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PREPARATION OF 4,6-*O*-BENZYLIDENE-2-*C*- AND -3-*C*-*p*-TOLYLSULFONYLHEX-2-ENOPYRANOSIDE DERIVATIVES AND A 2-*C*-*p*-TOLYLSULFONYLHEX-2-ENITOL DERIVATIVE*

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ABSTRACT

4,6-*O*-Benzylidenehex-2-enopyranoside derivatives having a 2-*C*- or 3-*C*-*p*-tolylsulfonyl group were synthesized from appropriate nitro sugars by the addition of *p*-toluenesulfinic acid followed by elimination of nitrous acid. 1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-D-*erythro*-hex-2-enitol was similarly prepared. Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*- and -3-*C*-*p*-tolylsulfonyl-α-D-*erythro*-hex-2-enopyranosides were alternatively ynthesized from methyl 2,3-anhydro-α-D-allo- and -mannopyranosides, respectively, by cleavage of the oxirane ring with sodium *p*-toluenethiolate, followed by oxidation.

INTRODUCTION

α-Sulfonylalkenes are unique and versatile intermediates in synthetic work, because the sulfonyl group, after introduction of a nucleophile at its β-position, may be converted into such useful functions as a carbonyl group[1] or a double bond[2]. Although pyranose derivatives having a 2-phenylsulfonyl-2-trimethylsilylvinyl group at position 5 have been used as key intermediates for the synthesis of maytansinoids[3], no studies of a sugar derivative having an α-sulfonylalkene moiety on a pyranose ring have been reported. Accordingly, we synthesized several 2-*C*- and 3-*C*-*p*-tolylsulfonylhex-2-enopyranoside derivatives†.

*Dedicated to Dr. R. Stuart Tipson.

†A part of the work was reported in preliminary form[4].

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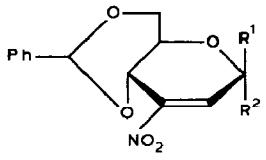

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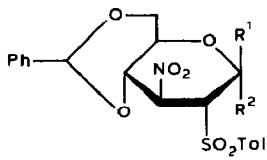
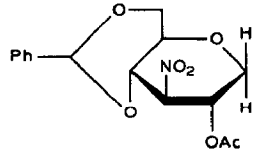
2 R^1 = OPh, R^2 = H
3 R^1 = R^2 = H
4 R^1 = H, R^2 = OMe



5 R^1 = OMe, R^2 = H
6 R^1 = OPh, R^2 = H
7 R^1 = R^2 = H
8 R^1 = H, R^2 = OMe



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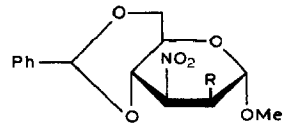
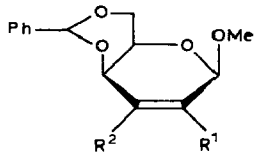
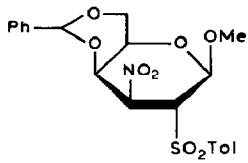


10 R = SO_2Tol



11 R^1 = H, R^2 = NO_2
12 R^1 = SO_2Tol, R^2 = H



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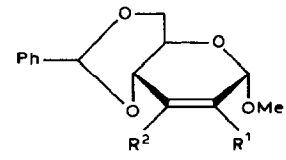
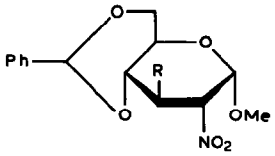


14 R^1 = NO_2, R^2 = H
15 R^1 = H, R^2 = SO_2Tol

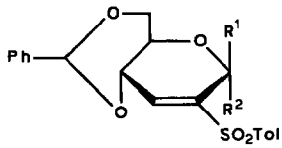
Tol = *p*-tolyl

RESULTS AND DISCUSSION

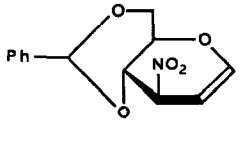
When methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**) was treated with sodium *p*-toluenesulfinate in benzene–water in the presence of tributylhexadecylphosphonium bromide as a phase-transfer catalyst, almost all of the starting material **1** was recovered. However, in the presence of acetic acid, a heterogeneous reaction was smoothly induced to give in high yield methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-2-*C*-*p*-tolylsulfonyl-β-D-glucopyranoside (**5**), identical with an authentic specimen[5]. Similar treatment of the phenyl glycoside **2** afforded the adduct **6** in 90% yield. Similar reaction of the 1,5-anhydro derivative **3** gave a mixture, from which the adduct **7** having the D-*gluco* configuration was isolated in moderate yield (64%) after chromatographic separation. The yield of **7** was raised to 77% by treatment of acetate **9** with sodium *p*-toluenesulfinate (2 mol. equiv.) in benzene–water with the phase-transfer catalyst for 4 days at 40°. The α-anomer **4** and *threo* isomer **11** afforded the α-D-manno-pyranoside **10** and the β-D-galactopyranoside **13**, respectively, in good yields by the heterogeneous reaction-system. Reaction of the 2-nitrohex-2-enopyranoside **14** afforded the adduct **16** having the α-D-*gluco* configuration in 73% yield. The structures of adducts thus prepared were determined by elemental analysis, and by i.r. and ^{1}H-n.m.r. (100 MHz) spectra. The 100-MHz ^{1}H-n.m.r. spectrum of **16** was



16 R = SO_2Tol
17 R = OH
18 R = NO_2



19 R^1 = OMe, R^2 = H
20 R^1 = OPh, R^2 = H
21 R^1 = R^2 = H
22 R^1 = H, R^2 = OMe



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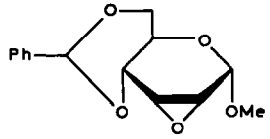

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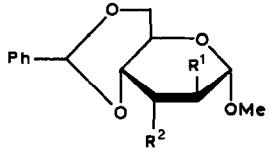
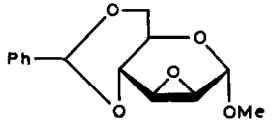


25 R^1 = SO_2Tol, R^2 = OH
26 R^1 = OH, R^2 = SO_2Tol
27 R^1 = OH, R^2 = STol
28 R^1 = OH, R^2 = SOTol



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difficult to analyze, and the structure of **16** was determined from its 200-MHz ^{1}H-n.m.r. spectrum and by comparison with the spectrum of a derivative of **16** partially deuterated at C-2.

The adducts thus prepared were respectively treated with triethylamine to convert them into the corresponding sulfonyl alkenes. Elimination of nitrous acid from the β-D-*gluco* isomers **5** and **6** occurred smoothly within 30 min at room temperature to afford methyl and phenyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-*erythro*-hex-2-enopyranosides (**19** and **20**, respectively) in high yields. The former compound was directly prepared from the corresponding nitro alkene **1** in high yield by treatment with *p*-toluenesulfinate (2.2 mol. equiv.) and triethylamine. The *galacto* isomer **13** gave the sulfonyl alkene **12** in 65% yield by treatment with triethylamine. Treatment of the 1,5-anhydro derivative **7** with triethylamine (1.2 mol. equiv.) in *N*,*N*-dimethylformamide for 2 h at room temperature afforded the sulfonyl alkene **21** in 78% yield, together with 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-D-*arabino*-hex-1-enitol[6,7] (**23**, 14% yield), which was formed[6] *via* the nitro alkene **3**. Such an elimination of *p*-toluenesulfinic acid, being competitive with that of nitrous acid, became more serious with the 2-nitro derivative **16** and the α-D-*manno* isomer **10**. The starting material (**16**) was recovered almost quantitatively upon treatment with triethylamine in dichloromethane for 1 h at room temperature. Even after 18 h, some compound **16** was still recovered (10% yield) together with the desired sulfonyl alkenes **15** (22% yield). Similar treatment of the α-D-*manno* isomer **10** for 1 h at room temperature gave a

mixture of sulfonyl alkene **22** and 2-*C*-nitro-3-*C*-sulfonyl-α-D-glucopyranoside **16** as the major products, as well as small proportions of the the α-D-*gluco* isomer **8**, the 2-nitro alkene **14**, and 2-nitro alcohol **17**; the latter two compounds were identical with the corresponding authentic samples[8]. As has been reported[9], elimination of *p*-toluenesulfinic acid from **10** afforded the 3-nitro alkene **4**, and **4** reacted with nitrous acid (which was generated during the formation of sulfonyl alkene **22**) to give the 2-nitro alkene **14**. The 2-nitro alkene **14** thus formed underwent addition with *p*-toluenesulfinic acid; the adduct **16** was stable under the conditions employed, as previously described. Several attempts to improve the yield of **22**, using potassium hydroxide, 1,8-diazabicyclo[5.4.0]undec-7-ene, and potassium *tert*-butoxide instead of triethylamine, failed.

Competitive elimination of *p*-toluenesulfinic acid thus decreased the yields of **22** and **15**. Apparently H-2 is more acidic than H-3 due to the inductive effects of O-5 and O-1; this factor is exemplified in the selective formation of 2-nitro alkene **14** from the 2,3-dinitro compound[9] **18**. Thus the greater extent of elimination of *p*-toluenesulfinic acid in **16** than in **5** is understandable. In the *gluco* isomer **5**, abstraction of H-3 should generate $A^{(1,3)}$ strain between the nitronate function and O-4, whereas this is not the case with the *galacto* isomer **13**; this rationalizes the lower yield of **12** as compared with **19**. Elimination of *p*-toluenesulfinic acid from the α-D-*manno* isomer **10** may be favored because of the arrangement of the sulfonyl group and H-3 appropriate for E2 elimination, and by the absence of $A^{(1,3)}$ strain between the generated nitronate and the sulfonyl group. If this is the case, the α-D-*gluco* isomer **8** should be a more-plausible precursor for **22** than the α-D-*manno* isomer **10**. This expectation was indeed realized; almost exclusive formation of **22** was observed on treating the α-D-*gluco* isomer **8** with triethylamine. It is noteworthy that the reactivity of **8** was much lower than that of the β-D-*gluco* isomer **5**; the reaction was complete within 1 h for the latter, but ~50% of **8** was recovered, even after 15 h, with the former. Although the yield of **22** was significantly improved by use of the α-D-*gluco* isomer **8** instead of the α-D-*manno* isomer **10**, no method suitable for preparing **8** has yet been established. Improved syntheses of **22** and **15** from the corresponding nitro alkenes have, therefore, been a matter of investigation, and an alternative method for their preparation was further investigated.

2,3-Anhydro-α-D-allopyranoside **24** was treated with sodium *p*-toluenethiolate, according to the method of Hanessian and Staub[10]. Subsequent oxidation with *m*-chloroperoxybenzoic acid afforded in 70% yield the sulfonyl derivative **25** having the α-D-*altro* configuration. Treatment of **25** with methanesulfonyl chloride in the presence of triethylamine gave the sulfonyl alkene **22** in almost quantitative yield. Similar treatment of the 2,3-anhydromannopyranoside **29** gave the desired sulfonyl alkene **15** in good yield.

EXPERIMENTAL

General methods. — All melting points are uncorrected. Optical rotations were determined with a JASCO DIP-4 polarimeter. ^{1}H-N.m.r. spectra were recorded at 100 MHz with a JEOL spectrometer (JNM-4H-100) unless otherwise noted, and Me_4Si was the internal standard. I.r. spectra were recorded for KBr pellets. Organic solutions were dried over anhydrous $MgSO_4$ and evaporated under diminished pressure. Column chromatography was conducted on silica gel (Wakogel C-300). T.l.c. was performed with Merck (Darmstadt) silica gel GF 254. The catalyst used refers to tributylhexadecylphosphonium bromide.

Methyl 4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-2-C-p-tolylsulfonyl-β-D-glucopyranoside (**5**). — A mixture of compound[11] **1** (1.20 g, 4.1 mmol), sodium *p*-toluenesulfinate dihydrate (1.05 g, 4.9 mmol), AcOH (0.28 mL, 4.9 mmol), the catalyst (90 mg), C_6H_6 (80 mL), and water (16 mL) was stirred for 4 h at room temperature. The mixture was diluted with water and extracted with C_6H_6. The extracts were combined and washed with water, dried, and evaporated to give a crystalline residue (1.74 g, 95%) of **5**, identified by comparison with an authentic sample[5] by ^{1}H-n.m.r. and i.r. spectroscopy.

Phenyl 4,6-O-benzylidene-2,3-dideoxy-2-C-nitro-3-C-p-tolylsulfonyl-β-D-glucopyranoside (**6**). — Treatment of compound[12] **2** (1.136 g, 3.2 mmol) as described in the preparation of **5** afforded 1.50 g (92%) of the crystalline adduct **6**. An analytical sample was obtained by recrystallization from EtOH; m.p. 141–143°, $[\alpha]_D^{25}$ −51° (*c* 1, $CHCl_3$); ν_{max} 1560 cm^{-1} (NO_2); n.m.r. δ 5.69 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.53 (q, 1 H, $J_{2,3}$ 11.6 Hz, H-2), 5.37 (q, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.09 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 4.4–3.5 (m, 3 H, H-5,6*a*,6*e*), 5.53 (s, 1 H, PhCH), and 2.46 (s, 3 H, Me).

Anal. Calc. for $C_{26}H_{25}NO_8S$: C, 61.05; H, 4.93; N, 2.74; S, 6.27. Found: C, 61.12; H, 4.91; N, 2.64; S, 6.44.

1,5-Anhydro-4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-2-C-p-tolylsulfonyl-D-glucitol (**7**). — A. *From nitro alkene* **3**. Treatment of compound[6,13] **3** (132 mg, 0.5 mmol) as described in the preparation of **5** gave a partially crystalline residue, which was chromatographed with 60:1 C_6H_6–EtOAc as eluant to afford 135 mg (64%) of **7**. An analytical sample was obtained by recrystallization from EtOH; m.p. 274° (dec.), $[\alpha]_D^{25}$ +17° (*c* 0.67, $HCONMe_2$); ν_{max} 1560 cm^{-1} (NO_2); n.m.r. (Me_2SO-d_6): δ 4.50 (sextet, 1 H, $J_{1a,2}$ 10.3, $J_{1e,2}$ 5.3, $J_{2,3}$ 10.3 Hz, H-2), 5.22 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.3–3.5 (m, 6 H, H-1*a*,1*e*,4,5,6*a*,6*e*), 5.67 (s, 1 H, PhCH), and 3.28 (s, 3 H, Me).

Anal. Calc. for $C_{20}H_{21}NO_7S$: C, 57.27; H, 5.05; N, 3.34; S, 7.64. Found: C, 56.98; H, 5.07; N, 3.30; S, 7.88.

B. *From nitro acetate* **9**. A mixture of acetate[6,13] **9** (534 mg, 1.7 mmol), sodium *p*-toluenesulfinate dihydrate (706 mg, 3.3 mmol), the catalyst (20 mg), C_6H_6 (20 mL), and water (4 mL) was kept for 4 days at ~40° with stirring. Similar processing to that just described gave 533 mg (77%) of **7**.

Methyl 4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-2-C-p-tolylsulfonyl-α-D-glu-

copyranoside (**8**). — To a solution of sodium *p*-toluenethiolate (80.3 mg, 0.55 mmol) in tetrahydrofuran (3 mL) was added the nitro alkene[14] **4** (147 mg, 0.50 mmol). After stirring for 24 h at room temperature, the mixture was diluted with water and extracted with EtOAc. The extracts were combined and washed successively with water, dilute HCl, and water, dried, and then evaporated. To the residue was added *m*-chloroperoxybenzoic acid (190 mg, purity ~80%, 0.9 mmol). After stirring for 5 h, the mixture was washed with $NaHCO_3$ and water, dried, and evaporated. Addition of 2-propanol afforded crystals (30 mg) of **8**. The filtrate was evaporated and chromatographed with 20:1 C_6H_6–EtOAc as eluant to give an additional amount of **8** (9 mg, total yield 17%). An analytical sample was obtained by recrystallization from 2-propanol; m.p. 212–213°, $[\alpha]_D^{20}$ +97° (*c* 0.87, $CHCl_3$); ν_{max} 1560 cm^{-1} (NO_2); n.m.r.: δ 5.26 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.11 (q, 1 H, $J_{2,3}$ 11.6 Hz, H-2), 5.10 (q, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 4.3–3.7 (4 H, H-4,5,6*a*,6*e*), 5.50 (s, 1 H, PhCH), 3.40 (s, 3 H, OMe), and 2.46 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{23}NO_8S$: C, 56.12; H, 5.16; N, 3.12; S, 7.13. Found: C, 56.29; H, 5.11; N, 2.82; S, 7.05.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-2-*C*-p-tolylsulfonyl-α-*D*-mannopyranoside* (**10**). — Treatment of compound[14] **4** (1.22 g, 4.16 mmol) as described in the preparation of **5** except for a reaction time of 6 h afforded 1.61 g (86%) of **10** (pure from its ^{1}H-n.m.r. spectrum) as crystals. An analytical sample was obtained by recrystallization from EtOH; m.p. 175–176°, $[\alpha]_D^{20}$ 0° (*c* 1.9, $CHCl_3$); ν_{max} 1570 cm^{-1} (NO_2); n.m.r.: δ 5.49 (s, 1 H, H-1), 4.24 (d, 1 H, $J_{2,3}$ 5.3 Hz, H-2), 5.07 (q, 1 H, $J_{3,4}$ 10.9 Hz, H-3), 4.81 (q, 1 H, $J_{4,5}$ 8.3 Hz, H-4), 3.8–3.9 (m, 2 H, H-5, 6*a*), 4.24 (1 H, H-6*e*), 5.64 (s, 1 H, PhCH), 3.42 (s, 3 H, OMe), and 2.48 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{23}NO_8S$: C, 56.12; H, 5.16; N, 3.12; S, 7.13. Found: C, 56.42; H, 5.14; N, 3.12; S, 7.36.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-2-*C*-p-tolylsulfonyl-β-*D*-galactopyranoside* (**13**). — Similar treatment of compound[15] **11** (380 mg, 1.3 mmol) with sodium *p*-toluenesulfinate afforded a precipitate (350 mg, 66%) of **13**. After filtration, the filtrate was diluted with C_6H_6 and washed with water, dried, evaporated, and crystallized from EtOH to give additional **13** (181 mg, total yield 91%). An analytical sample was obtained by recrystallization from $CHCl_3$; m.p. 239° (dec.), $[\alpha]_D^{20}$ +17° (*c* 1, Me_2CO); ν_{max} 1565 cm^{-1} (NO_2): n.m.r.: δ 4.89 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.35 (d, 1 H, $J_{2,3}$ 12.4 Hz, H-2), 5.39 (q, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 4.71 (d, 1 H, $J_{4,5}$ <1.5 Hz, H-4), 3.45–3.65 (overlapped with OMe, H-5), 4.11 (d, 1 H, $J_{6a,6e}$ 13.5 Hz, H-6*a*), 4.39 (q, 1 H, $J_{5,6e}$ 1.5 Hz, H-6*e*), 5.56 (s, 1 H, PhCH), 3.59 (s, 3 H, OMe), and 2.48 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{23}NO_8S$: C, 56.12; H, 5.16; N, 3.12; S, 7.13. Found: C, 56.23; H, 5.15; N, 3.05; S, 6.94.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-nitro-3-*C*-p-tolylsulfonyl-α-*D*-glucopyranoside* (**16**). — Treatment of compound[8,9] **14** (87.9 mg, 0.3 mmol) as described in the preparation of **5** gave pure crystalline **16** (127 mg, 94% yield), judging

from its ^{1}H-n.m.r. spectrum. An analytical sample was obtained from EtOH; m.p. 181.5–183.5°, $[\alpha]_D^{22}$ +110° (*c* 1, $CHCl_3$); ν_{max} 1570 cm^{-1} (NO_2); n.m.r. (200 MHz): δ 5.24 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 5.18 (d, 1 H, $J_{2,3}$ 11.0 Hz, H-2), 4.53 (t, 1 H, $J_{3,4}$ 11.0 Hz, H-3), 4.18 (q, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 3.91 (sextet, 1 H, $J_{5,6a}$ 9.5, $J_{5,6e}$ 3.8 Hz, H-5), 3.80 (t, 1 H, $J_{6a,6e}$ 9.5 Hz, H-6*a*), 4.28 (q, 1 H, H-6*e*), 5.59 (s, 1 H, PhCH), 3.36 (s, 3 H, OMe), and 2.37 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{23}NO_8S$: C, 56.12; H, 5.16; N, 3.12; S, 7.13. Found: C, 56.25; H, 5.26; N, 3.05; S, 6.87.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-*D*-erythro-hex-2-enopyranoside* (**19**). — A. *From 3-*C*-nitro-2-*C*-*p*-tolylsulfonyl derivative* **5**. To a solution of **5** (1.01 g, 2.25 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (0.38 mL, 2.8 mmol), and the mixture was stirred for 30 min at room temperature. The resulting mixture was diluted with $CHCl_3$ and washed with dilute HCl and water, dried, and then evaporated to give crystalline **19** (856 mg, 95%), which was pure, judging from its ^{1}H-n.m.r. spectrum. An analytical sample was obtained by recrystallization from 2-propanol; m.p. 149–150°, $[\alpha]_D^{20}$ −81° (*c* 1.5, $CHCl_3$); n.m.r.: δ 5.60 (s, 1 H, $J_{1,2}$ and $J_{1,4}$ <1.5 Hz), 7.36 (broad s, 1 H, $J_{3,4}$ <2.0 Hz, H-3), ~4.43 (m, 1 H, H-4), 4.4–3.6 (m, 3 H, H-5,6*a*,6*e*), 5.60 (s, 1 H, PhCH), 3.31 (s, 3 H, OMe), and 2.43 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.75; H, 5.51; S, 7.98.

B. *From nitro alkene* **1**. A mixture of compound[11] **1** (610 mg, 2.08 mmol), sodium *p*-toluenesulfinate dihydrate (980 mg, 4.58 mmol), Et_3N (0.58 mL, 4.16 mmol), and CH_2Cl_2 (30 mL) was stirred for 12 h at room temperature. Isolation as already described afforded 786 mg (94%) of **19**.

*Phenyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-*D*-erythro-hex-2-enopyranoside* (**20**). — Treatment of **6** (204 mg, 0.40 mmol) as described in the preparation of **19** from **5** afforded 156 mg (84%) of **20** (after recrystallization from C_6H_6–hexane); m.p. 178–180°, $[\alpha]_D^{25}$ −92° (*c* 1, $CHCl_3$); n.m.r.: δ 6.28 (d, 1 H, $J_{1,4}$ 2.4 Hz, H-1), 7.49 (s, 1 H, H-4), 4.52 (sextet, 1 H, $J_{3,4}$ 1.5 Hz, $J_{4,5}$ 6.8 Hz, H-4), 4.4–3.7 (3 H, m, H-5,6*a*,6*e*), 5.57 (s, 1 H, PhCH), and 2.43 (s, 3 H, Me).

Anal. Calc. for $C_{26}H_{24}O_6S$: C, 67.23; H, 5.21; S, 6.90. Found: C, 67.00; H, 4.94; S, 6.88.

*1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-*D*-erythro-hex-2-enitol* (**21**). — To a solution of **7** (43 mg, 0.10 mmol) in 2 mL of $HCONMe_2$ was added 0.017 mL (0.12 mmol) of Et_3N at room temperature. After stirring for 2 days at room temperature, the mixture was diluted with water (10 mL) and extracted with $CHCl_3$. The extracts were combined and washed with dilute HCl and water, dried, and evaporated. The resultant syrup was chromatographed with 30:1 (v/v) C_6H_6–EtOAc as eluant to afford 3.7 mg (14% yield) of compound[13] **23** as the fast-running fraction and 30 mg (78% yield) of **21** as the slow-running one. An analytical sample was obtained by recrystallization from 2-propanol; m.p. 147–148°, $[\alpha]_D^{20}$ +52° (*c* 0.9, $CHCl_3$); n.m.r.: δ 7.03 (broad s, 1 H, H-3), 3.41 (octet, 1

H, $J_{4,5}$ 7.5, $J_{5,6a}$ 10.0, $J_{5,6e}$ 4.1 Hz, H-5), 3.74 (t, 1 H, $J_{6a,6e}$ 10.0 Hz, H-6*a*), 4.5–4.2 (4 H, m, H-1*a*,1*e*,4,6*e*), 5.58 (s, 1 H, PhCH), and 2.46 (s, 3 H, Me).

Anal. Calc. for $C_{20}H_{20}O_5S$: C, 64.50; H, 5.41; S, 8.61. Found: C, 64.34; H, 5.34; S, 8.62.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-p-tolylsulfonyl-α-*D*-*erythro*-hex-2-enopyranoside* (**22**). — A. *From the* α-D-gluco *isomer* **8**. A solution of **8** (37 mg, 0.082 mmol) and Et_3N (50 mg, 0.50 mmol) in CH_2Cl_2 (7.5 mL) was kept for 3 days. Within the period, the spot of **8** completely disappeared and a single spot corresponding to **22** appeared in t.l.c. Similar processing as described for the preparation of **19** afforded a solid residue of **22** (32 mg, 97%), pure as judged from ^{1}H-n.m.r. spectroscopy. An analytical sample was obtained by recrystallization from 2-propanol; m.p. 133–134°, $[\alpha]_D^{20}$ +226° (*c* 1, $CHCl_3$); n.m.r.: δ 5.30 (s, 1 H, H-1), 7.24 (d, 1 H, $J_{3,4}$ 2.3 Hz, H-3), 4.4–3.7 (m, 4 H, H-4,5,6*a*,6*e*), 5.58 (s, 1 H, PhCH), 3.37 (s, 3 H, OMe), and 2.43 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.41; H, 5.52; S, 8.07.

B. *From the* α-D-manno *isomer* **10**. A solution of **10** (352 mg, 0.78 mmol) and Et_3N (0.13 mL, 0.93 mmol) in $CHCl_2$ (6 mL) was stirred for 1 h at room temperature. Similar processing as before afforded a residue, to which addition of 2-propanol gave crystals consisting of **22** and **16** (128 mg, 2:1, as estimated from ^{1}H-n.m.r. spectroscopy) as the first crop, 30 mg of pure **22** as the second one, and a mixture (28 mg) of **22** and **16** (1:2) as the third one. The residue was chromatographed, successively eluting with C_6H_6, 10:1, and then 3:1 C_6H_6–EtOAc, to give in turn 11.5 mg (5%) of **14**, 1:1.2 mixture (~36 mg) of **22** and **16**, a 1:1 mixture (18 mg) of **22** and **8**, 14 mg (5%) of **8**, and 14.6 mg (6%) of compound[8] **17**; compound **17** is presumably formed by addition of contaminating water to **14**.

C. *From 2-*C*-p-tolylsulfonyl-α-*D*-altropyranoside* **25**. To a solution of **25** (500 mg, 1.2 mmol) and methanesulfonyl chloride (165 mg, 1.4 mmol) in CH_2Cl_2 (6 mL) was added Et_3N (0.38 mL, 2.7 mmol). The mixture was stirred for 2 h at room temperature and then processed as for the preparation of **19**, affording 478 mg of crystalline residue, which was pure as judged from t.l.c. and ^{1}H-n.m.r. spectroscopy.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-p-tolylsulfonyl-β-*D*-threo-hex-2-enopyranoside* (**12**). — To a stirred solution of **13** (96 mg, 0.21 mmol) in Me_2CO (1.5 mL) was added Et_3N (0.16 mL, 1.14 mmol) at room temperature. After 21 h, the mixture was poured into $CHCl_3$–water. The organic layer was washed with dilute HCl and water, dried, and evaporated. The residue was chromatographed with C_6H_6 as eluant to give 56 mg (65%) of **12**. An analytical sample was obtained by recrystallization from 2-propanol; m.p. 154–158° $[\alpha]_D^{20}$ −185° (*c* 0.6, $CHCl_3$); n.m.r.: δ 5.61 (s, 1 H, H-1), 7.52 (broad s, 1 H, H-3), 4.52 (m, 1 H, H-4), 3.56 (t, 1 H, $J_{4,5}$ and $J_{5,6a}$ <1.5 Hz, H-5), 4.46 (d, 1 H, $J_{6a,6e}$ 13.5 Hz, H-6*a*), 4.20 (q, 1 H, $J_{5,6e}$ 3.6 Hz, H-6*e*), 5.64 (s, 1 H, PhCH), 3.27 (s, 3 H, OMe), and 2.46 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.84; H, 5.28; S, 7.79.

Methyl 4,6-O-benzylidene-2,3-dideoxy-3-C-p-tolylsulfonyl-α-D-erythro-hex-2-enopyranoside (**15**). — A. *From 2-C-nitro-3-C-p-tolylsulfonyl derivative* **16**. — A solution of **16** (116 mg, 0.26 mmol) and Et_3N (0.04 mL, 0.29 mmol) in CH_2Cl_2 (2 mL) was stirred for 18 h at room temperature. Similar processing as before gave a residue that was chromatographed with C_6H_6 and 30:1 C_6H_6–EtOAc as eluant to give successively 10 mg of nitro alkene **14**, a mixture (26 mg) of **16** and an unidentified compound (~1:2), and sulfonyl alkene **15** (23 mg, 22%). An analytical sample of **15** was obtained by recrystallization from 2-propanol; m.p. 147–148°, $[\alpha]_D^{20}$ −46° (*c* 1, $CHCl_3$); n.m.r.: δ 5.17 (q, 1 H, $J_{1,2}$ 2.2, $J_{1,4}$ 1.5 Hz, H-1), 7.03 (q, 1 H, $J_{2,4}$ 1.5 Hz, H-2), 4.60 (broad d, 1 H, $J_{4,5}$ 7.5 Hz, H-4), 4.3–3.7 (m, 3 H, H-5,6*a*,6*e*), 5.60 (s, 1 H, PhCH), 3.54 (s, 3 H, OMe), and 2.40 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.63; H, 5.54; S, 8.07.

B. *From 3-C-p-tolylsulfonyl-α-D-altropyranoside* **26**. — To a solution of **26** (100 mg, 0.24 mmol) and methanesulfonyl chloride (57 mg, 0.50 mmol) in CH_2Cl_2 (4 mL) was added Et_3N (101 mg, 1.0 mmol). The reaction was monitored by t.l.c. As the starting alcohol **26** still remained, additional methanesulfonyl chloride (33 mg) and Et_3N (50 mg) were added. Conventional processing afforded a crystalline residue that was recrystallized from 2 propanol to give 69 mg of **15**. the filtrate was evaporated and chromatographed with C_6H_6 as eluant to give an additional amount of **15** (4 mg, total yield 76%).

Methyl 4,6-O-benzylidene-2-deoxy-2-C-p-tolylsulfonyl-α-D-altropyranoside (**25**). — To a solution of sodium *p*-toluenethiolate (402 mg, 2.75 mmol) in 2-methoxymethanol (12 mL) was added 2,3-anhydro sugar **24** (660 mg, 2.5 mmol). The mixture was heated for 30 min at 80–90° in an atmosphere of nitrogen. After cooling, *m*-chloroperoxybenzoic acid (1.25 g, 80% purity, 5.8 mmol) and then Et_3N (587 mg, 5.8 mmol) were added to the solution. After 8 h, the mixture was diluted with saturated aqueous NaCl and extracted with EtOAc. The extracts were combined, washed with dilute HCl and water, dried, and then evaporated to a syrup. Addition of 2-propanol gave 527 mg (50% yield) of **25**. An analytical sample was obtained by recrystallization from 2-propanol; m.p. 164–165°, $[\alpha]_D^{25}$ +60° (*c* 1.2, $CHCl_3$); ν_{max} 3578 and 3445 cm^{-1} (OH); n.m.r.: δ 5.32 (s, 1 H, H-1), 4.46 (broad s, 1 H, H-3), 3.62 (d, 1 H, $J_{3,4}$ 1.6 Hz, H-4), 4.4–3.8 (m, 4 H, H-2,5,5*a*,6*e*), 2.70 (d, 1 H, $J_{2,OH}$ 4.1 Hz, OH), 5.68 (s, 1 H, PhCH), 3.43 (s, 3 H, OMe), and 2.49 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{24}O_7S$: C, 59.99; H, 5.75; S, 7.63. Found: C, 60.06; H, 5.76; S, 7.51.

The residue obtained by evaporation of the filtrate was chromatographed successively with 10:1 and 5:1 (v/v) C_6H_6–EtOAc, to give in turn 78 mg of **25**, a mixture (122 mg) of **25** and small amounts of unidentified product (from which 54 mg of **25** crystallized from EtOH), and a syrup (168 mg) that was similarly oxidized with *m*-chloroperoxybenzoic acid (86 mg), to afford 76 mg of **25**. Compound **25** was thus obtained in 70% yield.

*Methyl 4,6-O-benzylidene-3-deoxy-3-*C*-p-tolylthio-α-*D*-altropyranoside* (**27**). — To a solution of sodium *p*-toluenethiolate (80.4 mg, 0.55 mmol) in 2-methoxymethanol (10 mL) was added the 2,3-anhydro sugar **29** (132 mg, 0.5 mmol). The mixture was heated for 3 h at 80–90° in an atmosphere of nitrogen and poured into water. The precipitate generated was filtered off and chromatographed with 10:1 (v/v), C_6H_6–EtOAc, to give 19 mg of **29** and 137 mg (71%, 82% based on the consumed epoxide) of sulfide **27**. An analytical sample was prepared by recrystallization from C_6H_6; m.p. 155–156°, $[\alpha]_D^{25}$ −42° (*c* 1, $CHCl_3$); ν_{max} 3430 cm^{-1} (OH); n.m.r.: δ 4.60 (broad s, 1 H, H-1), 3.69 (broad s, 1 H, H-3), 3.83 (sextet, 1 H, $J_{5,6e}$ 5.1, $J_{5,6a}$ 11.6 Hz, H-5), 4.2–4.4 (m, 4 H, H-2,4,6*a*,6*e*), 2.37 (d, 1 H, $J_{2,OH}$ 6.4 Hz, OH), 5.60 (s, 1 H, PhCH), 3.43 (s, 3 H, OMe), and 2.26 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{24}O_5S$: C, 64.93; H, 6.23; S, 8.25. Found: C, 65.13; H, 6.32; S, 8.46.

*Methyl 4,6-O-benzylidene-3-deoxy-3-*C*-p-tolylsulfonyl-α-*D*-altropyranoside* (**26**). — To a stirred solution of **27** (26 mg, 0.067 mmol) in EtOAc (1 mL) was added *m*-chloroperoxybenzoic acid (14.5 mg, 0.067 mmol). A precipitate that formed immediately was stirred for 10 min. The precipitate (17.4 mg, 64.4%) then filtered off was almost pure sulfoxide **28** as judged from its ^{1}H-n.m.r. spectrum. The filtrate was washed successively with aqueous $NaHCO_3$, and water, dried, and evaporated to give almost pure **28** (10 mg, almost quantitative yield). An analytical sample was obtained by recrystallization from EtOH; m.p. 193° (dec.), $[\alpha]_D^{25}$ +108° (*c* 1, MeOH); ν_{max} 3565 (weak), 3500 (weak), and 3250 (strong) cm^{-1} (OH); n.m.r.: δ 4.79 (s, 1 H, H-1), 3.87 (broad s, 1 H, H-3), 4.8–4.2 (m, 6 H, H-2,4,5,*a*,6*e*,OH), 5.31 (s, 1 H, PhCH), 3.54 (s, 3 H, OMe), and 2.33 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{24}O_6S$: C, 62.36; H, 5.98; S, 7.93. Found: C, 62.39; H, 6.00; S, 8.11.

To a stirred suspension of sulfoxide (103 mg, 0.25 mmol) in EtOAc (3 mL) was added *m*-chloroperoxybenzoic acid (120 mg, 0.56 mmol). Within 1.3 h, the suspension turned gradually into a homogeneous solution that was diluted after 1.7 h with EtOAc. The mixture was successively washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated, to give a syrup (100 mg, ~93%), the ^{1}H-n.m.r. spectrum of which showed it to be almost pure **26**. An analytical sample was prepared by recrystallization from C_6H_6; m.p. 100–100.5°, $[\alpha]_D^{25}$ +31° (*c* 1, $CHCl_3$); ν_{max} 3610, 3520, and 3430 cm^{-1} (OH); n.m.r.: δ 4.73 (s, 1 H, H-1), 4.83 (broad d, 1 H, $J_{1,2}$ <1.0, $J_{2,OH}$ 5.1 Hz, H-2), 3.90 (q, 1 H, $J_{2,3}$ 1.6, $J_{3,4}$ 5.8 Hz, H-3), 4.25 (q, 1 H, $J_{4,5}$ 10.3 Hz, H-4), ~4.73 (sextet, 1 H, H-5), 3.66 (t, 1 H, $J_{5,6a} = J_{6a,6e}$ 10.3 Hz, H-6*a*), 4.31 (q, 1 H, $J_{5,6e}$ 5.1 Hz, H-6*e*), 3.90 (overlapped with signals due to H-3), 5.39 (s, 1 H, PhCH), 3.45 (s, 3 H, OMe), and 2.30 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{24}O_7S$: C, 59.99; H, 5.75; S, 7.63. Found: C, 59.89; H, 5.77; S, 7.46.

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