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Note

Titanium-mediated methylene transfer reactions on sugar esters, lactones, and uloses*

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The titanium alkylidene **1**, a versatile methylenating agent readily derived[1] from the rather costly Tebbe compound **2**, has been used in Wittig-type reactions to convert ketones into olefins and esters into vinyl ethers[2]. We now report‡ its application to a variety of sugar derivatives that contain carbonyl and/or ester functions, with the aim of delineating the scope of the reaction with respect to blocking groups and the structure of the ketone, ester, or lactone.

In order to simplify the procedure and increase the value of the method, the unpurified form of **2** was used (see Experimental). Pure, crystalline Tebbe reagent has been used by others[3,4] on some aldonolactones and, where comparisons can be made, both similarities and differences were found.

Reaction of the ulose **3** (X = O) and the aldehyde **5** (R = H) with **2** gave, after chromatography, 70% and 35%, respectively, of the olefins **4**[5,6] and **6** (R = H)[7] in experiments that were easier to execute than the customary Wittig procedure[5].

Mono-esters of sugars were converted smoothly into vinyl ethers. Thus, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-acetate, 3-benzoate, and 3-*p*-chlorobenzoate gave, in good yields, the respective substituted vinyl ethers **7** (R = Me, or Ph, or ClC_6H_4). Each of the vinyl ethers **7** was susceptible to hydrolysis and gave methyl ketones *via* hemiacetals. The stability of these compounds towards hydrolysis increased in the order cited.

Esters of glycuronic acids reacted readily with the crude **2**, thereby affording a route to chain-extended sugars. The methyl glucoronate derivative **8** gave the methylene compound **9**, and the methyl galacturonate derivative **5** (R = OMe) gave compound **6** (R = OMe), which needed more careful handling than **9** because it was rapidly hydrolysed on silica gel with neutral eluants to give the useful ketone **5** (R = Me).

The δ-lactones 2,3,4,6-tetra-*O*-methyl-D-glucono-1,5-lactone (**10**, R = Me) and

* Dedicated to Professor Leslie Hough in the year of his 65th birthday.
† Author for correspondence.
‡ The work reported was the subject of an SERC CASE project application (00893 in 1983).

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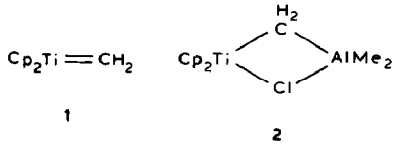

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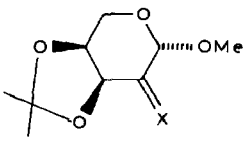

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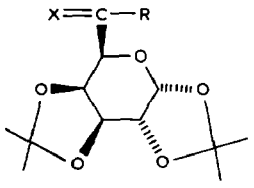

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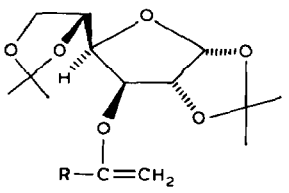

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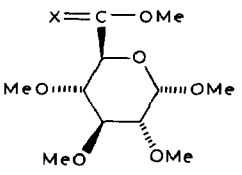

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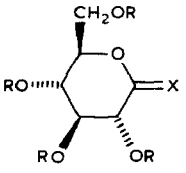

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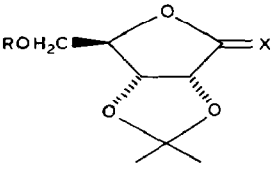

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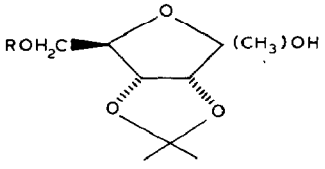

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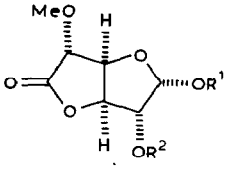

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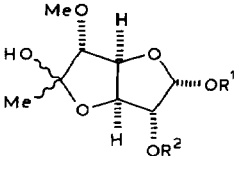

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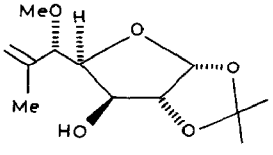

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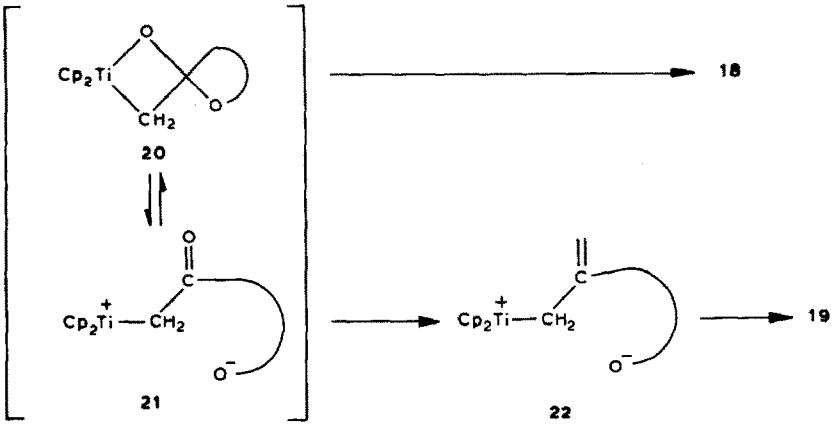
2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone (**10**, R = Bn) gave the corresponding 2,6-anhydroheptenitol derivatives (**11**, R = Me and R = Bn[8]) in yields as high as those obtained by others[4] working with pure **2**. Compounds **11** were stable on silica gel even in neutral solvents. Other methods[8,9] have also been used to prepare a wide selection of these exocyclic methylene sugars.

On the other hand, γ-lactones gave good yields of mixtures of olefins and the products of hydrolysis, the latter usually being present as lactol forms. The extent of hydrolysis varied with the structure of the lactone. For example, the ribono-1,4-lactone

derivatives **12** (R = Me or ^{t}BuMe$_2$Si) yielded crude 9:1 mixtures that contained the respective olefin (**13**, R = Me or ^{t}BuMe$_2$Si)[3] and lactol (**14**, R = Me or ^{t}BuMe$_2$Si). Although the olefins could be separated from the lactols by flash-column chromatography, even with slightly basic eluants[10], the product ratio changed dramatically in favour of the lactols and only 6% of the olefins were obtained. These olefins were characterised by their ^{1}H-n.m.r. spectra (see Experimental), which are the first for this class of furanose derivative to be reported fully assigned, even though such compounds were known hitherto.

The bicyclic lactones **15** and **16** reacted with **2** to give good yields of products, mainly lactols (**17** and **18**) with little of the expected olefins. However, in the reaction of **16**, **18** was accompanied by 10% of an olefin which had the structure **19** (see Experimental for the ^{1}H-n.m.r. data). The olefin **19** must be produced from **16** by the addition of two equiv. of **2**. This reaction could occur if some of the first-formed oxametalacycle (**20**) failed to collapse in the normal fashion to give olefin and Cp_2TiO, and was in equilibrium with its acyclic form **21**. Reaction with **1** would then give **22** and, after hydrolysis, **19**.



EXPERIMENTAL

General. — Melting points were determined with a Gallenkamp melting-point apparatus and are uncorrected. Optical rotations were determined with an Optical Activity polarimeter Model AA-100 for solutions in CH_2Cl_2. Evaporations were conducted under reduced pressure at 40°. Flash-column chromatography was performed on columns of SORBSILTH C60 silica gel (60–120 mesh). T.l.c. was performed on Silica Gel 60 F_{254} (Merck). ^{1}H-N.m.r. spectra were recorded, unless otherwise stated, on solutions in $CDCl_3$ (internal Me_4Si) with a Jeol JNM FX-200 instrument, except for **11** (R = Bn) for which a Varian VXR-400 spectrometer was used. Mass spectrometry was performed with a VG ZAB-SE instrument operated at 8 kV.

Reaction of the Tebbe compound **2** *with sugar ketones, esters, and lactones.* — 2M

Trimethylaluminium in toluene (10.2 mL, 20 mmol) at 20° was treated with titanocene dichloride (2.48 g, 10 mmol) for 72 h. This solution of the complex **2**, which could be stored at 0° for at least 3 months, was used without further purification as follows. The carbohydrate derivative (1 mmol) in toluene (3 mL), tetrahydrofuran (1 mL), and pyridine (5 μL) was stirred with a solution of **2** (2.14 mL) at −40° for 0.5 h. The solution was then allowed to reach ambient temperature during 1.5 h. The progress of the reaction was monitored by t.l.c. After cooling to −10°, aqueous 15% sodium hydroxide (0.1 mL), ether (15 mL), and sodium sulphate (1 g) were added sequentially. The mixture was filtered through Celite and then eluted from a short column of silica gel with eluents that usually contained ~0.3% of triethylamine. Evaporation of the solvents left the product.

*Methyl 2-deoxy-3,4-*O*-isopropylidene-2-*C*-methylene-β-*L*-*erythro*-pentopyranoside* (**4**). — A solution of methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose (**3**; 0.202 g, 1 mmol) (R_F 0.34) in toluene (3 mL), tetrahydrofuran (1 mL), and pyridine (5 μL) at −40° was treated with a solution of **2** (2.14 mL) under dry nitrogen as described above. T.l.c. (light petroleum–ether, 1:1) showed a single product (R_F 0.6). Column chromatography (light petroleum–ether, 3:1) gave **4** (0.142 g, 71%), $[\alpha]_D$ +182° (*c* 1.1); lit.[5] $[\alpha]_D$ +179°. ^{1}H-N.m.r. data: δ 5.4 (m, 2 H, $=CH_2$), 5.1 (s, 1 H, H-1), 4.75 (bd, 1 H, $J_{3,4}$ 5.8 Hz, H-3), 4.24 (m, 1 H, H-4), 3.78 (m, 2 H, H-5a,5b), 3.43 (s, 3 H, OMe), 1.50 and 1.35 (2 s, each 3 H, CMe_2).

*6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-*galacto*-hept-6-enopyranose* (**6**, *R* = *H*). — When 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-1,6-hexodialdo-1,5-pyranose (**5**, R = H) was treated with **2** as described above, t.l.c. (toluene–ethyl acetate, 3:2) revealed a faster-moving major product (R_F 0.71) and four minor ones. The major product, isolated by column chromatography (light petroleum–ether, 10:1), was **6** (R = H, 35%), $[\alpha]_D$ −190.5° (*c* 0.4); lit.[7] $[\alpha]_D$ −200°. ^{1}H-N.m.r. data: δ 5.94 (oct, 1 H, $J_{6,7a}$ 18.0, $J_{6,7b}$ 10.0, $J_{6,5}$ 6.0 Hz, H-6), 5.58 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 5.38 (dt, 1 H, $J_{7a,7b} = J_{7a,5}$ = 1.5 Hz, H-7a), 5.27 (dt, 1 H, $J_{7b,5}$ 1.5 Hz, H-7b), 4.62 (dd, 1 H, $J_{3,4}$ 7.8 Hz, H-3), 4.32 (dd, 1 H, $J_{2,3}$ 2.2 Hz, H-2), 4.28 (m, 1 H, H-5), 4.22 (dd, 1 H, $J_{4,5}$ 5.6 Hz, H-4), 1.54, 1.48, 1.24, and 1.13 (4 s, each 3 H, 2 CMe_2).

*Reactions of 1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose 3-esters with* **2**. — (*a*) *The 3-acetate*. The 3-acetate, R_F 0.44 (light petroleum–ether, 2:1), on treatment with **2** as described above followed by chromatography (light petroleum–ether, 4:1), gave 3-*O*-isopropenyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**7**; R = Me, 85%), R_F 0.6. ^{1}H-N.m.r. data: δ 5.87 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.58 (d, 1 H, $J_{2,3}$ <0.3 Hz, H-2), 4.41 and 4.29 (2 d, 2 H, J_{gem} 3.0 Hz, $=CH_2$), 4.34 (dd, 1 H, $J_{4,5}$ 6.0 Hz, H-4), 4.04 (m, 4 H, H-3, 5, 6a,6b), 1.8 (s, 3 H, CH_3), 1.5, 1.45, 1.36, and 1.31 (4 s, each 3 H, 2 CMe_2).

(*b*) *The 3-benzoate*. The 3-benzoate, R_F 0.42 (light petroleum–ether, 2:1), on treatment with **2**, followed by chromatography (light petroleum–ether, 2:1), gave 1,2:5,6-di-*O*-isopropylidene-3-*O*-(1-phenylvinyl)-α-D-glucofuranose (**7**; R = Ph, 75%), R_F 0.53. ^{1}H-N.m.r. data: δ 7.3–7.6 (m, 5 H, Ph), 5.92 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.84 and 4.65 (2 d, 2 H, J_{gem} 3.0 Hz, $=CH_2$), 4.72 (d, 1 H, $J_{2,3}$ <0.3 Hz, H-2), 4.50 (m, 1 H, $J_{5,6a} = J_{5,6b}$ = 5.5 Hz, H-5), 4.46 (d, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 4.35 (dd, 1 H, $J_{4,5}$ 7.8 Hz, H-4), 4.15

and 4.10 (2 dd, 2 H, $J_{6a,6b}$ 9.0 Hz, H-6a,6b), 1.59, 1.46, 1.39, and 1.35 (4 s, each 3 H, 2 CMe_2).

(*c*) *The 3-*p*-chlorobenzoate.* The 3-chlorobenzoate, on treatment with **2** followed by chromatography (light petroleum–ether, 7:1), gave 1,2:5,6-di-*O*-isopropylidene-3-*O*-(1-*p*-chlorophenylvinyl)-α-D-glucofuranose (**7**; R = ClC_6H_4, 78%). ^{1}H-N.m.r. data: 7.27–7.57 (m, 4 H, Ar), 4.94 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.82 and 4.63 (2 d, 2 H, J_{gem} 3.2 Hz, $=CH_2$), 4.70 (d, 1 H, $J_{2,3}$ <0.3 Hz, H-2), 4.49 (m, 2 H, H-3,5), 4.32 (dd, 1 H, $J_{4,5}$ 8.0 Hz, H-4), 4.15 and 4.05 (2 dd, 2 H, $J_{6a,6b}$ 9.0 Hz, H-6a,6b), 1.37, 1.38, 1.48, and 1.57 (4 s, each 3 H, 2 CMe_2).

*Methyl 7-deoxy-2,3,4,6-tetra-*O*-methyl-α-*D*-gluco-hept-6-enopyranoside* (**9**). — Treatment of methyl (methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranosid)uronate (**8**), R_F 0.20 (light petroleum–ether, 1:1), with **2**, as described above, gave, after chromatography, **9** (86%), R_F 0.19, $[\alpha]_D$ +123° (*c* 0.6). ^{1}H-N.m.r. data (C_6D_6): δ 4.71 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.30 and 4.01 (2 d, 2 H, J_{gem} 2.0 Hz, H-7a,7b), 4.18 (d, 1 H, $J_{5,4}$ 9.9 Hz, H-5), 3.82 (dd, 1 H, $J_{3,4}$ 9.1 Hz, H-3), 3.64 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.24 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2), 3.63, 3.47, 3.22, 3.20, and 3.16 (5 s, each 3 H, 5 MeO). Mass spectrum: *m/z* 262 ($M^{+\cdot}$).

*7-Deoxy-1,2:3,4-di-*O*-isopropylidene-6-*O*-methyl-α-*D*-gluco-hept-6-enopyranose* (**6**; *R = OMe*). — Treatment of methyl 1,2:3,4-di-*O*-isopropylidene-α-D-galacturonate (**5**, R = OMe), R_F 0.4 (light petroleum–ether, 1:1), with **2** as described above, followed by chromatography (light petroleum–ether, 4:1, plus 0.25% of Et_3N)[10], gave **6** (R = OMe, 86%), R_F 0.4, $[\alpha]_D$ −79°. ^{1}H-N.m.r. data: δ 5.61 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 4.61 (dd, 1 H, $J_{3,4}$ 7.7 Hz, H-3), 4.43 (dd, 1 H, $J_{4,5}$ 2.0 Hz, H-4), 4.38 and 4.16 (2 dd, 2 H, J_{gem} 2.5, $J_{7,5}$ 1.2 Hz, H-7a,7b), 4.33 (dd, 1 H, $J_{2,3}$ 2.2 Hz, H-2), 4.23 (1 H, H-5), 3.61 (s, 3 H, OMe), 1.53, 1.45, 1.35, and 1.34 (4 s, each 3 H, 2CMe_2). The use of neutral eluants for chromatography gave **6** (R = OMe, 5%) and the ketone **5** (R = Me, 90%), m.p. 42–44°, $[\alpha]_D$ −130° (*c* 1.7). ^{1}H-N.m.r. data: δ 5.65 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 4.64 (dd, 1 H, $J_{3,4}$ 7.9 Hz, H-3), 4.56 (dd, 1 H, $J_{4,5}$ 2.2 Hz, H-4), 4.36 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 4.18 (d, 1 H, H-5), 2.27 (s, 3 H, MeCO), 1.51, 1.45, 1.34, and 1.32 (4 s, each 3 H, 2CMe_2). Mass spectrum: *m/z* 286 ($M^{+\cdot}$).

*2,6-Anhydro-1-deoxy-3,4,5,7-tetra-*O*-methyl-*D*-gluco-hept-1-enitol* (**11**, *R = Me*). — Treatment of 2,3,4,6-tetra-*O*-methyl-D-gluconolactone[11] (**10**, R = Me) with **2**, as described above, gave a single faster-moving product, R_F 0.37 (light petroleum–ether, 2:1). Column chromatography (light petroleum–ether, 4:1) gave **11** (R = Me, 95%), $[\alpha]_D$ +67° (*c* 1). ^{1}H-N.m.r. data: δ 4.48 and 4.70 (2 bt, 2 H, $J_{1a,1b} = J_{1a,3} = J_{1b,3} = \sim 1.5$ Hz, H-1a,1b), 3.55–3.7 (m, 4 H, H-3,4,5,6), 3.29 (m, 2 H, H-7a,7b), 3.58, 3.52, 3.48, and 3.43 (4 s, each 3 H, 4 MeO).

*2,3,4,6-Tetra-*O*-benzyl-*D*-glucono-1,5-lactone* (**10**, *R = Bn*). — 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (0.2 g, 0.37 mmol) was treated with methyl sulphoxide (1.1 mL) and acetic anhydride (0.75 mL) at ~22° for 18 h. T.l.c. (light petroleum–ether, 1:1) showed a major product and traces of a minor one. The mixture was poured into ice–water, extracted into dichloromethane, and worked-up to give **10** (R = Bn) as a colourless syrup (0.2 g, 96%), $[\alpha]_D$ +68° (*c* 1.1). ^{1}H-N.m.r. data: δ 7.1–7.45 (m, 20 h, 4

Ph), 4.99 (d, 1 H, J_{gem} 11.6 Hz, PhC*H*), 4.41–4.76 (m, 7 H, 7 PhC*H*), 4.12 (m, 1 H, $J_{5,6a}$ 2.5, $J_{5,6b}$ 3.2 Hz, H-5), 3.87–3.99 (m, 2 H, H-3,4), 3.73 (dd, 1 H, $J_{6a,6b}$ 11.1 Hz, H-6a), and 3.65 (dd, 1 H, H-6b).

2,6-Anhydro-3,4,5,7-tetra-O-*benzyl-1-deoxy*-D-gluco-*hept-1-enitol* (**11**, *R = Bn*). — Treatment of the δ-lactone **10** (R = Bn) with **2** as described above, followed by chromatography (light petroleum–ether, 5:1), gave **11** (R = Bn, 88%), m.p. 60–62° (from ether), $[\alpha]_D$ +52° (*c* 1.5); lit.[4] m.p. 68–68.5°, $[\alpha]_D$ +60°. ^{1}H-N.m.r. data (400 MHz, C_6D_6): δ 7.04–7.3 (m, 20 H, 4 Ph), 4.66 and 4.90 (2 bs, 2 H, H-1a,1b), 4.83, 4.78, 4.61, 4.60, 4.59, 4.45, 4.44, and 4.34 (8 d, 8 H, J_{gem} 11.6–12.1 Hz, 8 PhC*H*), 4.00 (dd, 1 H, $J_{4,5}$ 7.2 Hz, H-4), 3.97 (d, 1 H, $J_{3,4}$ 9.9 Hz, H-3), 3.84 (dd, 1 H, $J_{5,6}$ 7.0 Hz, H-5), 3.71 (m, 2 H, H-7a,7b).

Reaction of 2,3-O-*isopropylidene-5*-O-*methyl*-D-*ribono-1,4-lactone* (**12**, *R = Me*) *with* **2**. — Treatment of **12** (R = Me), R_F 0.5 (light petroleum–ether, 1:1), with **2**, as described above, gave ~80% of a product with R_F 0.64 and ~10% of one with R_F 0.3. When the mixture was worked-up, t.l.c. showed a slight change in product composition (60% and 40%). Column chromatography (light petroleum–ether, 4:1, plus 0.25% of Et_3N) then gave only 7% of 2,5-anhydro-1-deoxy-3,4-*O*-isopropylidene-6-*O*-methyl-D-*ribo*-hex-1-enitol (**13**, R = Me), R_F 0.64, $[\alpha]_D$ −52.5° (*c* 0.3). ^{1}H-N.m.r. data (C_6D_6): δ 4.96 (bt, 1 H, $J_{3,4}$ 5.9, $J_{3,1a} = J_{3,1b} = \sim 1.5$ Hz, H-3), 4.65 and 4.32 (2 t, 2 H, $J_{1a,1b} \sim 1.5$ Hz, H-1a,1b), 4.46 (dd, 1 H, $J_{4,5} \sim 1$ Hz, H-4), 4.38 (td, 1 H, $J_{5,6a}$ 3.7, $J_{5,6b}$ 3.2 Hz, H-5), 3.03 (dd, 1 H, $J_{6a,6b}$ 10.4 Hz, H-6a), 2.93 (dd, 1 H, H-6b), 2.88 (s, 3 H, MeO), 1.54 and 1.28 (2 s, each 3 H, CMe_2).

When the polarity of the eluant was increased (light petroleum–ether, 1:1), 1-deoxy-3,4-*O*-isopropylidene-6-*O*-methyl-D-*ribo*-hexulose (**14**, R = Me) was obtained (78%), R_F 0.3, $[\alpha]_D$ −16° (*c* 1.2). ^{1}H-N.m.r. data (C_6D_6): δ 4.87 (b, 1 H, OH), 4.70 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.52 (d, 1 H, $J_{3,4}$ 5.9 Hz, H-3), 4.25 (m, 1 H, $J_{5,6a}$ 3.2, $J_{5,6b}$ 3.0 Hz, H-5), 3.16 (dd, 1 H, $J_{6a,6b}$ 10.1 Hz, H-6a), 2.95 (dd, 1 H, H-6b), 2.78 (s, 3 H, MeO), 1.83 (s, 3 H, CH_3), 1.47 and 1.21 (2 s, each 3 H, CMe_2).

Reaction of 5-O-(tert-*butyldimethylsilyl*)-*2,3*-O-*isopropylidene*-D-*ribono-1,4-lactone* (**12**, *R = 'BuMe$_2$*) *with* **2**. — Treatment of **12**, R_F 0.47, as described above gave products with R_F 0.74 and 0.53 (light petroleum–ether, 1:1) in the ratio 1:1. However, work-up and chromatography (light petroleum–ether, 15:1, plus 0.25% of Et_3N) gave only 6% of 2,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-3,4-*O*-isopropylidene-D-*ribo*-hex-1-enitol (**13**, R = ^{t}BuMe$_2$Si), $[\alpha]_D$ −107° (*c* 0.5); lit.[4] $[\alpha]_D$ −111°. ^{1}H-N.m.r. data: δ 5.0 (dt, 1 H, $J_{3,4}$ 5.9, $J_{3,1a} = J_{3,1b} = \sim 1.5$ Hz, H-3), 4.69 (dd, 1 H, $J_{4,5} \sim 1$ Hz, H-4), 4.38 (m, 2 H, $w_{\frac{1}{2}}$ 3 Hz, H-1a,1b), 4.14 (dd, 1 H, $J_{5,6}$ 1 Hz, H-5), 3.70 (dd, 1 H, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.74 (dd, 1 H, H-6b), 1.50 and 1.37 (2 s, each 3 H, CMe_2), 0.85 (s, 9 H, ^{t}Bu), 0.04 and 0.05 (2 s, each 3 H, $SiMe_2$). This was followed by an 84% yield of 6-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-3,4-*O*-isopropylidene-D-*ribo*-hexulose (**14**, R = ^{t}BuMe$_2$Si), $[\alpha]_D$ −20° (*c* 0.5). ^{1}H-N.m.r. data: δ 5.18 (b, 1 H, OH), 4.80 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.44 (d, 1 H, $J_{3,4}$ 5.9 Hz, H-3), 4.24 (dd, 1 H, $J_{5,6a}$ and $J_{5,6b}$ 3.5 Hz, H-5), 3.82 (dd, 1 H, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.75 (dd, 1 H, H-6b), 1.52 (s, 3 H, Me), 1.50 and 1.37 (2 s, each 3 H, 2 CH_3), 0.93 (s, 9 H, ^{t}Bu), 0.51 and 0.16 (2 s, each 3 H, $SiMe_2$).

Reaction of methyl 2,5-di-O-methyl-α-D-glucurono-6,3-lactone (**15**) *with* **2**. — T.l.c. (ether) of the mixture formed when **15** was treated with **2**, as described above, revealed products with R_F 0.36 and 0.55 (9:1) but no lactone (R_F 0.27). Column chromatography (light petroleum–ether, 1:2, plus 0.25% of Et_3N) gave insufficient of the minor product for identification. The major product, (6*R*,*S*)-7-deoxy-1,2,5-tri-*O*-methyl-α-D-*gluco*-heptofuranos-6-ulo-6,3-furanose (**17**, 72%), had $[\alpha]_D$ +76° (*c* 0.25). ^{1}H-N.m.r. data: δ 5.17 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.76 (dd, 1 H, $J_{4,5}$ 5.4 Hz, H-4), 4.59 (dd, 1 H, $J_{3,4}$ 5.6 Hz, H-3), 4.15 (dd, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 3.57 (d, 1 H, H-5), 3.61, 3.50, and 3.46 (3 s, each 3 H, 3 MeO), 2.85 (b, 1 H, OH), and 1.50 (s, 3 H, Me). Mass spectrum: *m/z* 247 ($M^+ + 1$), 246 (M^+), and 229 ($M^+ - OH$).

Reaction of 1,2-O-isopropylidene-5-O-methyl-α-D-glucurono-6,3-lactone (**16**) *with* **2**. — T.l.c. (light petroleum–ether, 1:2) of the mixture formed when **16** (R_F 0.19) was treated with **2**, as described above, revealed two products (9:1; R_F 0.36 and 0.58). Chromatography (light petroleum–ether, 1:1, plus 0.25% of Et_3N) gave 6,7-dideoxy-1,2-*O*-isopropylidene-6-*C*-methyl-5-*O*-methyl-α-D-*gluco*-hept-6-enofuranose (**19**, 9%), $[\alpha]_D$ +40° (*c* 1). ^{1}H-N.m.r. data: δ 5.98 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 5.15 (bs, 2 H, $w_{\frac{1}{2}} \sim 3$ Hz $=CH_2$), 4.52 (d, 1 H, H-2), 4.29 (bdd, 1 H, $J_{3,4}$ 2.0, $J_{3,OH} \sim 1$ Hz, H-3), 4.10 (d, 1 H, H-5), 4.06 (dd, 1 H, $J_{4,5}$ 5.0 Hz, H-4), 3.83 (b, 1 H, OH), 3.35 (s, 3 H, MeO), 1.80 (s, 3 H, Me), 1.49 and 1.32 (2 s, each 3 H, 2 CMe_2).

Further elution gave (6*R*,*S*)-7-deoxy-1,2-*O*-isopropylidene-5-*O*-methyl-α-D-*gluco*-heptofuranos-6-ulo-6,3-furanose (**18**, 70%), m.p. 83–85° (from ether–light petroleum), $[\alpha]_D$ +49° (*c* 0.4). ^{1}H-N.m.r. data (C_6D_6): δ 5.82 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.66 (d, 1 H, H-2), 4.48 (d, 1 H, $J_{4,5}$ 4.2 Hz, H-4), 4.36 (d, 1 H, $J_{3,4}$ 4.2 Hz, H-3), 3.89 (bs, 1 H, OH, exchanged with D_2O), 3.11 (s, 3 H, OMe), 2.85 (d, 1 H, H-5), 1.45 (s, 3 H, Me), 1.40 and 1.09 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{11}H_{18}O_6$: C, 53.66; H, 7.32. Found: C, 53.36; H, 7.51.

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