CONDITIONS FOR NEIGHBORING-GROUP PARTICIPATION IN DISPLACEMENT REACTIONS OF 5-*O*-SULFONYL-D-GLUCOFURANOSE DERIVATIVES*†

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ABSTRACT

Sulfonate displacement reactions of 6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose derivatives with acetate or chloride ions in acetic anhydride are shown to involve participation by the neighboring benzoyloxy group. Acetate displacement in *N*,*N*-dimethylformamide appears to occur by both this and the SN2 mechanism, but, with sodium azide in hexamethylphosphoramide, only the SN2 displacement product was formed.

Benzylidenation of 1,2-*O*-isopropylidene-β-L-idofuranose gave the 3,5-*O*-benzylidene derivative, and the reaction of this acetal with *N*-bromosuccinimide gave exclusively 5-*O*-benzoyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose.

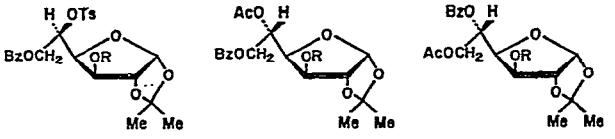
INTRODUCTION

An apparent anomaly in displacement reactions of carbohydrate sulfonates was noted in a review by L. Goodman[2] in 1967. The reactions of nucleophiles with 6-*O*-acyl-5-*O*-sulfonyl-D-glucofuranose derivatives had been reported as proceeding by direct attack at C-5 (SN2 reaction), whereas participation by the neighboring 6-acyloxy group might have been anticipated, especially with such relatively weak nucleophiles as acetate or benzoate ion. Examination of the literature revealed that, in those cases where different products would be formed were participation (as opposed to an SN2 reaction) involved, evidence confirming the structures of the products was lacking. For example, the reaction of 3-*O*-acetyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (**1**) with potassium acetate in acetic anhydride was reported[3] to give 3,5-di-*O*-acetyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose (**3**), the product of direct nucleophilic substitution, although the isomeric structure 3,6-di-*O*-acetyl-5-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose (**5**) was equally consistent with reactions subsequently performed on the product. Similarly, the reaction of 6-*O*-benzoyl-1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (**2**) in acetic anhydride with the acetate form of Dowex 1 ion-

*Dedicated to Dr. Nelson K. Richtmyer in honor of his 70th birthday.

†For a preliminary account of part of this work, see Ref. 1.

exchange resin was reported[4,5] to give the direct displacement product, namely, 5-*O*-acetyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-β-L-idofuranose (**4**), although subsequent reactions of the product were equally consistent with the isomeric structure **6***.

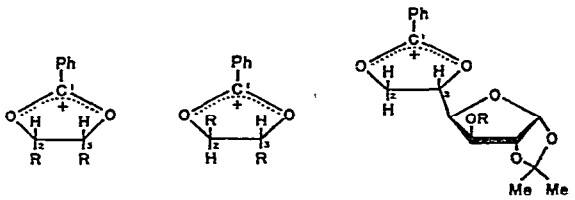


1 R = Ac **3** R = Ac **5** R = Ac

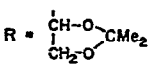
2 R = Ts **4** R = Ts **6** R = Ts

Participation by a neighboring benzoyloxy group has been observed in displacement reactions of 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-4-*O*-(methylsulfonyl)-D-mannitol with sodium acetate[7] or sodium benzoate[8] in moist *N*,*N*-dimethylformamide. The intermediate ion **7** has two adjacent, bulky groups on the same side of the five-membered ring, and, although the monobenzoate fraction isolated in each experiment probably arises by attack of water at C-1 of **7**, the products of SN2 reactions, also, were isolated in each. When the (more nucleophilic) azide ion was used, no evidence for benzoyloxy group participation was found[9]. The isomeric, *threo* ion **8** has also been postulated as an intermediate in a sulfonate displacement, and here, a dibenzoate resulting from attack of benzoate ion at C-2 (or C-3) of **8** was obtained, as well as a monobenzoate[10].

Formation of the ions **9** and **10** in displacement reactions of **1** and **2**, respectively, would appear to be even more favorable, and, in addition to opening by attack of water at C-1, these ions should be susceptible to nucleophilic attack at C-2, the primary carbon atom. Under anhydrous conditions, acetate displacements with **1** and **2** would then give the 6-acetates **5** and **6**. This paper describes proofs of the



7 **8** **9** R = Ac

R =  **10** R = Ts

structures of the displacement products, and also some of the parameters that influence the mechanism of displacements at C-5 of glucofuranose derivatives.

*In a subsequent Note by Miljkovic and Davidson[6], structure **6** was assigned to the acetate-displacement product, although the mechanism of the reaction was not discussed and structure **4** was implied at the end of the Discussion.

DISCUSSION

3-*O*-Acetyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (**1**) was prepared by a method that is a considerable improvement on published procedures. *p*-Toluenesulfonylation of 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose, which can be prepared in good yield[11] from 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, gave the 5,6-di-*p*-toluenesulfonate in 91% yield. H. Ohle and co-workers[12] were unable to obtain either a good yield or a pure product from this reaction, possibly due to initial acetyl migration or chloride displacement at C-6, or both, under their reaction conditions. The di-*p*-toluenesulfonate was readily converted into **1** (in 95% yield) by treatment with sodium benzoate in hexamethylphosphoramide at room temperature. Treatment of **1** with potassium acetate in boiling acetic anhydride gave a crystalline di-*O*-acetyl-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose, as previously reported[3].

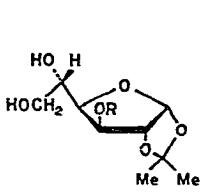
Catalytic deacylation of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-β-L-idofuranose[3] (or of **5**) gave 1,2-*O*-isopropylidene-β-L-idofuranose (**11**) in good yield. Monomolecular benzoylation of **11** gave a crystalline 6-benzoate, and treatment of this ester with acetic anhydride and pyridine afforded 3,5-di-*O*-acetyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose (**3**), having physical properties different from those of the displacement product already mentioned.

These results indicate that the acetate displacement product has the isomeric structure **5**, and, for confirmation, an unambiguous synthesis of **5** was devised. The introduction of a benzoyl group at O-5 by monomolecular benzoylation of 6-*O*-acetyl-1,2-*O*-isopropylidene-β-L-idofuranose did not appear to be a promising route, but previous work in the D-glucose series suggested that this objective might be achieved by the reaction of a benzylidene derivative of **11** (either 3,5 or 5,6) with *N*-bromosuccinimide[13]. The preponderant product formed by benzylidenation of **11** was obtained crystalline in 70% yield, and shown to be a 3,5-isomer (**13**) (probably having the conformation shown) by the following reactions. Reduction of the derived, crystalline *p*-toluenesulfonate (**14**) with lithium aluminum hydride gave mainly the alcohol **13**, together with a small proportion of the 6-deoxy derivative (**15**); however, the reaction of **14** with sodium iodide in boiling acetic anhydride gave the crystalline 6-iodo derivative (**16**) in good yield, and reduction with lithium aluminum hydride then gave, in good yield, **15** having physical constants in agreement with those previously reported[14]. The benzylidene derivative is, therefore, a 3,5-acetal (**13**) and it is, perhaps, not surprising that, in the conformation shown, C-6 of **14** is resistant to nucleophilic attack. The oxygen atom of the furanoid ring is axially disposed on the acetal ring, and C-6 is in an environment similar to that of C-6 of galactose[15].

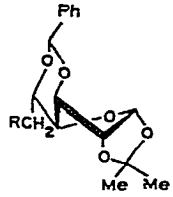
The reaction of 3,5-*O*-benzylidene-1,2-*O*-isopropylidene-α-D-glucofuranose with *N*-bromosuccinimide gave a mixture of 5-*O*-benzoyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose and 3,6-anhydro-5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose[13]. Under the same conditions, the isomeric L-idose derivative **13** gave one compound only (**17**); and, although this product crystallized,

attempted recrystallizations were unsuccessful and resulted in decomposition. The derived mono-(3,5-dinitrobenzoate) (**18**) crystallized, and had a satisfactory elemental analysis. In the p.m.r. spectrum of **17**, the H-5 signal occurred as a multiplet at τ 4.38, indicating that the benzoyl group was situated on O-5, and that for H-3 occurred as a doublet at τ 5.66. Addition of trichloroacetyl isocyanate resulted in a downfield shift of the H-3 resonance by 105 Hz, indicating that the hydroxyl group of **17** was on C-3, and that the structure of **17** was 5-*O*-benzoyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose. The mechanism of the *N*-bromosuccinimide reaction is, therefore, similar to that of the isomeric D-glucose derivative, in that the intermediate, 3,5-benzoxonium ion postulated rearranges to the 5,6-isomer prior to attack by bromide ion[13]. It was not evident from inspection of molecular models why a 3,6-anhydride should be formed from the *gluco* isomer, but not from **13**.

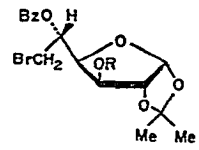
Acetylation of **17** gave the 3-acetate **19** as a homogeneous syrup, and treatment of **19** with silver acetate in acetic anhydride gave crystalline 3,6-di-*O*-acetyl-5-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose (**5**), identical in all respects with the product obtained from **1** by reaction with potassium acetate in acetic anhydride. The reaction of **1** under these conditions therefore involves neighboring-group participation *via* the intermediate benzoxonium ion **9**, which is opened by attack of acetate ion at the primary carbon atom to give **5**.



11 R = H
12 R = Ts

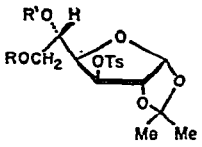


13 R = OH
14 R = OTs
15 R = H
16 R = I

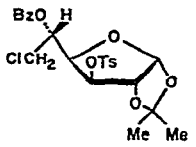


17 R = H
18 R = 3,5-dinitrobenzoyl
19 R = Ac

The crystalline product (shown later to be **6**) obtained, in 84% yield, by treatment of **2** (Ref. 16) with the acetate form of Dowex 1 ion-exchange resin in boiling acetic anhydride[6] was also conveniently prepared (in 80% yield) by using silver acetate instead of the resin. As noted previously[6], the use of potassium acetate results in more decomposition and a lower yield (52%). Catalytic deacylation of this product afforded, in high yield, crystalline 1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-β-L-idofuranose (**12**), previously obtained in noncrystalline form[5]. The *ido* configuration was established by reduction with lithium aluminum hydride to the known 1,2-*O*-isopropylidene-β-L-idofuranose[17] (**11**) already prepared. Moderate selectivity was observed in the monomolecular benzoylation of **12**. In addition to the major product, namely, crystalline 6-*O*-benzoyl-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-β-L-idofuranose (**20**), small proportions of the 5,6-dibenzoate (**21**) and the 5-benzoate



20 R = Bz, R' = H
21 R = R' = Bz
22 R = H, R' = Bz
23 R = Ac, R' = H



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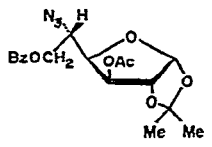

25

(**22**) were also obtained (in crystalline form). P.m.r. spectroscopy confirmed the structures assigned*. Acetylation of **20** gave the 5-acetate **4** as a homogeneous syrup that had a p.m.r. spectrum different from that of the crystalline product formed from **2** by acetate displacement.

Selective acetylation of **12** was similar to the foregoing benzoylation; however, neither the diacetate nor the major product, namely, 6-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-β-L-idofuranose (**23**), could be obtained crystalline. After chromatography on silica gel, **23** was obtained as a homogeneous syrup whose p.m.r. spectrum contained no evidence for the presence of the isomeric 5-acetate. Benzoylation of **23** gave, in 72% yield, crystalline **6**, identical in all respects with the acetate-displacement product. The reaction of **2** with the acetate form of Dowex 1 in acetic anhydride is, therefore, analogous to the reaction of **1** with potassium acetate–acetic anhydride, and occurs *via* the intermediate, benzoxonium ion **10**.

Because it might be expected that the mechanism of displacements at C-5 would be dependent on the nucleophile or the solvent, or both, the reaction of **2** with chloride ion in acetic anhydride, and the reaction of **1** with acetate ion in *N*,*N*-dimethylformamide and with sodium azide in hexamethylphosphoramide, were also examined.

From the reaction of **2** with the chloride form of Dowex 1 ion-exchange resin in boiling acetic anhydride, two products were formed that were successfully separated by chromatography on silica gel. The faster-moving compound (54%) was isolated as a homogeneous syrup that, in addition to the 3-*O*-*p*-tolylsulfonyl and benzoyl groups, contained a chlorine atom. Its p.m.r. spectrum clearly indicated that the benzoyl group was attached to O-5, and that the structure of the compound was 5-*O*-benzoyl-6-chloro-6-deoxy-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-β-L-idofuranose (**24**). Treatment of the syrup with silver acetate in acetic anhydride gave **6**. The second component from the column crystallized, and was identified as **6** (yield 43%). The formation of both **24** and **6** therefore involves neighboring-group participation and the ion **10**.

The reaction of **1** with potassium acetate in *N*,*N*-dimethylformamide gave a complex mixture of products, from which a mixture of the isomeric di-*O*-acetyl-*O*-benzoyl derivatives **3** and **5** was obtained by column chromatography. The p.m.r.

*When **2** was treated with silver acetate in moist *N*,*N*-dimethylformamide for 3 days at 110°, **20** was isolated in 60% yield; it is, presumably, formed by attack of water on the intermediate, benzoxonium ion **10**.

spectrum of the mixture indicated the ratio of **3** to **5** to be ~2:1, and, therefore, direct displacement is the principal mechanism in *N*,*N*-dimethylformamide. However, the yields were not good, as much deacylation occurred; these conclusions, therefore, are tentative.

Treatment of **1** with sodium azide in hexamethylphosphoramide for 3 h at 95° gave one product; this was precipitated by addition of water, and one recrystallization from ethanol afforded pure 3-*O*-acetyl-5-azido-6-*O*-benzoyl-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (**25**) in 83% yield. The structure was evident from the p.m.r. spectrum, and no trace of an isomeric 5-benzoate was detected.

Displacement reactions at C-5 of 6-*O*-benzoyl-5-*O*-*p*-tolylsulfonyl-D-glucofuranose derivatives can, therefore, occur either by SN2 displacement, or by participation of the neighboring benzoyloxy group (or by both pathways), and the mechanism operative is dependent on the strength of the nucleophile and the polarity of the solvent.

EXPERIMENTAL

General. — Unless otherwise stated, solutions were evaporated under diminished pressure below 50°. Melting points were determined in glass capillaries with a Thomas–Hoover apparatus, and optical rotations were measured with a Bendix Ericcson ETL-NPL automatic polarimeter. P.m.r. spectra were recorded at 100 MHz with a Varian HA-100 spectrometer operating in the frequency-sweep mode with tetramethylsilane ($\tau = 10.00$) as the internal reference standard. I. r. spectra were recorded with a Perkin–Elmer Model 137 Infracord spectrophotometer, and were calibrated against the 1600-cm^{-1} band of polystyrene. Ascending t.l.c. was performed on Silica Gel G or Silica Gel GF, and developed plates were examined under u.v. light (where appropriate) and then sprayed successively with a 1% solution of 1-naphthol in ethanol, and sulfuric acid, and then heated. Column chromatography was performed on Silica Gel (70–325 mesh, ASTM; E. Merck AG, Darmstadt, Germany; distributed by Brinkmann Instruments, Inc.)

Preparation of 3-O-acetyl-6-O-benzoyl-1,2-O-isopropylidene-5-O-p-tolylsulfonyl-α-D-glucofuranose (**1**). — To a solution of 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[11] (39.3 g, 0.15 mole) in chloroform (480 ml), cooled to ~ −10°, was slowly added a solution of recrystallized *p*-toluenesulfonyl chloride (80.1 g, 0.42 mole) in anhydrous pyridine (120 ml). The solution was allowed to attain room temperature, and the reaction was monitored by t.l.c. (ether), which indicated rapid mono-sulfonylation of O-6, followed by a slower sulfonylation of O-5 that was complete after 1 week. Water was then added, the mixture was stirred for 30 min to decompose the excess of *p*-toluenesulfonyl chloride, and the mixture was poured into ice water (~1 liter). The chloroform layer was separated, washed successively with iced 2M sulfuric acid and saturated sodium hydrogen carbonate solution, dried (sodium sulfate), and concentrated, to afford a syrup that crystallized from methanol; yield 77.5 g (91%); m.p. 92.5–94° (lit.[12] m.p. 92°).

To a solution of this product (5.70 g, 10 mmoles) in hexamethylphosphoramide (50 ml) was added sodium benzoate (5.76 g, 40 mmoles), and the suspension was stirred at room temperature. T.l.c. (ether) indicated the absence of starting material after ~4 days; water was then added slowly, first to dissolve salts, and then to precipitate the product. The solid was collected on a sintered-glass filter, washed with water, and recrystallized from ethanol; yield of **1**, 4.95 g (95%), m.p. 153.5–154° (lit.[12] m.p. 151°).

Reaction of **1** *with potassium acetate in acetic anhydride*[3]. — A mixture of **1** (2.08 g, 4 mmoles) and potassium acetate (1.58 g, 16 mmoles) in acetic anhydride (20 ml) was boiled under reflux for 15 h. Acetic anhydride was then removed by evaporation, and the dark residue was partitioned between ether and water. Evaporation of the dried (sodium sulfate) ether extracts gave a syrup that crystallized from ethanol; yield 1.03 g (63%) of a light-brown product. Recrystallization from ethanol, with treatment with charcoal, afforded analytically pure material (0.95 g) (shown later to be **5**); m.p. 119–121°, $[\alpha]_D^{24}$ −22.9° (*c* 1.4, chloroform); lit.[3] m.p. 121–122°, $[\alpha]_D$ −19.6° (*c* 2.8, chloroform). The p.m.r. spectrum indicated negligible (<2%) contamination of the product by starting material.

*Preparation of 1,2-*O*-isopropylidene-β-*L*-idofuranose* (**11**). — 3,5,6-Tri-*O*-acetyl-1,2-*O*-isopropylidene-β-L-idofuranose was prepared in 64% yield from 3-*O*-acetyl-1,2-*O*-isopropylidene-5,6-di-*O*-*p*-tolylsulfonyl-α-D-glucofuranose by the method of Vargha[3], it had m.p. 82–84°, as reported by Hough and co-workers[18]. To a solution of the triacetate (3.0 g) in chloroform (30 ml, cooled to 0°, was added 0.1% sodium methoxide in methanol (3 ml). T.l.c. (ether) indicated slow deacetylation that was complete after 6 h at room temperature. Concentration afforded a crystalline solid. This was dissolved in chloroform, the solution was stirred for several hours with anhydrous magnesium sulfate, the suspension was filtered, and the filtrate was evaporated to a crystalline residue which was recrystallized from chloroform and then from ethyl acetate; yield of **11**, 1.72 g (90%), m.p. 113–114.5°, $[\alpha]_D^{25}$ −27° (*c* 1.3, water); lit.[17] m.p. 112–114°, $[\alpha]_D^{14}$ −28.7° (*c* 1.36, water).

*3,5-Di-*O*-acetyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-β-*L*-idofuranose* (**3**). — To a stirred solution of **11** (1.10 g, 5 mmoles) in dry pyridine (50 ml), cooled to ~ −40°, was slowly added a solution of benzoyl chloride (0.61 ml, 5.3 mmoles) in dichloromethane (5 ml). The solution was kept for 20 h at −20° and for 4 h at 5°, and then concentrated to a syrup which was dissolved in a small volume of chloroform and fractionated on silica gel (150 g) with ether as the eluant. A small amount (0.32 g, 15%) of a crystalline dibenzoate was eluted first, followed by the major product (1.13 g, 53%), a crystalline monobenzoate. Recrystallization from water gave pure 6-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose, m.p. 109.5–110.5°, $[\alpha]_D^{25}$ −64° (*c* 1.3, chloroform); p.m.r. data (chloroform-*d*): τ 1.90–2.70 (5-proton multiplet, aromatic protons), 4.01 (doublet, $J_{1,2}$ ~3.5 Hz, H-1), 5.30–5.83 (6-proton multiplet, H-2,3,4,5,6,6′), 8.51, and 8.67 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.28; H, 6.16.

Treatment of the monobenzoate with acetic anhydride–pyridine afforded a

crystalline product which, on recrystallization from ethanol, gave pure **3**, m.p. 86–88° (depressed to 75–85° by admixture with the product obtained from reaction of **1** with potassium acetate in acetic anhydride), $[\alpha]_D^{25}$ −14.9° (*c* 1.0, chloroform); p.m.r. data (chloroform-*d*): τ 1.95–2.72 (5-proton multiplet, aromatic protons), 4.06 (doublet $J_{1,2}$ ~4 Hz, H-1), 4.50 (multiplet, H-5), 4.74 (doublet, $J_{3,4}$ ~3.5 Hz, H-3), 5.30–5.85 (4-proton multiplet, H-2,4,6,6'), 7.88, 7.90 (3-proton singlets, 2 OAc), 8.46, and 8.67 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{20}H_{24}O_9$: C, 58.82; H, 5.92. Found: C, 58.84; H, 5.94.

Benzylidenation of **11**. — To a solution of **11** (0.26 g, 1.2 mmoles) in dry *N,N*-dimethylformamide (4 ml) and benzaldehyde dimethyl acetal (0.75 ml, 5 mmoles) was added *p*-toluenesulfonic acid (10 mg). The solution was kept for 20 h at room temperature, and then stirred for 30 min with Rexyn AG-1 (OH^-) ion-exchange resin. The suspension was filtered, and the filtrate was evaporated to a syrup; to this was added xylene, and the solution was evaporated to a syrup which crystallized. Recrystallization from isopropyl ether gave a benzylidene derivative of **11**, shown later to be the 3,5-isomer **13*** (0.26 g, 70%), m.p. 120–121°, $[\alpha]_D^{25}$ +7° (*c* 1.3, chloroform); p.m.r. data (chloroform-*d*): τ 2.44–2.74 (5-proton multiplet, aromatic protons), 3.98 (doublet, $J_{1,2}$ ~3.5 Hz, H-1), 4.49 (singlet, benzylic proton), 5.39 (doublet, $J_{2,3}$ ~0 Hz, H-2), 5.59 (doublet, $J_{3,4}$ ~2.5 Hz, H-3), 5.74–6.24 (4-proton multiplet, H-4,5,6,6'), 7.77 (broad singlet, OH), 8.47, and 8.66 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54, Found: C, 62.34; H, 6.49.

Treatment of **13** with *p*-toluenesulfonyl chloride in pyridine, initially at 0° and then at room temperature, followed by evaporation of the pyridine, and isolation of the product by chromatography on silica gel with 3:1 ether–hexane as the eluant, afforded the crystalline *p*-toluenesulfonate **14** in 77% yield. After recrystallization from 95% ethanol, it had m.p. 120–121°, $[\alpha]_D^{25}$ −5° (*c* 1.2, chloroform); p.m.r. data chloroform-*d*): τ 2.15–2.76 (9-proton multiplet, aromatic protons), 4.07 (doublet, $J_{1,2}$ ~3.5 Hz, H-1), 4.56 (singlet, benzylic proton), 5.42 (doublet, H-2), 5.50–5.96 (5-proton multiplet, H-3, 4, 5, 6, 6'), 7.58 (3-proton singlet, Ar–Me), 8.50, and 8.68 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{23}H_{26}O_8S$: C, 59.73; H, 5.67; S, 6.93. Found: C, 59.72; H, 5.54; S, 6.73.

To a solution of **14** (0.31 g) in acetic anhydride (10 ml) was added sodium iodide (0.30 g), and the mixture was stirred and boiled under reflux for 16 h. Concentration afforded a syrup which was extracted with chloroform. The extracts were combined, and filtered, and the filtrate was washed successively with sodium hydrogen carbonate solution and water, dried (magnesium sulfate), and evaporated to a syrup which crystallized. Recrystallization from ethanol gave **16** (0.19 g, 68%); m.p.

*In some preparations of **13**, chromatographic fractionation of the products gave various proportions (5–15%) of an isomeric derivative having m.p. 156–157°, $[\alpha]_D^{25}$ −61° (*c* 1.1, chloroform). Its elemental analysis and p.m.r. spectrum were consistent with the structure 5,6-*O*-benzylidene-1,2-*O*-isopropylidene-β-L-idofuranose.

159–161°, $[\alpha]_D^{25}$ −4.1° (*c* 1.0, chloroform); p.m.r. data (chloroform-*d*): τ 2.42–2.74 (5-proton multiplet, aromatic protons), 4.01 (doublet, $J_{1,2}$ ~3.5 Hz, H-1), 4.52 (singlet, benzylic proton), 5.36 (doublet, H-2), 5.52–5.92 (3-proton multiplet, H-3,4,5), 6.44–6.62 (2-proton multiplet, H-6,6'), 8.46, 8.65 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{16}H_{19}IO_5$: C, 45.95; H, 4.58; I, 30.34. Found: C, 45.90; H, 4.72; I, 30.66.

To a stirred solution of **16** (0.18 g) in ether (6 ml) and benzene (4 ml), cooled to 0°, was slowly added a 4*M* solution of lithium aluminum hydride in ether (3.5 ml). The mixture was then boiled under reflux for 16 h, and cooled, and the excess of hydride was decomposed by successive addition of ethyl acetate and water. The resultant suspension was filtered, the residue was washed with chloroform, and the filtrates were combined and evaporated to a syrup (bath temperature <30°, to prevent loss of the volatile product). The syrup crystallized, and recrystallization from ethanol gave **15** (0.083 g, 66%); m.p. 125–125.5°, $[\alpha]_D^{25}$ +8° (*c* 1.8, chloroform); lit.[14] m.p. 126°, $[\alpha]_D^{14}$ +9° (chloroform); p.m.r. data (chloroform-*d*): τ 2.40–2.74 (5-proton multiplet, aromatic protons), 3.97 (doublet, $J_{1,2}$ ~3.5 Hz, H-1), 4.52 (singlet, benzylic proton), 5.38 (doublet, H-2), 5.63 (doublet, $J_{3,4}$ ~2 Hz, H-3), 5.72–6.04 (2-proton multiplet, H-4,5), 8.47, 8.66 (3-proton singlets, CMe_2), 8.53 (3-proton doublet, *J* ~6.5 Hz, C-6 protons).

Reaction of **13** *with* N-*bromosuccinimide*[13]. — To a stirred solution of **13** (0.39 g) in carbon tetrachloride (30 ml) were added *N*-bromosuccinimide (0.28 g) and barium carbonate (1.0 g), and the mixture was boiled under reflux for 2.5 h. Solids were removed by filtration, the filtrate was evaporated to a syrup which was dissolved in ether, and the solution was washed with water, dried (magnesium sulfate), and evaporated to a syrup which crystallized (0.36 g, 73%). T.l.c. (1:1 ether–hexane) indicated one product only, but attempts to recrystallize it resulted in decomposition. P.m.r. data (chloroform-*d*): τ 1.82–2.68 (5-proton multiplet, aromatic protons), 4.05 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.38 (multiplet, H-5), 5.46 (2-proton multiplet, H-2,4), 5.66 (doublet, $J_{3,4}$ ~3 H-3), 6.23 (2-proton doublet, H-6,6'), 7.07 (broad singlet, OH), 8.46, and 8.69 (3-proton singlets, CMe_2). Addition of trichloroacetyl isocyanate resulted in a spectrum having the following features: τ 1.18 (singlet, carbamate NH), 1.86–2.68 (5-proton multiplet, aromatic protons), 3.99 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.36 (multiplet, H-5), 4.61 (doublet, $J_{3,4}$ ~3.5 Hz, H-3), 5.19 (quartet, $J_{4,5}$ ~5.5 Hz, H-4), 5.31 (doublet, H-2), 6.35 (2-proton multiplet, H-6,6'), 8.43, and 8.67 (3-proton singlets, CMe_2).

These data indicated that the product was **17**. Treatment of **17** with 3,5-dinitrobenzoyl chloride in pyridine for 16 h at room temperature, followed by evaporation of the solvent, and isolation by chromatography on silica gel with 3:1 ether–hexane as the eluant, gave the crystalline 3,5-dinitrobenzoate **18**. After recrystallization from chloroform–hexane, it had m.p. 205–206°, $[\alpha]_D^{25}$ −8° (*c* 2.1, chloroform). The p.m.r. spectrum was consistent with structure **18**.

Anal. Calc. for $C_{23}H_{21}BrN_2O_{11}$: C, 47.52; H, 3.64; Br, 13.75; N, 4.82. Found: C, 47.54; H, 3.75; Br, 14.11; N, 4.83.

3,6-Di-O-acetyl-5-O-benzoyl-1,2-O-isopropylidene-β-L-idofuranose (**5**). — After treatment of **17** (90 mg) with acetic anhydride (1 ml) and pyridine (5 ml) for 7 h at room temperature, t.l.c. (3:1 ether–hexane) indicated the absence of **17** and complete conversion into a faster-moving compound. The solvents were removed by evaporation, and the resultant syrup was purified by chromatography on silica gel (15 g) with 3:1 ether–hexane as the eluant. Compound **19** was obtained as a chromatographically homogeneous syrup (80 mg), $[\alpha]_D^{25}$ −8° (*c* 4.0, chloroform); p.m.r. data (chloroform-*d*): τ 1.84–2.66 (5-proton multiplet, aromatic protons), 4.03 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.46 (multiplet, H-5), 4.68 (doublet, $J_{3,4}$ ~3.5 Hz, H-3), 5.25 (quartet, $J_{4,5}$ ~7 Hz, H-4), 5.47 (doublet, H-2), 6.18–6.58 (2-proton octet, the AB part of an ABX system, $J_{5,6} \approx J_{5,6'}$ ~5 Hz, $J_{6,6'}$ ~11 Hz), 7.97 (3-proton singlet, OAc), 8.43, and 8.66 (3-proton singlets, CMe_2).

Silver acetate (200 mg) was added to a stirred solution of **19** (74 mg) in acetic anhydride (7 ml), and the mixture was boiled under reflux for 28 h. Solids were removed by filtration, and the filtrate was evaporated to a syrup; this was dissolved in chloroform, and the solution was washed successively with sodium hydrogen carbonate solution and water, dried (magnesium sulfate), and evaporated to a syrup that crystallized (59 mg). Recrystallization from ethanol gave pure **5**; m.p. 119–121°, $[\alpha]_D^{25}$ −23° (*c* 1.1, chloroform). A mixture m.p. with the product obtained by reaction of **1** with potassium acetate in acetic anhydride was undepressed, and the p.m.r. spectra of the two products were identical, and different from that of **3**.

Reaction of **2** *with acetate ion in acetic anhydride. — A. With Dowex 1 (OAc^-).* Treatment of **2** with Dowex 1 (OAc^-) ion-exchange resin according to the method of Miljkovic and Davidson[4,6] gave a crystalline product (shown later to be **6**) in 84% yield; m.p. 125.5–126°, $[\alpha]_D^{25}$ −8° (*c* 1.0, chloroform); lit.[6] m.p. 125.5–126.5°, $[\alpha]_D^{27}$ −8.3° (*c* 1.0, chloroform).

B. With silver acetate. To a solution of **2** (1.10 g) in acetic anhydride (40 ml) was added silver acetate (1.0 g), and the mixture was stirred and boiled under reflux for 40 h. Solids were removed by filtration, and the filtrate was evaporated to a syrup; this was dissolved in chloroform, and the solution was washed successively with sodium hydrogen carbonate solution and water, dried (magnesium sulfate), and evaporated to a syrup that crystallized, Recrystallization from ethanol afforded pure **6** (0.57 g, 80%).

1,2-O-Isopropylidene-3-O-p-tolylsulfonyl-β-L-idofuranose (**12**). — To a cooled (0°) solution of **6** (5.55 g) in dichloromethane (60 ml) was added 0.2M sodium methoxide in methanol (60 ml). After 2 h at 0°, t.l.c. (ethyl acetate) indicated complete deacylation. Amberlite MB-3 ion-exchange resin was added, the suspension was stirred for 30 min and filtered, and the filtrate was evaporated to a syrup that crystallized. Recrystallization from chloroform–hexane gave pure **12** (3.62 g, 91%); m.p. 98–100°, $[\alpha]_D^{25}$ −27° (*c* 1.3, chloroform); p.m.r. data (chloroform-*d*): τ 2.12–2.70 (4-proton multiplet, aromatic protons), 4.08 (doublet, $J_{1,2}$ ~4 Hz, H-1), 5.11 (doublet, $J_{3,4}$ ~3 Hz, H-3), 5.31 (doublet, H-2), 5.71 (doublet of doublets, $J_{4,5}$ ~7.5 Hz, H-4), 6.14 (multiplet, H-5), 6.37–6.76 (2-proton octet, $J_{5,6}$ ~3.5 Hz, $J_{5,6'}$ ~5 Hz,

$J_{6,6'}$ ~11.5 Hz, H-6,6'), 7.52 (5-proton, broad singlet, Ar–Me, 2 OH), 8.51, and 8.70 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{16}H_{22}O_8S$: C, 51.33; H, 5.92; S, 8.56. Found: C, 51.40; H, 6.03; S, 8.51.

Reduction of **12** with lithium aluminum hydride in boiling tetrahydrofuran gave, in 73% yield, crystalline **11** having physical constants identical with those already reported.

Selective benzoylation of **12**. — A solution of benzoyl chloride (0.33 ml, 1.1 equivalents) in anhydrous pyridine (3 ml) was added dropwise to a stirred solution of **12** (1.0 g) in anhydrous pyridine (15 ml), below −25°; the mixture was then kept for 4 h at −20° and for 16 h at room temperature, and evaporated to a syrup which was dissolved in chloroform. The solution was washed successively with 2M hydrochloric acid, sodium hydrogen carbonate solution, and water, dried (magnesium sulfate), and evaporated to a syrup. T.l.c. (ether) indicated a major product and small proportions of a faster-moving compound (dibenzoate) and the slower-moving starting-material. The mixture was fractionated on silica gel (150 g) with 3:2 chloroform–ether as the eluant.

Fraction 1 crystallized, and recrystallization from ethanol afforded **21** (0.13 g, 9%); m.p. 149–150°, $[\alpha]_D^{25}$ −6° (*c* 1.0, chloroform); p.m.r. data (chloroform-*d*): τ 1.94–2.74 (14-proton multiplet, aromatic protons), 4.01 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.32 (multiplet, H-5), 4.95, (doublet $J_{3,4}$ ~3 Hz, H-3), 5.16 (doublet, H-2), 5.37 (doublet of doublets, $J_{4,5}$ ~7.5 Hz, H-4), 5.45–5.86 (2-proton octet, AB part of an ABX system, $J_{5,6}$ ~3 Hz, $J_{5,6'}$ ~5 Hz, $J_{6,6'}$ ~12.5 Hz, H-6,6'), 7.60 (3-proton singlet, Ar–Me), 8.48, and 8.67 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{30}H_{30}O_{10}S$: C, 61.85; H, 5.19; S, 5.50. Found: C, 61.76; H, 5.38; S, 5.45.

Fraction 2 (0.65 g) crystallized, and recrystallization from ethanol gave **20** (0.39 g, 32%); m.p. 134–135°, $[\alpha]_D^{25}$ −44.5° (*c* 1.4, chloroform); p.m.r. data (chloroform-*d*): τ 1.94–2.78 (9-proton multiplet, aromatic protons), 4.02 (doublet, $J_{1,2}$ ~4 Hz, H-1), 5.10 (doublet, $J_{3,4}$ ~3 Hz, H-3), 5.22 (doublet, H-2), 5.58–5.92 (4-proton multiplet, H-4,5,6,6'), 7.59 (4-proton, broad singlet, Ar–Me, OH), 8.51, and 8.68 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{23}H_{26}O_9S$: C, 57.73; H, 5.48; S, 6.70. Found: C, 57.68; H, 5.66; S, 6.69.

P.m.r. spectroscopy indicated that the mother liquors from the crystallization of **20** contained an isomeric monobenzoate. This was obtained crystalline, and recrystallization from ethanol afforded pure **22**; m.p. 114–116°, $[\alpha]_D^{25}$ +2.5° (*c* 1.0, chloroform); p.m.r. data (chloroform-*d*): τ 1.90–2.76 (9-proton multiplet, aromatic protons), 4.06 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.65 (multiplet, H-5), 4.90 (doublet, $J_{3,4}$ ~3 Hz, H-3), 5.20–5.39 (2-proton multiplet, H-2,4), 6.03–6.41 (2-proton multiplet, H-6,6'), 7.54 (3-proton singlet, Ar–Me), 8.07 (broad singlet, OH), 8.46, and 8.68 3-proton singlets, CMe_2).

Anal. Calc. for $C_{23}H_{26}O_9S$: C, 57.73; H, 5.48; S, 6.70. Found: C, 57.40; H. 5.46; S, 6.55.

5-O-Acetyl-6-O-benzoyl-1,2-O-isopropylidene-3-O-p-tolylsulfonyl-β-L-idofuranose (**4**). — Treatment of **20** (0.25 g) with acetic anhydride (1.0 ml) and pyridine (5 ml) for 20 h at room temperature, followed by evaporation of the solvents and conventional processing, gave **4** as a chromatographically and spectroscopically (p.m.r.) homogeneous syrup (0.25 g); $[\alpha]_D^{25}$ −7° (*c* 1.0, chloroform); p.m.r. data (chloroform-*d*): τ 1.98–2.76 (9-proton multiplet, aromatic protons), 4.04 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.60 (multiplet, H-5), 5.06 (doublet, $J_{3,4}$ ~3 Hz, H-3), 5.18 (doublet, H-2), 5.51 (doublet of doublets, $J_{4,5}$ ~7.5 Hz, H-4), 5.58–6.03 (2-proton octet, AB part of an ABX system, $J_{5,6}$ ~3 Hz, $J_{5,6'}$ ~5 Hz, $J_{6,6'}$ ~12 Hz, H-6,6'), 7.59 (3-proton singlet, Ar–Me), 7.96 (3-proton singlet, OAc), 8.49, and 8.67 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{25}H_{28}O_{10}S$: C, 57.68; H, 5.42; S, 6.16. Found: C, 57.68; H, 5.62; S, 6.01.

Selective acetylation of **12**. — A solution of acetyl chloride (0.22 ml, 1.1 equivalents) in dry ether (3 ml) was added dropwise during 30 min to a stirred solution of **12** in anhydrous pyridine (15 ml) kept at −25°. The mixture was kept for 2.5 h at −20° and then for 16 h at room temperature. Evaporation afforded a syrup which was dissolved in chloroform; the solution was successively washed with M sulfuric acid, sodium hydrogen carbonate solution, and water, dried (magnesium sulfate), and evaporated to a syrup (1.1 g). T.l.c. (ether) indicated a major product and small proportions of a faster-moving compound (diacetate) and the slower-moving starting-material. Fractionation on silica gel (150 g), with ether as the eluant, gave 50 mg of the diacetate, which could not be crystallized, and then the major product (**23**) as a chromatographically and spectroscopically (p.m.r.) homogeneous syrup (0.55 g, 55%); $[\alpha]_D^{25}$ −25° (*c* 1.2, chloroform); p.m.r. data (chloroform-*d*): τ 2.12–2.70 (4-proton multiplet, aromatic protons), 4.07 (doublet, $J_{1,2}$ ~4 Hz, H-1), 5.13 (doublet, $J_{3,4}$ ~3 Hz, H-3), 5.29 (doublet, H-2), 5.77 (multiplet, H-4), 5.86–6.12 (3-proton multiplet, H-5,6,6'), 7.37 (broad singlet, OH), 7.53 (3-proton singlet, Ar–Me), 7.93 (3-proton singlet, OAc), 8.51, and 8.69 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{18}H_{24}O_9S$: C, 51.92; H, 5.81; S, 7.70. Found: C, 51.44; H, 5.87; S, 7.48.

6-O-Acetyl-5-O-benzoyl-1,2-O-isopropylidene-3-O-p-tolylsulfonyl-β-L-idofuranose (**6**). — Treatment of **23** (0.26 g) with benzoyl chloride (0.2 ml) in pyridine (2 ml) for 16 h at room temperature, followed by evaporation of the solvent and conventional processing, gave a crystalline product. Recrystallization from ethanol afforded pure **6** (0.23 g, 72%); m.p. 125°, $[\alpha]_D^{25}$ −8° (*c* 1.1, chloroform). A mixture m.p. with the product obtained from reaction of **2** with acetate ion in acetic anhydride was undepressed, and the p.m.r. spectra of the two compounds were identical and different from that of **4**.

Reaction of **2** *with Dowex 1 (Cl^-) in acetic anhydride.* — Dowex 1 X-2 (Cl^-) ion-exchange resin (200–400 mesh) was washed with methanol, and dried overnight

at 70° in a vacuum oven. The resin (10 g) was added to a solution of **2** (1.6 g) in acetic anhydride, and the suspension was stirred and boiled under reflux for 40 h. The resin was removed by filtration, and washed with chloroform, and the filtrate and washings were combined, and evaporated to a syrup. A solution of the syrup in chloroform was washed successively with sodium hydrogen carbonate solution and water, dried (magnesium sulfate), and evaporated to a syrup that contained two products (t.l.c. in 1:1 ether–hexane). Complete separation of the two was obtained by fractionation on silica gel (150 g) with 2:3 ether–hexane as the eluant.

Fraction 1 (0.68 g, 54%) was obtained as a chromatographically and spectroscopically (p.m.r.) homogeneous syrup, $[\alpha]_D^{25}$ +9° (*c* 1.1, chloroform); p.m.r. data (chloroform-*d*): τ 1.90–2.75 (9-proton multiplet, aromatic protons), 4.06 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.52 (multiplet, H-5), 4.93 (doublet, $J_{3,4}$ ~3 Hz, H-3), 5.22–5.40 (2-proton multiplet, H-2,4), 6.12–6.51 (2-proton octet, AB part of an ABX system, $J_{5,6} \approx J_{5,6'}$ ~4 Hz, $J_{6,6'}$ ~12 Hz, H-6,6'), 7.53 (3 proton singlet, Ar–Me), 8.46, and 8.69 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{23}H_{25}ClO_8S$: C, 55.59; H, 5.07; Cl, 7.13; S, 6.45. Found: C, 55.56; H, 5.35; Cl, 7.08; S, 6.43.

Treatment of this compound with silver acetate in boiling acetic anhydride gave, in 63% yield, a crystalline product having m.p., mixture m.p., and p.m.r. spectrum identical with those of **6**, and the structure of the chloro sugar is, therefore, 5-*O*-benzoyl-6-chloro-6-deoxy-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-β-L-idofuranose (**24**).

Fraction 2 (0.56 g, 43%) crystallized, and recrystallization from ethanol gave **6**, identified by m.p., mixture m.p., and p.m.r. spectroscopy.

Reaction of **1** *with potassium acetate in* N,N-*dimethylformamide.* — A stirred solution of **1** (1.04 g, 2 mmoles) and potassium acetate (0.78 g, 8 mmoles) in *N*,*N*-dimethylformamide was heated for 16 h at 140°. T.l.c. (1:1 ether–hexane) indicated the absence of **1**, and the presence of a complex mixture of products. The solvent was removed by evaporation, and the residue was applied to a column of silica gel (100 g), which was eluted with 1:1 ether–hexane.

Fraction A (85 mg) contained several fast-moving compounds, and was not further investigated.

Fraction B (0.17 g) contained two compounds; these were identified from the p.m.r. spectrum as the isomeric di-*O*-acetyl-mono-*O*-benzoyl derivatives **3** and **5**. Integration of the spectrum indicated the ratio of **3** to **5** to be ~2:1.

Fraction C (0.11 g) contained slower-moving, deacylated products, and was not further examined.

Reaction of **1** *with sodium azide in hexamethylphosphoramide.* — To a stirred solution of **1** (1.04 g, 2 mmoles) in hexamethylphosphoramide (10 ml) was added sodium azide (0.52 g, 8 mmoles), and the mixture was kept for 3 h at 95°. T.l.c. (1:2 ether–hexane) indicated the presence of only one product, and the absence of **1**. Water (40 ml) was added slowly, and the precipitate was collected by filtration and recrystallized from ethanol, to give **25** (0.65 g, 83%); m.p. 147–149°, $[\alpha]_D^{25}$ −13°

(*c* 0.6, chloroform), $\nu_{max}^{CCl_4}$ 2105 (C-N_3), 1755, and 1725 cm^{-1} (acetate and benzoate C=O); p.m.r. data (chloroform-*d*): τ 1.90–2.66 (5-proton multiplet, aromatic protons), 4.04 (doublet, $J_{1,2}$ ~4 Hz, H-1), 4.76 (doublet, $J_{3,4}$ ~3 Hz, H-3). 5.40–6.10 (5-proton multiplet, H-2,4,5,6,6'), 7.89 (3-proton singlet, AcO), 8.49, and 8.69 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{18}H_{21}N_3O_7$: C, 55.24; H, 5.41; N, 10.74. Found: C, 55.28; H, 5.27; N, 10.81.

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