SOME REACTIONS OF UNSATURATED CARBOHYDRATES IN THE PRESENCE OF IODINE*

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ABSTRACT

The addition of the pseudohalogens nitryl iodide (NO_2I), iodine nitrate ($IONO_2$), and iodine azide (IN_3) to the terminal, unsaturated sugar, methyl 5,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hex-5-enofuranoside (**1**), is described. On treatment with iodine in ether solution, tri-*O*-acetyl-D-glucal dimerizes to yield the two anomers of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-*C*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-D-glucopyranose (**6**).

INTRODUCTION

In recent years, there has been considerable interest in addition reactions of unsaturated carbohydrates[1]. One aspect of our work in this area has been an investigation of the stereospecific introduction of nitrogen functions into carbohydrate molecules through pseudohalogen addition reactions. These reagents are conveniently prepared *in situ* by the reaction of the appropriate silver salts with iodine. Thus, for example, the reaction of silver nitrite with iodine generates the pseudohalogen, nitryl iodide (NO_2I), which has been shown to add to some unsaturated carbohydrate derivatives under mild conditions[2,3]. During the course of this work, a number of unexpected reactions of carbohydrate substrates in the presence of iodine were discovered. It has been found[4], for example, that epoxide rings are opened by treatment with iodine in methanol to give the corresponding methoxyalcohols; with methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside a preponderance of the di-equatorial product, namely, methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside, was obtained. More recently, it was shown[5] that iodine in ether converted methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside into furfuryl benzoate. The present article describes some pseudohalogen addition reactions of methyl 5,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hex-5-enofuranoside (**1**), and the results obtained on treatment of tri-*O*-acetyl-D-glucal (**5**) with silver nitrite and iodine.

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*Dedicated to Professor M. Stacey C.B.E., F.R.S., in honour of his 65th birthday.

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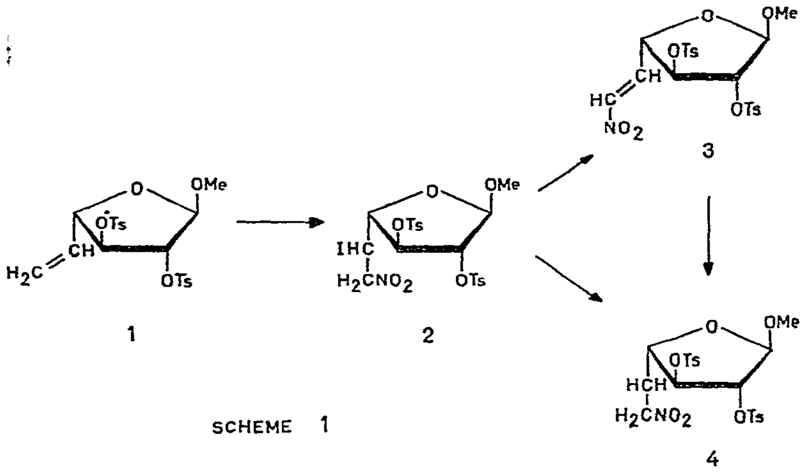
RESULTS AND DISCUSSION

Methyl 5,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hex-5-enofuranoside (**1**), prepared by the method of Ball *et al.*[6], had a complex n.m.r. spectrum, and the



SCHEME 1

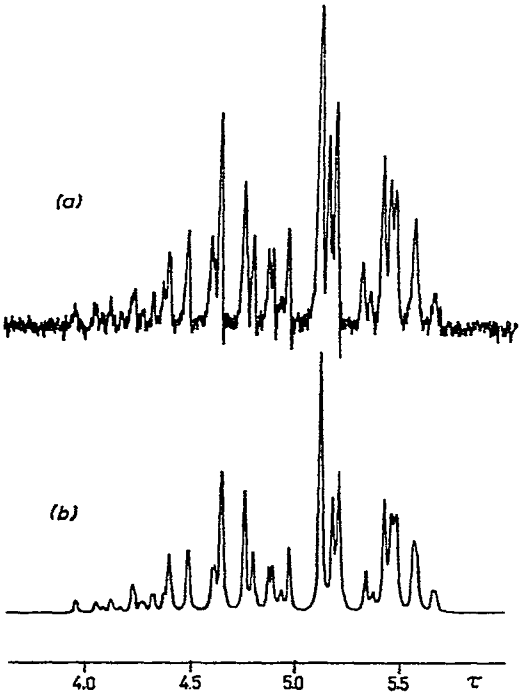


Fig. 1. (*a*). Partial n.m.r. spectrum (60 MHz) of methyl 5,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hex-5-enofuranoside (**1**) in chloroform-*d* solution. (*b*). Computer-simulated spectrum using the Laocoon II program.

parameters (see Experimental) were ascertained by comparing the experimental (Fig. 1*a*) and computer-simulated spectra (Fig. 1*b*). The observation of a 1-proton singlet at τ 5.11 for the anomeric proton confirms[7] a *trans* relationship for H-1 and H-2 on the furanoid ring and that the methoxyl group on C-1 has the α-L configuration.

Treatment of olefin **1** with silver nitrite and iodine in dry ether gave an iodo-*C*-nitro adduct (**2**, Scheme 1) in 71% yield. The crystalline adduct was stable in the dark, but decomposed on exposure to light. It could be dehydrohalogenated by sodium hydrogen carbonate in boiling benzene to give crystalline methyl 5,6-dideoxy-6-nitro-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hex-5-enofuranoside (**3**). In the n.m.r. spectrum of **3**, the vinyl protons, H-5 and H-6, were observed as the AB part of an ABX system. Comparison of this part of the spectrum with computed spectra yielded a value of 14.0 Hz for $J_{5,6}$, indicating[8] that the nitro-olefin has the *trans* stereochemistry. The double bond in compound **3** was selectively reduced with sodium borohydride in ethanol[2] to yield methyl 5,6-dideoxy-6-nitro-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hexofuranoside (**4**). A higher overall yield of **4** could be obtained by treatment of the adduct **2** directly with sodium borohydride. The regiochemistry of the reaction of silver nitrite and iodine in the presence of the unsaturated sugar **1** was established by n.m.r. spectroscopy. Thus, the spectrum of the reduced compound **4** shows a 2-proton multiplet in the region τ 7.50–8.00, characteristic of a methylene group in a carbon chain, but no signal at higher field attributable to a methyl group, thereby establishing C-6 as the position of the nitro-group. This observed regiochemistry is consistent with the free-radical pathway described by Hassner *et al.*[9] for the addition of nitryl iodide to terminal olefins.

When the reaction of olefin **1** with silver nitrite and iodine was performed in more-polar solvents, such as methanol and acetonitrile, a β-iodo nitrate was produced in addition to the iodo-*C*-nitro-adduct **2**; in methanol, the ratio of the two products was 3:2. The β-iodo nitrate was identical with the adduct obtained by Ball *et al.*[6] by the reaction of **1** with silver nitrate and iodine in acetonitrile*. The formation of the β-iodo nitrate in the silver nitrite–iodine reaction in polar solvents may be due to the increased solubility of the silver nitrite; the available nitrite ions could then be oxidized to nitrates. The positions of the iodo and nitrate groups in the adduct have not been determined by chemical methods, and attempts have been made to establish the structure of the compound by X-ray crystallographic analysis. It has been found, however, that the starting olefin **1** can be readily regenerated from the adduct. Thus, treatment of the adduct with sodium iodide in acetone at room temperature afforded **1** in quantitative yield, and treatment with lithium aluminium hydride or sodium borohydride gave **1** in ~80% yield. Hydrogenation of the β-iodo nitrate over palladium-on-carbon or palladium-on-calcium carbonate afforded the previously reported[6] methyl 5,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hexofuranoside.

The addition of the pseudohalogen iodine azide[10] (prepared from iodine

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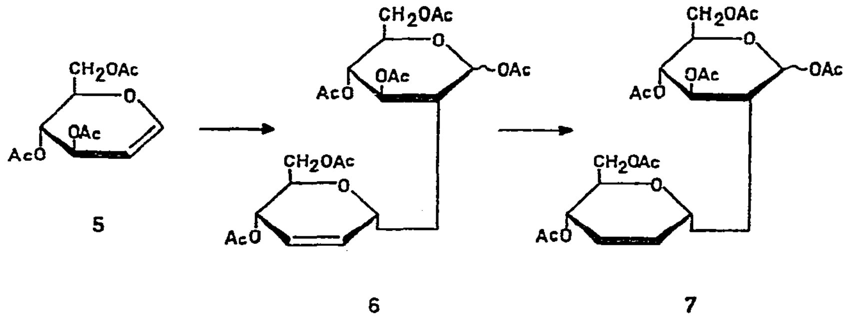
*In the work of Ball *et al.*[6], the crystalline adduct was isolated in only 11% yield. By the modified procedure (see Experimental) employed in the present work, the β-iodo nitrate was obtained in 70% yield.

monochloride and sodium azide in acetonitrile) to the olefin **1** has also been achieved; a crystalline β-iodo azide was isolated in 69% yield, which was stable in the dark, but became colored on exposure to light. Attempts were made to convert the adduct into an unsaturated azide[10,11] by treatment with base. Treatment with potassium *tert*-butoxide in dry ether, however, gave the starting olefin **1**; the adduct was unaffected by sodium hydrogen carbonate or triethylamine in boiling benzene. The olefin **1** was also obtained when the iodo azide was treated with sodium borohydride in refluxing ethanol or with lithium aluminium hydride in ether. The addition of iodine azide to a terminal, unsaturated sugar, 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose, has been reported by Brimacombe *et al.*[12]; X-ray crystallographic analysis established that the product is 6-azido-5,6-dideoxy-5-iodo-1,2-*O*-isopropylidene-β-L-idofuranose.

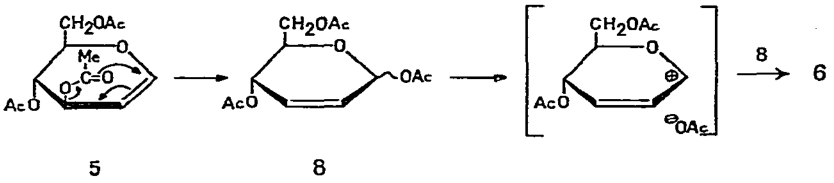
In the present work, the addition of nitryl iodide to tri-*O*-acetyl-D-glucal (**5**) was also attempted. After treatment of the glycal ester with silver nitrite and iodine in dry ether for 1 h at room temperature, the presence of at least five new components was detected by t.l.c. The crude mixture was isolated after 4 h and treated with sodium hydrogen carbonate in boiling benzene; however, no absorption attributable to a nitro group was observed in the i.r. spectrum of the product. Compound **5** was therefore treated with iodine alone in dry ether, and after 1 h, the same thin-layer chromatogram was observed as for the reaction in the presence of silver nitrite. Trituration with ethanol of the crude mixture of products afforded a low yield of crystalline material. A higher yield (~30%) could be obtained by a longer reaction time (2–12 h) and a temperature of ~27°. The crystalline product migrated as an elongated spot in t.l.c., and an osmometric determination of molecular weight suggested that it was a dimer of the starting material. Ferrier and Prasad[13] have reported that, on treatment with boron trifluoride–diethyl ether in benzene solution, tri-*O*-acetyl-D-glucal dimerizes to produce 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-*C*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-D-glucopyranose (**6**, Scheme 2). A comparison of the n.m.r. spectral data for the crystalline product obtained in the present work with that reported for the dimer isolated by Ferrier and Prasad[13] indicated that the product was a mixture of the two anomers of **6**; the product consisted predominantly of the β-D anomer, although the relative proportions of the two forms could not be accurately determined from the n.m.r. spectrum, because of an overlap of other signals with the H-1 signal of the β-D anomer. Hydrogenation of the mixture of unsaturated dimers over palladium black in ethyl acetate afforded a crystalline mixture of the α and β anomers of the dihydro derivative **7** in the ratio of 2:5, respectively.

An attractive mechanism for the dimerization of **5** in the presence of iodine is that suggested[13] for the reaction with boron trifluoride–diethyl ether, and is shown in Scheme 3. It is envisaged that the initial step is an isomerization of the tri-*O*-acetyl-D-glucal to 1,4,6-tri-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranose (**8**). One molecule of **8**, ionized as shown in Scheme 3, could then add in a *trans* manner to another, un-ionized molecule to give the unsaturated dimer **6**. Very recently, Jordaan and Lourens[14] reported that isocyanatosulfonyl chloride (OCN–SO_2Cl) reacts with tri-*O*-



SCHEME 2

acetyl-D-glucal in ether to give the β anomer of **6** in 50% yield. Thus, this reagent (or the trace of sulfur trioxide present) catalyzes the dimerization in the same way as boron trifluoride or iodine.



SCHEME 3

EXPERIMENTAL

General. — Melting points were determined on a Fisher–Johns melting-point apparatus and are uncorrected. Optical rotations were measured at 22 ±3°. I.r. spectra were recorded with a Beckman IR5A spectrophotometer. N.m.r. spectra were recorded at 60 MHz in chloroform-*d* with tetramethylsilane as the internal standard, unless otherwise stated; theoretical spectra were calculated with an IBM 360 computer, equipped with a CALCOMP plotter, by use of a modification of the Laocoon II program of Castellano and Bothner-By[15]. T.l.c. was performed with Silica Gel G and benzene–chloroform–ether, 3:3:1 (*A*); petroleum ether (b.p. 60–80°)–ethyl acetate, 1:1 (*B*) or 2:3 (*C*). The developed plates were air-dried, sprayed with 5% ethanolic sulfuric acid, and heated at about 150°.

*Methyl 5,6-dideoxy-2,3-di-*O-p-*tolylsulfonyl-α-*L-arabino-*hex-5-enofuranoside* (**1**). — Olefin **1**, prepared essentially as described by Ball *et al.*[6], had m.p. 105–107°, $[\alpha]_D$ −60° (*c* 1.0, chloroform); lit.[6] m.p. 109–110°, $[\alpha]_D$ −62° (*c* 0.5, chloroform); R_F 0.7 (solvent *A*), 0.3 (solvent *B*); λ_{max}^{KBr} 6.09 (C=C), 6.23, 8.36, 8.46 μm (OTs); n.m.r. data: τ 2.10–2.75 (8 protons, aromatic H), 4.29 (1-proton multiplet, $J_{5,6(cis)}$ 10.9, $J_{5,6'(trans)}$ 16.8, $J_{4,5}$ 7.0 Hz, H-5), 4.73 (1-proton multiplet, $J_{4,6'}$ −0.4, $J_{6,6'}$ 1.2 Hz, H-6'), 4.85 (1-proton multiplet, $J_{4,6}$ −1.2 Hz, H-6), 5.11 (1-proton broadened singlet, $J_{1,3}$ 0.6 Hz, H-1), 5.20 (1-proton doublet, $J_{2,3}$ 2.2 Hz, H-2), 5.41 (1-proton quartet,

$J_{3,4}$ 5.9 Hz, H-3), 5.58 (1-proton multiplet, H-4), 6.71 (3-proton singlet, OMe), 7.54 (6-proton singlet, aromatic Me).

Reaction of **1** *with silver nitrite and iodine in ether.* — Freshly prepared silver nitrite (0.38 g) and iodine (0.76 g) were stirred in dry ether (50 ml), in a flask covered with aluminium foil, for 5 min at 5°. Olefin **1** (1.00 g) was then added, and the reaction mixture was stirred for 18 h at room temperature. Solid material was removed by filtration, the filtrate was evaporated, the syrupy residue was dissolved in chloroform, and the solution was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and evaporated to a pale-orange syrup. Crystallization from ether or chloroform–petroleum ether (b.p. 30–60°) gave the iodo-*C*-nitro adduct **2** (0.93 g, 71%), m.p. 128–132°, $[\alpha]_D$ −75° (*c* 1.3, chloroform); $\lambda_{\max}^{\mathrm{KBr}}$ 6.23, 8.35, 8.45 (OTs), 6.40 μm (C–NO_2); n.m.r. data: τ 2.10–2.75 (8 protons, aromatic H), 4.97 (1-proton singlet, H-1), 5.08 (1-proton doublet, H-2), 5.16–5.78 (5 protons, H-3, H-4, H-5, and H-6,6′), 6.70 (3-proton singlet, OMe), 7.50 (6-proton singlet, aromatic Me).

Anal. Calc. for $C_{21}H_{24}INO_{10}S_2$: C, 39.3; H, 3.8; I, 19.8; N, 2.2; S, 10.0. Found: C, 39.5; H, 4.2; I, 20.0; N, 2.3; S, 10.3.

*Methyl 5,6-dideoxy-6-nitro-2,3-di-*O-p-*tolylsulfonyl-α-*L-arabino-*hex-5-enofuranoside* (**3**). — The iodo-*C*-nitro adduct **2** (1.05 g) was stirred for 3 days in boiling benzene (100 ml) with anhydrous sodium hydrogen carbonate (10 g). The filtered solution was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and concentrated to a pale-yellow syrup which crystallized from ether. Recrystallization from chloroform–petroleum ether (b.p. 30–60°) gave **3** (0.56 g, 68%), m.p. 124–125°, $[\alpha]_D$ −41 ±2° (*c* 1.0, chloroform); $\lambda_{\max}^{\mathrm{KBr}}$ 6.03 (C=C), 6.23, 8.36, 8.46 (OTs), 6.51 μm (olefinic NO_2); n.m.r. data: τ 2.18–2.78 (8 protons, aromatic H), 2.88 (2 protons, $J_{4,5}$ 2.0, $J_{5,6}$ 14.0 Hz, H-5 and H-6), 5.02 (1-proton singlet, H-1), 5.21 (1-proton doublet, $J_{2,3}$ 1.5 Hz, H-2), 5.29 (1-proton quartet, $J_{3,4}$ 5.4 Hz, H-4), 5.45 (1-proton quartet, H-3), 6.69 (3-proton singlet, OMe), 7.51 (6-proton singlet, aromatic Me).

Anal. Calc. for $C_{21}H_{23}NO_{10}S_2$: C, 49.1; H, 4.5; N, 2.7. Found: C, 49.0; H, 4.5; N, 2.5.

*Methyl 5,6-dideoxy-6-nitro-2,3-di-*O-p-*tolylsulfonyl-α-*L-arabino-*hexofuranoside* (**4**). — A mixture of adduct **2** (0.342 g), ethanol (25 ml), and sodium borohydride (65 mg) was stirred for 18 h at room temperature. Water was then added dropwise until the solution became cloudy, and the mixture was concentrated to dryness. The residue was extracted with chloroform, and the extracts were washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and concentrated to a syrup which crystallized from chloroform–ether to give **4** (0.257 g, 75%), m.p. 124–125°, $[\alpha]_D$ +24° (*c* 1.3, chloroform); R_F 0.65 (solvent *A*), 0.12 (solvent *B*); $\lambda_{\max}^{\mathrm{KBr}}$ 6.23, 6.36, 6.46 (OTs), 6.41 μm (C–NO_2); n.m.r. data: τ 2.08–2.70 (8 protons, aromatic H), 5.18 (1-proton singlet, H-1), 5.20 (1-proton doublet, $J_{2,3}$ 3.2 Hz, H-2), 5.32–6.15 (4 protons, H-3, H-4, and H-6,6′), 6.76 (3-proton singlet, OMe), 7.53 (6-proton singlet, aromatic Me), 7.50–8.00 (2 protons, H-5,5′).

Anal. Calc. for $C_{21}H_{25}NO_{10}S_2$: C, 48.9; H, 4.9; N, 2.7. Found: C, 48.9; H, 5.0; N, 2.6.

Compound **4** was obtained also in 68% yield by treatment of nitro-olefin **3** (0.24 g) in ethanol (50 ml) with sodium borohydride (0.125 g) for 5 h at room temperature.

Reactions of **1**. — (*a*) *With silver nitrite and iodine in methanol and in acetonitrile.* Olefin **1** (1.75 g) was added to a mixture of silver nitrite (1.5 g) and iodine (2.5 g) at 5° in methanol (50 ml), in a flask covered with aluminium foil. The mixture was stirred for 5 days at room temperature and then filtered, and the filtrate was evaporated. A solution of the deep red, syrupy residue in chloroform was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and evaporated. A solution of the residue in methanol (20 ml) was kept for 1 week at 5° to afford a crystalline product (0.74 g, 30%), m.p. 124–127°, which was shown (m.m.p., i.r. and n.m.r. spectra) to be identical with the β-iodo nitrate obtained by the reaction of olefin **1** with silver nitrate and iodine in acetonitrile (see below). The methanolic mother liquor was evaporated, and a solution of the residue in chloroform–petroleum ether (b.p. 30–60°) was kept for several days at 5°; crystals (0.48 g, 20%) of the iodo-*C*-nitro adduct **2** were obtained having m.p. 126–128°. T.l.c. examination of the mother liquor showed the presence of more of the iodonitrate and iodo-*C*-nitro adducts, in addition to trace amounts of two other components. Only the two adducts were obtained when the reaction was performed in acetonitrile.

(*b*) *With silver nitrate and iodine.* A mixture of olefin **1** (1.03 g), silver nitrate (0.38 g), and iodine (0.55 g) in acetonitrile (25 ml) was shaken for 6 days in a flask covered with aluminum foil. The filtered mixture was then evaporated, and the reddish-brown, syrupy residue was dissolved in chloroform. The solution was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and evaporated to a yellow syrup. Crystallization from methanol or chloroform–petroleum ether (b.p. 30–60°) gave a β-iodo nitrate (0.97 g, 70%), m.p. 125–127°, $[\alpha]_D$ $-48.3°$ (*c* 2.6, chloroform); n.m.r. data: τ 2.10–2.76 (8 protons, aromatic H), 4.99–5.82 (7 protons, H-1, H-2, H-3, H-4, H-5, and H-6,6'), 6.70 (3 protons, OMe), 7.50 (6-proton singlet, aromatic Me). There was no depression of the melting point on admixture with a sample of an iodo nitrate prepared and reported earlier[6].

Reactions of the β-iodo nitrate derivative of **1**. — (*a*) *With sodium iodide in acetone.* A solution of the β-iodo nitrate derivative of **1** (0.32 g) in acetone (45 ml) was stirred with sodium iodide (0.5 g) for 9 h at room temperature. The acetone was evaporated to leave a dark-red syrup that was dissolved in chloroform. The solution was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and evaporated to a yellow syrup that crystallized on standing. Recrystallization from methanol gave the olefin **1** (0.22 g, 95%), m.p. 105–107°, not depressed on admixture with an authentic sample. The infrared spectrum (KBr) was also indistinguishable from that of an authentic sample of **1**.

(*b*) *Hydrogenation.* A solution of the β-iodo nitrate derivative of **1** (1.23 g) in ethanol (30 ml) containing palladium-on-calcium carbonate (100 mg) was subjected, with shaking, to a hydrogen pressure of 1 atm. for 24 h. The filtered solution was evaporated, and the solid residue was recrystallised from petroleum ether to give methyl 5,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-L-*arabino*-hexofuranoside (0.77 g, 93%), m.p. 93–94°, not depressed on admixture with a sample prepared and reported earlier[6]. The same compound was obtained when palladium-on-carbon in the presence of pyridine was used instead of palladium-on-calcium carbonate.

Reaction of **1** *with iodine azide.* — To a vigorously stirred solution of sodium azide (0.42 g) in acetonitrile (75 ml) at 5° was added, dropwise, iodine monochloride (0.3 ml); after 5 min, olefin **1** (1.51 g) was added, and the solution was stirred for 30 h at room temperature. The acetonitrile was evaporated, and a solution of the syrupy residue in chloroform was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and evaporated to a syrup, which crystallized from ether to give a β-iodo azide (1.42 g, 69%), m.p. 97–98°, $[\alpha]_D$ $-59 \pm 2°$ (*c* 1.7, chloroform); λ_{max}^{KBr} 4.72 (N_3), 6.23 μm (OTs); n.m.r. data τ 2.10–2.80 (8 protons, aromatic H), 4.99–6.40 (7 protons, H-1, H-2, H-3, H-4, H-5, and H-6,6'), 7.58 (6-proton singlet, aromatic Me).

Anal. Calc. for $C_{21}H_{24}IN_3O_8S_2$: C, 39.6; H, 3.8. Found: C, 39.6; H, 4.0.

Treatment of β-iodo azide derivative of **1** *with lithium aluminium hydride.* — The β-iodo azide derivative of **1** (0.72 g) and lithium aluminium hydride (40 mg) in dry ether were stirred for 3 h at room temperature. Ethyl acetate was added, and the solvents were evaporated. The residue was extracted with chloroform, the extracts were filtered, and the filtrate was evaporated. T.l.c. examination of the residue showed the presence of several components. The major component could be crystallized from methanol and was shown to be the olefin **1** (0.41 g, 81%); the m.p. was not depressed on admixture with an authentic sample.

*Treatment of tri-*O*-acetyl-D-glucal* (**5**) *with silver nitrite and iodine.* — Iodine (4.05 g, 16 mmoles) and silver nitrite (2.63 g, 17 mmoles) were stirred in dry ether (50 ml), in a flask covered with aluminium foil, for 10 min at room temperature. A solution of **5** (4.08 g, 15 mmoles) in dry ether (5 ml) was then added portionwise, and stirring was continued. After 1 h, t.l.c. examination (solvent *C*) revealed the presence of at least five new components. After 4 h, the reaction mixture was filtered, and the filtrate was evaporated. A solution of the residue in chloroform (50 ml) was washed with 10% aqueous sodium thiosulfate, dried ($MgSO_4$), and evaporated. The residue was heated at reflux temperature in benzene (50 ml) containing sodium hydrogen carbonate (3 g) for 3 h. The filtered mixture was evaporated, and a chloroform solution of the residue was washed with aqueous sodium thiosulfate and afforded a syrupy mixture of compounds. The i.r. spectrum (film) did not show any absorption attributable to a nitro group.

*Reaction of tri-*O*-acetyl-D-glucal* (**5**) *with iodine in ether.* — A solution of **5** (2.0 g) [R_F 0.78 (solvent *C*)] and iodine (2.0 g) in ether (25 ml) was kept at 22° under normal laboratory lighting. After 1 h, the same thin-layer chromatogram (solvent *C*) was observed as for the preceding experiment. The solution was concentrated, and a solution of the residue in chloroform was washed with aqueous sodium thiosulfate dried ($MgSO_4$), and evaporated. Trituration of the residue with ethanol gave a crystalline material, which was identified as a mixture of the two anomers of the unsaturated dimer **6**; yield 0.15 g (7%), m.p. 192–197°, R_F 0.45 (elongated spot, solvent *C*). Higher yields (~30%) could be obtained when the reaction was performed at 27° and for longer times (2–12 h); the isolation of a crystalline product became difficult when reaction times longer than 12 h were used, because of the formation of a tarry, intractable material. In a separate experimental, the isolated, crystalline material was recrystallized several times from ethanol to give a product having m.p. 203–205°, $[\alpha]_D$ +72° (*c* 1.0, chloroform); mol. wt., 544 ±2 (osmometry), $C_{24}H_{32}O_{14}$ calc.: 544. The product was revealed on a thin-layer chromatogram with a potassium permanganate spray reagent, an observation consistent with the presence of a double bond. The 100-MHz n.m.r. spectrum of this product in chloroform-*d* was essentially the same as that published by Ferrier and Prasad[13] for 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-*C*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-β-D-glucopyranose, except for the appearance of a small doublet, with a spacing of 3.5 Hz, 0.42 p.p.m. downfield from the H-1 signal of the β-D anomer; this small doublet is attributed to H-1 of the α-D anomer. The relative proportions of the two anomers could not be determined by integration of their H-1 signals, because of an overlap of the signal for the β-D anomer with the H-2 and H-3 signals of the unsaturated moiety.

Hydrogenation of the unsaturated dimer sample (0.15 g), having m.p. 192–197°, over palladium black in ethyl acetate for 7 h gave a syrup which partially crystallized. Crystallization from ethanol gave a product, m.p. 165–170°, which did not react with potassium permanganate on a thin-layer chromatogram. The 100-MHz n.m.r. spectrum in chloroform-*d* showed the presence of the α and β anomers of the saturated dimer 7 in the ratio of 2:5, respectively; the H-1 signal of the α-D anomer appeared as a doublet, with a spacing of 3.1 Hz, 0.50 p.p.m. downfield from the H-1 signal of the β-D anomer. The spectral features were very similar to those of the unsaturated product **6**, except for the absence of the H-2 and H-3 signals of the unsaturated moiety, overlapping the H-1 signal of the β-D anomer, and the appearance of signals corresponding to four protons at higher field.

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REFERENCES

1 R. J. Ferrier, *Advan. Carbohyd. Chem.*, 20 (1965) 67; 24 (1969) 199.

2 W. A. Szarek, D. G. Lance, and R. L. Beach, *Chem. Commun.*, (1968) 356; *Carbohyd. Res.*, 13 (1970) 75.

3 W. A. Szarek, J. S. Jewell, I. Szczerek, and J. K. N. Jones, *Can. J. Chem.*, 47 (1969) 4473.

4 J. S. Jewell and W. A. Szarek, *Carbohyd. Res.*, 16 (1971) 248.

5 R. G. S. Ritchie and W. A. Szarek, *Carbohyd. Res.*, 18 (1971) 443.

6 D. H. Ball, A. E. Flood, and J. K. N. Jones, *Can. J. Chem.*, 37 (1959) 1018.

7 S. J. Angyal, *Angew. Chem.*, 81 (1969) 172; J. D. Stevens and H. G. Fletcher, Jr., *J. Org. Chem.*, 33 (1968) 1799.

8 W. E. Noland, B. A. Langager, J. W. Manthey, A. G. Zacchei, D. L. Petrak, and G. L. Eian, *Can. J. Chem.*, 45 (1967) 2969.

9 A. Hassner, J. E. Kropp, and G. J. Kent, *J. Org. Chem.*, 34 (1969) 2628.

10 A. Hassner and L. A. Levy, *J. Amer. Chem. Soc.*, 87 (1965) 4203; F. W. Fowler, A. Hassner, and L. A. Levy, *ibid.*, 89 (1967) 2077; A. Hassner, *Accounts Chem. Res.*, 4 (1971) 9.

11 G. L'Abbé and A. Hassner, *Angew. Chem. Int. Ed. Engl.*, 10 (1971) 98.

12 J. S. Brimacombe, J. G. H. Bryan, T. A. Hamor, and L. C. N. Tucker, *Chem. Commun.*, (1968) 1401; J. S. Brimacombe, J. G. H. Bryan, and T. A. Hamor, *J. Chem. Soc.*, (*B*), (1970) 514. See also J. S. Brimacombe, F. Hunedy, and M. Stacey, *Carbohyd. Res.*, 13 (1970) 447.

13 R. J. Ferrier and N. Prasad, *J. Chem. Soc.*, (*C*), (1969) 581.

14 A. Jordaan and G. J. Lourens, *Chem. Commun.*, (1971) 581.

15 S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41 (1964) 3863.