Addition of Pseudohalogens to Unsaturated Carbohydrates. V. Addition of Iodine Trifluoroacetate[1]

R. G. S. RITCHIE AND W. A. SZAREK

Department of Chemistry, Queen's University, Kingston, Ontario

Received August 20, 1971

Treatment of 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**1**) with silver trifluoroacetate and iodine in acetonitrile gave 3,6-anhydro-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-gluco(and β-L-ido)-furanose (**2**) and 5-deoxy-5-iodo-1,2-*O*-isopropylidene-6-*O*-trifluoroacetyl-α-D-gluco(and/or β-L-ido)furanose (**3**). Component **2** was converted into 3,6-anhydro-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**5**) by hydrogenation over Raney nickel, and component **3** was converted into 5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**6**) by treatment with methanol, followed by hydrogenation. Treatment of 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-trifluoroacetyl-α-D-*xylo*-hex-5-enofuranose (**7**) with silver trifluoroacetate and iodine in acetonitrile gave the addition product **8**, but no 3,6-anhydro derivative; **8** was converted into the iodohydrin **4** by treatment with methanol. The preparation of the 5-deoxy derivative **6** by way of the iodohydrin **4** represents an overall anti-Markovnikov hydration of the olefin **1**; the reactions described are a convenient alternative to the hydroboration–oxidation procedure for the preparation of **6**.

Le traitement du 5,6-didéoxy-1,2-*O*-isopropylidène-α-D-*xylo*-hex-5-énofuranose (**1**) par le trifluoracétate d'argent et l'iode dans l'acétonitrile conduit aux 3,6-anhydro-5-déoxy-5-iodo-1,2-*O*-isopropylidène-α-D-gluco(et β-L-ido)furanose (**2**) et 5-déoxy-5-iodo-1,2-*O*-isopropylidène-6-*O*-trifluoroacétyl-α-D-gluco(et/ou β-L-ido)furanose (**3**). Le composé **2** a été transformé en 3,6-anhydro-5-déoxy-1,2-*O*-isopropylidène-α-D-*xylo*-hexafuranose (**5**) par hydrogénation sur nickel de Raney et le composé **3** a été transformé en 5-déoxy-1,2-*O*-isopropylidène-α-D-*xylo*-hexofuranose (**6**) par traitement avec le méthanol puis par hydrogénation. Le traitement du 5,6-didéoxy-1,2-*O*-isopropylidène-3-*O*-trifluoroacétyl-α-D-*xylo*-hex-5-énofuranose (**7**) par le trifluoroacétate d'argent et l'iode dans l'acétonitrile conduit au produit d'addition **8**, mais pas au dérivé 3,6-anhydro; le composé **8** a été transformé en iodohydrine **4** par traitement dans le méthanol. La préparation du dérivé 5-déoxy **6** au moyen de l'iodohydrine **4** représente une hydratation anti-Markovnikov de l'oléfine **1**; les réactions décrites représentent un autre moyen possible d'hydroboration-oxydation pour la préparation de **6**.

Canadian Journal of Chemistry, 50, 507 (1972)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 141.114.238.19 on 11/09/14
For personal use only.

Introduction

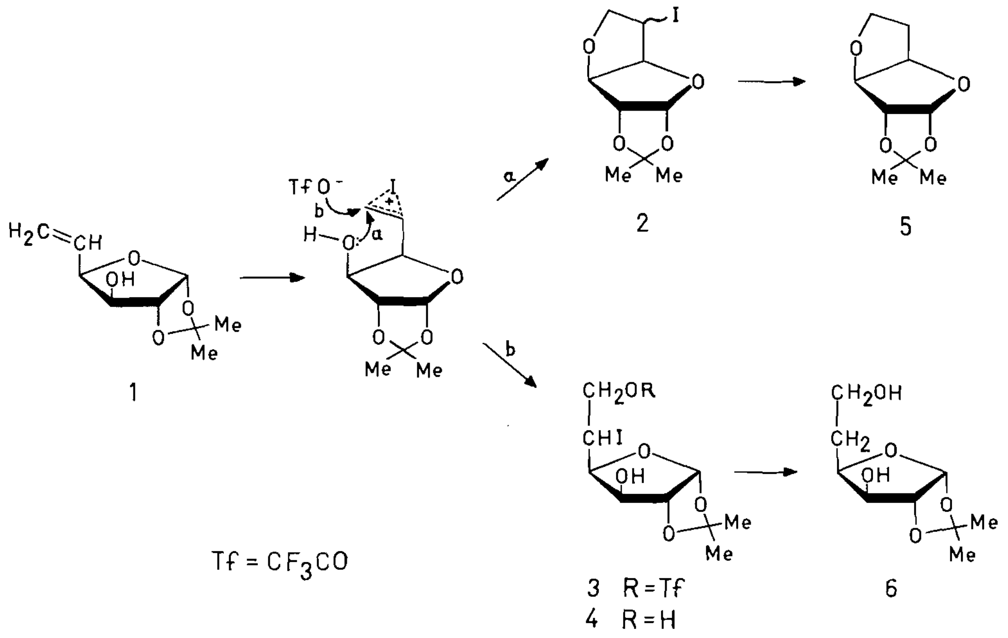
The addition of pseudohalogens to unsaturated carbohydrates, as a method of introducing nitrogen-containing functional groups, has been the subject of several recent publications (1–6). In connection with a study (7) of the addition of iodine nitrate, it was necessary to prepare some carbohydrate iodohydrins. Such compounds have been obtained mainly from sugar epoxides (8). Recently, the preparation of iodohydrins directly from olefins, by reaction with iodine in the presence of water and a suitable oxidizing agent, was described by Cornforth and Green (9). Here we report some results of an investigation of the synthesis of carbohydrate iodohydrins by way of the addition of iodine trifluoroacetate to unsaturated carbohydrates. The trifluoroacetyl group has been used in carbohydrate chemistry as a blocking group, particularly, because of its ease of hydrolysis; removal of the group has been achieved under extremely mild conditions at room temperature with anhydrous methanol, aqueous acetone, or aqueous pyridine (10).

Iodine trifluoroacetate is produced by the reaction of iodine and silver trifluoroacetate; the positive iodine generated in this way has been shown (11) to be very reactive in electrophilic aromatic substitution. Henbest (12) first reported the addition of iodine trifluoroacetate to ethylenic compounds, although in that work, the adducts were not isolated. In 1966 Hey *et al.* (13) showed that iodine trifluoroacetate adds stereospecifically to 5α-cholest-2-ene to give 3α-iodo-5α-cholestan-2β-yl trifluoroacetate in high yield. In the present work the reaction of iodine trifluoroacetate with 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**1**) (14) and a 3-*O*-substituted derivative (**7**) has been studied.

---

[1] For part IV in this series, see ref. 6.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 141.114.238.19 on 11/09/14
For personal use only.



SCHEME 1

Results and Discussion

Addition of silver trifluoroacetate and olefin **1** to a solution of iodine in acetonitrile[2] at room temperature gave in 5 min a syrupy mixture of two components; the i.r. spectrum showed absorptions at 3460 and 1790 cm^{-1} attributable to the presence of hydroxyl and trifluoroacetate groups, respectively. The isolation of a compound containing a trifluoroacetate group could not, however, be achieved by column chromatography on silica gel, because of the lability of this group. Instead, the mixture was briefly treated with methanol, and the resultant syrupy material was fractionated on silica gel. Two components were obtained, which were assigned the structures **2** and **4** (Scheme 1). The first component was a crystalline solid with a 5° m.p. range; its i.r. spectrum and elemental analysis were consistent with the assigned structure (**2**). However, the presence in the n.m.r. spectrum of two doublets with equal spacings (3.7 Hz) at τ 3.76 and 4.06, attributable to H-1, indicated that this component was a mixture of two compounds; the ratio of peak areas was 2:15, respectively. Hydrogenation over a Raney nickel catalyst gave only one compound, which was assigned the structure of 3,6-anhydro-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**5**) on the basis of its n.m.r. spectrum. The first component was, therefore, a 2:15 mixture of epimers: 3,6-anhydro-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-glucofuranose and the β-L-*ido* isomer. The isomer distribution was assigned on the basis of the chemical shifts of the H-1 signals in the n.m.r. spectrum. In the L-*ido* compound, the iodine is *exo* in the bicyclic system formed by the furanose and 3,6-anhydro rings, whereas, in the D-*gluco* compound, it is *endo*, and relatively close to H-1. The H-1 signal in the former compound should, therefore, be less affected by the iodine at C-5, and it is reasonable to expect that its chemical shift would be very close to that of the H-1 signal in the 5-deoxy compound **5** (τ 4.08). Thus, the preponderant isomer, whose H-1 signal is at τ 4.06, has been assigned the L-*ido* structure.

The second component (**4**) was isolated as a syrup in 37% yield. Its i.r. spectrum showed a very strong hydroxyl absorption at 3460 cm^{-1}, but no absorption attributable to a trifluoroacetate group. The assignation of the iodine to

---

[2] The use of acetonitrile for the *in situ* generation of iodine trifluoroacetate gave satisfactory results with equimolar amounts of silver trifluoroacetate and iodine; other workers used an excess of the silver salt with nitrobenzene (11) or methylene chloride (13).

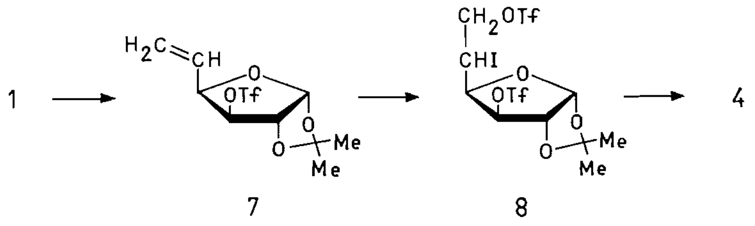
Can. J. Chem. Downloaded from www.nrcresearchpress.com by 141.114.238.19 on 11/09/14
For personal use only.

C-5 was established by the conversion of **4** into 5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**6**) by hydrogenation over a Raney nickel catalyst. The preparation, in the present work, of the 5-deoxy derivative **6** by way of the iodohydrin **4** represents an overall anti-Markovnikov hydration of the unsaturated sugar **1**. An improved protocol for the conversion of **1** into **6** is described later in this paper. A synthesis of **6** from **1** has been reported previously (15), namely, by hydroboration. A number of other syntheses of compound **6** have also been achieved (16).

Component **4** was unstable on standing, and an iodine-colored syrup was formed even in the dark at 5°. The structure proposed for **4** was supported by its mass spectrum, which shows many of the features of the spectra of monosaccharide isopropylidene derivatives (17). A weak molecular ion was observed at *m*/*e* 330 ($C_9H_{15}O_5I$), and a more intense peak at *m*/*e* 315 (M-15) owing to the ion formed from the molecular ion by elimination of one of the methyl groups; the most intense peak was at *m*/*e* 59, attributable to protonated acetone.

The reaction of 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**1**) with silver trifluoroacetate and iodine in acetonitrile is considered to proceed by way of an intermediate cationic species such as that shown in Scheme 1. Attack by the C-3 hydroxyl group at the less-hindered C-6 position (route *a*) would then yield a 3,6-anhydro derivative (**2**), whereas attack by trifluoroacetate ion (route *b*) would give a 5-deoxy-5-iodo-6-*O*-trifluoroacetyl derivative (**3**). Treatment of **3** with methanol afforded the iodohydrin **4**. The possibility of the formation of **2** from the adduct **3** in the reaction mixture was excluded by the observation that the proportion of the products remained unchanged when the time of the reaction was extended from 5 to 40 min. Moreover, the formation of **2** was not observed, within 40 min, when olefin **1** was treated with only iodine in acetonitrile; a decomposition of **1**, involving elimination of acetone, was observed with longer reaction times. Since the two faces of the double bond in **1** are diastereotopic, the addition of iodine trifluoroacetate by the mechanism suggested above would be expected to yield two diastereoisomers. Although the presence of two isomers of **2** was clearly discernible in its n.m.r. spectrum by the observation of two anomeric signals, such was not the case for **4**. The spectrum of **4** showed what appeared to be only one anomeric signal. It is interesting that, in the reaction of the pseudohalogen iodine azide (IN_3) with olefin **1**, the formation of a 3,6-anhydro derivative was not reported (4); the product isolated was the adduct 6-azido-5,6-dideoxy-5-iodo-1,2-*O*-isopropylidene-β-L-idofuranose. The addition of iodine azide presumably also occurs by way of the cyclic iodonium ion intermediate shown in Scheme 1. In the present work, the formation of the 3,6-anhydro component **2** as the preponderant product is probably attributable to the trifluoroacetate anion's low nucleophilicity.

In order to obviate the formation of a 3,6-anhydro derivative, it was clearly necessary to block the hydroxyl group at C-3 in the olefin **1** with a non-participating group. For this purpose, the highly electronegative trifluoroacetyl group was selected. Thus, treatment of olefin **1** with trifluoroacetic anhydride – sodium trifluoroacetate gave an almost quantitative yield of the 3-*O*-trifluoroacetyl derivative **7** (Scheme 2). The reaction of **7** with silver trifluoroacetate and iodine in acetonitrile then gave the adduct **8** in high yield without the formation of a 3,6-anhydro derivative. A brief treatment of **8** with methanol afforded the iodohydrin **4**. The preceding reactions constitute a convenient procedure for the preparation of **4**, and hence of



SCHEME 2

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 141.114.238.19 on 11/09/14
For personal use only.

the 5-deoxy sugar derivative **6** with subsequent hydrogenation.

Hey *et al.* (13) have reported that heating 3α-iodo-5α-cholestan-2β-yl trifluoroacetate, the adduct from the reaction of 5α-cholest-2-ene and iodine trifluoroacetate, with silver trifluoroacetate and hydrolyzing the intermediate (presumably the 2β,3β-diester) gave the 2β,3β-diol. In the present work, an attempted displacement of an iodo group by trifluoroacetate in **8**, using silver trifluoroacetate in acetonitrile, gave only an intractable material. With dichloromethane–toluene as the solvent, even after refluxing for 24 h, no change in the starting material was observed.

Experimental

Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Microdistillations were performed with a Gallenkamp heating block. Optical rotations were measured using a Perkin–Elmer Model 141 automatic polarimeter at 23 ± 2°. The i.r. spectra were recorded on a Unicam SP 1000 or a Perkin–Elmer 180 spectrophotometer. The n.m.r. spectra were obtained on a Varian A-60 spectrometer in chloroform-*d* with tetramethylsilane (τ 10.00) as internal standard; coupling constants were measured at a 250 Hz sweep width. High resolution mass spectra were determined with a JEOLCO double focusing spectrometer, Model JMS-01SC, equipped with a heated, direct sample-injection system operated at 83°, and fitted to record data by a photoplate; ionizing potential 75 eV. The t.l.c. was performed with silica gel G as the adsorbent in the following solvent systems (v/v): (A) petroleum ether (b.p. 60–80°) – ethyl acetate, 3:2; (B) 3:1; (C) 2:3. The developed plates were air-dried, sprayed with 5% ethanolic sulfuric acid, and heated at about 150°. Column chromatography was performed on Brinkmann silica gel (70–325 mesh) with the following eluants (v/v): (D) carbon tetrachloride – ethyl acetate, 3:1; (E) 1:1; the glass columns were covered with aluminum foil to exclude light. Carbon tetrachloride was freshly distilled, and acetonitrile was kept over Type 3A molecular sieves for at least 1 week prior to its use. Solvents were evaporated under reduced pressure below 35°. Silver trifluoroacetate was prepared as described by Janssen and Wilson (18).

Reaction of 5,6-Dideoxy-1,2-O-isopropylidene-α-D-xylo-hex-5-enofuranose (1) with Silver Trifluoroacetate and Iodine

Olefin **1** (395 mg, 2.1 mmol) and silver trifluoroacetate (563 mg, 1.2 equiv) in dry acetonitrile (15 ml) were added, in one portion, to a stirred solution of iodine (647 mg, 1.2 equiv) in dry acetonitrile (25 ml) in a flask covered with aluminum foil. After 5 min, the reaction mixture was filtered, and the filtrate was concentrated to a dark red syrup. The syrupy residue was extracted with carbon tetrachloride (50 ml), and the extract was washed with aqueous sodium thiosulfate solution, dried over anhydrous sodium sulfate in the presence of decolorizing charcoal, and filtered through Celite. The clear, colorless filtrate was concentrated to a syrup (761 mg). The t.l.c. (solvent A) showed that all of the starting olefin (R_F 0.5) had been consumed and revealed the presence of two new components, one as a well defined spot (R_F 0.8) and the other as a tailing spot (R_F 0.6). The i.r. spectrum (film) showed absorptions at 3460 (OH) and 1790 cm^{-1} ($CF_3C{=}O$). The syrup was dissolved in methanol; after 1 min, t.l.c. (solvent A) showed the presence of two components having R_F values of 0.8 and 0.2. The solvent was evaporated to leave a pale yellow syrup (633 mg), which was fractionated on silica gel, with solvent D as eluant, to yield the two components **2** and **4**.

Component **2** was obtained from ethanol as a crystalline solid (295 mg, 45%), m.p. 105–110°, $[\alpha]_D$ +4° (*c*, 1.0 in chloroform); ν_{max} ($CHCl_3$) 1380, 1390 cm^{-1} (CMe_2), no absorption attributable to OH or $CF_3C{=}O$; n.m.r. data: τ 3.76, 4.06 (1-proton, two doublets with a ratio of peak areas of 2:15, respectively, $J_{1,2} = 3.7$ Hz, H-1 of two isomers), 5.15 (1-proton quartet, $J_{3,4} = 3.4$ Hz, $J_{4,5} = 2.4$ Hz, H-4), 5.25 (1-proton doublet, $J_{2,3} < 0.5$ Hz, H-2), 5.45 (1-proton doublet, H-3), 5.7–6.3 (3-proton multiplets, H-5, 2H-6's), 8.50, 8.67 (3-proton singlets, CMe_2).

Anal. Calcd. for $C_9H_{13}O_4I$: C, 34.6; H, 4.2; I, 40.7. Found: C, 34.8; H, 4.2; I, 40.4.

Component **4** was obtained as a syrup (260 mg, 37%), $[\alpha]_D$ −2°, $[\alpha]_{365}$ +10° (*c*, 0.9 in chloroform), ν_{max} (film) 1380, 1390 (CMe_2), 3440 cm^{-1} (very strong, OH), no absorption attributable to $CF_3C{=}O$; n.m.r. data: τ 4.04 (1-proton doublet, $J_{1,2} = 3.6$ Hz, H-1), 5.32 (1-proton doublet, $J_{2,3} <$ 0.5 Hz, H-2), 5.68 (3-proton broad singlet), 5.88 (2-proton singlet, disappeared on deuteration, 2OH's), 6.03 (2-proton multiplet), 8.48, 8.64 (3-proton singlets, CMe_2).

Anal. Calcd. for $C_9H_{15}O_5I$: C, 32.7; H, 4.6. Found: C, 32.4; H, 4.7.

Syrupy **4** was unstable on standing, and a satisfactory analysis for iodine could not be obtained. The molecular formula was confirmed by mass spectrometry: M^+ 329.994, M^+-Me 314.970 (Calcd. for $C_9H_{15}O_5I$: 329.996; M^+-Me: 314.973).

3,6-Anhydro-5-deoxy-1,2-O-isopropylidene-α-D-xylo-hexofuranose (5)

A solution of component **2** (168 mg, 0.54 mmol) in ethanol containing W-4 Raney nickel catalyst and triethylamine (1 ml) was subjected to a hydrogen pressure of 40 p.s.i.g. The t.l.c. (solvent B) showed that the reaction was complete in 80 min. The catalyst was removed by filtration and extracted with boiling ethanol. The combined filtrate and extract were concentrated, and the residue was partitioned between ether and water. The dried (sodium sulfate) ether solution was decolorized with charcoal and then concentrated to give **5** as an oil (79 mg, 79%), b.p. 56–60°/0.06 Torr, $[\alpha]_D$ +15.5° (*c*, 2.0 in chloroform); n.m.r. data: τ 4.08 (1-proton doublet, $J_{1,2} = 3.9$ Hz, H-1), 5.02 (1-proton multiplet, H-4), 5.39 (1-proton doublet, $J_{2,3} <$ 0.5 Hz, H-2), 5.58 (1-proton doublet, $J_{3,4} = 3.4$ Hz, H-3), 5.86–6.34 (2-proton multiplet, 2H-6's), 7.75–8.18 (2-proton multiplet, 2H-5's), 8.49, 8.67 (3-proton singlets, CMe_2). The i.r. spectrum did not show any absorptions attributable to OH or $CF_3C{=}O$.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.0; H, 7.6. Found: C, 57.9; H, 7.7.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 141.114.238.19 on 11/09/14
For personal use only.

5-Deoxy-1,2-O-isopropylidene-α-D-xylo-hexofuranose (6)

A solution of freshly prepared component **4** (264 mg, 0.8 mmol) in ethanol containing W-4 Raney nickel catalyst and triethylamine (1 ml) was subjected to a hydrogen pressure of 40 p.s.i.g. for 3 h; the progress of the reaction was followed by t.l.c. (solvent C). The catalyst was removed by filtration and extracted with boiling ethanol. The combined filtrate and extract were concentrated to a crystalline residue, which was extracted with ether. The ether was evaporated, and the residue was chromatographed on silica gel (60–120 mesh), with, initially, 1:2 carbon tetrachloride–ethyl acetate and, finally, ethyl acetate as eluants, to yield compound **6** (104 mg, 64%). After recrystallization from ether–petroleum ether (b.p. 60–80°), the compound had m.p. 93–94.5° and $[\alpha]_D$ −10.5° (*c*, 1.7 in chloroform). These physical constants are in agreement with those reported for compound **6** by other workers (15, 16); its n.m.r. spectrum was identical with that published by Wolfrom *et al.* (15).

5,6-Dideoxy-1,2-O-isopropylidene-3-O-trifluoroacetyl-α-D-xylo-hex-5-enofuranose (7)

5,6-Dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**1**) (312 mg, 1.68 mmol) and sodium trifluoroacetate (77 mg) were treated with ice-cold trifluoroacetic anhydride (1 ml). The vigorous, exothermic reaction subsided in 5 min, and the mixture was then concentrated to dryness, under reduced pressure and a bath temperature of less than 35°, three times with 50 ml portions of carbon tetrachloride. The residue was extracted with hot carbon tetrachloride, and the solvent was evaporated to give **7** as a colorless oil (450 mg, 95%), b.p. 40–43°/0.008 Torr, $[\alpha]_D$ +24.4° (*c*, 3.0 in carbon tetrachloride); ν_{max} (film) 1385, 1390 (CMe_2), 1790 cm^{-1} (strong, $CF_3C{=}O$), no absorption attributable to OH; n.m.r. data: τ 3.95 (1-proton doublet, $J_{1,2} = 3.8$ Hz, H-1), 3.9–4.8 (4-protons, H-3, H-5, 2H-6's), 5.13 (1-proton multiplet, H-4), 5.34 (1-proton doublet, $J_{2,3} < 0.5$ Hz, H-2), 8.45, 8.65 (3-proton singlets, CMe_2). As would be expected, the n.m.r. spectrum of **7** showed an "acylation shift" compared with the spectrum of olefin **1**; the magnitudes of the shifts were even greater than those observed with the 3-*O*-acetate of **1** (19).

Anal. Calcd. for $C_{11}H_{13}O_5F_3$: C, 46.8; H, 4.6; F, 20.2. Found: C, 46.3; H, 4.6; F, 20.4.

Reaction of 5,6-Dideoxy-1,2-O-isopropylidene-3-O-trifluoroacetyl-α-D-xylo-hex-5-enofuranose (7) with Silver Trifluoroacetate and Iodine

Olefin **7** (300 mg, 1.06 mmol) and silver trifluoroacetate (277 mg, 1.2 equiv) in dry acetonitrile (8 ml) were added to a stirred solution of iodine (319 mg, 1.2 equiv) in dry acetonitrile (10 ml) in a flask covered with aluminum foil. After 10 min, the reaction mixture was filtered through Celite, and the filtrate was concentrated to dryness. The residue was extracted with hot carbon tetrachloride, and the extract was washed with aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The solvent was evaporated to leave an oil (498 mg) from which **8** was obtained by distillation, b.p. 88–92°/0.008 Torr, $[\alpha]_D$ −5°, $[\alpha]_{365}$ −9° (*c*, 1.2 in carbon tetrachloride); ν_{max} (film) 1378, 1385 (CMe_2), 1790 cm^{-1} (very strong, $CF_3C{=}O$), no absorption attributable to OH; n.m.r. data: τ 3.98 (1-proton doublet, $J_{1,2} = 3.7$ Hz, H-1), 4.55 (1-proton doublet, $J_{3,4} =$ 1.5 Hz, H-3), 5.1–5.7 (5-protons, H-2, H-4, H-5, 2H-6's), 8.45, 8.66 (3-proton singlets, CMe_2).

Anal. Calcd. for $C_{13}H_{13}O_7IF_6$: C, 29.9; H, 2.5. Found: C, 30.4; H, 2.6.

A portion (470 mg) of the crude oil obtained above was dissolved in methanol (15 ml), and the solvent was subsequently evaporated to leave a syrup (274 mg). Chromatography of this material on silica gel, with solvent E as eluant, gave the expected 4 (190 mg) and some 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**1**) (21 mg). The presence of **1** was probably the result of incomplete addition of iodine trifluoroacetate to olefin 7.

The authors thank Professor J. K. N. Jones for his interest and encouragement, and the National Research Council of Canada for financial support of this work.

1. W. A. Szarek, D. G. Lance, and R. L. Beach. Chem. Commun. 356 (1968); Carbohydr. Res. **13**, 75 (1970).
2. W. A. Szarek, J. S. Jewell, I. Szczerek, and J. K. N. Jones. Can. J. Chem. **47**, 4473 (1969).
3. E. L. Albano, D. Horton, and J. H. Lauterbach. Carbohydr. Res. **9**, 149 (1969).
4. J. S. Brimacombe, J. G. H. Bryan, and T. A. Hamor. J. Chem. Soc. B, 514 (1970).
5. J. S. Brimacombe, F. Hunedy, and M. Stacey. Carbohydr. Res. **13**, 447 (1970).
6. R. G. S. Ritchie and W. A. Szarek. Carbohydr. Res. **18**, 443 (1971).
7. J. S. Jewell, R. G. S. Ritchie, W. A. Szarek, and J. K. N. Jones. To be published.
8. F. H. Newth. Quart. Rev. (London), **13**, 30 (1959); R. U. Lemieux, E. Fraga, and K. A. Watanabe. Can. J. Chem. **46**, 61 (1968).
9. J. W. Cornforth and D. T. Green. J. Chem. Soc. C, 846 (1970).
10. T. G. Bonner. Advan. Carbohydr. Chem. **16**, 59 (1961).
11. R. N. Haszeldine. J. Chem. Soc. 584 (1951); R. N. Haszeldine and A. G. Sharpe. J. Chem. Soc. 993 (1952).
12. H. B. Henbest. Proc. Chem. Soc. 159 (1963).
13. D. G. Hey, G. D. Meakins, and M. W. Pemberton. J. Chem. Soc. C, 1331 (1966).
14. J. K. N. Jones and J. L. Thompson. Can. J. Chem. **35**, 955 (1957).
15. M. L. Wolfrom, K. Matsuda, F. Komitsky, Jr., and T. E. Whiteley. J. Org. Chem. **28**, 3551 (1963).
16. E. J. Hedgley, O. Mérész, and W. G. Overend. J. Chem. Soc. C, 888 (1967); H. Paulsen and D. Stoye. Ber. **99**, 908 (1966); J. G. Buchanan and E. M. Oakes. Tetrahedron Lett. 2013 (1964); R. E. Gramera, T. R. Ingle, and R. L. Whistler. J. Org. Chem. **29**, 878, 2074 (1964).
17. D. C. De Jongh and K. Biemann. J. Am. Chem. Soc. **86**, 67 (1964); N. K. Kochetkov and O. S. Chizhov. Advan. Carbohydr. Chem. **21**, 39 (1966).
18. D. E. Janssen and C. V. Wilson. Inorg. Syn. Coll. Vol. IV, 547 (1963).
19. D. G. Lance and W. A. Szarek. Carbohydr. Res. **10**, 306 (1969).