Carbohydrate Research, 35 (1974) 203–219

REACTION OF HEXOPYRANOSIDE α-KETO TOLUENE-*p*-SULFONATES WITH TRIETHYLAMINE–METHANOL*†

WALTER A. SZAREK, ALEXANDER DMYTRACZENKO‡, AND J. K. N. JONES
Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6 (Canada)
(Received January 29th, 1974; accepted for publication, March 11th, 1974)

ABSTRACT

Treatment of methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-*ribo*-hexopyranosid-3-ulose (**1**) with triethylamine–methanol at reflux temperature yields methyl 2,3-anhydro-4,6-*O*-benzylidene-3-methoxy-α-D-allopyranoside (**2**), a derivative (**3**) of 3-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one, and methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose dimethyl acetal (**4**). The reaction of methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-*arabino*-hexopyranosid-2-ulose (**12**) with triethylamine–methanol afforded methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-2-ulose dimethyl acetal (**19**) and methyl 2,3-anhydro-4,6-*O*-benzylidene-2-methoxy-α-D-allopyranoside (**20**); from the reaction of the β-D anomer (**13**) of **12**, methyl 4,6-*O*-benzylidene-β-D-*ribo*-hexopyranosid-2-ulose dimethyl acetal (**21**) was isolated. Syntheses of the α-keto toluene-*p*-sulfonates **12** and **13** are described. Mechanisms for the formation of the compounds isolated from the reactions with triethylamine–methanol are proposed.

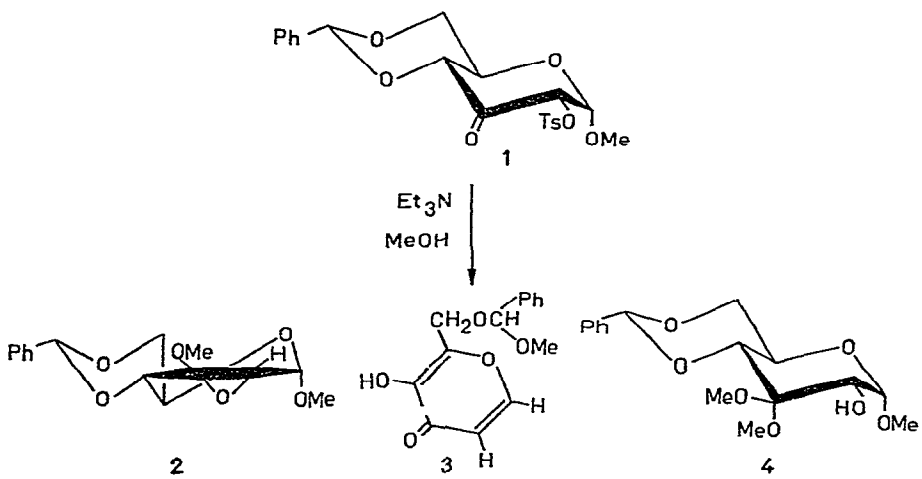
INTRODUCTION

A project in this laboratory is concerned with ground-state and photochemical reactions of carbohydrate α-keto-toluene-*p*-sulfonates[2]. Thus, for example, it has been reported[3] that the reaction of methyl 2,3-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-α-D-*lyxo*-hexofuranosid-5-ulose, a carbohydrate derivative containing the α-keto toluene-*p*-sulfonate grouping in an exocyclic side-chain, with triethylamine–methanol led to some unusual compounds, namely, methyl 2,3-*O*-isopropylidene-α-D-*lyxo*-hexofuranosid-5-ulose dimethyl acetal and methyl 6-deoxy-2,3-*O*-isopropylidene-4-methoxy-α-D-*lyxo*-hexofuranosid-5-ulose. We now describe the reaction of some hexopyranoside α-keto toluene-*p*-sulfonates with triethylamine–methanol.

*Dedicated to Dr. Horace S. Isbell, in honor of his 75th birthday.
† For a preliminary report of part of this work, see Ref. 1.
‡Present address: Universidade Federal do Paraná, Instituto de Bioquímica, Curitiba, Paraná, Brasil.

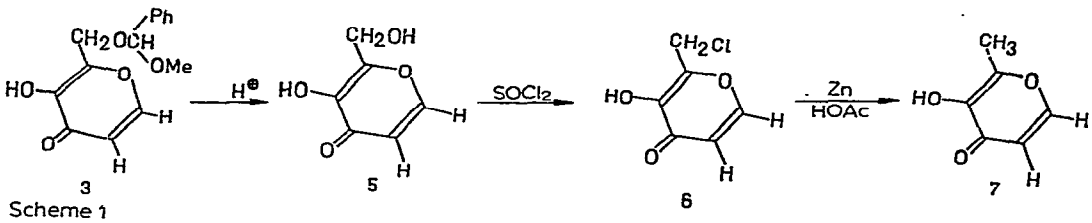
RESULTS AND DISCUSSION

Methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-*ribo*-hexopyranosid-3-ulose (**1**) was readily obtained from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside by selective tosylation[4] at C-2, followed by oxidation with the Pfitzner–Moffatt reagent (methyl sulfoxide–*N*,*N*′-dicyclohexylcarbodi-imide–orthophosphoric acid)[5]. When a solution of compound **1** in methanol containing 2 equiv. of triethylamine was heated at reflux temperature, t.l.c. (solvent *B*) showed the early formation of two new compounds [R_F 0.61 and ~0.29 (elongated spot)], in addition to the starting material (R_F 0.65) and material which did not migrate. After 50 min, t.l.c. revealed that all the starting material had been consumed. The faster-moving component, R_F 0.61, which crystallized from the reaction mixture on cooling (yield 30%), was identified as methyl 2,3-anhydro-4,6-*O*-benzylidene-3-methoxy-α-D-allopyranoside (**2**). The n.m.r. spectrum in chloroform-*d* showed two 3-proton singlets at τ 6.55 and 6.60 which were assigned to the methoxyl groups at C-1 and C-3. The D-*allo* configuration was assigned to **2** on the basis of the magnitude (3 Hz) of $J_{1,2}$; it has been shown[6] in several 2,3-anhydroglycopyranosides that, when the 2,3-epoxy group and the anomeric alkoxyl group are *trans*, $J_{1,2}$ is ~0, whereas when the groups are *cis*, $J_{1,2}$ is 2.5–4.5 Hz.



The slower-moving component, R_F ~0.29, isolated (38%) by fractional crystallization, was shown to be a derivative (**3**) of 3-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one. Compound **3** gave a positive ferric chloride test, and the i.r. spectrum showed absorptions at 1658 and 1640 cm^{-1} consistent with the presence of the grouping –C=C–CO–C=C–. The n.m.r. spectrum in methyl sulfoxide-d_6 showed, at τ 1.90 and 3.62, two 1-proton doublets with a spacing of 5.6 Hz assigned to H-5 and H-6, a 5-proton multiplet at τ 2.60 for the phenyl hydrogens, a 1-proton singlet at τ 4.80 for the acetal-methine hydrogen, a 2-proton singlet at τ 5.45 for the methylene group, and a 3-proton singlet at τ 6.70 for the methoxyl group. The structure assigned

to **3** was confirmed by the conversion of **3** into maltol (**7**) (Scheme 1). Thus, acid-catalyzed hydrolysis of **3** gave 3-hydroxy-2-(hydroxy methyl)-4*H*-pyran-4-one (**5**), which was converted into maltol (**7**) essentially by the procedure described by Stodola[7], namely, by treatment of **5** with thionyl chloride to give the chloro derivative (**6**), followed by reduction of **6** with zinc dust and acetic acid.



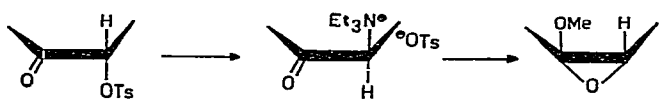
Scheme 1

Compound **3** gave a crystalline 3-*O*-*p*-tolylsulfonyl derivative which, on acid-catalyzed hydrolysis, afforded 2-(hydroxymethyl)-3-*p*-tolylsulfonyloxy-4*H*-pyran-4-one. The n.m.r. spectrum of the hydrolysis product in methyl sulfoxide-d_6 showed a 1-proton triplet at τ 4.27 attributable to the primary hydroxyl proton and a 2-proton doublet at τ 5.65 attributable to the methylene group. Treatment of the hydrolysis product with acetic anhydride–pyridine gave crystalline 2-(acetoxymethyl)-3-*p*-tolyl-sulfonyloxy-4*H*-pyran-4-one.

When a solution of **1** in triethylamine–methanol was heated at reflux temperature for more than 50 min, a third component (R_F 0.54) was formed. A maximum yield of this component was obtained after 48 h, at which time the presence of the α-methoxy epoxide (**2**) could no longer be detected by t.l.c. The pure compound was isolated by column chromatography as a syrup (yield 21%) and was shown to be methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose dimethyl acetal (**4**). The i.r. spectrum showed absorption at 3500 cm^{-1} for a hydroxyl group. The n.m.r. spectrum showed a 1-proton doublet at τ 7.20 ($J_{2,OH}$ 12 Hz) which disappeared on deuteration and was assigned to the hydroxyl proton, a 1-proton doublet at τ 5.35 ($J_{1,2}$ 4 Hz) assigned to H-1, and three 3-proton singlets at τ 6.38, 6.45, and 6.55 assigned to the methoxyl group at C-1 and the two methoxyl groups at C-3. The magnitude of the splitting observed for H-1 is consistent with values reported[8] for an equatorial–axial arrangement of H-1 and H-2, respectively, in methyl 4,6-*O*-benzylidene-α-D-hexopyranosides. Compound **4** afforded a crystalline toluene-*p*-sulfonate.

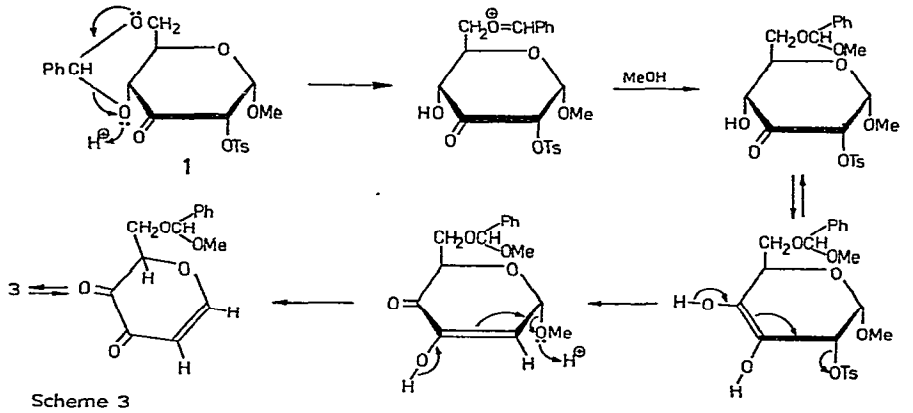
A possible mechanism for the formation of the α-methoxy epoxide **2** from **1** involves initial epimerization to give the axial toluene-*p*-sulfonate, followed by equatorial attack by methanol on the carbonyl carbon, and finally internal displacement of the toluene-*p*-sulfonyloxy group by the carbonyl oxygen. Alternatively, an initial displacement of the toluene-*p*-sulfonyloxy group at C-2 by triethylamine could occur to give a quaternary ammonium salt with inversion of configuration (see Scheme 2). Equatorial attack by methanol on the carbonyl carbon and then internal displacement of triethylamine would give the α-methoxy epoxide **2**. It was felt that,

if this mechanism were operative, the use, of *N,N*-di-isopropylethylamine or of 1,8-bis(dimethylamino)naphthalene, in place of triethylamine, would suppress the formation of the α-methoxy epoxide **2**; 1,8-bis(dimethylamino)naphthalene is a highly strained, strong base, which is almost completely non-nucleophilic[9]. With *N,N*-di-isopropylethylamine, all of the starting material had been consumed after 1 h, and the α-methoxy epoxide **2** and the derivative (**3**) of 3-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one were isolated in yields of 11% and 60%, respectively, (*cf.* 30 and 38% with triethylamine). Similarly, with 1,8-bis(dimethylamino)naphthalene, compound **2** was isolated in only 10% yield. These results suggest that, if *N,N*-di-isopropylethylamine and 1,8-bis(dimethylamino)naphthalene are in fact non-nucleophilic, then the formation of **2** occurs with these bases by way of the epimerization mechanism. The higher yield of the α-methoxy epoxide obtained with triethylamine suggests that at least some of compound **2** may be formed, in this reaction, by way of an initial displacement of TsO-2 by the base; it is possible, however, that the higher yield of **2** may simply be the result of a less-rapid consumption of the starting material (**1**), by its conversion into the γ-pyrone **3**, than in the reactions with *N,N*-di-isopropylethylamine and 1,8-bis(dimethylamino)naphthalene.

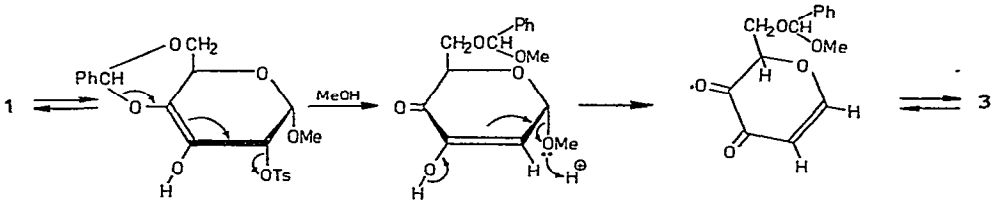


Scheme 2

Although there exists considerable literature[10] on the formation and cleavage of α-alkoxy epoxides (epoxy ethers) in non-carbohydrate systems, the preliminary communication (Ref. 1) is the first report of an analogous carbohydrate derivative. Aspinall and King[11] subsequently reported the formation of 2,3-anhydro-2-methoxy-α-D-allopyranose derivatives on treatment of 3-deoxyhex-2-enopyranoses with *m*-chloroperbenzoic acid. It is interesting that, in the present work, treatment of methyl 2,3-anhydro-4,6-*O*-benzylidene-3-methoxy-α-D-allopyranoside (**2**) with lithium aluminum hydride in tetrahydrofuran resulted in its conversion into methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside[12]. The formation of this compound may involve displacement of methoxide followed by further reduction of the resulting methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside. Stevens and Coffield[10e] have reported that reduction with lithium aluminum hydride of a series of non-carbohydrate α-methoxy epoxides afforded the corresponding methoxy alcohols by attack of hydride ion upon the carbon bearing the methoxyl group. However, 1,2-diphenyl-1-methoxyethylene oxide was found[10d] to react rapidly to give 1,2-diphenylethanol in 75% yield, a course of reaction analogous to that observed with **2**. For **2**, the possibility of an alternative mechanism for the formation of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside, namely, by way of an initial attack by hydride ion at C-2, cannot be excluded.

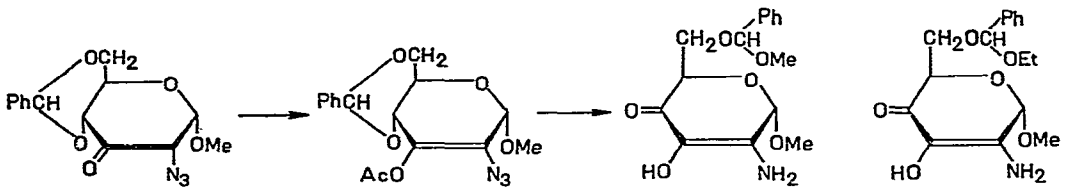


Scheme 3



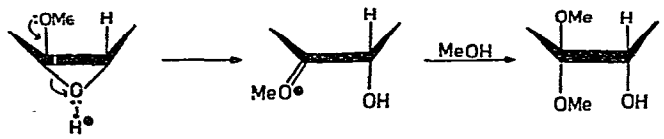
Scheme 4

A possible rationalization for the formation of the γ-pyrone **3** from the sulfonate **1** on treatment with triethylamine–methanol is shown in Scheme 3. In this mechanism, the acid catalyst would be the triethylammonium toluene-*p*-sulfonate formed as a result of the conversion of **1** into the α-methoxy epoxide **2**. A modification of this mechanism is shown in Scheme 4, which involves an attack by methanol on the benzylidene-acetal carbon atom; it might be expected, therefore, that the γ-pyrone **3** obtained by this route would be optically active. In the mechanism shown in Scheme 3, however, the asymmetry at this carbon is lost by formation of the oxocarbonium ion, and the product **3** might be expected to be optically inactive. In the present study, the specific rotation of compound **3** was not determined, but that of the 3-*O*-*p*-tolylsulfonyl derivative was zero; although this result is consistent with the mechanism outlined in Scheme 3, more work is required before the validity of either of these (or other) mechanisms can be established. Of relevance to the present study is the observation by Meyer zu Reckendorf[13] that treatment of the azidoketone **8** with acetic anhydride–pyridine gave the enolacetate **9** which, with sodium methoxide in methanol, afforded the vinylogous amide **10**. The mechanism suggested[13] for the conversion of **9** into **10** requires attack by methanol at the benzylidene–acetal carbon atom. It was also reported[13] that simply heating a solution of azidoketone **8** in ethanol for 3 h afforded the corresponding ethyl derivative (**11**).



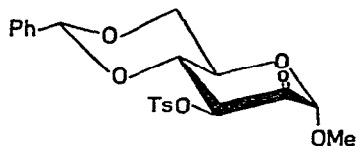
8 9 10 11

Finally, the mechanism of formation of the dimethyl acetal **4** was considered. The observation that a maximum yield of **4** was obtained when the sulfonate **1** was treated with triethylamine–methanol for 48 h, at which time the α-methoxy epoxide **2** could no longer be detected (t.l.c.), suggested that **4** was derived from **2**. In a separate experiment, **2** was heated at reflux temperature in triethylamine–methanol; after 6 days, almost all of **2** was consumed, and t.l.c. showed the presence of the dimethyl acetal **4** and some minor components near the baseline but did not reveal the presence of any of the γ-pyrone **3**. This experiment established that the α-methoxy epoxide **2** was converted into the dimethyl acetal **4**, but that a much greater time (6 days) was required, compared to that (48 h) observed when the α-keto toluene-*p*-sulfonate **1** was treated with triethylamine–methanol. The two experiments are not, however, strictly comparable, since triethylammonium toluene-*p*-sulfonate is formed as **1** is converted into the α-methoxy epoxide **2** and the γ-pyrone **3**. Moreover, when **2** was heated at reflux temperature in methanol containing 2 equiv. of triethylamine and 1 equiv of toluene-*p*-sulfonic acid (as the monohydrate), after only 15 min, t.l.c. (solvent *B*) revealed the dimethyl acetal **4** (R_F 0.54) as the major component, in addition to a small amount of a component which migrated at the same rate as **2** (R_F 0.61) and a small amount of a component having R_F 0.05. The reaction mixture was processed after 5 h, and the dimethyl acetal **4** was isolated in 44% yield. Thus triethylammonium toluene-*p*-sulfonate is implicated in the conversion of the α-methoxy epoxide **2** into the dimethyl acetal **4**, and the acid-catalyzed mechanism shown in Scheme 5 is suggested.

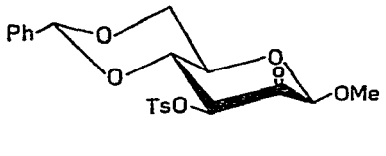


Scheme 5

The results obtained with methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-*ribo*-hexopyranosid-3-ulose and triethylamine–methanol prompted an investigation of the effect of this reagent mixture on other carbohydrate α-keto toluene-*p*-sulfonates, namely, methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-*arabino*-hexopyranosid-2-ulose (**12**) and its β-D anomer (**13**). Both of these compounds were obtained from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**14**) in the following

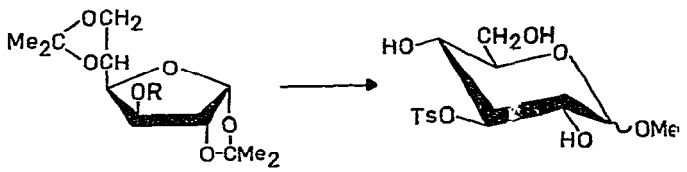


12



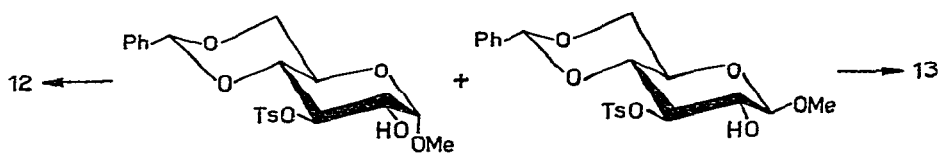
13

manner. Treatment of **14** with toluene-*p*-sulfonyl chloride–pyridine gave the 3-*O*-*p*-tolylsulfonyl derivative **15** which, on methanolysis, afforded syrupy methyl 3-*O*-*p*-tolylsulfonyl-αβ-D-glucopyranoside (**16**). Treatment of **16** with benzaldehyde and zinc chloride gave a crystalline product which was resolved by column chromatography on silica gel to give methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**17**) and the β-D anomer (**18**), each of which was crystalline. Oxidation of **17** and **18** with methyl sulfoxide–acetic anhydride afforded the 2-keto-3-*O*-*p*-tolylsulfonyl derivatives **12** and **13**, respectively.



14 R=H
15 R=Ts

16

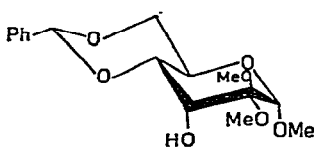


17 18

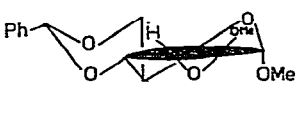
The anomeric configurations were initially assigned to **17** and **18** on the basis of the $J_{1,2}$ values, namely, 4.0 Hz for **17**, consistent with an equatorial–axial arrangement for H-1 and H-2, and 7.5 Hz for **18**, consistent with a diaxial arrangement of these protons[8]. These assignments were corroborated by a comparison of the spectral and chromatographic properties of **17** and **18** with those of methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**17**) obtained by an alternative synthesis. This synthesis involved selective benzoylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside to give the 2-*O*-benzoyl derivative, followed by toluene-*p*-sulfonylation and debenzoylation to give **17** in a low, overall yield.

When methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-*arabino*-hexopyranosid-2-ulose (**12**) was heated at reflux temperature in methanol containing

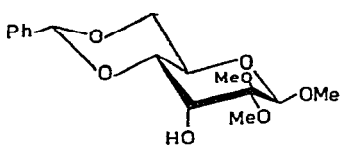
2 equiv. of triethylamine, after 2 h, t.l.c. (ethyl ether) revealed one new component (R_F 0.70) in addition to starting material (R_F 0.44); a second new component (R_F 0.35) was revealed after 3 h. The reaction mixture was processed after 20 h, at which time t.l.c. indicated that almost all of the starting material had been consumed. Moreover, the product having R_F 0.35 was now the major component, and the spot having R_F 0.70 was greatly diminished in intensity compared to its appearance after 2 or 3 h, an observation suggesting the conversion of the faster-moving component into the slower-moving component during the course of the experiment. Only the slower-moving component and a small amount of starting material could be isolated by column chromatography on silica gel; the former was identified as methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-2-ulose dimethyl acetal (**19**) and was obtained crystalline in an 86% yield. The i.r. spectrum showed absorption at 3530 cm^{-1} for a hydroxyl group. The n.m.r. spectrum in chloroform-*d* showed a 5-proton multiplet at τ 2.38–2.84 attributable to the aromatic protons, a 1-proton singlet at τ 4.44 for the benzylidene-methine proton, a 1-proton doublet at τ 5.23 (J 1.4 Hz), three 3-proton singlets at τ 6.52, 6.65, and 6.76 assigned to three methoxyl groups, a broad signal at τ 7.03 assigned to the hydroxyl proton, and signals corresponding to five protons in the region τ 5.53–6.37. The doublet at τ 5.23 was assigned to H-1, and the splitting of 1.4 Hz was attributed to long-range coupling with an equatorial proton at C-3. It has been shown[14–16] that a pair of protons in a "1,3-diequatorial" ("W") disposition produce a small, long-range coupling. In the spectrum of compound **19**, a definitive assignment of a 1-proton signal in the region τ 5.53–6.37 could not be made for H-3. However, **19** formed a crystalline 3-*O*-methanesulfonyl derivative, whose n.m.r. spectrum showed a 1-proton doublet at τ 5.37 for H-1 with a spacing of 1.0 Hz, and a clearly discernible, 1-proton quartet at τ 4.85 assigned to H-3 ($J_{3,4}$ and $J_{1,3}$ equal to 2.8 Hz and 1.0 Hz, respectively). These assignments were confirmed by spin decoupling; thus, irradiation at τ 5.37 (H-1) caused the quartet at 4.85 to collapse to a doublet with a spacing of 2.8 Hz, and irradiation at 4.85 caused the doublet at 5.37 to collapse to a singlet. The value of 2.8 Hz for $J_{3,4}$ is consistent with an equatorial–axial arrangement[17] for these protons, and hence an axial orientation for HO-3.



19



20



21

Since none of the faster-moving component (R_F 0.70) could be obtained from the above experiment with methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-*arabino*-hexopyranosid-2-ulose (**12**) and triethylamine–methanol, a sample of **12** was heated at reflux temperature in this reagent mixture for only 2.5 h, at which time the formation of the slower-moving component (R_F 0.35) could just be detected by t.l.c.

From this experiment, the faster-moving component was isolated crystalline in 13% yield; the structure of methyl 2,3-anhydro-4,6-*O*-benzylidene-2-methoxy-α-D-allopyranoside (**20**) has been assigned to this compound. The i.r. spectrum did not show any absorptions attributable to hydroxyl or carbonyl groups. The n.m.r. spectral data (see Experimental section) were consistent with the assigned structure. Thus, the signal for H-1 appeared as a singlet at τ 5.05, and there were two methoxyl signals at τ 6.53 and 6.72. Unfortunately, it was not possible to definitely assign signals to either H-3 or H-4, and hence to obtain a value for $J_{3,4}$, which would permit the assignment of either the D-*allo* or D-*manno* configuration (see Ref. 6). However, the D-*allo* configuration was assigned on the basis of the observation that the α-methoxy epoxide was converted into the dimethyl acetal **19** during the reaction of methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-*arabino*-hexopyranosid-2-ulose with triethylamine–methanol.

The mechanisms proposed for the formation of the α-methoxy epoxide **20** and the dimethyl acetal **19** on treatment of methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-*arabino*-hexopyranosid-2-ulose (**12**) with triethylamine–methanol are analogous to those suggested for the formation of the α-methoxy epoxide **2** and the dimethyl acetal **4** in the reaction with methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-*ribo*-hexopyranosid-3-ulose (**1**). Thus, axial attack by methanol on the carbonyl carbon in **12**, followed by internal displacement of the *p*-tolylsulfonyloxy group by the carbonyl oxygen, would give the α-methoxy epoxide **20**. The dimethyl acetal **19** would be obtained by an acid-catalyzed opening with methanol of the epoxide ring in compound **20**.

When methyl 4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-β-D-*arabino*-hexopyranosid-2-ulose (**13**) was heated at reflux temperature in methanol containing 2 equiv. of triethylamine, after 10 h, t.l.c. (solvent *D*) revealed a major component (R_F 0.41) and two minor components (R_F 0.59 and R_F 0.33). The component having R_F 0.41 was isolated in crystalline form in 62% yield, and was identified as methyl 4,6-*O*-benzylidene-β-D-*ribo*-hexopyranosid-2-ulose dimethyl acetal (**21**). The i.r. spectrum showed a sharp peak at 3550 cm^{-1} for a hydroxyl group. The n.m.r. spectrum in chloroform-*d* indicated the presence of three methoxyl groups with 3-proton singlets at τ 6.40, 6.48, and 6.56. The C-1 proton in **21** is axial, and its signal was readily recognized as a singlet at τ 5.22. The H-3 signal was observed as a doublet at τ 5.75 with $J_{3,4}$ equal to 2.1 Hz. Compound **21** gave a crystalline 3-*O*-methanesulfonyl derivative; the H-3 doublet was now observed at τ 4.87. The structures of the two minor components from the reaction of **13** with triethylamine–methanol have not been elucidated.

EXPERIMENTAL

General. — Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 141 automatic polarimeter at 26 ±3°. I.r. spectra were recorded with a Unicam SP 1000

spectrophotometer. N.m.r. spectra were recorded at 60 MHz in chloroform-*d* with tetramethylsilane as the internal standard, unless otherwise stated. T.l.c. was performed on Silica Gel G, using (*A*) 1:1 ethyl acetate–petroleum ether (b.p. 60–80°); (*B*) 2:1 ethyl acetate–petroleum ether (b.p. 60–80°); (*C*) diethyl ether; (*D*) 5:1 diethyl ether–petroleum ether (b.p. 30–60°); (*E*) 2:1:1 chloroform–petroleum ether (b.p. 30–60°)–methanol. The air-dried plates were sprayed with either 5% ethanolic sulfuric acid or 10% aqueous sulfuric acid containing 1% of cerium sulfate and 1.5% of molybdic acid, unless otherwise stated, and heated at ~150°. Column chromatography was performed on Silica Gel 60 (70–230 mesh, Merck).

*Methyl 4,6-*O*-benzylidene-2-*O*-p-tolylsulfonyl-α-*D*-ribo-hexopyranosid-3-ulose* (**1**). — This compound was prepared from methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside[4] (120 g) by the method of Baker and Buss[5]. The product was recrystallized from chloroform–ethanol to give white needles (62 g, 52%), m.p. 162–164°; lit. m.p. 165–167° [5], 162–164° [18], 163–164° [19].

*Reaction of methyl 4,6-*O*-benzylidene-2-*O*-p-tolylsulfonyl-α-*D*-ribo-hexopyranosid-3-ulose* (**1**) *with triethylamine–methanol.* — (*a*) *Reaction time of 50 min.* Compound **1** (2.5 g) was dissolved in methanol (65 ml) containing triethylamine (1.6 ml). The solution was heated at reflux temperature, and the reaction was followed by t.l.c. (solvent *B*). After 50 min, all starting material (R_F 0.65) had been consumed, and two new components [R_F 0.61 and ~0.29 (elongated spot)] were present, in addition to material which did not migrate. The solution was cooled to room temperature, and the faster-moving component was obtained by crystallization; recrystallization from chloroform–ethanol gave methyl 2,3-anhydro-4,6-*O*-benzylidene-3-methoxy-α-D-allopyranoside (**2**; 0.495 g, 30%), m.p. 187–190°, $[\alpha]_D$ +108° (*c* 1.32, chloroform); n.m.r. data: τ 2.4–2.7 (5-proton multiplet, Ph), 4.40 (1-proton singlet, benzylidene–methine H), 5.13 (1-proton doublet, $J_{1,2}$ 3 Hz, H-1), 6.30 (1-proton doublet, H-2), 6.55 (3-proton singlet, MeO-3), 6.60 (3-proton singlet, MeO-1); no hydroxyl or carbonyl absorptions in i.r. spectrum.

Anal. Calc. for $C_{15}H_{18}O_6$: C, 61.2; H, 6.2. Found: C, 61.0; H, 6.1.

The filtrate, remaining after the separation of compound **2**, was evaporated to give a residue, which crystallized from chloroform–petroleum ether (b.p. 60–80°) to give the γ-pyrone **3** (0.563 g, 38%), m.p. 115–117°. The product gave a positive ferric chloride test, and on t.l.c. was revealed as a yellow spot with 0.01N potassium permanganate solution. For i.r. and n.m.r. data, see Discussion.

Anal. Calc. for $C_{14}H_{14}O_5$: C, 64.1; H, 5.3. Found: C, 64.4; H, 5.5.

(*b*) *Reaction time of 48 h.* Compound **1** (5.0 g) was dissolved in methanol (130 ml) containing triethylamine (3.2 ml), and the solution was heated at reflux temperature. After 5 h, t.l.c. (solvent *B*) showed the presence of a new component having R_F 0.54, in addition to the two components obtained in (*a*) having R_F 0.61 and R_F ~0.29. After 48 h, the component having R_F 0.61 could no longer be detected. The reaction mixture was concentrated to a syrup, which was chromatographed on a column of silica gel, with solvent *B*, to give methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose dimethyl acetal (**4**) as a homogeneous syrup (21%), $[\alpha]_D$

+112° (*c* 1.24, chloroform). N.m.r. data: τ 2.35–2.90 (5-proton multiplet, Ph); 4.60 (1-proton singlet, PhC*H*); 5.35 (1-proton singlet, $J_{1,2}$ 4 Hz, H-1); 5.51–6.35 (5-protons, H-2,4,6,6′); 6.38, 6.45, and 6.55 (3-proton singlets, MeO-1 and 2 × MeO-3) 7.20 (1-proton doublet, $J_{2,OH}$ 12 Hz, disappeared on deuteration, OH).

Methyl 4,6-O-benzylidene-2-O-p-tolylsulfonyl-α-D-ribo-hexopyranosid-3-ulose dimethyl acetal. — Compound **4** (0.404 g) was treated with *p*-tolylsulfonyl chloride (0.46 g, 3 equiv.) in dry pyridine overnight at room temperature. The solution was processed in the usual manner to a syrup which crystallized from chloroform-hexane. Recrystallization from this solvent gave the title compound (0.303 g, 58%), m.p. 136–138° (dec.), $[\alpha]_D$ +3.5° (*c* 1.2, chloroform). N.m.r. data: τ 4.55 (1-proton singlet, PhC*H*); 5.29 (1-proton doublet, $J_{1,2}$ 4 Hz, H-1); 5.48 (1-proton doublet, H-2); 5.55–6.46 (4-protons, H-4,5,6,6′); 6.58, 6.70, and 6.72 (3-proton singlets, MeO-1 and 2 × MeO-3); 7.58 (3-proton singlet, aromatic Me).

Anal. Calc. for $C_{23}H_{28}O_9S$: C, 57.5; H, 5.9; S, 6.7. Found: C, 57.5; H, 5.9; S, 6.5.

Conversion of γ-pyrone **3** *into maltol* (**7**). — The γ-pyrone **3** (2.43 g) was stirred with Amberlite IR-120(H^+) resin in water at room temperature. When the hydrolysis was complete (t.l.c.; solvent *E*, detection with 0.01N potassium permanganate), the resin was removed by filtration, and the aqueous filtrate was extracted three times with petroleum ether (b.p. 60–80°). Lyophilization of the aqueous solution gave 3-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one (**5**). A portion (500 mg) of **5** was dissolved, with heating, in purified thionyl chloride (5 ml), and the solution was kept overnight at room temperature. The mixture was filtered, and the solid residue was sublimed. The sublimate was recrystallized from benzene to give the chloro derivative **6** (300 mg). Compound **6** (116 mg) was then treated with zinc dust in acetic acid for ~20 min at room temperature. The excess of zinc was precipitated by hydrogen sulfide, the mixture was filtered, and the filtrate was nearly neutralized with sodium hydrogen carbonate and then extracted with ethyl ether. The ether extracts were evaporated, and the residue was sublimed to give a crystalline product whose m.p. and i.r. and n.m.r. spectra were identical with those of an authentic sample of maltol (**7**).

2-(Hydroxymethyl)-3-p-tolylsulfonyloxy-4H-pyran-4-one. — The γ-pyrone derivative **3** (0.354 g) was treated with *p*-tolylsulfonyl chloride (3 equiv.) in dry pyridine overnight at room temperature. The solution was processed in the usual manner to give a syrup which crystallized from chloroform–petroleum ether (b.p. 60–80°), m.p. 83.5–85.5°, $[\alpha]_D$ 0° (*c* 1.07, chloroform). The toluene-*p*-sulfonate (0.355 g) was hydrolyzed with M hydrochloric acid (0.75 ml) in acetone (20 ml) and water (5 ml) at room temperature. After 30 min, no starting material could be detected by t.l.c. (solvent *B*, detection with 0.01N potassium permanganate), and the solution was neutralized with barium carbonate and filtered; the filtrate was extracted with chloroform. Concentration of the chloroform extract gave a syrup, which crystallised from chloroform–petroleum ether (b.p. 60–80°) to give the title compound (0.118 g), m.p. 118–118.5°. N.m.r. data: τ 2.01, 2.12, 2.56, 2.72 (4-proton A_2B_2 system, aryl

protons); 2.95 (2-proton AB quartet, $J_{A,B}$ 5.6 Hz, $\Delta\nu$ 85.5 Hz, H-5,6); 5.38 (2-proton singlet, methylene protons); 6.60 (1-proton singlet, disappeared on deuteration, OH); 7.58 (3-proton singlet, aromatic Me). N.m.r. data (methyl sulfoxide-d_6): τ 2.05, 2.21, 2.50, 2.71 (4-proton A_2B_2 system, aryl protons); 2.71 (2-proton AB quartet $J_{A,B}$ 5.6 Hz, $\Delta\nu$ 110 Hz, H-5,6); 4.32 (1-proton triplet, J 3 Hz, primary OH); 5.72 (2-proton doublet, J 3 Hz, methylene protons); 7.57 (3-proton singlet, aromatic Me).

The product obtained above, on treatment with acetic anhydride and dry pyridine overnight at room temperature, gave a syrup; crystallization from ethyl ether gave 2-(acetoxymethyl)-3-*p*-tolylsulfonyloxy-4*H*-pyran-4-one, m.p. 119–120°; ν_{max} (Nujol) 1745 cm^{-1} (OAc). N.m.r. data: τ 1.95, 2.09, 2.55, 2.72 (4-proton A_2B_2 system, aryl protons); 2.95 (2-proton AB quartet, $J_{A,B}$ 5.6 Hz, $\Delta\nu$ 80.2 Hz, H-5,6); 4.85 (2-proton singlet, methylene protons); 7.58 (3-proton singlet, aromatic Me); 7.90 (3-proton singlet, OAc).

*Reaction of methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-*D*-ribo-hexopyranoside* (**1**) *with* N,N-*di-isopropylethylamine–methanol and with 1,8-bis(dimethylamino)naphthalene–methanol.* — A solution of **1** (5.0 g) in methanol (100 ml) and *N,N*-di-isopropylethylamine (3.2 ml) was heated at reflux temperature. After 1 h, no starting material could be detected by t.l.c. (solvent *B*). The α-methoxy epoxide **2** (0.378 g, 11%) crystallized from the reaction mixture on cooling and was removed by filtration. Concentration of the filtrate gave a syrup which crystallized from chloroform–petroleum ether (b.p. 60–80°) to yield the γ-pyrone **3** (1.83 g, 60%). These products had the same physical constants and n.m.r. spectra as those for compounds **2** and **3**, respectively, isolated from the reaction of **1** with triethylamine–methanol.

A solution of compound **1** (2.0 g) in methanol (40 ml) and 1,8-bis(dimethylamino)naphthalene (2.0 g) was heated at reflux temperature for 1 h, after which time no starting material could be detected by t.l.c. (solvent *B*). The α-methoxy epoxide **2** (0.129 g, 10%) crystallized from the reaction mixture on cooling. The filtrate was concentrated to a syrup which crystallized from chloroform–petroleum ether (b.p. 60–80°) to give the γ-pyrone **3** contaminated with 1,8-bis(dimethylamino)naphthalene; the crude product was dissolved in chloroform, and the solution was washed with 2M potassium carbonate and then with water, and dried ($MgSO_4$). Concentration of the chloroform extract to a syrup and crystallization from chloroform–petroleum ether (b.p. 60–80°) afforded a sample (0.221 g) of pure compound **3**. Both products had the same physical constants and n.m.r. spectra as those for compounds **2** and **3**, respectively, isolated from the reaction of **1** with triethylamine–methanol.

*Treatment of methyl 2,3-anhydro-4,6-*O*-benzylidene-3-methoxy-α-*D*-allopyranoside* (**2**) *with lithium aluminum hydride.* — Compound **2** (500 mg) was dissolved in tetrahydrofuran (100 ml) and lithium aluminum hydride (500 mg) was added. The reaction mixture was heated at reflux temperature, and the reaction was followed by t.l.c. (solvent *B*); after 15 min, no starting material could be detected. A syrupy product was obtained, which crystallized from ethyl acetate–petroleum ether (b.p. 60–80°), to give methyl 4,6-*O*-benzylidene-2-deoxy-α-*D*-*ribo*-hexopyranoside (248 mg), m.p. 128–130°, $[\alpha]_D$ +138° (*c* 1.16, chloroform); lit.[12] m.p. 127–129°, $[\alpha]_D$ +155.6

±3° (*c* 0.649, chloroform). The n.m.r. spectrum was indistinguishable from that of a sample obtained by reduction of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside with lithium aluminum hydride.

Anal. Calc. for $C_{14}H_{18}O_5$: C, 63.1; H, 6.8. Found: C, 62.8; H, 6.5.

Treatment of **2** *with triethylamine–methanol.* — (*a*) A solution of the α-methoxy epoxide **2** (300 mg) in methanol (25 ml) and triethylamine (0.28 ml, 2 equiv.) was heated at reflux temperature; the progress of the reaction was monitored by t.l.c. (solvent *B*). After 24 h, only a small amount of the dimethyl acetal **4** had been formed; at this stage, more triethylamine (0.28 ml, 2 equiv.) was added. After 2 days, more triethylamine (0.56 ml, 4 equiv.) was added, followed by a final addition (1.14 ml, 8 equiv.) after 3 days, to give a total concentration of triethylamine of 16 equiv. (2.26 ml). Most of the α-methoxy epoxide **2** was transformed into the dimethyl acetal **4** after 6 days of reaction. The product, isolated by preparative t.l.c., had the same n.m.r. spectrum as **4** obtained from the reaction of **1** with triethylamine–methanol.

(*b*) *In the presence of toluene-*p*-sulfonic acid.* A solution of the α-methoxy epoxide **2** (329 mg) in methanol (25 ml) containing triethylamine (0.31 ml, 2 equiv.) and toluene-*p*-sulfonic acid monohydrate (215 mg, 1 equiv.) was heated at reflux temperature; the progress of the reaction was monitored by t.l.c. (solvent *B*). After 15 min, only a small amount of starting material (R_F 0.61) remained, and the major product was the dimethyl acetal **4** (R_F 0.54); a small amount of a new component having R_F 0.05 was also present. After 5 h, the reaction mixture was cooled, and the unreacted **2** (25 mg) then crystallized. The filtrate was concentrated to a syrup, and the pure dimethyl acetal **4** (170 mg, 44%) was isolated by column chromatography on silica gel, with solvent *B* as eluant. The n.m.r. spectrum was identical with that of **4** obtained in (*a*).

*Methyl 4,6-O-benzylidene-3-*O*-*p*-tolylsulfonyl-α- and -β-*D*-glucopyranoside* (**17** *and* **18**). — A solution of 1,2:5,6-di-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose[20] (**15**, m.p. 120–121°) (43 g) in methanol (800 ml) containing acetyl chloride (32 ml) was heated at reflux temperature. After 4 h, t.l.c. (solvent *B*) revealed that all of the starting material had reacted. The reaction mixture was neutralized with lead carbonate, water (150 ml) was added, and the mixture was stirred for 1 h. The filtrate was concentrated to ~150 ml and lyophilized. The syrupy residue (35 g) was treated with benzaldehyde (300 ml) and zinc chloride (35 g) at room temperature. After 6 h, t.l.c. (solvent *B*) showed that all of the starting material had reacted and that two new components had been formed. The reaction mixture was partitioned between chloroform and water, and the organic layer was extracted several times with 10% aqueous sodium bisulfite, washed with 5% aqueous sodium hydrogen carbonate, and water, and concentrated to a syrup which crystallized from ethyl acetate–petroleum ether (b.p. 60–80°). T.l.c. (solvent *C* or solvent *D*) showed that this material was a mixture of two components. The mixture was resolved by column chromatography on silica gel, with solvent *D* as eluant, to yield the α-D anomer **17** (R_F 0.28) and the β-D anomer **18** (R_F 0.38). Compound **17** had m.p. 164–165°, $[\alpha]_D$ +32.3° (*c* 1.08, chloroform); ν_{max} (Nujol) 3420 cm^{-1} (OH). N.m.r. data: τ 2.21, 2.37, 2.98, and 3.11 (A_2B_2 system,

four aryl protons); 2.71 (5-proton broad singlet, Ph); 4.65 (1-proton singlet, PhC*H*); 4.91–4.34 (2 protons, $J_{1,2}$ 4 Hz, H-1,3); 4.58–4.83 (1 proton-multiplet, H-2); 4.92–6.42 (4 protons, H-4,5,6,6′); 6.56 (3-proton singlet, OMe); 7.28 (1-proton doublet, $J_{2,OH}$ 9.5 Hz, disappeared on deuteration, OH); 7.72 (3-proton singlet, aromatic Me). Compound **18** had m.p. 160–162°, $[\alpha]_D$ −75.3° (*c* 0.46, chloroform), $[\alpha]_{546}$ −92° (*c* 0.66, chloroform); ν_{max} (Nujol) 3400 cm^{-1} (OH). N.m.r. data: τ 2.22, 2.39, 3.00, and 3.12 (A_2B_2 system, four aryl protons); 2.71 (5-proton singlet, Ph); 4.69 (1-proton singlet, PhC*H*); 5.07–5.38 (1-proton triplet, H-3); 5.52–5.81 (2 protons, $J_{1,2}$ 7.5 Hz, H-1,2); 6.08–6.58 (7 protons, H-4,5,6,6′, and OMe as a sharp singlet at τ 6.45); 6.64 (1-proton doublet, $J_{2,OH}$ 3.2 Hz, disappeared on deuteration, OH); 7.73 (3-proton singlet, aromatic Me). For compound **18**: lit.[21] m.p. 162–163°, $[\alpha]_{546}$ −86.5 ±5° (*c* 0.5, chloroform).

*Alternative synthesis of methyl 4,6-*O*-benzylidene-3-*O*-p-tolylsulfonyl-α-*D*-glucopyranoside* (**17**). — Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was selectively benzoylated, as described by Jeanloz and Jeanloz[22], to give methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (33%), m.p. 169–170°. Treatment of the 2-benzoate with *p*-tolylsulfonyl chloride, as described by Robertson and Griffith[4], afforded the crystalline 3-sulfonate (73%), m.p. 184.5–186°; lit.[4] m.p. 184–186°. Treatment of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (2.0 g) with sodium methoxide in methanol at 0° gave a mixture of products from which **17** was separated by column chromatography on silica gel, with solvent *B* as eluant. Recrystallization from ethyl acetate–petroleum ether (b.p. 60–80°) gave a sample of **17** (0.84 g, 52%) having the same physical constants and i.r. and n.m.r. spectra as the product obtained in the preceding experiment.

*Methyl 4,6-*O*-benzylidene-3-*O*-p-tolylsulfonyl-α-*D*-arabino-hexopyranosid-2-ulose* (**12**). — Compound **17** (3.4 g) was treated with methyl sulfoxide (34 ml) and acetic anhydride (25 ml) at room temperature. After t.l.c. (solvent *D*) had revealed that all of the starting material had reacted, the pH of the solution was adjusted to ~8.5 with 2M potassium carbonate, and the solution was extracted with chloroform. The extract was washed with 5% aqueous sodium hydrogen carbonate and then with water, dried ($MgSO_4$), and concentrated to a syrup which crystallized from ethyl acetate–petroleum ether (b.p. 60–80°). Recrystallization from this solvent mixture afforded **12** (1.76 g, 51%), m.p. 162–164°, $[\alpha]_D$ +6.3° (*c* 1.11, chloroform); ν_{max} (Nujol) 1760 cm^{-1} (C=O), no absorption attributable to OH. N.m.r. data: τ 2.19, 2.32, 2.85, and 3.00 (4-proton A_2B_2 system, aryl protons); 2.70 (5-proton singlet, Ph); 4.52 (1-proton doublet, $J_{3,4}$ 8.0 Hz, H-3); 4.64 (1-proton singlet, PhC*H*); 5.20 (1-proton singlet, H-1); 5.34–6.34 (4 protons, H-4,5,6,6′); 6.52 (3-proton singlet, OMe); 7.67 (3-proton singlet, aromatic Me).

Anal. Calc. for $C_{21}H_{22}O_8S$: C, 58.0; H, 5.1; S, 7.4. Found: C, 57.7; H, 5.3; S, 7.3.

*Methyl 4,6-*O*-benzylidene-3-*O*-p-tolylsulfonyl-β-*D*-arabino-hexopyranosid-2-ulose* (**13**). — Compound **18** was oxidized with methyl sulfoxide–acetic anhydride as described for the α-D anomer **17**, and **13** was obtained in crystalline form from

chloroform–petroleum ether (b.p. 60–80°), m.p. 211.5–213°, $[\alpha]_D$ −94.2° (*c* 0.53, chloroform); ν_{max} (Nujol) 1765 cm^{-1} (C=O), no absorption attributable to OH. N.m.r. data (methyl sulfoxide-d_6): τ 2.15–3.00 (9 protons, aromatic H's); 4.18–4.55 (2 protons, H-3 and PhC*H*); 4.68 (1-proton singlet, H-1); 5.53–6.45 (4 protons, H-4,5,5,6′); 6.56 (3-proton singlet, OMe); 7.68 (3-proton singlet, aromatic Me).

Anal. Calc. for $C_{21}H_{22}O_8S$: C, 58.0; H, 5.1; S, 7.4. Found: C, 57.8; H, 5.0; S, 7.2.

Reaction of **12** *with triethylamine–methanol.* — A solution of compound **12** (1.28 g) in methanol (40 ml) containing triethylamine (0.83 ml, 2 equiv.) was heated at reflux temperature. After 2 h, t.l.c. (solvent *C*) revealed the presence of one new component having R_F 0.70, in addition to the starting material (R_F 0.44); a second component having R_F 0.35 was revealed after 3 h. After 20 h, almost all of the starting material had reacted, and the component having R_F 0.35 was the major component, with only a small amount of the faster-moving component (R_F 0.70) remaining. The reaction mixture was partitioned between chloroform–water; the organic extract was washed with 50mM sulfuric acid, 5% aqueous sodium hydrogen carbonate, and finally with water, dried ($MgSO_4$), and concentrated to a syrup. This material was chromatographed on silica gel, with ethyl acetate as eluant, to yield starting material (72 mg) and the slower-moving component (R_F 0.35) (771 mg, 86%); none of the faster-moving component (R_F 0.70) could be isolated. Recrystallization of the component having R_F 0.35 from ethyl acetate–petroleum ether (b.p. 60–80°) gave pure methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-2-ulose dimethyl acetal (**19**), m.p. 112–113°, $[\alpha]_D$ +81.2° (*c* 2.08, chloroform); ν_{max} (Nujol) 3530 cm^{-1} (OH). N.m.r. data: τ 2.38–2.84 (5-proton multiplet, Ph); 4.44 (1-proton singlet, PhC*H*); 5.23 (1-proton doublet, $J_{1,3}$ 1.4 Hz, H-1); 5.53–6.37 (5 protons, H-3,4,5,6,6′); 6.52, 6.65, and 6.76 (3-proton singlets, 3 × MeO); 7.03 (1-proton broad singlet, disappeared on deuteration, OH).

Anal. Calc. $C_{16}H_{22}O_7$: C, 58.9; H, 6.8. Found: C, 59.0; H, 6.8.

In a separate experiment, a solution of **12** (487 mg) in methanol (20 ml) and triethylamine (0.32 ml, 2 equiv.) was heated at reflux temperature for 2.5 h, at which time the formation of the slower-moving component (R_F 0.35) could just be detected by t.l.c. (solvent *C*). The reaction mixture was processed as described above, and the faster-moving component was isolated by column chromatography on silica gel (solvent *A*); this component was identified as methyl 2,3-anhydro-4,6-*O*-benzylidene-2-methoxy-α-D-allopyranoside (**20**), and was obtained in crystalline form (42 mg, 13%). Recrystallization from ethyl acetate–petroleum ether (b.p. 60–80°) gave a pure sample, m.p. 182.5–184.5°; no absorption attributable to OH or C=O in the i.r. spectrum. N.m.r. data: τ 2.39–2.70 (5-proton multiplet, Ph); 4.46 (1-proton singlet, PhC*H*); 5.05 (1-proton singlet, H-1); 5.60–6.36 (5 protons, H-3,4,5,6,6′); 6.53 and 6.72 (3-proton singlets, 2 × MeO).

Anal. Calc. for $C_{15}H_{18}O_6$: C, 61.2; H, 6.2. Found: C, 60.8; H, 5.9.

*Methyl 4,6-*O*-benzylidene-3-*O*-methanesulfonyl-α-*D*-ribo-hexopyranosid-2-ulose dimethyl acetal.* — Methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-2-ulose di-

methyl acetal (**19**) (200 mg) was treated with methanesulfonyl chloride (1.0 ml, 2 equiv.) in dry pyridine (5 ml) for 2 h at room temperature. The reaction mixture was processed in the usual manner to give the title compound which, after crystallisation from ethyl acetate–petroleum ether (b.p. 60–80°), had m.p. 200–203° (dec.) and no absorption attributable to OH in the i.r. spectrum. N.m.r. data: τ 2.44–2.79 (5-proton multiplet, Ph); 4.44 (1-proton singlet, PhC*H*); 4.85 (1-proton quartet, $J_{1,3}$ 1.0, $J_{3,4}$ 2.8 Hz, H-3); 5.37 (1-proton doublet, $J_{1,3}$ 1.0 Hz, H-1); 5.58–6.44 (4 protons, H-4,5,6,6'); 6.60, 6.67, and 6.70 (3-proton singlets, 3 × MeO); 7.05 (3-proton singlet, mesyl Me).

Anal. Calc. for $C_{17}H_{24}O_9S$: C, 50.5; H, 6.0; S, 7.9. Found: C, 50.5; H, 5.9; S, 8.0.

*Reaction of methyl 4,6-*O*-benzylidene-3-*O*-p-tolylsulfonyl-β-*D*-arabino-hexopyranosid-2-ulose* (**13**) *with triethylamine–methanol.* — A solution of compound **13** (2.0 g) in methanol (100 ml) and triethylamine (1.3 ml, 2 equiv.) was heated at reflux temperature. After 10 h, t.l.c. (solvent *D*) revealed the presence of a major component having R_F 0.41, and two minor components having R_F 0.59 and 0.33; only traces of the starting material (R_F 0.17) remained. The reaction mixture was processed by the procedure described for the α anomer (**12**), and the component having R_F 0.41 crystallized in pure form (0.919 g, 62%) from ethyl acetate–petroleum ether (b.p. 60–80°). The mother liquors were chromatographed on silica gel (solvent *D*) and yielded the components having R_F 0.59 (42 mg) and 0.33 (71 mg) as syrups. The crystalline component (R_F 0.41) was methyl 4,6-*O*-benzylidene-β-D-*ribo*-hexopyranosid-2-ulose dimethyl acetal (**21**), m.p. 178–180°, $[\alpha]_D$ −44.3° (*c* 1.85, chloroform); ν_{max} (Nujol) 3550 cm^{-1} (OH). N.m.r. data: τ 2.30–2.58 (5-proton multiplet, Ph); 4.33 (1-proton singlet, PhC*H*); 5.22 (1-proton singlet, H-1); 5.75 (1-proton doublet, $J_{3,4}$ 2.1 Hz, H-3); 6.05 (2-proton singlet, H-6,6'); 6.40, 6.48, and 6.56 (3-proton singlets, 3 × MeO); 7.59 (1-proton singlet, disappeared on deuteration, OH).

Anal. Calc. for $C_{16}H_{22}O_7$: C, 58.9; H, 6.8. Found: C, 58.8; H, 6.8.

*Methyl 4,6-*O*-benzylidene-3-*O*-methanesulfonyl-β-*D*-ribo-hexopyranosid-2-ulose dimethyl acetal.* — Compound **21** (200 mg) was treated with methanesulfonyl chloride (1.0 ml, 2 equiv.) in dry pyridine (5 ml) for ~1 h at room temperature. The reaction mixture was processed in the usual manner to give the title compound, m.p. 148–149° [from ethyl acetate–petroleum ether (b.p. 60–80°)]; no absorption attributable to OH in the i.r. spectrum. N.m.r. data: τ 2.50–2.75 (5-proton mutiplet, Ph); 4.43 (1-proton singlet, PhC*H*); 4.87 (1-proton doublet, $J_{3,4}$ 2.1 Hz, H-3); 5.37 (1-proton singlet, H-1); 5.51–6.33 (4 protons, H-4,5,6,6'); 6.48, 6.53, and 6.59 (3-proton singlets, 3 × MeO); 7.03 (3-proton singlet, mesyl Me).

Anal. Calc. for $C_{17}H_{24}O_9S$: C, 50.5; H, 6.0; S, 7.9. Found: C, 50.4; H, 5.7; S, 7.9.

ACKNOWLEDGMENTS

The authors thank the National Research Council of Canada for financial

support of this work. One of us (A.D.) is also grateful to the Universidade Federal do Paraná, Brasil, foi a leave of absence to pursue studies at Queen's University.

REFERENCES

1 A. DMYTRACZENKO, W. A. SZAREK, AND J. K. N. JONES, *Chem. Commun.*, (1971) 1220.
2 W. A. SZAREK, *Abstr. Papers VIth Intern. Symp. Carbohyd. Chem.*, Madison, Wisconsin, August 14–18, 1972, p. 3.
3 A. DMYTRACZENKO, W. A. SZAREK, AND J. K. N. JONES, *Carbohyd. Res.*, 26 (1973) 297.
4 G. J. ROBERTSON AND C. F. GRIFFITH, *J. Chem. Soc.*, (1935) 1193.
5 B. R. BAKER AND D. H. BUSS, *J. Org. Chem.*, 30 (1965) 2304.
6 D. H. BUSS, L. HOUGH, L. D. HALL, AND J. F. MANVILLE, *Tetrahedron*, 21 (1965) 69. See also F. SWEET AND R. K. BROWN, *Can. J. Chem.*, 46 (1968) 1481.
7 F. H. STODOLA, *J. Amer. Chem. Soc.*, 73 (1951) 5912.
8 B. COXON, *Tetrahedron*, 21 (1965) 3481.
9 R. W. ALDER, P. S. BOWMAN, W. R. S. STEELE, AND D. R. WINTERMAN, *Chem. Commun.*, (1968) 723.
10 See, for example, (*a*) C. L. STEVENS AND E. FARKAS, *J. Amer. Chem. Soc.*, 74 (1952) 618; (*b*) C. L. STEVENS AND S. J. DYKSTRA, *ibid.*, 75 (1953) 5975; (*c*) C. L. STEVENS AND A. J. WEINHEIMER, *ibid.*, 80 (1958) 4072; (*d*) C. L. STEVENS AND T. H. COFFIELD, *J. Org. Chem.*, 23 (1958) 336; (*e*) C. L. STEVENS AND T. H. COFFIELD, *J. Amer. Chem. Soc.*, 80 (1958) 1919; (*f*) C. L. STEVENS AND C. H. CHANG, *J. Org. Chem.*, 27 (1962) 4392; (*g*) H. PATEL AND G. HITE, *ibid.*, 30 (1965) 4337; (*h*) A. L. MORI, M. A. PORZIO, AND L. L. SCHALEGER, *J. Amer. Chem. Soc.*, 94 (1972) 5034; (*i*) A. L. MORI AND L. L. SCHALEGER, *ibid.*, 94 (1972) 5039.
11 G. O. ASPINALL AND R. R. KING, *Can. J. Chem.*, 51 (1973) 394. See also G. O. ASPINALL, R. R. KING, AND Z. PAWLAK, *ibid.*, 51 (1973) 388.
12 D. A. PRINS, *J. Amer. Chem. Soc.*, 70 (1948) 3955.
13 W. MEYER ZU RECKENDORF, *Naturwissenschaften*, 56 (1969) 328; *Chem. Ber.*, 103 (1970) 2418.
14 D. R. DAVIS, R. P. LUTZ, AND J. D. ROBERTS, *J. Amer. Chem. Soc.*, 83 (1961) 246; J. MEINWALD AND A. LEWIS, *ibid.*, 83 (1961) 2769.
15 L. D. HALL AND L. HOUGH, *Proc. Chem. Soc.*, (1962) 382.
16 D. HORTON AND J. S. JEWELL, *Carbohyd. Res.*, 5 (1967) 149; D. HORTON, J. S. JEWELL, E. K. JUST, AND J. D. WANDER, *ibid.*, 18 (1971) 49.
17 L. D. HALL, *Advan. Carbohyd. Chem.*, 19 (1964) 51.
18 K. ONODERA, S. HIRANO, AND N. KASHIMURA, *Carbohyd. Res.*, 6 (1968) 276.
19 G. B. HOWARTH, W. A. SZAREK, AND J. K. N. JONES, *Can. J. Chem.*, 46 (1968) 3375.
20 K. FREUDENBERG AND O. IVERS, *Ber.*, 55B (1922) 929.
21 S. STIRM, O. LÜDERITZ, AND O. WESTPHAL, *Ann.*, 696 (1966) 180.
22 R. W. JEANLOZ AND D. A. JEANLOZ, *J. Amer. Chem. Soc.*, 79 (1957) 2579.