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Preparation of 2-Deoxy-sugars by Hydrogenolysis of Benzoylated Glycopyranosyl Bromides

STEFFEN JACOBSEN and CHRISTIAN PEDERSEN

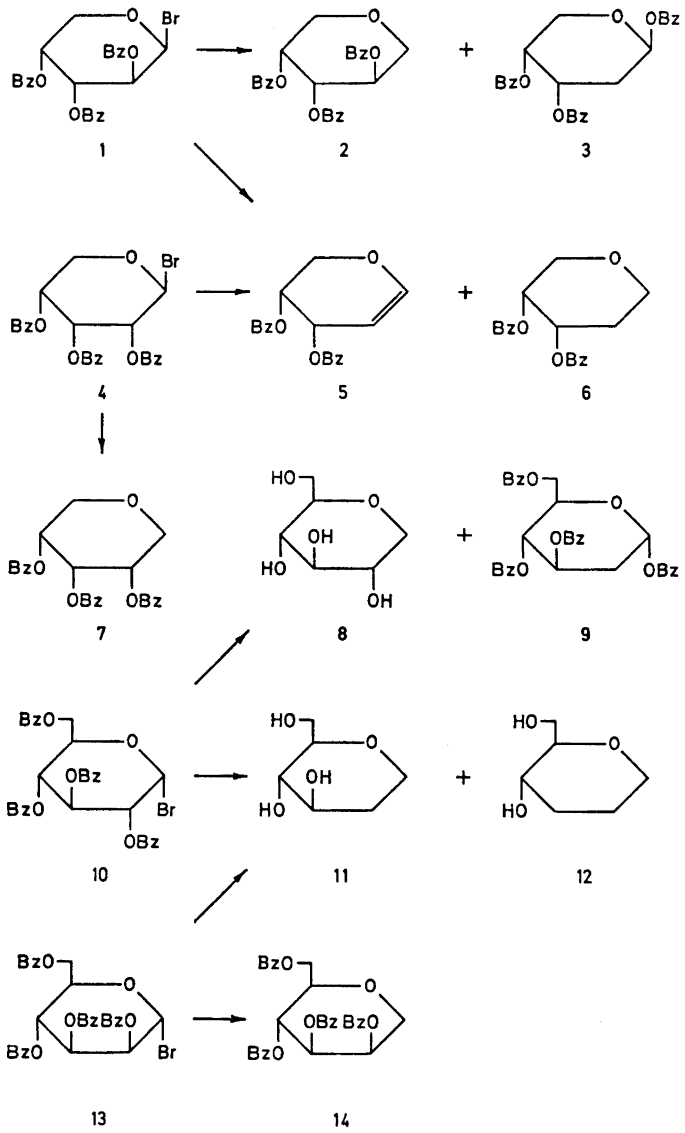
Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

Hydrogenolysis of tri-*O*-benzoyl-β-D-arabinopyranosyl bromide with palladium on carbon as catalyst gives, in addition to the expected 1,5-anhydro-tri-*O*-benzoyl-D-arabinitol, considerable amounts of 1,3,4-tri-*O*-benzoyl-2-deoxy-β-D-*erythro*-pentose. A similar treatment of tetra-*O*-benzoyl-α-D-glucopyranosyl bromide yields tetra-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranose. Hydrogenolysis of tetra-*O*-benzoyl-α-D-mannopyranosyl bromide, or of tri-*O*-benzoyl-β-D-ribopyranosyl bromide, does not give 2-deoxy-sugars.

The preparation of acetylated or benzoylated 1,5-anhydroalditols by reductive dehalogenation of acylated glycopyranosyl bromides, using palladium on carbon as catalyst in the presence of triethylamine, has been described by Zervas and Zioudrou [1] and by Hedgley and Fletcher.[2] Later Gray and Barker [3] investigated this reaction more closely and found that better yields of 1,5-anhydroalditols were obtained when platinum was used as the catalyst.

In connection with other work we reduced tri-*O*-benzoyl-β-D-arabinopyranosyl bromide (*1*) with hydrogen in the presence of palladium on carbon and triethylamine with ethyl acetate as solvent, *i.e.* under conditions which are reported to give an 86 % yield of 1,5-anhydro-tri-*O*-benzoyl-D-arabinitol (*2*).[2] The product was, however, rather impure and examination of it revealed that it contained considerable amounts of 1,3,4-tri-*O*-benzoyl-2-deoxy-β-D-*erythro*-pentopyranose (*3*). In view of this rather unexpected result the hydrogenolysis of (*1*), and of other acylated pyranosyl bromides, has been investigated more closely.

In order to optimize the yield of the 2-deoxy-derivative (*3*) a number of exploratory experiments were carried out (Table 1). From these it is seen that only when palladium on carbon, or on barium sulfate, was used as catalyst could significant amounts of (*3*) be obtained. With palladium oxide, platinum oxide, or Raney-nickel (experiments 10, 12, and 13, respectively) only traces of (*3*) were found.



The amount of triethylamine should not be less than 2 molar equivalents (using 200 mg of catalyst) since this resulted in a lower yield of the 2-deoxyribose derivative (*3*) (experiment No. 7). A larger amount of triethylamine did, on the other hand, not give more (*3*) (experiments 8 and 9). A larger amount of catalyst gave less (*3*) (experiment 5) unless the amount of triethylamine was increased proportionally (experiment 6). The catalyst is presumably modified by absorption of triethylamine and it is probably this modified catalyst which

Table 1. Hydrogenolysis of tri-*O*-benzoyl-β-D-arabinopyranosyl bromide (*1*) (1.0 g was used in each of the experiments). For further details see the experimental section.

Experiment no.	Ethyl acetate ml	Triethylamine ml; molar eqv.'s	Catalyst	Yield (%) of (*3*) as determined from NMR spectra
1	7.0	0.53; 2	200 mg, 5 % Pd-C	40 – 50
2	9.5	0.53; 2	200 mg, 5 % Pd-C	40
3	15.0	0.53; 2	200 mg, 5 % Pd-C	24
4	7.0	0.53; 2	50 mg, 5 % Pd-C	45
5	15.0	0.53; 2	1.0 g, 5 % Pd-C	11
6	7.0	2.65; 10	1.0 g, 5 % Pd-C	30
7	7.0	0.26; 1	200 mg, 5 % Pd-C	20
8	5.0	5.0; 19	200 mg, 5 % Pd-C	43
9	0	8.0; 31	200 mg, 5 % Pd-C	34
10	15.0	0.53; 2	150 mg, PdO	trace
11	7.0	0.53; 2	200 mg, 5 % Pd-$BaSO_4$	40
12	9.5	0.53; 2	50 mg, PtO_2	trace
13	7.0	0.53; 2	*ca.* 200 mg, Ra.-Ni	trace
14	dioxane, 14 ml	0.53; 2	200 mg, 5 % Pd-C	24

is responsible for the formation of the 2-deoxy-ribose derivative (*3*). Gray and Barker [3] observed that diethylamine has a profound effect on the properties of palladium or platinum when used for the reduction of unsaturated sugars. Addition of more ethyl acetate (experiments 2 and 3) gave less (*3*), probably because the complex formation between the catalyst and the triethylamine was suppressed by dilution. The use of 10 % palladium on carbon gave very nearly the same results as 5 % palladium.

The optimum conditions for the preparation of (*3*) from the bromide (*1*) are those given for experiment No. 1 (Table 1). When the reduction of (*1*) was carried out on a larger scale, using these conditions, (*3*) was readily isolated in 32 % yield. Besides, 1,5-anhydro-tri-*O*-benzoyl-D-arabinitol (*2*) was obtained together with small amounts of 3,4-di-*O*-benzoyl-1,2-dideoxy-D-*erythro*-pent-1-enopyranose (*5*) and its reduction product (*6*).

Hedgley and Fletcher [2] carried out the reduction under almost identical conditions. They, however, used a crude bromide which probably contained some acetic acid and hydrogen bromide. The triethylamine would therefore be partly neutralized and this could affect the reaction. When we carried out the reduction under the conditions of Hedgley and Fletcher the 1,5-anhydride (*2*) was the major product; it did, however, not crystallize well due to the presence of small amounts of other products.

Hydrogenolysis of tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (*10*) under the conditions described above gave a 40 % yield of tetra-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranose (*9*). After debenzoylation of the remaining product 1,5-anhydro-D-glucitol (*8*) and smaller amounts of 1,5-anhydro-2-deoxy-D-*arabino*-hexitol (*11*) and 1,5-anhydro-2,3-dideoxy-D-*erythro*-hexitol (*12*) were

isolated. The latter two products were probably formed *via* unsaturated sugars, analogous to the results described by Gray and Barker.[3]

Both the arabinosyl bromide (*1*) and the glucosyl bromide (*10*) have the bromine atom *cis* to the benzoyloxy-group at C-2, and in both cases the benzoyloxy-group migrated to C-1 without change in configuration. It was therefore of interest to study the hydrogenolysis of compounds in which the bromine is *trans* to the benzoyloxy-group at C-2.

Hydrogenolysis of tetra-*O*-benzoyl-α-D-mannopyranosyl bromide (*13*) gave no detectable amounts of 2-deoxy-derivatives. The main product was 1,5-anhydro-tetra-*O*-benzoyl-D-mannitol (*14*); besides, the 2-deoxy- and the 2,3-dideoxy-1,5-anhydrides (*11*) and (*12*) were isolated as their tri- and di-benzoates, respectively.

Hydrogenolysis of tri-*O*-benzoyl-β-D-ribopyranosyl bromide (*4*) gave 53 % of 1,5-anhydro-tri-*O*-benzoyl-ribitol (*7*) and a trace of the 2-deoxy-1,5-anhydride (*6*). Besides, a very small amount of 1,3,4-tri-*O*-benzoyl-2-deoxy-α-D-*erythro*-pentopyranose was isolated. It seems most likely that this product was formed by hydrogenolysis of tri-*O*-benzoyl-α-D-ribopyranosyl bromide, which could be present as an impurity in the β-bromide (*4*),[4] or it could be formed by anomerization of the latter in the course of the hydrogenolysis.

From the results described above it may be concluded that hydrogenolysis of benzoylated 1,2-*cis*-glycopyranosyl bromides with palladium on carbon in the presence of triethylamine yields substantial amounts of 2-deoxy-sugars in addition to the expected 1,5-anhydro-alditols. Hydrogenolysis of 1,2-*trans*-bromides does not give 2-deoxy-sugars. Similar results have been found for other benzoylated glycosyl bromides; details will be published later.

Hydrogenolysis of tri-*O*-acetyl-β-D-arabinopyranosyl bromide gave a good yield of tri-*O*-acetyl-1,5-anhydro-D-arabinitol and only traces of 2-deoxy-ribose derivatives were formed.

The structure of tetra-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranose (*9*) was confirmed by its reaction with hydrogen bromide, which gave the known tri-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranosyl bromide.[5] The anomeric structure of (*9*) was seen from its NMR spectrum, which showed H-1 at δ 6.64 as a double doublet, $J_{12e} = 1$ Hz, $J_{12a} = 3$ Hz. Bergmann *et al.*[5] benzoylated 2-deoxy-D-*arabino*-hexose and obtained a tetrabenzoate to which they assigned structure (*9*). However, an NMR spectrum of a product prepared according to Bergmann *et al.* showed H-1 as a double doublet at δ 6.32, $J_{12e} = 2.5$, $J_{12a} = 9.5$ Hz, clearly indicating that the substance is tetra-*O*-benzoyl-2-deoxy-β-D-*arabino*-hexopyranose. The anomeric structures were further confirmed by the optical rotations, the α-anomer (*9*) being the more dextrorotatory.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were obtained on Varian A-60 or HA-100 instruments using deuteriochloroform as solvent. Thin layer chromatography (TLC) was performed on silica gel PF_{254} ("Merck"); for preparative work 1 mm layers were used on 20 × 40 cm plates. Zones were visualized under UV light.

Catalysts. Palladium (5 %) on carbon was purchased from "Fluka" (*puriss.*; two different batches were used), or it was prepared according to Ref. 6. No differences were observed between these. 10 % Palladium on carbon was obtained from "Merck". The

palladium oxide was a "Fluka" *puriss.* grade and the platinum oxide was obtained from Johnson Matthey and Co. (England). The Raney nickel was prepared according to Ref. 7.

Experiments in Table 1. Tri-*O*-benzoyl-β-D-arabinopyranosyl bromide [8] (1.0 g) was dissolved in ethyl acetate in a 100 ml roundbottomed flask, the catalyst was added followed by triethylamine. The mixture was then hydrogenated with efficient magnetic stirring at ambient temp. and pressure for 14 – 16 h. The hydrogen uptake was usually completed in *ca.* 6 h.

The mixture was then filtered through a layer of activated carbon and the filter was washed several times with dichloromethane. The filtrate was washed twice with water, dried ($MgSO_4$), and evaporated. The residue (*ca.* 800 mg) was dissolved in tetrachloromethane which was evaporated. This was repeated and an NMR spectrum was then measured in deuteriochloroform solution. The spectra showed H-1 of 1,3,4-tri-*O*-benzoyl-2-deoxy-β-D-*erythro*-pento-pyranose (*3*) as a broad triplet at δ 6.7. H-3,4 of (*3*) and H-2,3,4 of the 1,5-anhydride (*2*) gave a broad signal at δ 5.75. From the integrals of these two signals the yields of (*3*) (Table 1) were calculated. Since products other than (*2*) and (*3*) are present (see below) the values thus obtained are approximations only.

*Hydrogenolysis of tri-*O*-benzoyl-β-D-arabinopyranosyl bromide* (*1*). *A.* To (*1*) (5.0 g) in ethyl acetate (35 ml) was added triethylamine (2.64 ml) and 5 % palladium on carbon (1.0 g). The mixture was then hydrogenated and worked up as described above. The product (4.2 g) was crystallized from ether-pentane to give 1.2 g (28 %) of 1,3,4-tri-*O*-benzoyl-2-deoxy-β-D-*erythro*-pentopyranose (*3*), m.p. 150 – 152°C. After two additional recrystallizations from ether-pentane the product melted at 156 – 157°C, $[\alpha]_D^{22} = -190°$ (*c* 1.7, $CDCl_3$). (Reported [9] m.p. 159 – 161°C, $[\alpha]_D = -195°$).

A sample (1.50 g) of the material in the mother liquors was separated into 4 fractions by preparative TLC using ethyl acetate-pentane (1:4) as eluent. The fast moving fraction gave 49 mg of 3,4-di-*O*-benzoyl-1,2-dideoxy-D-*erythro*-pent-1-enopyranose (*5*) as seen from an NMR spectrum, which was identical with that of an authentic sample.[10] The next fraction (114 mg) was crystallized from methanol to give 75 mg of (*3*), m.p. 156 – 157°C. The third fraction (640 mg) was also crystallized from methanol and gave 450 mg (21 %) of 1,5-anhydro-tri-*O*-benzoyl-D-arabinitol, m.p. 117 – 119°C, $[\alpha]_D^{22} = -214°$ (*c* 1.3, $CHCl_3$). (Reported [2,11] m.p. 120 – 121°C $[\alpha]_D = -220°$). A fourth fraction (120 mg) contained impure (*6*) (see below).

B. A suspension of (1) (41.0 g) in ethyl acetate (280 ml) and triethylamine (22 ml) was hydrogenated in the presence of 8.0 g of 5 % palladium on carbon. The product was crystallized from ether to give 13.2 g (38 %) of crude (*3*), m.p. 150 – 153°C. One recrystallization from methanol gave 11.2 g (32 %) of (*3*), m.p. 157 – 158°C, $[\alpha]_D^{23} = -195°$ (*c* 1.2, $CHCl_3$).

The mother liquor material was boiled for 3 h with methanol and excess sodium methoxide. The methanol was removed, water was added and the mixture was deionized by passage through columns of Amberlite IR-120 and IR-4 B. The solution was then filtered through activated carbon and evaporated. The residue (3.7 g) was crystallized from ethanol-ethyl acetate to give 800 mg (7.6 %) of 1,5-anhydro-D-arabinitol, m.p. 90 – 93°C.

The remaining material was separated into 4 fractions by chromatography on a column of silica gel (150 g) using butanone-2, saturated with water, as eluent. The first two fractions (91 mg) were not investigated. The third fraction gave 271 mg (3 %) of 1,5-anhydro-2-deoxy-D-*erythro*-pentitol as a syrup. Benzoylation yielded the di-*O*-benzoate (*6*) which was recrystallized from methanol, yield 200 mg, m.p. 86 – 87°C, $[\alpha]_D^{22} = -64.9°$ (*c* 4.7, $CHCl_3$). (Reported [12] m.p. 89 – 91°C, $[\alpha]_D = -65.1°$). The last fraction (1.119 g) was crystallized from ethanol-ethyl acetate to give 700 mg (6.7 %) of 1,5-anhydro-D-arabinitol, m.p. 93 – 95°C. Recrystallization from ethanol gave a product with m.p. 95 – 97°C, $[\alpha]_D^{22} = -97.5°$ (*c* 3.7, H_2O). (Reported [11] m.p. 96 – 97°C, $[\alpha]_D = -98.6°$).

*Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide* (44.0 g) in ethyl acetate (250 ml) and triethylamine (24 ml) was hydrogenated in the presence of 8.5 g of 5 % palladium on carbon. Work up as described above gave a syrup which was crystallized from ether-pentane. The product (17.5 g), m.p. 149 – 152°C, was recrystallized from ethanol to give 15.6 g (40 %) of tetra-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranose (*9*), m.p. 152 – 153°C. An additional recrystallization gave the pure product, m.p. 153 – 154°C, $[\alpha]_D^{22} = +68.6°$ (*c* 3.2, $CHCl_3$). (Found: C 70.07; H 4.91. Calc. for $C_{34}H_{28}O_9$: C 70.36; H 4.86).

The material in the mother liquor was boiled for 3 h with methanolic sodium methoxide, evaporated, dissolved in water, and deionized as described above. The product

was crystallized from ethanol to give 2.55 g (22 %) of 1,5-anhydro-D-glucitol (*8*), m.p. 135 – 137°C. Additional recrystallization gave a product with m.p. 139 – 141°C, $[\alpha]_D^{23} = +42.0°$ (*c* 3.2, H_2O). (Reported [13] m.p. 142 – 143°C, $[\alpha]_D = +42.3°$).

The material in the mother liquor (1.5 g) was separated into 3 fractions by chromatography on a column of silica gel (150 g) using butanone-2, saturated with water, as eluent. The fastest moving fraction (370 mg, 4.2 %) was pure 1,5-anhydro-2,3-dideoxy-D-*erythro*-hexitol (*12*) as seen from an NMR spectrum. To confirm its structure it was converted into the 4,6-benzylidene derivative, m.p. 135 – 136°C, $[\alpha]_D^{22} = -3.5°$ (*c* 0.2, $CDCl_3$). [Reported [3] m.p. 137.5 – 138.5°C, $[\alpha]_D = -4.1°$ (tetrachloroethane)].

The next fraction gave 510 mg (5 %) of syrupy 1,5-anhydro-2-deoxy-D-*arabino*-hexitol (*11*) as seen from an NMR spectrum, which was identical with that of the product described below. Benzoylation and recrystallization from ethanol gave 1,5-anhydro-tri-*O*-benzoyl-2-deoxy-D-*arabino*-hexitol, m.p. 89 – 90°C, $[\alpha]_D = -8.7°$ (*c* 2.5, $CHCl_3$), identical with the product described below.

The last fraction to come off the column gave 1.28 g of rather impure 1,5-anhydro-D-glucitol (*8*), which was only identified through its NMR spectrum.

Tetra-O-*benzoyl*-α-D-*mannopyranosyl bromide* [14] (3.8 g) was hydrogenated in ethyl acetate (29 ml) and triethylamine (3.0 ml) with 5 % Pd-C (760 mg) as catalyst. Work up as described above gave 2.9 g of a syrup which crystallized slowly from ether-pentane to give 600 mg (18 %) of crude 1,5-anhydro-tetra-*O*-benzoyl-D-mannitol (*14*), m.p. 135 – 138°C.

The material in the mother liquor was separated into 4 fractions by preparative TLC using 2 elutions with ethyl acetate-pentane (1:4). The fastest moving fraction gave 238 mg (12 %) of 1,5-anhydro-di-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hexitol [the dibenzoate of (*12*)] as a syrup. The product was identified through its 100 MHz NMR spectrum only, which gave the following δ-values and coupling constants (Hz): H-1*e* = 4.0; H-1*a* = 3.46; H-2*e*, H-2*a* and H-3*a* = 1.5 – 2.0; H-3*e* = 2.3 – 2.5; H-4 = 5.06; H-5 = 3.88; H-6 = 4.4; H-6′ = 4.6. $J_{1e1a} = 11$; $J_{1a2a} = 10$; $J_{1a2e} = \sim 4$; $J_{43e} = 4.8$; $J_{43a} = 10$; $J_{45} = 10$; $J_{56} = 5.5$; $J_{56'} = 2.8$.

The next fraction gave 240 mg (9 %) of 1,5-anhydro-tri-*O*-benzoyl-2-deoxy-D-*arabino*-hexitol which was crystallized from ethanol, m.p. 89 – 90°C. A mixed melting point proved the identity with the product described below. The third fraction (822 mg) was crystallized from ether-pentane to give 633 mg (19 %) of (*14*), m.p. 140 – 141°C. Further recrystallizations from ethanol gave a product with m.p. 141 – 142°C, $[\alpha]_D^{22} = -145°$ (*c* 2.0, $CHCl_3$). (Reported [15] m.p. 145 – 146°C, $[\alpha]_D = -148.4°$). The last fraction (237 mg) was not investigated closely. Its NMR spectrum indicated that it was a hydrolysis product of the bromide (*13*).

Tri-O-*benzoyl*-β-D-*ribopyranosyl bromide* [4] (2.0 g) in ethyl acetate (14 ml) and triethylamine (1.1 ml) was hydrogenated in the presence of 5 % Pd-C (400 mg). Work up as described above gave 1.6 g of syrup which was separated into several fractions by chromatography on a column of silica gel (150 mg) using ethyl acetate-pentane (1:4) as eluent.

The fastest moving fraction gave 26 mg of a crystalline product which was shown by NMR spectra [16] to be 1,3,4-tri-*O*-benzoyl-2-deoxy-α-D-*erythro*-pentopyranose, recrystallized from ether-pentane, m.p. 149 – 150°C, $[\alpha]_D^{22} = +42.0°$ (*c* 0.4, $CHCl_3$). (Reported [9] m.p. 151 – 152°C, $[\alpha]_D = +41.6°$). The next fraction (55 mg) was a mixture. The third fraction (16 mg) was shown by NMR spectroscopy, melting point, and mixed melting point to be identical with (*6*), described above.

Fraction 4 (1.3 g) was crystallized from ether-pentane to give 900 mg (53 %) of 1,5-anhydro-tri-*O*-benzoyl-ribitol (*7*), m.p. 154 – 155°C, $[\alpha]_D = 0°$. (Reported [17] m.p. 156 – 157°C). The last fraction (150 mg) was not investigated closely. An NMR spectrum indicated that it was a hydrolysis product of the bromide (*4*).

Hydrogenolysis with Raney-nickel. Tri-*O*-benzoyl-β-D-*arabino*-pyranosyl bromide (5.0 g) in ethyl acetate (40 ml) and triethylamine (2.7 ml) was hydrogenated in the presence of Raney-nickel (*ca.* 1 g). Work up as described above gave a syrup (4.0 g) which was crystallized from methanol to give 2.2 g (52 %) of (*2*), m.p. 116 – 118°C, $[\alpha]_D^{22} = -214°$ (*c* 3.6, $CHCl_3$). The mother liquor deposited an additional batch of crystals (250 mg) which were recrystallized from ether-pentane to give 120 mg (3 %) of the 2-deoxy-compound (*3*), m.p. 155 – 157°C.

Tri-O-*benzoyl*-2-*deoxy*-α-D-arabino-*hexopyranosyl bromide.* To tetra-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranose (5.0 g) was added 15 ml of a solution of 32 % hydrogen bromide

in glacial acetic acid and 15 ml of dichloromethane. After 3 h at room temperature more dichloromethane was added and the solution was washed with water and aqueous sodium hydrogen carbonate, dried and evaporated. The residue (4.3 g) was crystallized from ether-pentane to give 2.9 g (62 %) of the α-bromide, m.p. 140–141°C. After an additional recrystallization the melting point was unchanged, $[\alpha]_D^{22} = +115°$ (*c* 1.5, $CHCl_3$). [Reported [5] m.p. 139°C, $[\alpha]_D^{16} = +121°$ (tetrachloroethane)]. The structure was further confirmed through an NMR-spectrum.

1,5-Anhydro-tri-O-*benzoyl-2-deoxy*-D-arabino-*hexitol.* Tri-*O*-acetyl-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (5.0 g) in ethyl acetate (25 ml) was hydrogenated in the presence of platinum oxide (200 mg). The product was deacetylated with methanolic sodium methoxide to give 1,5-anhydro-2-deoxy-D-*arabino*-hexitol (*11*) [18] which was purified by distillation, boiling point 170°C (1 mmHg). The product was chromatographically homogeneous, but it could not be induced to crystallize. Benzoylation in the usual manner gave the tribenzoate which crystallized from ether-pentane and was recrystallized from ethanol, m.p. 90–91°C, $[\alpha]_D^{22} = -7.9°$ (*c* 5.0, $CHCl_3$). (Found: C 70.33; H 5.09. Calc. for $C_{27}H_{24}O_7$: C 70.42; H 5.25).

Microanalyses were performed by Dr. A. Bernhardt.

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