Carbohydrate Research, 179 (1988) 77–86
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

REACTIONS OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-2-*C*-*p*-TOLYLSULFONYL-α-D-*erythro*-HEX-2-ENOPYRANOSIDE AND ITS PHENYL ANALOGUE WITH SODIUM METHOXIDE*

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(Received October 31st, 1987; accepted for publication, February 1st, 1988)

ABSTRACT

Reaction of the title methyl glycoside **5** with methanolic sodium methoxide afforded mainly the isomeric α-D-*erythro*-hex-3-enopyranoside derivative **13**, formed by migration of the double bond from C-2 to C-3, together with 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-D-*ribo*-hex-1-enitol (**7**) and the methyl 4,6-*O*-benzylidene-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α-D-hexopyranosides having the *gluco* (**15**), *allo* (**14**), and *altro* (**12**) configurations. Similar reaction of the phenyl glycoside analogue (**6**) of **5** resulted in loss of the phenyl group to give **7** and **12**–**14** together with phenyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α-D-glucopyranoside (**18**).

INTRODUCTION

The products formed by the attack of nucleophiles on alkyl 4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides carrying electron-withdrawing substituents at C-2 depend not only on the characteristics and stereochemistry of the ring substituents but also on the nature of the electron-withdrawing groups. For example, cyanide ion added from the equatorial (β) side of the double bond in methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-nitro-β-D-*erythro*-hex-2-enopyranoside[1] (**1**) and from the axial (α) side in the 2-cyano analogue[2] (**2**). With the α anomer (**3**) of **1**, the reactions are more complicated, as exemplified by the facts that methanol added almost exclusively from the axial side, but from the equatorial side in the presence of small amounts of sodium methoxide[3]. In order to compare these results with those of other Michael-type reactions, similar reactions were performed with the methyl 2-*C*-*p*-tolylsulfonyl-β-D-hex-2-enopyranoside derivative[4]

*Dedicated to Professor Bengt Lindberg.
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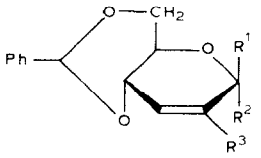
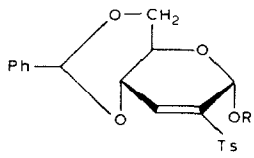
0008-6215/88/$ 03.50

(**4**), in which nucleophiles added from the equatorial side. We now describe the reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-α-D-*erythro*-hex-2-enopyranoside[5] (**5**), its phenyl analogue **6**, and 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-D-*ribo*-hex-1-enitol (**7**) with sodium methoxide.



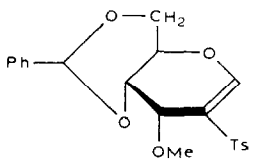


1 $R^1 = OMe, R^2 = H, R^3 = NO_2$
2 $R^1 = OMe, R^2 = H, R^3 = CN$
3 $R^1 = H, R^2 = OMe, R^3 = NO_2$
4 $R^1 = OMe, R^2 = H, R^3 = Ts$

5 R = Me
6 R = Ph

RESULTS AND DISCUSSION

Compounds **6** and **7** were prepared as follows. Addition of *p*-toluenesulfinic acid to phenyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-hex-2-enopyranoside (**9**) and subsequent elimination of nitrous acid gave **6** (19.3% from **8**). Methylation (MeI–Ag_2O) of methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-*p*-tolylsulfonyl-α-D-altropyranoside (**11**) afforded the 3-*O*-methyl derivative **12**. On the basis of the fact[3] that treatment of the corresponding 2-nitro derivatives having the *altro* and *allo* configurations with a base afforded the 3-*O*-methyl-2-nitro-D-*ribo*-hex-1-enitol derivative, a similar reaction was applied to **12**. Thus, **7** was obtained in 78% yield by treatment of **12** with butyl-lithium.



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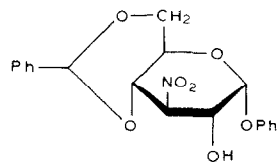

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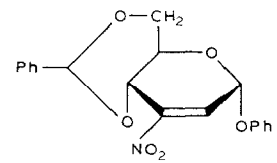

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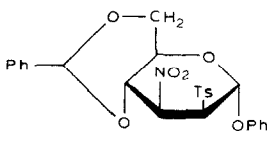

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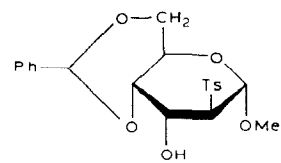

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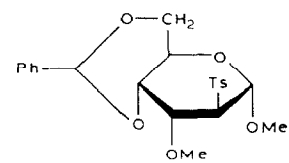

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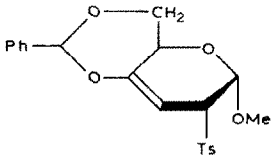
Treatment of **5** with methanolic sodium methoxide afforded a complex mixture of products from which methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-α-D-*erythro*-hex-3-enopyranoside (**13**) was isolated as the major product, together with **7** and the methyl 4,6-*O*-benzylidene-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α-D-hexopyranosides having the *altro* (**12**), *allo* (**14**), and *gluco* (**15**) configurations. The *allo* and *gluco* configurations of **14** and **15** were assigned on the basis of n.m.r. data ($J_{1,2}$ 3.9, $J_{2,3}$ 2.6, $J_{3,4}$ 2.6 Hz for **14**; $J_{1,2}$ 3.3, $J_{2,3}$ 10.5, $J_{3,4}$ 9.3 Hz for **15**). The *allo* structure of **14** accorded with the fact that the *altro* isomer **12** was partially empimerised to **14** (see below). The 3-enopyranoside structure of **13**, suggested by elemental analysis, and i.r. [1690 cm^{-1} (–O–C=C–)], ^{1}H- (δ 5.29*, alkenic proton), and ^{13}C-n.m.r. spectra, was confirmed chemically. Debenzylidenation of **13** with aqueous 70% acetic acid afforded the 4-ulose derivative **16**, which was also formed partially during the recrystallisation of **13**. Assignment of almost all of the signals in the n.m.r. spectra of **13** was performed by the COSY method. The α-D-*erythro* configuration for **13** was suggested by the coupling constants ($J_{1,2}$ 5.2 Hz for **13**, and $J_{1,2}$ 3.3, $J_{2,3a}$ 8.4, and $J_{2,3e}$ 6.9 Hz for **16**). In the ^{1}H-n.m.r. spectrum of **13**, however, the signal (δ 2.66, t, *J* 10.3 Hz) for H-6*a* resonated at higher field than the signal (δ 3.48) due to the aglyconic methyl group. To the best of our knowledge, such an example is unprecedented[7]. Thus, further evidence was required for the configuration of **13**.

Since **13** was also obtained from the phenyl analogue **6** (see below), the possibility of the β-D structure for **13** was not excluded. Therefore, **5** was treated with methanol-d_4 in tetrahydrofuran in the presence of sodium methoxide. In this reaction, axial attack to give the adducts having the α-D-*allo* and -*altro* configura-



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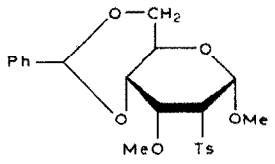

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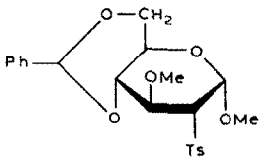

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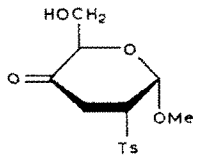

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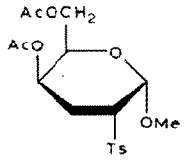

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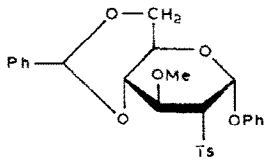

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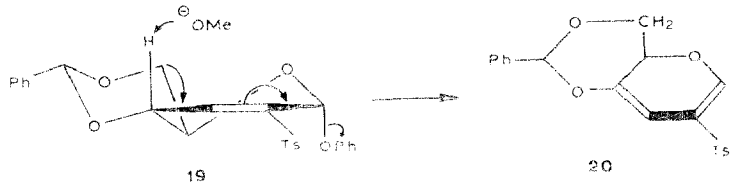
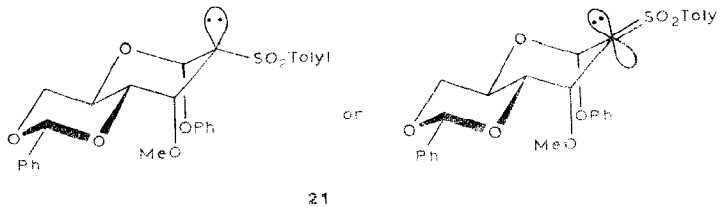
*Two singlets at δ 5.24 and 5.29 correlated with those at δ 102.578 and 94.919, respectively, in its ^{13}C-n.m.r. spectrum. Since the benzylidene methine carbon of several 4,6-*O*-benzylidene derivatives[6] resonated at δ 101–102, the peak appearing at δ 5.24 was tentatively assigned to the benzylidene methine proton.

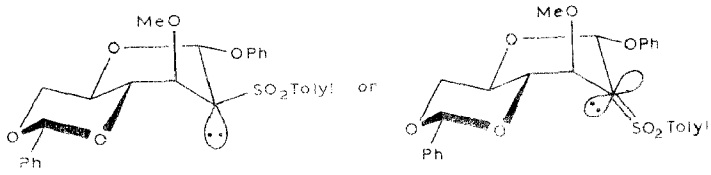
tions was almost negligible and the product having the α-D-*gluco* configuration and the 2-deuterio derivative of **13** were obtained. Although the 2-position of these products was completely deuterated, the anomeric methoxyl group (MeO-1) was not deuterated, indicating that **13** was the α anomer because replacement of MeO-1 did not occur. Reduction of **16** with sodium borohydride and subsequent acetylation afforded, at least, two products, from which the diacetate **17** was isolated. The α-D-*xylo* configuration of **17** was determined from the coupling constants ($J_{1,2}$ 3.9, $J_{2,3a}$ 9.0, $J_{2,3e}$ 5.4, $J_{3a,4} = J_{3e,4}$ = 5.4 Hz). Thus, the α-D-*erythro* structure for **13** was established unequivocally, but the reason why the H-6*a* signal appeared at so high field remains unexplained.

In contrast with the β anomer[4] (**4**) of **5**, methoxide ion behaved mainly as a base and to some extent as a nucleophile. The ratio of axial and equatorial attack at the 3-position was ~2:1 in methanol, but equatorial attack occurred almost exclusively in tetrahydrofuran–methanol-d_4. A similar 2→3 migration of the double bond was reported[8] in the reaction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-β-D-*erythro*-hex-2-enopyranoside with methanolic sodium methoxide.

Treatment of **6** with methanolic sodium methoxide also gave many products, from which **7** and **12–14** were isolated together with the phenyl α-D-*gluco* isomer **18**. The ^{1}H-n.m.r. spectrum of the 2-deuterio derivative of **18**, prepared by reaction of **6** with methanol-*d*, confirmed the α-D-*gluco* configuration ($J_{1,2}$ 3.3, $J_{2,3}$ 10.5, $J_{3,4}$ 9.6 Hz).







Assuming that the formation of the 3-enopyranoside **13** from **6** involves the formation of a reactive 1,3-diene intermediate (**19**→**20**), addition of methanol to **20** is highly stereoselective, because formation of the β-D anomer of **13** was not detected. The 1-enitol derivative **7** was the intermediate in the formation of the α-D-*altro* (**12**) and α-D-*allo* (**14**) derivatives from **6**. In fact, treatment of **7** with methanolic sodium methoxide afforded **7**, **12**, and **14**, together with a small amount of an unidentified product. Under the same conditions, **12** gave a 1:2.7:2.2 mixture of **7**, **12**, and **14**. In the reaction of the phenyl analogue, no evidence for the formation of the 3-epimer of **7** and methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α- and -β-D-glucopyranosides[4] was obtained. Therefore, it may be concluded that the equatorial attack of a nucleophile resulted in an addition reaction, whereas the axial attack resulted in an S_N2' reaction. These results can be explained in terms of the stereoelectronic control. Axial and equatorial attack should give a chair-like (**21**) and boat-like intermediate (**22**), respectively, in which the former is more suitable for the elimination of phenoxyl group. It was not established whether the axial attack gave rise to the S_N2' reaction or not in the methyl glycoside **5**; the ratio of axial and equatorial attack was comparable to that observed with the phenyl glycoside **6**.

EXPERIMENTAL

General methods. — All melting points are uncorrected. Optical rotations were determined with a Horiba High Sensitive Polarimeter (SEPA-200). I.r. spectra were recorded for KBr pellets. Solvents were evaporated under diminished pressure. Column chromatography was conducted on Wakogel C-300. ^{1}H-N.m.r. spectra were recorded at 90 (JNM-FX90Q) and 200 MHz (JNM-FX200) with a JEOL spectrometer, or at 300 MHz (VXR 300) with a Varian spectrometer, for solutions in $CDCl_3$ (internal Me_4Si).

Phenyl 4,6-O-benzylidene-3-deoxy-3-C-nitro-α-D-glucopyranoside (**8**). — A mixture of phenyl α-D-mannopyranoside (12.88 g, 50 mmol) and $NaHCO_3$ (4.2 g, 50 mmol) was added in portions during 20 min to a stirred solution of sodium metaperiodate (22.1 g, 103 mmol) in water (250 mL). After stirring for an additional 3 h, the sodium iodate was removed and the filtrate was concentrated to a partly crystalline mass, to which EtOH (40 mL) was added. Insoluble material was removed, the filtrate was concentrated to a syrup, which was dissolved in EtOH, and the solution was filtered and concentrated. This procedure was repeated if the dissolution of the syrup caused an appreciable quantity of salt to separate. To a solution of the syrupy dialdehyde in MeOH (7 mL) was added $MeNO_2$ (3 mL, 56 mmol), the solution was cooled, and the pH was adjusted to 9 by the addition of methanolic M MeONa. The solution was then kept overnight at room temperature, and concentrated at <30°. Powdered anhydrous $ZnCl_2$ (15 g) was added to a mixture of the syrup and benzaldehyde (35 mL), and the mixture was stirred for 24 h, then poured into water (70 mL) and light petroleum. The organic layer was

decanted, diluted with light petroleum, decanted, and extracted with EtOAc. The combined extracts were washed with aqueous $NaHCO_3$ and water, dried, and concentrated. Column chromatography (C_6H_6) of the residue gave benzaldehyde and then **8**. Compound **8** (2.5 g, 13%), isolated after recrystallisation from EtOH, had m.p. 198–200°, $[\alpha]_D^{25}$ +175° (*c* 1, acetone); ν_{max} 3350 (broad, OH) and 1550 cm^{-1} (NO_2). ^{1}H-N.m.r. data (CD_3COCD_3): δ 5.76 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.42 (ddd, 1 H, $J_{2,3}$ 10.0, $J_{2,OH}$ 9.0 Hz, H-2), 5.14 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), ~4.31 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.8–4.3 (m, 3 H, H-5,6*a*,6*e*), 5.34 (d, 1 H, OH), and 5.70 (s, 1 H, PhC*H*).

Anal. Calc. for $C_{19}H_{19}NO_7$: C, 61.12; H, 5.13; N, 3.75. Found: C, 61.07; H, 5.19; N, 3.75.

*Phenyl 4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-α-*D-erythro-*hex-2-enopyranoside* (**9**). — To a solution of **8** (1.119 g, 3 mmol) and methanesulfonyl chloride (361 mg, 3.2 mmol) in tetrahydrofuran (10 mL) was added Et_3N (685 mg, 6.8 mmol) dropwise. The mixture was stirred for 30 min, then partitioned between C_6H_6 and water. The organic layer was washed with water, dried, and concentrated. Column chromatography (C_6H_6) of the residue gave **9** in almost quantitative yield. The crude product was used directly for the next reaction. An analytical sample, prepared by recrystallisation from EtOAc–hexane, had m.p. 161.5–162°, $[\alpha]_D^{25}$ −2° (*c* 1, chloroform); ν_{max} 1542 (sh), 1532 cm^{-1} (C=C–NO_2). ^{1}H-N.m.r. data: δ 5.91 (dd, 1 H, $J_{1,2}$ 3.2, $J_{1,4}$ 1.0 Hz, H-1), 6.96 (dd, 1 H, $J_{2,4}$ 1.9 Hz, H-2), 4.74 (m, 1 H, $J_{4,5}$ 8.4 Hz, H-4), 3.7–4.4 (m, 3 H, H-5,6*a*,6*e*), and 5.70 (s, 1 H, PhC*H*).

Anal. Calc. for $C_{19}H_{17}NO_6$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.21; H, 4.80; N, 4.02.

*Phenyl 4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-2-C-*p*-tolylsulfonyl-α-*D-*mannopyranoside* (**10**). — A mixture of **9** [prepared from **8** (1.347 g)], sodium *p*-toluenesulfinate (784 mg, 4.40 mmol), AcOH (264 mg, 4.40 mmol), tributylhexadecylphosphonium bromide (as a phase-transfer catalyst, 60 mg), C_6H_6 (40 mL), and water (8 mL) was stirred. The reaction was monitored by i.r. spectroscopy. Within 6 h, **9** had disappeared. The mixture was diluted with C_6H_6, and the organic layer was washed with water, dried, and concentrated. The resulting syrup crystallised from 2-propanol to give **10** (1.670 g, 90.5%). An analytical sample, prepared by recrystallisation from 2-propanol, had m.p. 147–148°, $[\alpha]_D^{25}$ +54° (*c* 1, chloroform); ν_{max} 1567 cm^{-1} (NO_2). ^{1}H-N.m.r. data: δ 6.38 (s, 1 H, H-1), 4.47 (dd, 1 H, $J_{2,3}$ 5.1, $J_{2,4}$ 1.0 Hz, H-2), 5.32 (dd, 1 H, $J_{3,4}$ 10.9 Hz, H-3), 4.97 (bdd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.7–4.4 (m, 3 H, H-5,6*a*,6*e*), 5.70 (s, 1 H, PhC*H*), and 2.47 (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, 60.96; H, 4.95; N, 2.86; S, 6.18.

*Phenyl 4,6-O-benzylidene-2,3-dideoxy-2-C-*p*-tolylsulfonyl-α-*D-erythro-*hex-2-enopyranoside* (**6**). — To a solution of **10** (384 mg, 0.75 mmol) in tetrahydrofuran (7.5 mL) was added Et_3N (90 mg, 0.89 mmol). After 25 min at room temperature, the mixture was diluted with EtOAc, washed successively with dilute HCl, water,

aqueous $NaHCO_3$, and water, dried, and concentrated. The resulting syrup was combined with that from 51 mg of **10** and subjected to column chromatography (8:5 C_6H_6–CCl_4) to afford **6** (84 mg, 21.3%), which crystallised from 2-propanol and had m.p. 135–136°, $[\alpha]_D^{25}$ +217° (*c* 1, acetone). ^{1}H-N.m.r. data: δ 6.13 (bs, 1 H, H-1), 7.2–7.3 (H-3, overlapped with aromatic ring protons), 4.37 (bd, 1 H, $J_{1,4} = J_{3,4} = 1.3$, $J_{4,5}$ 8.5 Hz, H-4), 3.7–4.4 (m, 3 H, H-5,6*a*,6*e*), 5.64 (s, 1 H, PhC*H*), and 2.46 (s, 3 H, Me).

Anal. Calc. for $C_{26}H_{24}O_6S$: C, 67.23; H, 5.21; S, 6.90. Found: C, 67.28; H, 5.24; S, 6.95.

*Methyl 4,6-O-benzylidene-2-deoxy-3-O-methyl-2-*C*-p-tolylsulfonyl-α-*D*-altropyranoside* (**12**). — A mixture of **11**[5] (136 mg, 0.32 mmol), Ag_2O (313 mg, 1.35 mmol), molecular sieves (3 Å, 450 mg), and MeI (5 mL) was heated under reflux for 9 h, then filtered, and concentrated. The residue was recrystallised from EtOH to give **12** (97 mg, 69.0%), m.p. 175–177°, $[\alpha]_D^{25}$ +63° (*c* 1, chloroform). ^{1}H-N.m.r. data (300 MHz): δ 5.15 (s, 1 H, H-1), 3.63 (bs, 1 H, H-2), 4.12 (bd, 1 H, H-3), 4.06 (dd, 1 H, $J_{3,4}$ 3.9, $J_{4,5}$ 9.5 Hz, H-4), 4.10–4.35 (m, 2 H, H-5,6*e*), 3.72 (t, 1 H, $J_{5,6a}$ 11.6, $J_{6a,6e}$ 11.6 Hz, H-6*a*), 5.54 (s, 1 H, PhC*H*), 3.35 (s, 3 H, OMe), 3.39 (s, 3 H, OMe), and 2.48 (s, 3 H, Me).

Anal. Calc. for $C_{22}H_{26}O_7S$: C, 60.81; H, 6.03; S, 7.38. Found: C, 60.88; H, 6.06; S, 7.21.

*1,5-Anhydro-4,6-O-benzylidene-2-deoxy-3-O-methyl-2-*C*-p-tolylsulfonyl-*D*-ribo-hex-1-enitol* (**7**). — A solution of **12** (1.110 g, 2.56 mmol) in tetrahydrofuran (51 mL) was cooled with dry ice–acetone under nitrogen. 1.6M BuLi in hexane (1.8 mL, 1.1 mol) was added, followed, after 20 min, by saturated aqueous NH_4Cl (70 mL). The resulting solution was brought to room temperature and extracted with C_6H_6 (3 × 100 mL), and the combined extracts were washed with water, dried, and concentrated to give **7** (808 mg, 78.6%). An analytical sample, prepared by recrystallisation from 2-propanol, had m.p. 154.5–155.0°, $[\alpha]_D^{25}$ +202° (*c* 1, chloroform); ν_{max} 1605 cm^{-1} (O–C=C). ^{1}H-N.m.r. data: δ 7.55 (s, 1 H, H-1), 4.34 (d, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 3.83 (dd, 1 H, $J_{4,5}$ 10.1 Hz, H-4), 4.28 (dt, 1 H, $J_{5,6a}$ 10.1, $J_{5,6e}$ 4.9 Hz, H-5), 3.81 (t, 1 H, $J_{6a,6e}$ 10.1 Hz, H-6*a*), 4.50 (dd, 1 H, H-6*e*), 5.51 (s, 1 H, PhC*H*), 3.39 (s, 3 H, OMe), and 2.44 (s, 3 H, Me).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.60; H, 5.53; S, 7.75.

Reaction of **5** *with methanolic sodium methoxide.* — To a stirred dispersion of **5**[5] (297 mg, 0.74 mmol) in MeOH (30 mL) was added methanolic M MeONa (1.5 mL). Dissolution occurred within 10 min. The solution was stirred for 45 min, then neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. Column chromatography (5:1 C_6H_6–CCl_4 then C_6H_6) of the residue gave, in turn, mainly **13** (170 mg), 1.2:1 (54 mg), 1:3 (15 mg), and 1:6 (38 mg) mixtures of the α-D-*altro* (**12**) and α-D-*gluco* (**15**) isomers, and the α-D-*allo* isomer **14** (35 mg). Recrystallisation of the first fraction from 2-propanol gave **13** (102 mg) as the first crop, **7** (18 mg) as the second, and **16** (21 mg) as the third. Compound **16** was formed during

the recrystallisation of **13**, since it was not detected by ^{1}H-n.m.r. spectroscopy before recrystallisation. An analytical sample of methyl 2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-α-D-*erythro*-hexopyranosid-4-ulose (**16**), obtained by recrystallisation from 2-propanol, had m.p. 146.5–148°, $[\alpha]_D^{25}$ +185° (*c* 1, chloroform); ν_{max} 1740 cm^{-1} (CO). ^{1}H-N.m.r. data: δ 5.33 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 3.54 (ddd, 1 H, $J_{2,3a}$ 8.4, $J_{2,3e}$ 6.9 Hz, H-2), 2.83 (d, 1 H, H-3*a*), 2.77 (d, 1 H, H-3*e*), 4.10 (t, 1 H, $J_{5,6} = J_{5,6'}$ = 4.2 Hz, H-5), 3.86 (d, 2 H, H-6,6'), 3.39 (s, 3 H, OMe), and 2.47 (s, 3 H, Me).

Anal. Calc. for $C_{14}H_{18}O_6S$: C, 53.49; H, 5.77; S, 10.20. Found: C, 53.56; H, 5.77; S, 10.28.

From the 1:6 mixture of **12** and **15**, methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α-D-glucopyranoside (**15**, 17 mg) was isolated by recrystallisation from EtOH and had m.p. 164–165°, $[\alpha]_D^{25}$ +3.0° (*c* 0.5, acetone). ^{1}H-N.m.r. data (300 MHz): δ 5.20 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 3.43 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 4.14 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 3.54 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 3.87 (dt, 1 H, $J_{5,6a}$ 10.0, $J_{5,6e}$ 4.6 Hz, H-5), 3.70 (t, 1 H, $J_{6a,6e}$ 10.0 Hz, H-6*a*), 4.26 (dd, 1 H, H-6*e*), 5.48 (s, 1 H, PhC*H*), 3.49 (s, 6 H, 2 OMe), and 2.43 (s, 3 H, Me).

Anal. Calc. for $C_{22}H_{26}O_7S$: C, 60.81; H, 6.03; S, 7.38. Found: C, 60.60: H, 6.04; S, 7.34.

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-α-D-*erythro*-hex-3-enopyranoside (**13**), recrystallised from 2-propanol, had m.p. 124.5–125.5°, $[\alpha]_D^{25}$ +143° (*c* 1, chloroform); ν_{max} 1690 cm^{-1} (O–C=C). ^{1}H-N.m.r. data (300 MHz): δ 5.45 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 3.89 (dd, 1 H, $J_{2,5}$ 2.4 Hz, H-2), 5.29 (s, 1 H, H-3), 4.18 (m, 1 H, $J_{5,6a}$ 10.3, $J_{5,6e}$ 5.1 Hz, H-5), 2.66 (t, 1 H, $J_{6a,6e}$ 10.3 Hz, H-6*a*), 4.05 (dd, 1 H, H-6*e*), 5.24 (s, 1 H, PhC*H*), 3.48 (s, 3 H, OMe), and 2.49 (s, 3 H, Me); ^{13}C (75 MHz), δ 95.744 (C-1), 65.323 (C-2), 94.919 (C-3), 94.876 (C-4), 59.906 (C-5), 68.448 (C-6), 102.578 (PhCH), 55.712 (OMe), and 21.567 (Me).

Anal. Calc. for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51; S, 7.97. Found: C, 62.50; H, 5.56; S, 8.22.

Recrystallisation of the last fraction from 2-propanol gave methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α-D-allopyranoside (**14**, 22 mg), m.p. 216–217°, $[\alpha]_D^{25}$ +141° (*c* 1, acetone). ^{1}H-N.m.r. data: δ 5.11 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 3.37–3.40 (H-2, partially overlapped with the methoxyl signals), 4.40 (t, 1 H, $J_{2,3} = J_{3,4}$ = 2.6 Hz, H-3), 3.57 (dd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), ~4.25 (m, H-5, overlapped with the H-6*e* signals), 3.67 (dd, 1 H, $J_{5,6a}$ 10.9, $J_{6a,6e}$ 12.9 Hz, H-6*a*), 4.20 (dd, $J_{5,6e}$ 5.1 Hz, H-6*e*), 5.47 (s, 1 H, PhC*H*), 3.35 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), and 2.44 (s, 3 H, Me).

Anal. Calc. for $C_{22}H_{26}O_7S$: C, 60.81; H, 6.03; S, 7.38. Found: C, 60.90; H, 6.11; S, 7.63.

To a stirred solution of **5** (201 mg, 0.50 mmol) in tetrahydrofuran (3 mL) and CD_3OD (1 mL) was added 16 mg of powdered MeONa. The mixture was stirred for 30 min and then processed as described above. Column chromatography (5:1 C_6H_6–CCl_4) of the product gave successively the 2-deuterio derivative of **13** [75 mg; 55 mg (27.3%) after recrystallisation; the anomeric methoxyl group of which was

retained as judged from the ^{1}H-n.m.r. spectrum], the trideuteriomethyl analogue of **7** [9 mg; 3 mg (1.5%) after recrystallisation from 2-propanol], and the compound (129 mg, 58.9%) having the α-D-*gluco* configuration, derived by addition of CD_3OD to **5**.

Reaction of **6** *with methanolic sodium methoxide.* — To a stirred dispersion of **6** (93 mg, 0.20 mmol) in MeOH (16 mL) was added methanolic M MeONa (0.2 mL) at 22°. The mixture, which gave a clear solution within 30 min, was stirred for 70 min, then neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was partitioned between EtOAc and water, and the organic layer was washed with water, dried, and concentrated. Column chromatography (8:5 C_6H_6–CCl_4) of the syrupy residue (125 mg) gave successively **13** (12 mg), a 5:1 mixture (14 mg) of **13** and **7**, a 1:1.2 mixture (35 mg) of **18** and **7**, a 1:1:1 mixture (12 mg) of **18, 12**, and **14**, and a 1.2:1 mixture (8 mg) of **12** and **14**. The calculated yields of **7, 13, 18, 14**, and **12** (by ^{1}H-n.m.r. spectroscopy) were 24.6, 29.4, 21.8, 9.6, and 8.6%, respectively. Phenyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-α-D-glucopyranoside (**18**), after recrystallisation from 2-propanol, had m.p. 193.5–194°, $[\alpha]_D^{25}$ +65° (*c* 1, acetone). ^{1}H-N.m.r. data (200 MHz): δ 5.99 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 3.57 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 4.31 (dd, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 4.17 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), ~4.20 (dt, $J_{5,6a}$ 9.5, $J_{5,6e}$ 4.8 Hz, H-5), 3.69 (dd, 1 H, $J_{6a,6e}$ 10.5 Hz, H-6*a*), 4.07 (dd, 1 H, H-6*e*), 5.49 (s, 1 H, PhC*H*), 3.55 (s, 3 H, OMe), and 2.43 (s, 3 H, Me).

Anal. Calc. for $C_{27}H_{28}O_7S$: C, 65.31; H, 5.68; S, 6.46. Found: C, 65.31; H, 5.72; S, 6.36.

Similar treatment of **6** with CH_3OD afforded the 2-deuterio derivative of **18**.

Reaction of **7** *with methanolic sodium methoxide.* — Under the same conditions employed for the reaction of **5, 7** (120 mg, 0.30 mmol) was treated with methanolic sodium methoxide. Column chromatography (2:1 C_6H_6–CCl_4) of the syrupy product afforded, in turn, **7** (14 mg, 11.7%), **12** (60 mg, containing small amounts of unidentified product), a 1:1.2 mixture (15 mg) of **12** and **14** (containing a small amount of an unidentified product), and **14** (38 mg). The estimated yields of **7, 12**, and **14** were 11.7, 48, and 34%, respectively.

Reaction of **12** *with methanolic sodium methoxide.* — To a stirred dispersion of **12** (21.7 mg) in MeOH (2 mL) was added methanolic M MeONa (0.1 mL). The mixture was stirred for 90 min; during that time a precipitate formed. After dilution with EtOAc, the mixture was washed successively with dilute HCl and water, dried, and concentrated to a crystalline residue, the ^{1}H-n.m.r. data of which showed it to be a 1:2.7:2.2 mixture of **7, 12,** and **14**.

Methyl 2,3-dideoxy-2-C-p-*tolylsulfonyl*-α-D-erythro-*hexopyranosid-4-ulose* (**16**). — A solution of **13** (101 mg, 0.25 mmol) in aqueous 70% AcOH (5 mL) was heated for 2.5 h at ~80°. After evaporation of the acid, a solution of the residue in water was concentrated. The procedure was repeated until no AcOH remained. Column chromatography (15:1 and 7:1 C_6H_6–EtOAc) of the product gave **16** (45 mg, 57.0%).

*Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-p-tolylsulfonyl-α-*D*-xylo-hexopyranoside* (**17**). — To a solution of **16** (32 mg, 0.1 mmol) in MeOH (1 mL) was added $NaBH_4$ (6 mg). After 30 min, the mixture was partitioned between EtOAc and water, and the organic layer was concentrated. To the residue was added pyridine (0.5 mL) and Ac_2O (0.4 mL). After 5 h, the mixture was poured into water and extracted with EtOAc, and the extract was concentrated. Addition of water to the residue gave a precipitate that was washed with water, and a solution in EtOAc was concentrated. The same reaction was performed again, and the precipitates (63 mg) were combined and subjected to column chromatography (20:1 C_6H_6–EtOAc), to give first a syrup (8 mg) and then **17** (31 mg). The ^{1}H-n.m.r. spectrum (300 MHz) of the first fraction suggested that it was the 4-epimer of **17** ($J_{3a,4}$ 8.7, $J_{3e,4}$ 5.4, and $J_{4,5}$ 8.7 Hz). However, the H-2 and H-3*a* signals overlapped with those of MeO-1 and AcO-4,6, respectively, and it was difficult to determine the configuration at C-2.

The second fraction crystallised from EtOH–cyclohexane to give **17**, m.p. 91.5–92°, $[\alpha]_D^{25}$ +3° (*c* 1.1, chloroform); ν_{max} 1745 (sh) and 1736 cm^{-1} (OCOMe). ^{1}H-N.m.r. data (300 MHz): δ 5.05 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 3.10 (ddd, 1 H, $J_{2,3a}$ 9.0 and $J_{2,3e}$ 5.4 Hz, H-2), 2.24 (m, 1 H, $J_{3a,3e}$ 14.4, $J_{3a,4}$ 5.4 Hz, H-3*a*), 2.39 (dt, 1 H, $J_{3e,4}$ 5.4 Hz, H-3*e*), 4.96 (dt, 1 H, $J_{4,5}$ 3.0 Hz, H-4), 4.02 (dt, $J_{5,6} = J_{5,6'} = 3.9$ Hz, H-5), 4.19 (AB type, 2 H, H-6,6'), 3.25 (s, 3 H, OMe), 2.45 (s, 3 H, Me), 2.10 (s, 3 H, OAc), and 2.03 (s, 3 H, OAc).

Anal. Calc. for $C_{18}H_{24}O_8S$: C, 53.99; H, 6.04; S, 8.01. Found: C, 54.14; H, 6.13; S, 8.10.

REFERENCES

1 T. SAKAKIBARA, Y. TACHIMORI, AND R. SUDOH, *Tetrahedron*, 40 (1984) 1533–1539.
2 T. SAKAKIBARA AND R. SUDOH, *Carbohydr. Res.*, 85 (1980) 33–40.
3 T. SAKAKIBARA, Y. TACHIMORI, AND R. SUDOH, *Carbohydr. Res.*, 131 (1984) 197–208.
4 T. SAKAKIBARA, I. TAKAI, A. YAMAMOTO, Y. TACHIMORI, R. SUDOH, AND Y. ISHIDO, *Carbohydr. Res.*, 160 (1987) c3–c5.
5 T. SAKAKIBARA, I. TAKAI, A. YAMAMOTO, Y. TACHIMORI, R. SUDOH, AND Y. ISHIDO, *Carbohydr. Res.*, 169 (1987) 189–199.
6 M. MILJKOVIĆ, M. GLIGORIJEVIĆ, T. SATOH, AND D. GLIŠIN, *J. Org. Chem.*, 39 (1974) 3847–3850.
7 Y. CHAPLEUR, F. GERMAIN, A. AUBRY, AND D. BAYEUL, *J. Carbohydr. Chem.*, 3 (1984) 443–459.
8 P. M. COLLINS, D. GARDINER, S. KUMAR, AND W. G. OVEREND, *J. Chem. Soc., Perkin Trans. 1*, (1972) 2596–2610.