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Reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-*erythro*-hex-2-enopyranoside and its phenyl analog with several nucleophiles; stereoselective preparation of 3-*O*-acyl-D-*arabino*- and -D-*ribo*-hex-1-enitol derivatives

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ABSTRACT

Reactions of methyl 2-*C*-*p*-tolylsulfonyl-2-enopyranoside (**6**) with nucleophiles (methoxide, nitromethane, 2,4-pentanedione, and ammonia) afforded the β-D-*gluco* adducts with high stereoselectivity. However, similar treatment of the phenyl analog **11** with sodium borodeuteride, nitromethane, methoxide, and lithium hydroxide led mainly to an SN2′ process to give 1-enitol derivatives having the *arabino* configuration. Conversely, treatment of **11** with carboxylic acids in pyridine gave the 1-enitol derivatives having the *ribo* configuration as the major product.

INTRODUCTION

Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-nitro-α-D-*erythro*-hex-2-enopyranoside (**1**) with methanolic sodium methoxide afforded the adduct **3** having the α-D-*gluco* configuration as the major product[1]. On the other hand, similar treatment of 2-*C*-*p*-tolylsulfonyl analog **2** gave mainly the 3-enopyranoside **4**, the sodium methoxide thus acting as a base[2]. These results suggest that the electrophilicity of the nitroalkene **1** is higher than that of the sulfonyl alkene **2**. Similar reactions of methyl 2-*C*-nitro-β-D-*erythro*-hex-2-enopyranoside (**5**) also gave adducts having the β-D-*gluco* configuration[3].

We examined[4] the reaction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-*erythro*-hex-2-enopyranoside (**6**) with several nucleophiles to throw light on the stereochemistry of these nucleophilic addition reactions and to determine whether addition predominates over abstraction of H-4. The phenyl analog **11** was also subjected to reactions with the nucleophiles.

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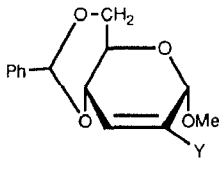
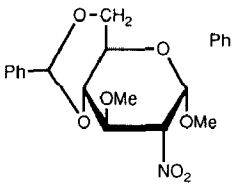


1 Y = NO_2
2 Y = SO_2Tol



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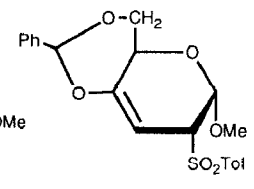

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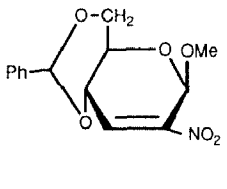

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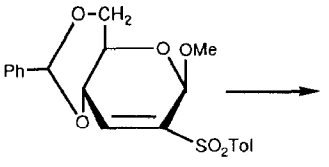

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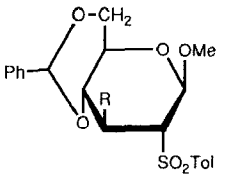
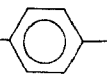


7 R = OMe
8 R = CH_2NO_2
9 R = $CHAc_2$
10 R = NHAc

Tol = Me 

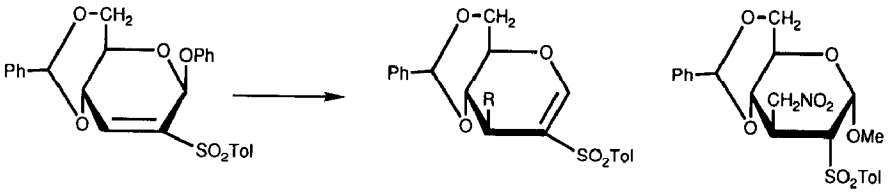
RESULTS AND DISCUSSION

Treatment of compound **6** with sodium methoxide in methanol afforded the *β*-D-*gluco* adduct **7** in 93% yield. A solution of **6** in nitromethane containing triethylamine was heated under reflux for 6 h, gave at least two products (as judged from the ^{1}H-n.m.r. spectrum), and the *β*-D-*gluco* isomer **8** was isolated by fractional crystallization in 78% yield. Similar treatment of **6** in 2,4-pentanedione in the presence of triethylamine for 8.75 h at ~80° gave the *β*-D-*gluco* product **9** in 92% yield. The reaction of **6** with aqueous ammonia in tetrahydrofuran, followed by acetylation with acetic anhydride, provided **10** in 81% yield, together with an unidentified product. The *β*-D-*gluco* configuration and the $^4C_1$ conformation was assigned for **7**, **8**, **9**, and **10** from the large values of the $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ coupling constants.

All nucleophiles investigated thus added principally to the electron-deficient C-3 position from the equatorial side of **6**, and did not abstract the hydrogen atom[2] at C-4.

Similar nucleophilic addition reactions to the phenyl analog **11** were undertaken. In contrast to the methyl glycoside **6**, the phenyl analog **11** might be expected to form 1-enitol derivatives, because the aglyconic phenoxyl group is a better leaving group than the methoxyl group, as exemplified in the reactions of nitroepoxide derivatives[5].

Treatment of **11** with sodium borohydride led to an SN2′ reaction to give the 3-deoxy-1-enitol derivative **12**. In the ^{1}H-n.m.r. spectrum of **12**, the quasi-axial and quasi-equatorial protons at C-3 appeared respectively at δ 2.29 and 2.67 (in $CDCl_3$) having $J_{3qa,4}$ 9.5 and $J_{3qe,4}$ 5.8 Hz. When compound **11** was reduced with sodium borodeuteride, the quasi-equatorial signal disappeared almost completely from the



11

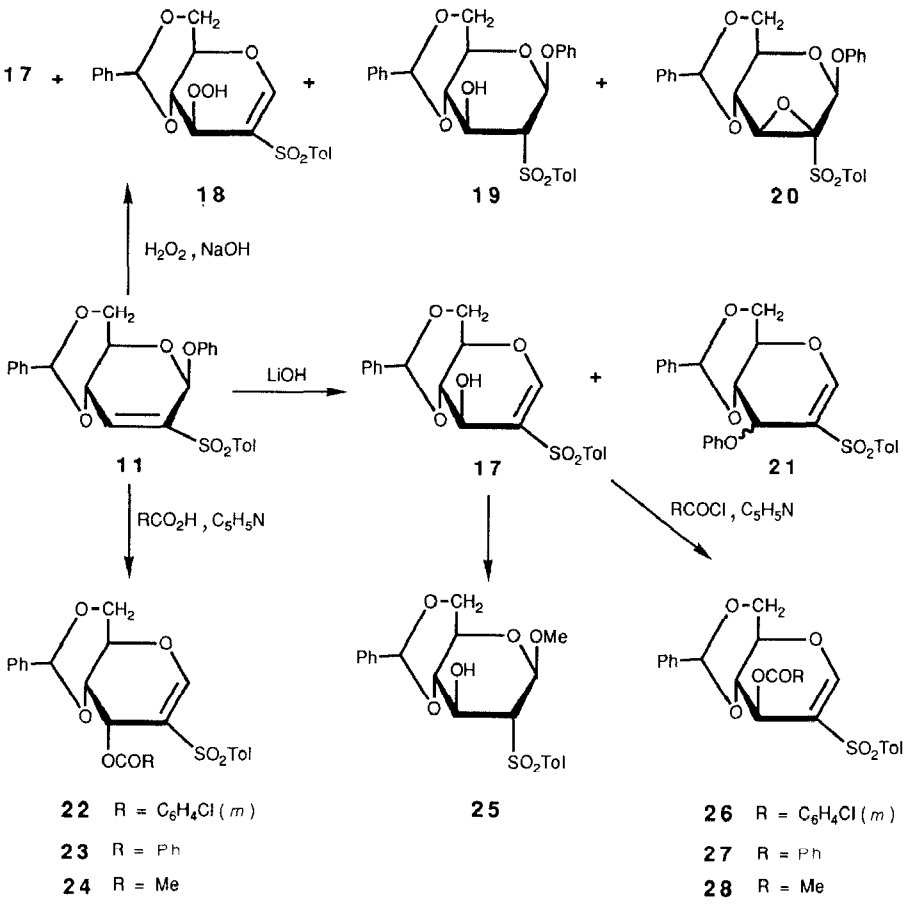
12 R = H
13 R = D
14 R = CH_2NO_2
15 R = OMe

16

^{1}H-n.m.r. spectrum. Treatment of **11** with nitromethane in the presence of triethylamine for 3 days at room temperature afforded the 3-*C*-nitromethyl-1-enitol derivative **14** in 75% yield. The *arabino* configuration for **14** was suggested by the coupling constants ($J_{1,3}$ 1.6 and $J_{3,4}$ 9.2 Hz) and confirmed by the formation of a ~2:3 mixture of α-D-glucopyranoside **16** and β-D-glucopyranoside **8** (as judged by its ^{1}H-n.m.r. spectrum) on treatment of **14** with methanolic sodium methoxide. These two products were separated by fractional crystallization from ethanol. The β anomer **8** was identical with an authentic sample derived from **6**, and the α-D-*gluco* structure with the $^4C_1$ conformation for **16** was deduced from the coupling constants ($J_{1,2}$ 3.3 and $J_{2,3}$ 11.9 Hz). When **11** was treated with methanolic sodium methoxide, methyl 3-*O*-methyl-β-D-glucopyranoside (**7**) was obtained in 95% yield. Obviously, **7** was formed *via* the 3-*O*-methyl-1-enitol derivative **15**. In fact, under mild conditions, compound **15** was isolated in almost quantitative yield, but no evidence for the formation of a potential adduct, phenyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-β-D-glucopyranoside, was obtained. The *arabino* configuration for **15** was suggested by the coupling constants, $J_{1,3}$ 1.0 and $J_{3,4}$ 7.3 Hz, and supported by the formation of **7** from **15***.

Treatment of **11** with lithium hydroxide in tetrahydrofuran afforded the 1-enitol derivative **17** in 63% yield, together with the epimeric 3-*O*-phenyl derivatives **21** (~11%). The *arabino* configuration for **17** was again suggested by the coupling constants, $J_{1,3}$ 0.8 and $J_{3,4}$ 7.2 Hz, and chemically determined by formation of the methyl β-D-glucopyranoside derivative **25** on treatment with methanolic sodium methoxide. A phenoxide ion concomitantly generated during the reaction attacked the sulfonyl alkene **11** to give an epimeric mixture of 3-*O*-phenyl derivatives **21**. Assuming that the formation of **21** should be suppressed by the use of a reagent more reactive than phenoxide ion, we then performed a heterogeneous reaction of **11** with hydrogen peroxide in the presence of aqueous sodium hydroxide and tributylhexadecylphosphonium bromide (added as a phase-transfer catalyst). As expected, there was no evidence for the formation of **21**, but the reaction afforded a complex mixture containing the desired compound **17** (7%), the 3-hydroperoxy-1-enitol derivative **18** (39%), the phenyl glucopyranoside derivative **19** (11%), and the epoxide **20** (~14%). The yield of **17** was

* The 3-epimer of **15** had $J_{1,3}$ ~0 and $J_{3,4}$ 3.0 Hz (ref. 2).



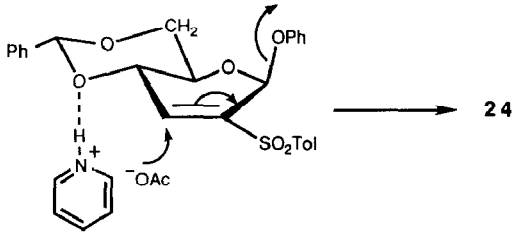
increased to 42% by treatment of the crude product with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

As pyridine *N*-oxide seemed to be a suitable reagent, compound **11** was treated with *m*-chloroperoxybenzoic acid in pyridine. Although compound **17** was not obtained, a new compound (**22**) was isolated in moderate yield. The same compound (**22**) was obtained in 80% yield by treatment of **11** with *m*-chlorobenzoic acid in pyridine in the presence of benzoic anhydride (added as a scavenger of phenol). The spectral data for **22** were different from those of the *arabino* isomer **26**, prepared by *m*-chlorobenzoylation of the 1,5-anhydro-D-*arabino*-hex-1-enitol derivative **17**. Similar treatment of **11** with benzoic and acetic acids in pyridine in the presence of benzoic and acetic anhydride afforded the corresponding 3-*O*-acyl derivatives **23** and **24** in high yield, together with small amounts of the corresponding 3-epimers **27** and **28**, respectively. The latter two compounds were identical with respective authentic samples prepared by benzoylation and acetylation of **17**. When compound **11** was similarly treated with acetic acid-*d* instead of acetic acid*, the compound **24** isolated had no deuterium at C-4,

* Epimerization at C-4, enough possible from the data[2], should be taken into consideration for determining the configuration for **17**–**19**.

indicating that epimerization at C-4 did not occur during the reaction.

The H-3 signal of the 3-*O*-acyl derivatives having the *arabino* configuration appeared as a broad doublet having $J_{1,3}$ 0.7–1.0 Hz and $J_{3,4}$ 6.6–6.9 Hz, whereas that of the 3-epimers, **22–24**, gave a sharp doublet having $J_{3,4}$ 3.6–3.8 Hz. The 3-*O*-acyl derivatives **22**, **23**, and **24** could thus be assigned as having the *ribo* configuration and they are respectively the 3-epimers of **26**, **27**, and **28***. Thus the nucleophiles were incorporated almost exclusively at the equatorial and quasi-equatorial positions of products arising from **6** and **11**, respectively. In contrast, carboxylic acids in pyridine exceptionally added from the axial side of **11**. One possible explanation for this fact could be hydrogen bonding between O-4 and the N-H atom of a pyridinium salt, where a counter anion (carboxylate in the present case) should then be activated for attack at C-3 from the same side as O-4. Such an assumption was reinforced by a similar observed



reaction of **11** with acetic acid in γ-collidine (2,6-dimethylpyridine), where the reaction was much slower and gave a small amount of a ~1:1 mixture of **24** and **28** along with unchanged **11**, even under forcing conditions.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were determined with a Jasco DIP-4 polarimeter. ^{1}H-N.m.r. spectra were recorded at 270 MHz (JNM-EX270) with a Jeol spectrometer for solutions in $CDCl_3$ (internal Me_4Si). I.r. spectra were recorded for KBr pellets. Organic solutions were dried over $MgSO_4$ and evaporated under diminished pressure. Column chromatography was conducted on silica gel (Wakogel C-300). The catalyst refers to tributylhexadecylphosphonium bromide.

Methyl 4,6-O-benzylidene-2-deoxy-3-O-methyl-2-C-p-tolylsulfonyl-β-D-glucopyranoside (**7**). — (*a*) *From methyl 2-enopyranoside* **6**. To a stirred dispersion of sulfonyl alkene **6** (ref. 7, 39 mg, 0.1 mmol) in MeOH (5 mL) was added methanolic M NaOMe (0.12 mL). After stirring for 1.5 h at room temperature, the mixture was partitioned between EtOAc and sat. aq. NaCl. The organic layer was washed with water, dried, and evaporated to give a solid residue, which was subjected to column chromatography (20:1 C_6H_6–EtOAc) to give 39 mg (93%) of **7**. An analytical sample, prepared by

* The configurational assignment was confirmed by the reaction of **24** with methanolic sodium methoxide and sodium borodeuteride[6].

recrystallization, had m.p. 130–130.5° (from EtOH), $[\alpha]_D^{22}$ −80° (*c* 0.87, $CHCl_3$); ^{1}H-n.m.r.: δ 4.86 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.38 (dd, 1 H, $J_{2,3}$ 8.9 Hz, H-2), 4.03 (t, 1 H, $J_{3,4}$ 8.8 Hz, H-3), 3.76 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.46 (dt, 1 H, $J_{5,6a}$ 10.2, $J_{5,6e}$ 5.2 Hz, H-5), 3.72 (t, 1 H, $J_{6a,6e}$ 9.8 Hz, H-6*a*), 4.33 (dd, 1 H, H-6*e*), 5.55 (s, 1 H, PhCH), 3.49 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 2.45 (s, 3 H, Me), 7.80 (d, 2 H, *J* 8.3 Hz, C_6H_4), and 7.35–7.49 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{22}H_{26}O_7S$: C, 60.81; H, 6.03; S, 7.38. Found: C, 60.92; H, 5.98; S, 7.24.

(*b*) *From 1-enitol* **15**. Similar treatment of **15** (39 mg, 0.1 mmol) gave **7** in 91% yield.

(*c*) *From phenyl 2-enopyranoside* **11**. To a stirred dispersion of **11** (ref. 7, 93 mg, 0.2 mmol) in MeOH (6 mL) was added methanolic M NaOMe (0.6 mL) and the mixture was stirred for 40 min at room temperature and then partitioned between $CHCl_3$ and dilute HCl–sat. aq. NaCl. The organic layer was washed with water, dried, and evaporated to give 117 mg of a residue that smelled of phenol. Addition of EtOH gave 83 mg (95%) of **7**.

*Methyl 4,6-O-benzylidene-2,3-dideoxy-3-*C*-nitromethyl-2-*C*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**8**). — A solution of **6** (90 mg, 0.22 mmol) in $MeNO_2$ (4 mL) in the presence of Et_3N (0.4 mL) was heated under reflux for 6 h. To the mixture was added dilute HCl, sat. aq. NaCl, and EtOAc. The organic layer was washed with sat. NaCl, dried, and evaporated. Column chromatography (20:1 C_6H_6–EtOAc) gave **8** as a crude powder (102 mg) whose ^{1}H-n.m.r. spectrum revealed it to be contaminated by a small amount of unidentified product(s). Compound **8** (81 mg, 78%), isolated by recrystallization, had m.p. 185.5–186° (from 2-propanol), $[\alpha]_D^{22}$ −54° (*c* 1, $CHCl_3$); ν_{max} 1550 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 4.82 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 3.81 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2), 2.98 (tt, 1 H, $J_{3,4}$ 10.6, $J_{3,CH}$ 4.0, $J_{3,CH}$ 3.3 Hz, H-3), 3.77 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.56 (dt, $J_{5,6a}$ 10.2, $J_{5,6e}$ 4.6 Hz, H-5), 3.70 (t, 1 H, $J_{6a,6e}$ 10.2 Hz, H-6*a*), 4.32 (dd, 1 H, H-6*e*), 5.41 (dd, 1 H, J_{gem} 13.2 Hz, CH_2NO_2), 4.97 (dd, 1 H, CH_2NO_2), 5.54 (s, 1 H, PhCH), 3.24 (s, 3 H, OMe), 2.46 (s, 3 H, Me), 7.73 (d, 2 H, *J* 6.6 Hz, C_6H_4), and 7.35–7.49 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{22}H_{25}NO_8S$: C, 57.01; H, 5.44; N, 3.02; S, 6.92. Found: C, 57.20; H, 5.45; N, 3.04; S, 7.00.

*Methyl 3-*C*-(1-acetyl-2-oxopropyl)-4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**9**). — A solution of **6** (98 mg, 0.24 mmol) in 2,4-pentanedione (3 mL) in the presence of Et_3N (0.4 mL) was warmed for 8.75 h at ~80°. The mixture was partitioned between EtOAc and dilute HCl. The organic layer was washed with water, dried, and evaporated. A precipitate caused by addition of large excess of water was filtered off, dissolved in Me_2CO, and the solution evaporated. The remaining water was evaporated azeotropically with EtOH. The ^{1}H-n.m.r. spectrum of the residue showed it to be **9**, together with small amounts of unidentified product(s). Column chromatography (C_6H_6) of the residue gave 113 mg (92%) of **9**, which was pure as judged by t.l.c. and ^{1}H-n.m.r. spectroscopy. An analytical sample, prepared by recrystallization, had m.p. 131–132° (from diisopropyl ether), $[\alpha]_D^{25}$ −85° (*c* 1, $CHCl_3$); ν_{max}

1724 and 1703 cm^{-1} (CO); ^{1}H-n.mr.: δ 4.60 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 3.73 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 3.23 (dt, 1 H, $J_{3,4}$ 10.5, $J_{3,CH}$ 4.0 Hz, H-3), 4.40 (dd, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.41 (dt, 1 H, $J_{5,6a}$ 10.5, $J_{5,6e}$ 5.0 Hz, H-5), 3.71 (t, 1 H, $J_{6a,6e}$ 10.5 Hz, H-6*a*), 4.27 (dd, 1 H, H-6*e*), 4.86 (d, 1 H, $CHAc_2$), 5.44 (s, 1 H, PhCH), 2.99 (s, 3 H, OMe), 2.45 (s, 3 H, Me), 2.26 (s, 3 H, COMe), 2.19 (s, 3 H, COMe), 7.66 (d, 2 H, *J* 8.6 Hz, C_6H_4) and 7.33–7.36 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{26}H_{30}O_8S$: C, 62.14; H, 6.02; S, 6.38. Found: C, 62.28; H, 6.09; S, 6.52.

*Methyl 3-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**10**). — To a solution of **6** (90 mg, 0.22 mmol) in tetrahydrofuran (4 mL) was added aq. NH_3 (~30%, 0.6 mL). After stirring for 2 h at room temperature, the mixture was evaporated. To the resulting residue was added MeOH (4 mL) and Ac_2O (1 mL) and the mixture was stirred for 5.7 h and then evaporated. To the residue was added a large excess of water to give a precipitate. After stirring for 30 min, the mixture was filtered. The precipitate was dissolved in Me_2CO and the solution evaporated. The residue was chromatographed with 10:1 (v/v) C_6H_6–EtOAc to give successively 84 mg (81%) of **10** and 18 mg (17%) of an unidentified product. An analytical sample of **10**, prepared by recrystallization, had m.p. 203–204° (from EtOH), $[\alpha]_D^{22}$ −61° (*c* 0.87, $CHCl_3$); ν_{max} 1663 and 1546 cm^{-1} (NHAc); ^{1}H-n.m.r. (100 MHz): δ 4.71 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.52 (dd, 1 H, $J_{2,3}$ 10.6 Hz, H-2), 3.93 (dt, 1 H, $J_{3,4}$ 10.3, $J_{3,NH}$ 6.6 Hz, H-3), 4.45 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.39 (dt, 1 H, $J_{5,6a}$ 10.2, $J_{5,6e}$ 5.0 Hz, H-5), 3.74 (t, 1 H, $J_{6a,6e}$ 10.3 Hz, H-6*a*), 4.29 (dd, 1 H, H-6*e*), 5.96 (d, 1 H, NH), 5.53 (s, 1 H, PhCH), 3.27 (s, 3 H, OMe), 2.44 (s, 3 H, Me), 1.96 (s, 3 H, NCOMe), 7.71 (d, 2 H, *J* 8.6 Hz, C_6H_4), and 7.32–7.47 (m, 7 H, C_6H_4 and C_6H_5).

Anal. Calc. for $C_{23}H_{27}NO_7S$: C, 59.86; H, 5.90; N, 3.03; S, 6.95. Found: C, 59.86; H, 5.89; N, 2.96; S, 7.08.

*1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-p-tolylsulfonyl-*D*-erythro-hex-1-enitol* (**12**). — To a solution of **11** (93 mg, 0.2 mmol) in MeCN (7 mL) was added $NaBH_4$ (26 mg). After stirring for 15.5 h at room temperature, the mixture was evaporated and addition of large excess of water caused a precipitate, which was filtered to give 72 mg (97%) of **12**. An analytical sample, prepared by recrystallization, had m.p. 185.5–186.5° (from C_6H_6–hexane), $[\alpha]_D^{22}$ +114° (*c* 1, CH_2Cl_2); ν_{max} 1620 (O–C=C); ^{1}H-n.m.r.: δ 7.57 (d, 1 H, $J_{1,3qa}$ 2.2 Hz, H-1), 2.29 (ddd, 1 H, $J_{3qa,4}$ 9.5, $J_{3qa,3qe}$ 15.2 Hz, H-3*qa*), 2.67 (dd, 1 H, $J_{3qe,4}$ 5.8 Hz, H-3*qe*), 3.85 (dt, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.45 (m, 1 H, H-5), 3.75–3.80 (m, 2 H, H-6*a*, and -6*e*), 5.56 (s, 1 H, PhCH), 2.44 (s, 3 H, Me), 7.75 (d, 2 H, *J* 8.5 Hz, C_6H_4), and 7.3–7.5 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{20}H_{20}O_5S$: C, 64.50; H, 5.41; S, 8.61. Found: C, 64.39; H, 5.20; S, 8.73.

Similar treatment of **11** (93 mg) with $NaBD_4$ (26 mg) afforded the 3-deuterio derivative **13** in 95% yield.

*1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitromethyl-2-*C*-p-tolylsulfonyl-*D*-arabino-hex-1-enitol* (**14**). — A solution of **11** (127 mg, 0.27 mmol) in $MeNO_2$ (5 mL) in the presence of Et_3N (0.6 mL) was kept for 3 days at room temperature. To the

solution was added EtOAc, sat. aq. NaCl, and dilute HCl. The organic layer was washed with water, dried, and evaporated. The resulting syrup was dissolved in EtOAc, washed successively with M NaOH to remove the phenol generated and water, dried, and evaporated. Crystallization gave 88 mg (75%) of **14**; m.p. 164–174° (from EtOH), $[\alpha]_D^{25}$ +136° (*c* 1, Me_2CO); ν_{max} 1602 (O–C=C) and 1550 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 7.74 (d, 1 H, $J_{1,3}$ 1.6 Hz, H-1), 3.20 (m, 1 H, $J_{3,4}$ 9.2, $J_{3,CH}$ 4.0, and $J_{3,CH}$ 6.5 Hz, H-3), 4.05 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.47 (m, 1 H, H-5), 3.56–3.58 (m, 2 H, H-6*a*, and -6*e*), 5.06 (dd, 1 H, $J_{CH,CH}$ 14.2 Hz, CH_2NO_2), 4.64 (dd, 1 H, CH_2NO_2), 5.55 (s, 1 H, PhCH), 2.45 (s, 3 H, Me), 7.73 (d, 2 H, *J* 8.3 Hz, C_6H_4), and 7.31–7.41 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{21}H_{21}NO_7S$: C, 58.46; H, 4.91; N, 3.25; S, 7.43. Found: C, 58.59; H, 4.97; N, 3.04; S, 7.24.

Addition of methanol to **14**. — To a solution of **14** (112 mg, 0.26 mmol) in MeOH (9 mL) was added methanolic M NaOMe (1.5 mL) and the mixture was stirred for 4 h at room temperature. The mixture was partitioned between EtOAc and sat. aq. NaCl. The organic layer was washed with dilute HCl and water, dried, and evaporated to give a solid residue (119 mg), whose ^{1}H-n.m.r. spectrum showed that it consisted of the α anomer **16** and β anomer **8** in the ratio of ~2:3. These were separated by fractional crystallization from EtOH; the first crop was 27 mg (22%) of **16** and the second 35 mg (29%) of **8**, the latter compound being identical with an authentic sample. Physical data for **16**: m.p. 243–244°, $[\alpha]_D^{25}$ +58° (*c* 1, $CHCl_3$); ν_{max} 1558 cm^{-1} (NO_2); ^{1}H-n.m.r.: δ 4.59 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.00 (dd, 1 H, $J_{2,3}$ 11.9 Hz, H-2), 3.06 (m, 1 H, $J_{3,CH}$ 2.8, $J_{3,CH}$ 4.6 Hz, H-3), 3.56–3.58 (m, 2 H, H-4, and -5), 3.69 (t, 1 H, $J_{5,6a}$ 10.0, $J_{6a,6e}$ 10.3 Hz, H-6*a*), 4.22 (dd, 1 H, $J_{5,6e}$ 3.6 Hz, H-6*e*), 5.10 (t, 1 H, $J_{CH,CH}$ 15.5 Hz, CH_2NO_2), 4.95 (dd, 1 H, CH_2NO_2), 5.51 (s, 1 H, PhCH), 3.27 (s, 3 H, OMe), 2.48 (s, 3 H, Me), 7.78 (d, 2 H, *J* 8.3 Hz, C_6H_4), and 7.26–7.40 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{22}H_{25}NO_8S$: C, 57.01; H, 5.44; N, 3.02; S, 6.92. Found: C, 57.12; H, 5.36; N, 3.08; S, 6.95.

*1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-*D*-arabino-hex-1-enitol* (**15**). — To a solution of **11** (24 mg, 0.05 mmol) in MeOH (2.5 mL) was added methanolic M NaOMe (0.06 mL). After stirring for 40 min at room temperature, the mixture was partitioned between EtOAc and sat. aq. NaCl. The organic layer was washed with dilute HCl and water, dried, and evaporated. The ^{1}H-n.m.r. spectrum of the residue (25 mg; contaminated by a trace of phenol) showed that it was almost pure **15**. An analytical sample, prepared by recrystallization, had m.p. 146–147.5° (from EtOH), $[\alpha]_D^{15}$ −59° (*c* 1.2, $CHCl_3$); ν_{max} 1620 cm^{-1} (O–C=C); ^{1}H-n.m.r.: δ 7.58 (d, 1 H, $J_{1,3}$ 1.0 Hz, H-1), 4.47 (dd, 1 H, $J_{3,4}$ 7.3 Hz, H-3), 3.90 (dd, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 4.04 (dt, 1 H, $J_{5,6a}$ 10.0, $J_{5,6e}$ 5.0 Hz, H-5), 3.83 (t, 1 H, $J_{6a,6e}$ 10.0 Hz, H-6*a*), 4.44 (dd, 1 H, H-6*e*), 5.52 (s, 1 H, PhCH), 3.48 (s, 3 H, OMe), 2.42 (s, 3 H, Me), 7.76 (m, 2 H, *J* 8.3 Hz, C_6H_4), and 7.28–7.57 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.70; H, 5.38; S, 8.05.

Reaction of **11** *with hydrogen peroxide*. A mixture of **11** (485 mg, 1.0 mmol), 35% H_2O_2 (22 mL), the catalyst (11 mg), C_6H_6 (10 mL), and M aq. NaOH (2 mL) was stirred.

Additional amounts of H_2O_2 (2 mL) and M NaOH (2 mL) were added after 3 and 4 h, respectively. After stirring for 21 h, the mixture was partition between EtOAc and water. The organic layer was washed with 10% aq. thiosulfate and water, dried, and evaporated. The residue was chromatographed with 50:1 and 3:1 (v/v) C_6H_6–EtOAc to give successively 72 mg of almost pure epoxide **20** (~14%) contaminated with small amounts of **11** and an unidentified product, 165 mg (39%) of the peroxide **18**, 58 mg (11%) of the sulfonyl alcohol **19**, and 28 mg (7%) of the 1-enitol **17**. Physical data for **18**: m.p. 154.5–156° (washed with acetone), $[\alpha]_D^{15}$ −102° (*c* 1.0, $CHCl_3$); ν_{max} 3358 (OOH), 1616 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.75 (d, 1 H, $J_{1,3}$ 1.3 Hz, H-1), 4.37 (dd, 1 H, $J_{3,4}$ 8.0 Hz, H-3), 4.48 (dd, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 3.87–4.01 (m, 2 H, H-5 and -6*a*), 4.43 (dd, 1 H, $J_{5,6e}$ 4.2, $J_{6a,6e}$ 9.7 Hz, H-6*e*), 5.64 (s, 1 H, PhCH), 2.45 (s, 3 H, Me), 9.84 (broad s, 1 H, OOH), 7.86 (d, 2 H, *J* 8.3 Hz, C_6H_4), and 7.32–7.47 (m, 7 H, C_6H_4 and C_6H_5).

Anal. Calc. for $C_{20}H_{20}O_7S$: C, 59.40; H, 4.98; S, 7.93. Found: C, 59.65; H, 5.05; S, 7.96.

Physical data for **19**: m.p. 148.5–149° (from C_6H_6–hexane), $[\alpha]_D^{15}$ −35° (*c* 1.1, CH_2Cl_2); ν_{max} 3530 cm^{-1} (OH); ^{1}H-n.m.r.: δ 5.52 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 3.69 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 4.71 (dt, 1 H, $J_{3,4}$ 9.2, $J_{3,OH}$ 2.3 Hz, H-3), 3.78 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 3.64 (dt, 1 H, $J_{5,6a}$ 10.2, $J_{5,6e}$ 4.4 Hz, H-5), 3.76 (t, 1 H, $J_{6a,6e}$ 10.2 Hz, H-6*a*), 4.33 (dd, 1 H, H-6*e*), 5.60 (s, 1 H, PhCH), 2.46 (s, 3 H, Me), 7.72 (d, 2 H, *J* 8.3 Hz, C_6H_4), and 7.35–7.49 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{26}H_{26}O_7S$: C, 64.72; H, 5.43; S, 6.64. Found: C, 64.75; H, 5.30; S, 6.41.

Physical data for **20**: m.p. 167–168° (from C_6H_6–hexane, twice), $[\alpha]_D^{15}$ −64° (*c* 0.9, CH_2Cl_2); ^{1}H-n.m.r. (100 MHz, JNM-4H-100, Jeol): δ 6.33 (s, 1 H, H-1), 4.44 (s, 1 H, H-3), 3.6–4.6 (m, 5 H, H-2, -4, -5, -6*a*, and -6*e*), 5.57 (s, 1 H, PhCH), 2.48 (s, 3 H, Me), 7.66 (d, 2 H, *J* 8.3 Hz, C_6H_4), 6.7–7.5 (m, 12 H, 2 × C_6H_5 and C_6H_4).

Anal. Calc. for $C_{26}H_{24}O_7S$: C, 64.99; H, 5.03; S, 6.67. Found: C, 65.09; H, 5.12; S, 6.77.

*1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-arabino-hex-1-enitol* (**17**). — A. *Method I.* A mixture of **11** (940 mg, 2.0 mmol), 35% H_2O_2 (20 mL), the catalyst (117 mg), C_6H_6 (40 mL), and M aq. NaOH (3 mL) was stirred for 70 min and then extracted with CH_2Cl_2 (100 mL) and 1,2-dichloroethane (100 mL). The organic layer combined was washed with water, dried, and evaporated. The residue was dissolved in CH_2Cl_2 (20 mL) and 0.3 mL (equimolar) of DBU was added. After 20 min, 0.3 mL of DBU was again added and the mixture was stirred for 15 min, diluted with C_6H_6, and washed successively with water, sat. aq. $NaHCO_3$, water, and dried. After filtration through active charcoal, the filtrate was evaporated. The residue was chromatographed with silica gel (C-200) eluting with 20:1 and 10:1 (v/v) C_6H_6–EtOAc to give 333 mg (42%) of **17**. Physical data for **17**: m.p. 181–183° (from C_6H_6), $[\alpha]_D^{15}$ +99° (*c* 1.1, CH_2Cl_2); ν_{max} 3500 (OH), 1610 cm^{-1} (O–C=C); ^{1}H-n.m.r.: δ 7.57 (d, 1 H, $J_{1,3}$ 0.8 Hz, H-1), 4.59 (m, 1 H, $J_{3,4}$ 7.2, $J_{3,OH}$ 3.0 Hz, H-3), 3.81–3.96 (m, 3 H, H-4, 5, and 6*a*), 4.41 (dd, 1 H, $J_{5,6e}$ 3.5, $J_{6a,6e}$ 9.8 Hz, H-6*e*), 3.79 (d, 1 H, OH), 5.58 (s, 1 H, PhCH), 2.42 (s, 3 H, Me), 7.79 (m, 2 H, *J* 8.3 Hz, C_6H_4), and 7.33–7.57 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{20}H_{20}O_6S$: C, 61.84; H, 5.19; S, 8.25. Found: C, 61.65; H, 5.16; S, 7.98.

B. *Method II.* To a solution of **11** (53 mg, 0.11 mmol) in tetrahydrofuran (5 mL) was added 0.7M aq. LiOH (0.5 mL, 3.2 mol. equiv.) and the mixture was stirred for 4 h at room temperature. After dilution with EtOAc, AcOH (0.5 mL) was added. The mixture was washed successively with water, dilute aq. NaOH, water, dilute aq. HCl, aq. Na_2CO_3, and water and then dried over Na_2SO_4, and evaporated. The residue was chromatographed with 100:1 (v/v) CH_2Cl_2–EtOAc and then 15:1 (v/v) C_6H_6–EtOAc to give **21** as the first-eluted fraction (6 mg, 11%) and then **17** as the second one (28 mg, 63% yield). The latter was identical with an authentic sample.

*A mixture of 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-phenyl-2-*C*-p-tolylsulfonyl-*D*-arabino- and -*D*-ribo-hex-1-enitols* (**21**). — To a solution of **11** (216 mg, 0.46 mmol) in C_6H_6 (10 mL) in the presence of the catalyst (20 mg) was added 0.05M NaOH (12 mL, 2.6 mmol) and the mixture was stirred for 6 h at room temperature. After dilution with C_6H_6, the organic layer was washed with water, dried, and evaporated. The residue was chromatographed with 50:1 and then 10:1 (v/v) C_6H_6–EtOAc to afford successively 20 mg (9%) of **11**, 137 mg (63%) of **21**, and 28 mg (16%) of **17**. Compound **21** crystallized from 2-propanol proved to be a mixture of 3-epimers from its ^{1}H-n.m.r. spectrum; the methyl group of the tolyl moiety appeared as two peaks in the ratio of 8:1 (by integration); m.p. 146–154°, ν_{max} 1630 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 2.43 (s, Me, major) and 2.38 (s, Me, minor).

Anal. Calc. for $C_{26}H_{24}O_6S$: C, 67.23; H, 5.21; S, 6.90. Found: C, 67.28; H, 5.21; S, 6.66.

*Methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**25**). — To a solution of **17** (111 mg, 0.29 mmol) in MeOH (3 mL) and tetrahydrofuran (3 mL) was added NaOMe (3 mg, 0.06 mmol) and the mixture was kept for a long time (2 days), because a good solvent system for t.l.c. was not found. After addition of AcOH (0.5 mL) and C_6H_6, the organic layer was washed with aq. NaCl, water, sat. aq. $NaHCO_3$, and water, dried, and evaporated. The residue was chromatographed with 15:1 (v/v) C_6H_6–EtOAc to give 111 mg (92%) of **25** as a syrup that crystallized from diisopropyl ether; m.p. 111–112° (from diisopropyl ether), $[\alpha]_D^{15}$ −51° (*c* 0.7, $CHCl_3$); ν_{max} 3530 cm^{-1} (OH); ^{1}H-n.m.r.: δ 4.68 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 3.33 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 4.59 (dt, 1 H, $J_{3,4}$ 9.0, $J_{3,OH}$ 2.0 Hz, H-3), 3.66 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.49 (dt, 1 H, $J_{5,6a}$ 10.3, $J_{5,6e}$ 4.9 Hz, H-5), 3.75 (t, 1 H, $J_{6a,6e}$ 10.3 Hz, H-6*a*), 4.32 (dd, 1 H, H-6*e*), 5.57 (s, 1 H, PhCH), 3.35 (s, 3 H, OMe), 2.47 (s, 3 H, Me), 7.77 (d, 2 H, *J* 8.3 Hz, C_6H_4), and 7.35–7.52 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{21}H_{24}O_7S$: C, 59.99; H, 5.75; S, 7.62. Found: C, 60.10; H, 5.74; S, 7.58.

*1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-m-chlorobenzoyl-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-ribo-hex-1-enitol* (**22**). — To a stirred solution of **11** (372 mg, 0.80 mmol) in pyridine (3.2 mL) at ~40° was added Ac_2O (0.2 mL, 1.80 mmol) and *m*-chlorobenzoic acid (1.064 g, 6.8 mmol). After stirring for 16 h, the mixture was diluted with EtOAc and washed successively with water, sat. aq. $NaHCO_3$, and water, and then dried and

evaporated. The resulting residue was washed with water and evaporated; the ^{1}H-n.m.r. spectrum showed the product to be **22** contaminated with its 3-epimer **26** (<8%). Recrystallization gave 337 mg (80% yield) of **22**; m.p. 221–223° (from 2-propanol), $[\alpha]_D^{15}$ +180° (*c* 1.0, $CHCl_3$); ν_{max} 1723 (C=O) and 1612 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.87 (d, 1 H, $J_{1,5}$ 0.7 Hz, H-1), 6.34 (d, 1 H, $J_{3,4}$ 3.8 Hz, H-3), 4.02 (dd, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 4.25 (dt, 1 H, $J_{5,6a}$ 10.5, $J_{5,6e}$ 5.0 Hz, H-5), 3.90 (t, 1 H, $J_{6a,6e}$ 10.6 Hz, H-6*a*), 4.54 (dd, 1 H, H-6*e*), 5.58 (s, 1 H, PhCH), 2.16 (s, 3 H, Me), 7.70 (m, 2 H, *J* 8.5 Hz, C_6H_4), and 7.33–7.57 (m, 11 H, C_6H_5 and 2 × C_6H_4).

Anal. Calc. for $C_{27}H_{23}O_7SCl$: C, 61.54; H, 4.40; S, 6.08. Found: C, 61.51; H, 4.44; S, 6.28.

*1,5-Anhydro-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-ribo-hex-1-enitol* (**23**). — To a stirred solution of **11** (100 mg, 0.22 mmol) in pyridine (0.86 mL) was added benzoic anhydride (108.5 mg, 0.48 mmol) and benzoic acid (414 mg, 1.8 mmol) at ~40° and the mixture was stirred for 14 h at ambient temperature. Addition of EtOAc (15 mL) and sat. aq. $NaHCO_3$ (10 mL) caused a precipitate, which was washed with small amounts of EtOAc to give 64 mg (60% yield) of **23**. Its ^{1}H-n.m.r. spectrum showed it to be pure **23**; m.p. ~245° (dec.) (from 2-propanol), $[\alpha]_D^{15}$ +199° (*c* 1.0, $CHCl_3$); ν_{max} 1722 (C=O) and 1608 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.85 (d, 1 H, $J_{1,5}$ 0.7 Hz, H-1), 6.36 (d, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 4.01 (dd, 1 H, $J_{4,5}$ 10.5 Hz, H-4), 4.28 (dt, 1 H, $J_{5,6a}$ 10.4, $J_{5,6e}$ 5.3 Hz, H-5), 3.90 (t, 1 H, $J_{6a,6e}$ 10.4 Hz, H-6*a*), 4.51 (dd, 1 H, H-6*e*), 5.58 (s, 1 H, PhCH), 2.12 (s, 3 H, Me), and 7.05–7.73 (m, 12 H, 2 × C_6H_5 and C_6H_4).

Anal. Calc. for $C_{27}H_{24}O_7S$: C, 65.84; H, 4.91; S, 6.51. Found: C, 66.00; H, 4.98; S, 6.56.

The organic layer was washed with water, sat. aq. $NaHCO_3$, dried, and evaporated. The residue was chromatographed with 30:1 (v/v) C_6H_6–EtOAc to give 16 mg of **23**, 20 mg of a mixture of **23** and **27** (~1:1), and 4 mg (4%) of **27**, identical with an authentic sample.

*3-*O*-Acetyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-ribo-hex-1-enitol* (**24**). — To a stirred solution of **11** (372 mg, 0.8 mmol) in pyridine (3.2 mL) was added AcOH (408 mg, 6.8 mmol) and Ac_2O (0.2 mL) at ~40° and the mixture was stirred for 10 h at room temperature. The mixture was partitioned between EtOAc (15 mL) and sat. aq. $NaHCO_3$ (10 mL) and the organic layer was washed with water, dried, and evaporated. The residue was chromatographed with C_6H_6 to give successively 276 mg (80%) of **24**, 48 mg (14%) of a 1:1 mixture of **24** and **28**, and 17 mg (5%) of **28**. Physical data for **24**; m.p. 158.5–159.5° (from 2-propanol), $[\alpha]_D^{15}$ +142° (*c* 1.1, $CHCl_3$); ν_{max} 1735 (C=O) and 1608 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.77 (d, 1 H, $J_{1,5}$ 0.7 Hz, H-1), 6.05 (d, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 3.84 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4), 4.19 (dt, 1 H, $J_{5,6a}$ 10.3, $J_{5,6e}$ 5.3 Hz, H-5), 3.85 (t, 1 H, $J_{6a,6e}$ 10.6 Hz, H-6*a*), 4.51 (dd, 1 H, H-6*e*), 5.54 (s, 1 H, PhCH), 2.16 (s, 3 H, Me), 2.43 (s, 3 H, Ac), 7.75 (m, 2 H, *J* 7.3 Hz, C_6H_4), and 7.31–7.37 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{22}H_{22}O_7S$: C, 61.38; H, 5.15; S, 7.45. Found: C, 61.48; H, 5.27; S, 7.49.

Treatment of **11** (186 mg, 0.4 mmol) with AcOH (0.2 mL, 3.4 mmol) in pyridine

(1.6 mL) in the presence of Ac_2O (0.1 mL, 0.9 mmol) for 68 h at room temperature, followed by similar processing afforded the 3-acetate **24** (131 mg, 76%).

The same reaction of **11** (186 mg) except the use of acetic acid-*d* instead of AcOH gave **24** (129 mg, 75%).

Similar treatment of **11** (186 mg) in γ-collidine (3 mL) instead of pyridine for 70 h at room temperature resulted in the recovery of **11**. Even after 70 h at 70°, almost all starting material was recovered, together with small amount (< 5%) of a ~1:1 mixture of **24** and **28**.

*1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-m-chlorobenzoyl-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-arabino-hex-1-enitol* (**26**). — To a solution of **17** (58.2 mg, 0.15 mmol) in pyridine (5 mL) was added *m*-chlorobenzoyl chloride (185 mg, 1.06 mmol) at room temperature and the mixture was stirred for 5 h. A precipitate generated by the addition of water w as filtered off and washed with dilute aq. $NaHCO_3$. The precipitate, which showed two spots on t.l.c., was chromatographed with 40:1 (v/v) C_6H_6–EtOAc to give 65 mg (82%) of **26**; m.p. ~215° (from 2-propanol–acetone), $[\alpha]_D^{15}$ −19° (*c* 1.0, $CHCl_3$); ν_{max} 1738 (C=O) and 1618 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.83 (br s, 1 H, $J_{1,3} = J_{1,4} = 1.0$ Hz, H-1), 6.39 (dd, 1 H, $J_{3,4}$ 6.9 Hz, H-3), 4.10–4.22 (m, 2 H, H-4, and -5), 3.90 (t, 1 H, $J_{5,6a} = J_{6a,6e} = 10.5$ Hz, H-6*a*), 4.49 (dd, 1 H, $J_{5,6e}$ 4.6 Hz, H-6*e*), 5.50 (s, 1 H, PhCH), 2.34 (s, 3 H, Me), 7.09–7.75 (m, 13 H, C_6H_5 and 2 × C_6H_4).

Anal. Calc. for $C_{27}H_{23}O_7SCl$: C, 61.54; H, 4.40; S, 6.08. Found: C, 61.68; H, 4.41; S, 6.26.

*1,5-Anhydro-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-arabino-hex-1-enitol* (**27**). — To a solution of **17** (58.2 mg, 0.15 mmol) in pyridine (3 mL) was added BzCl (168 mg, 1.20 mmol) and the mixture was stirred overnight at room temperature and then partitioned between water and EtOAc. After filtration of a precipitate (44 mg), the filtrate was washed with water, dilute aq. $NaHCO_3$, water, dilute aq. HCl, and water, dried, and then evaporated to give 28 mg of crystalline material. The residue and the precipitate, whose ^{1}H-n.m.r. spectra showed them to be almost pure **27**, were combined and recrystallized to give 59 mg (80%) of **27**; m.p. 219–221° (from EtOAc), $[\alpha]_D^{15}$ −13° (*c* 0.9, $CHCl_3$); ν_{max} 1728 (C=O) and 1615 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.82 (br s, 1 H, $J_{1,3} = J_{1,4} = 1.0$ Hz, H-1), 6.36 (dd, 1 H, $J_{3,4}$ 6.6 Hz, H-3), 4.10–4.18 (m, 2 H, H-4, and -5), 3.98 (t, 1 H, $J_{5,6a} = J_{6a,6e} = 10.5$ Hz, H-6*a*), 4.49 (dd, 1 H, $J_{5,6e}$ 4.5 Hz, H-6*e*), 5.49 (s, 1 H, PhCH), 2.31 (s, 3 H, Me), 7.06–7.73 (m, 13 H, 2 × C_6H_5 and C_6H_4).

Anal. Calc. for $C_{27}H_{24}O_7S$: C, 65.84; H, 4.91; S, 6.51. Found: C, 65.81; H, 4.97; S, 6.41.

*3-*O*-Acetyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-2-*C*-p-tolylsulfonyl-*D*-arabino-hex-1-enitol* (**28**). — To a solution of **17** (58.2 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL) in the presence of pyridine (0.6 mL) was added Ac_2O (0.74 mL). The mixture was kept overnight and partitioned between C_6H_6 and water. The organic layer was washed with sat. aq. $NaHCO_3$, and water, dried, and evaporated to give almost pure **28** in quantitative yield; m.p. 179–181° (from 2-propanol–acetone), $[\alpha]_D^{15}$ +57° (*c* 0.9, $CHCl_3$); ν_{max} 1745 (C=O) and 1620 cm^{-1} (O–C=C–Ts); ^{1}H-n.m.r.: δ 7.74 (br s, 1 H, $J_{1,3} = J_{1,4} = 1.0$

Hz, H-1), 6.02 (dd, 1 H, $J_{3,4}$ 6.9 Hz, H-3), 3.97–4.05 (m, 2 H, H-4, and -5), 3.86 (t, 1 H, $J_{5,6a}$ 10.3, $J_{6a,6e}$ 10.6 Hz, H-6*a*), 4.44 (dd, 1 H, $J_{5,6e}$ 4.3 Hz, H-6*e*), 5.50 (s, 1 H, PhCH), 2.44 (s, 3 H, Me), 1.96 (s, 3 H, OAc), 7.73 (d, 2 H, *J* 7.9 Hz, C_6H_4), and 7.31–7.42 (m, 7 H, C_6H_5 and C_6H_4).

Anal. Calc. for $C_{22}H_{22}O_7S$: C, 61.38; H, 5.15; S, 7.45. Found: C, 61.54; H, 5.20; S, 7.73.

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