s, 5-H_2), 5.9—6.0 (2 H, m, 2- and 3-H), and 9.68 (1 H, s, 1-H); $\delta_C(CDCl_3)$ 22.3 (CH_3CO), 32.3 (C-5), 75.5 and 76.9 (C-2 and -3), 177.2 ($CH_3C{=}O$), 194.7 (C-1), and 201.9 p.p.m. (C-4) + ester resonances.

2,3-*Di*-O-*benzoyl*-5-*deoxy*-D-threo-*pentos*-4-*ulose* (**12**).—The mercurial (**10**) was dissolved in dichloromethane (15 ml) and hydrogen sulphide was passed through the solution. The precipitated mercury(II) sulphide and the solvent were removed and the product was purified by preparative t.l.c. to give the methyl ketone (**12**) (0.22 g, 66%), $\delta_H(CDCl_3)$ 2.33 (3 H, s, 5-H_3), 5.8—5.9 (2 H, m, 2- and 3-H), 7.2—8.2 (10 h, m, ArH), and 9.70 (1 H, s, 1-H); $\delta_C(CDCl_3)$ 26.8 (C-5), 76.2 and 76.9 (C-2 and -3), 196.2 (C-1), and 203.2 p.p.m. (C-4). The dicarbonyl compound was characterised by treatment in dichloromethane with ethane-1,2-dithiol and boron trifluoride–diethyl ether [as for compound (**6**) above] to give the *bis*(*ethylenedithioacetal*) (**13**) which, after preparative t.l.c., had $[\alpha]_D$ +68° (Found: C, 56.2, H, 5.0. $C_{23}H_{24}O_4S_4$ requires C, 56.1; H, 4.9%); $\delta_H(CDCl_3)$ 1.81 (3 H, s, 5-H_3), 3.2—3.4 (8 H, m, 4 × CH_2), 4.64 (1 H, d, $J_{1,2}$ 9.1 Hz, 1-H), 5.78 (1 H, dd, $J_{2,3}$ 1.2 Hz, 2-H), 5.84 (1 H, d, 3-H), and 7.3—8.1 (10 H, ArH); $\delta_C(CDCl_3)$ 26.7 (C-5), 37.9, 38.4, 39.6, and 39.9 (CH_2), 55.4 (C-1), 68.7 (C-4), and 74.0 and 76.8 p.p.m. (C-2 and -3).

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