Carbohydrate Research 60 (1978) 210–218

Note

Synthesis of 6-deoxy-1,2:3,5-di-*O*-methylidene-α-D-*xylo*-hex-5-enofuranose

HARISH C. SRIVASTAVA AND VINAI K. SRIVASTAVA*
Ahmedabad Textile Industry's Research Association, Ahmedabad 380015 (India)
(Received February 16th, 1977; accepted for publication in revised form, May 20th, 1977)

In connection with previous work on the preparation of deoxyhalogenated and unsaturated celluloses[1,2] in our laboratory, work was undertaken to investigate suitable methods for halogenation and elimination in model carbohydrates. Recent reports have used similar reagents as those we have employed for synthesis of halogenated sugars[3,4]. Based on investigations by Kent *et al.*[5], treatment of 1,2:3,5-di-*O*-methylidene-6-*O*-*p*-tolylsulfonyl (tosyl)-α-D-glucofuranose (**2**) with anhydrous potassium fluoride in dry 1,2-dihydroxyethane for 3 min gave a mixture of three major compounds, namely the 6-deoxy-6-fluoro- (**3**, 60%), alkene (**7**, 18%), and 6-*O*-(2-hydroxyethyl) (**6**, 12%) derivatives. Hall *et al.*[3], and Barnett[6] have also observed *O*-(2-hydroxyethyl) derivatives as by-products in this reaction. Compound **3** had been prepared earlier as a syrup in low yield[3,7]. The ^{19}F n.m.r. spectrum of **3** showed a multiplet at +226.6 p.p.m. from $CFCl_3$ in $CDCl_3$ solution; displaying geminal (^{19}F–^{1}H, 48.1 Hz) and vicinal (^{19}F–^{1}H, 32.8 Hz) coupling.

TABLE I

TREATMENT OF 1,2:3,5-DI-*O*-METHYLENE-6-*O*-TOSYL-α-D-GLUCOFURANOSE WITH ANHYDROUS POTASSIUM FLUORIDE

Solvent	*Time*	*Temperature (0°C)*	*Yield of derivatives (%)*			
			3	**7**	**6**	**2**
1 1,2-Dihydroxyethane	2 min	180 (±5)	40	14	10	10
2 1,2-Dihydroxyethane	3 min	180 (±5)	60	18	12	
3 1,2-Dihydroxyethane	5 min	180 (±5)	52	20	12	
4 1,2-Dihydroxyethane	1 h	180 (±5)	30	50	12	
5 Abs. methanol	18 h	100 (±1)	53	22		

The remaining products of the reaction were contaminated with other, minor, compounds, which could not be identified.

*Present address: Department of Biochemistry, Downstate Medical Center, 450 Clarkson Ave., Brooklyn, NY 11203, U.S.A.

To study the effect of longer reaction times, the mixture was treated for different periods and the various products formed were analyzed quantitatively. The results are given in Table I, which shows that the fluoro product reaches a maximum after 3 min and longer reaction-time results in higher yields of the alkene **7**, with a decreased yield of **3**. The formation of the 6-*O*-(2-hydroxyethyl) derivative is fairly constant.

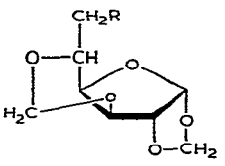
Treatment of **2** with anhydrous potassium fluoride in abs. methanol in a sealed tube gave **3** and **7** as major products, together with traces of two other, unidentified products.

The 6-chloro-6-deoxy derivative (**4**) was prepared from the alcohol **1** in 90–95% yield by treatment with methanesulfonyl chloride in *N,N*-dimethylformamide (DMF)[8] or (chloromethylene)dimethylimminium chloride in DMF[9]. The 6-bromo-6-deoxy derivative (**5**) was prepared in 84% yield by treatment[4] of **2** with lithium bromide in DMF. Acid hydrolysis of **3**, **4**, and **5** with an ion-exchange resin in the acid form afforded crystalline 6-fluoro-, 6-bromo, and 6-chloro-6-deoxy-D-glucoses.

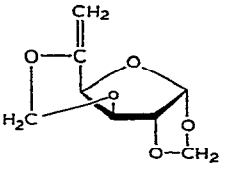
Dehydrohalogenation of the 6-deoxy-6-iodo-derivative **8** with 1.1 mol of potassium *tert*-butoxide in dimethyl sulfoxide for 10 min at room temperature gave 96% of the alkene **7**. Similar treatment of the bromo (**5**) and chloro (**4**) derivatives afforded alkene **7** in high yields. Dehydrohalogenation of **8** with silver nitrate in dimethyl sulfoxide at 60–65° gave **7** in 98% yield. The silver nitrate–dimethyl sulfoxide reagent has been employed by Mehta[10] for dehydrohalogenation of terpene hydrochlorides. Treatment of **4** and **5** with this reagent under similar conditions gave no reaction. Treatment of **4** and **5** at 100° (±1°) in a sealed tube gave the 6-nitrate **9** as a syrup, instead of the expected alkene **7**. Compound **9** showed strong i.r. absorption at ν_{max} 850, 1270, and 1635 cm^{-1}, suggesting the presence of the $-ONO_2$ group. Compound **9** gave positive tests with diphenyl[11] and N,N′-diphenylbenzidine[12], also indicating presence of a nitrate group. Conversion of **9** into the iodo derivative **8** with sodium iodide in dry acetone also confirmed that it was a *O*-nitrate.

Elimination of the tosyl group from **2** was achieved by treatment with potassium *tert*-butoxide–dimethyl sulfoxide at room temperature, to afford the alkene **7** in 96% yield. Elimination of the tosyl group from **2** with methylsulfinyl carbanion (produced by the action of sodium hydride on dimethyl sulfoxide) gave **7** in 75% yield. The ease of elimination of the primary tosyl group from **2** with potassium *tert*-butoxide–dimethyl sulfoxide provides a useful, quantitative synthesis of **7**. Ferrier and Srivastava[13] have recently utilized the alkene **7** as a starting material for synthesis of 3-methoxy-2-oxa-6-oxabicyclo[2,2,1]heptan-7-ol.

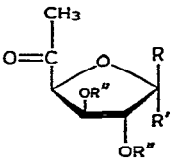
Treatment of **7** with 2% methanolic hydrogen chloride gave methyl 6-deoxy-α,β-D-*xylo*-hexofuranosid-5-ulose (**10**, **11**) in 15% yield, after chromatographic separation. Acetylation of this anomeric mixture afforded mixed α (**12**) and β diacetates (**13**) by conventional procedures as a syrup, $[\alpha]_D$ −5.4°; n.m.r. spectra indicated a 3:7 mixture of α and β anomers. Crystallization of the syrup from ethanol gave the crude β anomer, contaminated by α anomer having $[\alpha]_D$ −28.6°. Three



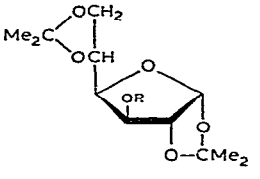
1 R = OH
2 R = OTs
3 R = F
4 R = Cl
5 R = Br
6 R = OCH_2CH_2OH
8 R = I
9 R = ONO_2



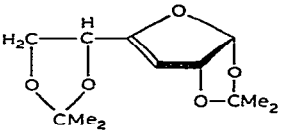
7



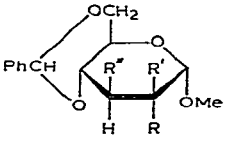
10 R = H, R′ = OMe, R″ = H
11 R = OMe, R′ = R″ = H
12 R = H, R′ = OMe, R″ = Ac
13 R = OMe, R′ = H, R″ = Ac



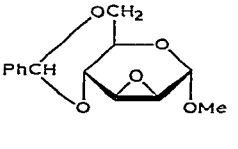
14 R = H
15 R = Ts



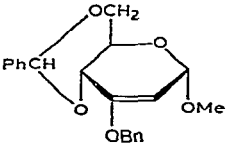
16



17 R = OTs, R′ = H, R″ = OBz
19 R = OTs, R′ = H, R″ = OBn
20 R = OH, R′ = H, R″ = OBn
21 R = H, R′ = OTs, R″ = OBn



18



22

(Bn = $PhCH_2$)

recrystallizations from ethanol afforded the analytically pure β anomer of methyl 2,3-di-*O*-acetyl-β-D-*xylo*-hexofuranosid-5-ulose (**13**), $[\alpha]_D$ −88°, whose purity was confirmed by n.m.r. spectroscopy.

As the elimination of the primary tosyloxy group was very facile, it was of interest to see whether these bases could also eliminate a secondary tosyl group in the five-membered, furanose ring-system. Thus, 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose (**15**) was treated with potassium *tert*-butoxide–dimethyl sulfoxide at room temperature to afford 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose (**16**) in 40% yield, together with the detosylated product **14**. Reaction at lower temperature (10°) increased the yield of alkene **16** (69%). Alkene **16** had been prepared earlier, but in only moderate yields[14–16]. Partial detosylation with this reagent has been reported by Goodman *et al.*[17]. Treatment of **15** with

dimethylsulfinyl carbanion in dimethyl sulfoxide, or sodium hydride in dimethyl sulfoxide, under similar conditions gave a low yield of the alkene **16**.

It was of interest to see whether potassium *tert*-butoxide-dimethyl sulfoxide could bring about facile elimination of a secondary tosyloxy group in the pyranoid ring system. This would provide a direct method for the introduction of a 2,3-double bond in the cellulose molecule. Thus, methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-tosyl-α-D-glucofuranose (**17**) was treated with the reagent for 10 min. Instead of an unsaturated derivative, methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**18**) was obtained in 82% yield. This result is not unexpected, as the benzoyl group is readily hydrolyzed by the base, and generation of a hydroxyl group results in the formation of the 2,3-anhydro derivative **18**. In order to avoid this situation, methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-tosyl-α-D-glucopyranoside (**19**) was treated in the same way; it afforded only the detosylated product **20**. The failure of elimination in compound **19** may be attributed to the unfavorable, equatorial disposition of the eliminating group. To overcome these difficulties, methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-tosyl-α-D-mannopyranoside (**21**) was treated identically with potassium *tert*-butoxide–dimethyl sulfoxide; it gave a mixture of three products. Chromatographic separation gave methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hex-2-enopyranoside (**22**) as the major product (R_F 0.65) in 40% yield. The other two, minor fractions failed to crystallize and were not identified.

EXPERIMENTAL

General methods. — All melting points are uncorrected. Optical rotations were determined for solutions at ambient temperature with a Hilger polarimeter. Organic solutions were dried with anhydrous sodium sulfate, and solvents then removed below 50° *in vacuo*. N.m.r. spectra were recorded on HA-60 or HA-100 instruments and tetramethylsilane was used as an internal reference. All proton shifts are given on the τ scale. Mass spectra were recorded on an AEI MS-902 instrument. T.l.c. was performed on 0.1-mm plates of silica gel (NCL, Poona), and detection was effected with 15% sulfuric acid in ethanol. Column chromatography was conducted with silica gel (NCL, Poona), and 3:2 hexane–ethyl acetate as eluant. Potassium *tert*-butoxide[18], sodium acetylide[19], methylsulfinyl carbanion[20], and (chloromethylene)-dimethylimminium chloride[21] were prepared by standard methods.

Nucleophilic displacement-reactions. — Treatment[5] of 1,2:3,5-di-*O*-methylidene-6-*O*-tosyl-α-D-glucofuranose (**2**) with anhydrous potassium fluoride in boiling 1,2-dihydroxyethane gave, after column chromatography, three major products. Fraction 1 gave crystalline 6-deoxy-1,2:3,5-di-*O*-methylidene-α-D-*xylo*-hex-5-enofuranose (**7**), m.p. 72–73°, $[\alpha]_D$ +173° (*c* 1, chloroform); ν_{max} 1680 cm^{-1} (C=C); *m/e* 186 (M^+); 114, 85, 72, 55, 43, and 42; n.m.r. data ($CDCl_3$): τ 3.98 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 4.89 (d, 1H, $J_{3,4}$ 3.8 Hz, H-4), 4.96 (d, 2H, 1,2-methylidene), 5.18 (d, 1H, $J_{6,6'}$ 0.5 Hz, H-6), 5.27 (d, 1H, H-3), 5.36 (d, 1H, H-6'), 5.48 (d, 1H, $J_{2,3}$ 0.0 Hz, H-2), 5.62–5.74 (q, 2H, 3,5-methylidene).

Anal. Calc. for $C_8H_{10}O_5$: C, 51.6: H, 5.4; Br no. 86.0. Found: C, 51.9; H, 5.5; Br no. 86.0.

Fraction 2, on crystallization from ethanol–ether, afforded 6-deoxy-6-fluoro-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose (**3**), m.p. 58° $[\alpha]_D$ +56° (*c.* 1, chloroform).

Anal. Calc. for $C_8H_{11}FO_5$: C, 46.60; H, 5.38; F, 9.22. Found: C, 46.90; H, 5.00; F, 9.50.

Fraction 3 gave 6-*O*-(2-hydroxyethyl)-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose (**6**), $[\alpha]_D$ +30° (*c* 0.8, chloroform); n.m.r. data ($CDCl_3$): τ 3.99 (H-1), 5.48 (H-2), 5.72 (H-3), 5.94 (H-4), 5.9 (H-5), 6.12 (H-6), 6.22 (H-6'), ~6.32 ($-OCH_2CH_2O-$), 7.5 (OH), ~4.94 (1,3-dioxolane), and ~4.8 (3,5-dioxane).

Treatment of **2** with anhydrous potassium fluoride in dry methanol in a sealed tube for 18 h at 100° gave **3** and **7**, having identical m.p., optical rotation, and n.m.r. spectra as those of authentic samples.

A solution of **2** (1 g) and lithium bromide (0.8 g) in *N,N*-dimethylformamide (20 ml) was heated for 3 h at 65° (±1°) and allowed to cool. Dilution of the solution with water (50 ml) was followed by extraction with chloroform (2 × 40 ml). The extract was washed with water (2 × 30 ml), dried, and evaporated to a syrup that crystallized on trituration with ethanol, to give 6-bromo-6-deoxy-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose (0.62 g, 84%), m.p. 100–101°, $[\alpha]_D$ +32° (*c* 1, chloroform).

Anal. Calc. for $C_8H_{11}BrO_5$: C, 35.98, H, 4.15, Br, 29.92. Found: C, 35.92; H, 4.07; Br, 30.10.

Hydroxyl-group displacement. — *(a)* To a solution of **1** (4 g) in *N,N*-dimethylformamide (40 ml) and methanesulfonyl chloride (4.5 ml) was added dropwise a stirred solution at 60 (±1°) during 1 h. After 16 h at this temperature, the mixture was diluted with water and the product was extracted with chloroform (3 × 40 ml). The extract was washed with water, dried, and evaporated to a syrup (4.6 g). T.l.c. of the crude, syrupy product indicated the presence of some impurities (*O*-formates). The syrupy residue was eluted from silica gel to give 6-chloro-6-deoxy-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose (**4**, 90%), which was crystallized from methanol; yield 3.9 g; m.p. 70–71°, $[\alpha]_D$ +40° (*c.* 1, chloroform).

Anal. Calc. for $C_8H_{11}ClO_5$: C, 43.16; H, 4.98; Cl, 15.92. Found: C, 42.89; H, 4.73; Cl, 16.14.

(b) To a solution of (chloromethylene)dimethylimminum chloride (0.71 g) in *N,N*-dimethylformamide (10 ml) was added a solution of **1** (1.2 g) in DMF (10 ml). After stirring for 30 min at room temperature, the mixture was heated for an additional 30 min at 65°. The pale-yellow mixture was cooled and treated with aqueous, saturated sodium hydrogen carbonate (10 ml) and the product was isolated conventionally to yield the 6-chloro-6-deoxy derivative (1.1 g, 88%), m.p. and mixed m.p. 71°, $[\alpha]_D$ +39.5° (*c* 1, chloroform).

Resin hydrolyses[4,6]. — An aqueous, ethanolic solution–suspension of compound **3** (0.7 g) was heated for 7 h at 70° in the presence of Amberlite IR-120 (H^+)

resin. Concentration of the filtered hydrolyzate, and elution of the residue from silica gel with ethyl acetate, gave 6-deoxy-6-fluoro-D-glucose (0.44 g 72%); m.p. 150–151° (from ethyl acetate–ethanol), $[\alpha]_D$ +81 (2 min) → +46 (*c* 1, equil. water); +90.2 → +48.2°; lit.[4] m.p. 152°, $[\alpha]_D$ +92 (min) → +47°. (equil. water).

Resin hydrolysis (5 h, 70°) of 6-bromo-6-deoxy-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose gave 6-bromo-6-deoxy-D-glucose (70%), m.p. 127–129°, $[\alpha]_D$ +81° (2 min) → +46° (*c* 1, equil., water); lit.[4] m.p. 129–130°, $[\alpha]_D$ +82 (2 min) → +45° (equil., water).

Resin hydrolysis (5 h, 70°) of **4** gave 6-chloro-6-deoxy-D-glucose (65%), m.p. 135–136° (ethyl acetate–ethanol), $[\alpha]_D$ +97.8 (2 min) → +43° (*c* 2, equil., water), +98° (ethanol); lit.[22] m.p. 134–135° $[\alpha]_D$ +100° (*c* 0.5, ethanol).

*6-Deoxy-1,2:3,5-di-*O*-methylidene-α-D-xylo-hex-5-enofuranose* (**7**). — (*a*) 6-Deoxy-6-iodo-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose[23] (**8**, 0.7 g) was dissolved in dimethyl sulfoxide (5 ml), and to the resulting solution potassium *tert*-butoxide (0.52 g) in dimethyl sulfoxide (5 ml) was added. The mixture was kept for 10 min at room temperature, diluted with cold water (20 ml), and then extracted with chloroform (3 × 20 ml). The chloroform extract was washed with cold water (3 × 20 ml), dried, and evaporated to a syrup that crystallized to afford crude alkene **7** (0.42 g, 96%). Recrystallization from methanol gave pure **7**, m.p. 73–74%, $[\alpha]_D$ +174° (*c* 1, chloroform).

Similar treatment of **4** and **5** also afforded **7**.

(*b*) Similar treatment of 1,2:3,5-di-*O*-methylidene-6-*O*-tosyl-α-D-glucofuranose[23] (**2**, 20 g) with potassium *tert*-butoxide in dimethyl sulfoxide gave alkene **7** (10.2 g, 96%), m.p. 74°, $[\alpha]_D$ +173.5° (*c* 1, chloroform).

(*c*) Compound **2** (1.0 g) was dissolved in dimethyl sulfoxide (6 ml) and the resulting solution was added slowly with stirring to a solution of dimethylsulfinyl carbanion (from 0.5 g of sodium hydride in 5 ml of dimethyl sulfoxide). The reaction was allowed to continue for 1.5 h. Conventional isolation of the product gave **7** (0.41, 82%), m.p. 73°, $[\alpha]_D$ +173° (*c* 1 chloroform).

(*d*) Compound **2** (0.8 g) was treated with sodium acetylide in the same way as the foregoing to give alkene **7** (0.3 g, 75%), m.p. 73° $[\alpha]_D$ +174° (*c* 1 chloroform).

Dehydrohalogenation of **8** (0.2 g) with silver nitrate (0.12 g) in dimethyl sulfoxide (4 ml) was performed in the dark for 3 h at 65° (±1°). The mixture was diluted with chloroform (10 ml), the precipitated silver iodide was filtered off, the residue washed with chloroform (5 ml), and the combined solution was extracted with water (20 ml), dried, and evaporated to a syrup that crystallized from methanol to afford alkene **7** (0.12 g, 98%), m.p. 73° $[\alpha]_D$ +174° (*c* 1, chloroform).

Treatment of **5** (0.5 g) with silver nitrate (0.2 g) in dimethyl sulfoxide (10 ml) in a sealed tube for 8 h at 100 (±1°), afforded 1,2:3,5-di-*O*-methylidene-α-D-glucofuranose 6-nitrate (**9**) as a syrup (0.252 g, 54%) that crystallized from ether–petroleum ether (b. p. 40–60°), but the crystals melted at room temperature; $[\alpha]_D$ +140° (*c* 1, chloroform): ν_{max} 850, 1270, and 1635 cm^{-1} (–ONO_2 group).

Anal. Calc. for $C_8H_{11}NO_8$: N, 5.62, Found: 5.68.

Similar treatment of **4** for 12 h gave **9** (53%), $[\alpha]_D$ +140°.

Treatment of **9** (0.2 g) with sodium iodide (0.2 g) in dry acetone (5 ml) for 8 h at 100° in a sealed tube afforded the 6-deoxy-6-iodo derivative **8** (0.15 g, 71%), m.p. 97° (alone and in admixture with an authentic sample[23]), $[\alpha]_D$ +57° [lit.[23] m.p. 97–97.5°, $[\alpha]_D$ +57 ±1.5° (*c* 1, acetone)]. The i.r. spectra of the two iodo compounds were identical.

*Methyl 6-deoxy-α,β-*D-xylo-*hexofuranosid-5-ulose* (**10, 11**). — Alkene **7** (2 g) was boiled under reflux with 2% methanolic hydrogen chloride (40 ml) for 12 h. The mixture was neutralized with Amberlite resin IR-45 [OH^-], (10 g). Removal of resin and solvent gave a syrup (1.5 g) that was resolved on a column of silica gel, with 9:1 chloroform–ethanol as eluant. The last fraction, having R_F 0.29, afforded a mixture of the anomeric methyl furanosides (0.3 g, 15%), $[\alpha]_D$ −16.5° (*c* 0.5, water).

*Methyl 2,3-di-*O*-acetyl-6-deoxy-α,β-*D-xylo-*hexofuranosid-5-ulose* (**12, 13**). — The α,β-mixture of methyl glycosides (0.2 g) was acetylated conventionally with acetic anhydride (5 ml) in pyridine (5 ml) to afford a syrup that was crystallized from ethanol to give the diacetate (0.25 g, 83%), m.p. 118–120°, $[\alpha]_D$ −28.6° (*c* 1, chloroform). The n.m.r. spectrum indicated the presence of both anomers [τ 6.53 (methoxyl), 4.62 (H-1 of β anomer, 70%), 6.63 (methoxyl), and 4.78 (H-1 of α anomer, 30%)]. After three recrystallizations from ethanol, the pure β anomer was obtained; m.p. 122°, $[\alpha]_D$ −88° (*c* 0.6 chloroform); *m/e* 260 (M^+); n.m.r. data ($CDCl_3$): τ 4.63 (H-1), 5.32 (H-2), 5.05 (H-3 and H-4), 6.53 (OCH_3), 7.74, 7.90, and 7.99 (3 OAc).

Anal. Calc. for $C_{11}H_{16}O_7$: C, 50.77, H, 6.19; OCH_3, 11.92. Found: C, 50.97; H, 5.90; OCH_3; 12.3.

*3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-*D-erythro-*hex-3-enofuranose* (**16**). — 1,2:5,6-Di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose[24] (**15**, 2 g) was dissolved in dimethyl sulfoxide (15 ml) and to the resulting solution potassium *tert*-butoxide (1 g) in dimethyl sulfoxide (10 ml) was added slowly with stirring for 4.5 h at 10°. It was then diluted with cold water (20 ml) and conventional isolation of the product gave a syrup (1.15 g) which, on chromotographic purification on silica gel, gave crystalline alkene **16** (Fraction 1). Recrystallization from methanol–petroleum ether (b.p. 40–60°) gave pure alkene (0.8 g, 69%); m.p. 58°, $[\alpha]_D$ +21.2° (*c* 1, chloroform), $[\alpha]_D$ +19.8° (*c* 0.8, ethanol) [lit.[15] m.p. 51°, $[\alpha]_D$ +19.8 ±1° (*c* 3.03 in abs. ethanol)]; *m/e* 227 (M^+ −15), 184, 158, 131, 114, 101, 85, 73, and 43.

Anal. Calc. for $C_{12}H_{18}O_5$: C, 59.5; H, 7.48. Found: C, 59.9, H, 7.07.

Fraction 2 (0.18 g) crystallized from cyclohexane to afford **14** (0.15 g, 12%), m.p. 108–109°, $[\alpha]_D$ −10° (*c* 1, chloroform); lit.[25] m.p. 110°, $[\alpha]_D$ −10°.

*Reaction of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-tosyl-α-*D*-glucopyranoside* (**17**) *with potassium* tert*-butoxide–dimethyl sulfoxide.* — Treatment of **17** (ref. 26) (1.24 g) as before gave a crude product (0.52 g) that was recrystallized from ethanol to give pure methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**18**, 92%); m.p. 143°, alone or admixed with an authentic sample[27], $[\alpha]_D$ +109°, (*c* 1, chloroform).

*Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-tosyl-α-*D*-glucopyranoside* (**19**). — (*a*)

To a solution of methyl 4,6-*O*-benzylidene-2-*O*-tosyl-α-D-glucopyranoside[26] (2 g) in *N*,*N*-dimethylformamide (20 ml), benzyl bromide (5 g), and silver oxide (5.7 g) were added, and mixture was stirred for 20 h in the dark. Thereafter, pyridine (8 ml) was added and the mixture was set aside for 20 h. It was then diluted with water (20 ml), silver salts were filtered off, and the filtrate was extracted with chloroform (3 × 20 ml), washed with water (3 × 20 ml), dried, and evaporated to a syrup (1.6 g) which, on trituration with methanol, gave **19** (1.35 g, 56%), m.p. 114°, $[\alpha]_D$ +22° (*c* 0.9, chloroform); *m/e* 526 (M^+), 248, 233, 217, 205, 155, 147, 139, and 105.

Anal. Calc. for $C_{28}H_{30}O_8S$: C, 63.88; H, 5.74; S, 6.08. Found: C, 63.90; H. 5.74; S. 6.36.

(*b*) Routine tosylation of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (2.5 g) afforded **19** (3.5 g, 98%), m.p. 114°, $[\alpha]_D$ +22° (*c* 0.8 chloroform).

Reaction of methyl 3-O-benzyl-4,6-O-benzylidene-2-O-tosyl-α-D-glucopyranoside with potassium tert-butoxide–dimethyl sulfoxide. — Treatment of **19** with potassium *tert*-butoxide–dimethyl sulfoxide as before gave the detosylated compound **20** (91%); m.p. 178° (alone or in admixture with an authentic sample), $[\alpha]_D$ +52.4° (*c* 1, chloroform); lit.[28] m.p. 178–180°, $[\alpha]_D$ +47°. The i.r. spectra of the two samples were identical; *m/e* 372 (M^+), 191, 179, 175, 149, 147, 132, 105, and 91.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-O-tosyl-α-D-mannopyranoside (**21**). — Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside[29] (1 g) was tosylated conventionally to afford **21** as a thick syrup (1.2 g, 84%), which crystallized from 3:2 hexane–abs. ethanol, m.p. 89–91°. Recrystallization from butanol gave pure **21**; m.p. 100°, $[\alpha]_D$ +22.8° (*c* 1, chloroform) 526 (M^+), 248, 233, 155, 149, 105, 99, 91, and 81.

Anal. Calc. for $C_{28}H_{30}O_8S$: C, 63.88; H, 5.74; S. 6.08. Found: C, 64.37; H, 5.60; S, 6.12.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-α-D-erythro-hex-2-enopyranoside (**22**). — Treatment of **21** (0.5 g) with potassium *tert*-butoxide (0.2 g) in dimethyl sulfoxide (5 ml) as before afforded a syrupy mixture (0.32 g) of three products that was fractionated on silica gel. Fraction 1 gave a syrup (0.14 g, 40%) which crystallized from methanol to give the title compound **22**, m.p. 62°, $[\alpha]_D$ +41° (0.8, chloroform); n.m.r. data ($CDCl_3$): τ 2.58 (m, 10H, Ph), 4.40 (s, 1H, PhCH), 4.22 (bs. 1H, H-2), 5.12 (bd, 1H, $J_{1,2}$ 2.5 Hz, H-1), 5.6 (m, 2H,-CH_2), 5.64 (bd, 1H, $J_{4,5}$ 8.0 Hz, H-4), 6.08 (td, 1H, $J_{5,6a}$ 10.0 Hz, H-5), 6.18 (t, 1H, $J_{6a,6e}$ −10.5 Hz, H-6a), 6.38 (t, 1H, H-6e), 6.55 (s, 3H, OCH_3).

Anal. Calc. for $C_{21}H_{22}O_6$: C, 71.17, H, 6.28; OCH_3; 8.76. Found: C, 70.70; H, 6.40; OCH_3; 8.60.

ACKNOWLEDGEMENTS

We thank Prof. L. D. Hall, University of British Columbia, Vancouver, for details concerning 6-deoxy-6-fluoro-1,2:3,5-di-*O*-methylidene-α-D-glucofuranose,

and Prof. L. Hough, Queen Elizabeth College, University of London, for recording the HA-100 n.m.r. spectra.

REFERENCES

1 H. C. SRIVASTAVA, A. K. KULSHRESHTHA, AND V. K. SRIVASTAVA, *Polymer Lett.*, 13 (1975) 65–70; V. K. SRIVASTAVA, Ph.D. Thesis, Gujarat University, India (1973).
2 H. C. SRIVASTAVA, S. N. HARSHE, AND M. M. GHARIA, *Text. Res. J.*, 42 (1972) 150–154.
3 L. E. EVELYN AND L. D. HALL, *Carbohydr. Res.*, 47 (1976) 285–297; L. D. HALL, personal communication.
4 E. M. BESSEL, A. B. FOSTER, J. H. WESTWOOD, L. D. HALL, AND R. N. JOHNSON, *Carbohydr. Res.*, 19 (1971) 39–48.
5 N. F. TAYLOR AND P. W. KENT, *J. Chem. Soc.*, (1958) 872–875.
6 J. E. G. BARNETT, *Adv. Carbohydr. Chem.*, 22 (1967) 177–227.
7 H. ARITA AND Y. MATSUSHIMA, *J. Biochem. Jpn.*, 69 (1971) 409–413.
8 M. E. EVANS, L. LONG, JR., AND F. W. PARRISH, *J. Org. Chem.*, 33 (1968) 1074–1076.
9 S. HANESSIAN AND N. R. PLESSAS, *J. Org. Chem.*, 34 (1969) 2163–2170.
10 G. MEHTA, *Indian J. Chem.*, 9 (1971) 559–562.
11 J. W. H. OLDHAM, *J. Chem. Soc.*, (1925) 2840–2845.
12 J. DEWAR AND G. FORT, *J. Chem. Soc.*, (1944) 492–495.
13 R. J. FERRIER AND V. K. SRIVASTAVA, *Carbohydr. Res.*, 59 (1977) 333–341.
14 K. FREUDENBERG AND F. BRAUNS, *Ber.*, 55 (1922) 3237–3238.
15 F. WEYGAND AND H. WOLZ, *Chem. Ber.*, 85 (1952) 256–260.
16 K. W. BUCK, A. B. FOSTER, R. HEMS, AND J. M. WEBBER, *Carbohydr. Res.*, 3 (1966) 137–138.
17 H. ARZOUMANIAN, E. M. ACTON, AND L. GOODMAN, *J. Am. Chem. Soc.*, 86 (1964) 74–77.
18 W. G. DAUBEN, *Org. Syn.*, 45 (1965) 33–36.
19 T. F. RUTLEDGE, *J. Org. Chem.*, 22 (1957) 649–652.
20 E. J. COREY AND M. CHAYKOVSKY, *J. Am. Chem. Soc.*, 87 (1965) 1345–1353.
21 H. H. BOSSHARD, R. MORY, M. SCHMID, AND H. ZOLLINGER, *Helv. Chim. Acta*, 42 (1959) 1653–1658.
22 R. L. BOEHM, *J. Org. Chem.*, 23 (1958) 1716–1720.
23 O. T. SCHMIDT, A. DISTELMAIR, AND H. REINHARD, *Chem. Ber.*, 86 (1953) 741–749.
24 K. FREUDENBERG AND O. IVERS, *Ber.*, 55 (1922) 929–941.
25 O. T. SCHMIDT, *Methods Carbohydr. Chem*, 2 (1963) 320–322.
26 G. J. ROBERTSON AND C. E. GRIFFITH, *J. Chem. Soc.*, (1935) 1193–1201.
27 M. GUT AND D. A. PRINS, *Helv. Chim. Acta*, 30 (1947) 1223–1232.
28 J. G. BUCHANAN AND J. C. P. SCHWARZ, *J. Chem. Soc.*, (1962) 4770–4777.
29 H. C. SRIVASTAVA AND V. K. SRIVASTAVA, *Carbohydr. Res.*, 58 (1977) 227–229.