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STEREOCONTROLLED PREPARATION OF C-2-DEOXY-α- AND -β-D-GLUCOPYRANOSYL COMPOUNDS FROM TRIBUTYL-(2-DEOXY-α- AND -β-D-GLUCOPYRANOSYL)STANNANES*

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ABSTRACT

Tributylstannyllithium treatment of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl chloride (**2**) provided selectively tributyl (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)stannane (**3**) in 85% yield. Isomeric tributyl (3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)stannane (**6**) could be prepared in 70% yield by reductive lithiation of **2** and reaction with tributyltin chloride. Tin–lithium exchange reaction, performed on **3** and **6** with butyllithium in oxolane at −78°, generated the corresponding, configurationally stable 2-deoxy-β- and -α-D-hexopyranosyllithium compounds which reacted with electrophilic compounds with retention of configuration. Addition of these glycosyllithium reagents to prochiral carbonyl compounds gave variable degrees of facial selectivity. A significant diastereofacial discrimination (10:1) was observed by condensation of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyllithium reagent with hexanal and isobutyraldehyde. The structure of all *C*-glycopyranosyl compounds obtained was established by ^{1}H-n.m.r. spectroscopy.

INTRODUCTION

Carbohydrate-based methods of synthesis have often proved to be very appropriate in the preparation of enantiomerically pure, natural and artificial compounds[2]. One particular area which has grown rapidly in the past few years is the synthesis of 2,6-dialkylated oxolane units (*C*-glycopyranosyl compounds). These structural systems are not only frequently found in a wide variety of natural products, but are also good starting points for other synthetic objectives in which stereocontrolled lengthening of a carbohydrate chain is needed. Reactions of carbon nucleophiles with the electrophilic anomeric center of carbohydrates are the most exploited routes to *C*-glycopyranosyl syntheses[3]. Less common

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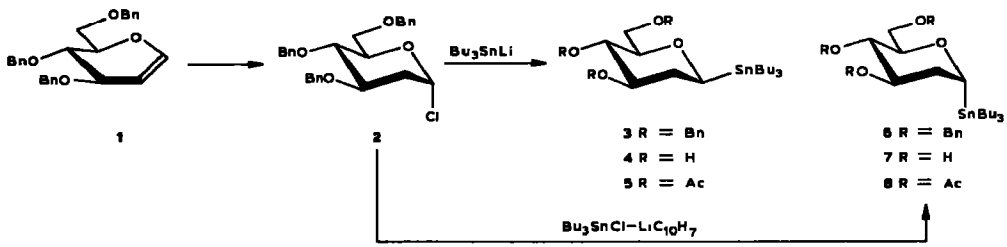
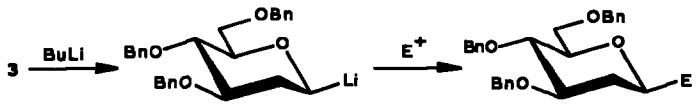
approaches may also be realized by use of a nucleophilic anomeric center. Thus, the efficient and stereocontrolled introduction of carbon side-chains has been described by use of either a stabilized nucleophilic intermediate derived from anomeric phosphonium salts[4], nitro[5] and phenylsulfonyl[6] sugar derivatives, and pentacarbonyl glycosylmanganese complexes[7], or 2-deoxy-D-glucopyranosyllithium reagents[8]. As part of an ongoing research program in this area, we report herein a stereocontrolled method for the preparation of *C*-glycopyranosyl compounds from tributyl (2-deoxy-D-glucopyranosyl)stannanes.

RESULTS AND DISCUSSION

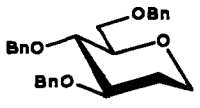
α-Alkoxy organostannanes, prepared by the addition of organotin nucleophiles to aldehydes or ketones[9], followed by immediate protection of the intermediate alcohol[10], have been shown to be useful precursors of α-alkoxy organolithium compounds through a fast, low-temperature, exchange reaction with alkyllithium reagents[10,11]. In addition, tin–lithium exchange on stereodefined α-alkoxy organostannanes occurs with retention of configuration and the tetrahydral lithiated compounds, thus formed, accept electrophiles with retention of configuration as well[12,13]. In view of these observations, a stereoselective anomeric trialkylstannylation of carbohydrates would provide, *via* the corresponding glycosyllithium reagents, a stereocontrolled route to *C*-glycopyranosyl compounds. Reaction of the tri-*O*-benzyl-D-glucal[14] **1** with hydrogen chloride in toluene[8,15] gave unstable 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl chloride (**2**) which was treated immediately with tributylstannyllithium[10] in oxolane at 0°. The products formed were easily separated on a column of silica gel, providing the tributyl-β-D-glycosylstannane **3** as the major compound (85% from glucal **1**), along with a small proportion of its α-D anomer **6** (1.5% from **1**). The reaction of triorganotin–alkali reagents with organic halides is a well-known route for synthesis of tetraorganotin compounds[16]. That the substitution reaction on chloride **2** was indeed possible was strongly indicated by the preparation of 1-tributylstannyl-1-methoxyheptane from 1-chloro-1-methoxyheptane by Still[10]. The stereoselectivity observed (50~60:1) in favor of the β-D anomer **3** suggests a preponderant direct (SN2) displacement, although this statement must await further mechanistic investigation. The tributyl-α-D-glycosylstannane **6** was selectively obtained from chloride **2** by reductive lithia-





9

10 E = ^2H
11 E = CH(OH)Ph
12 E = $CH(OH)C_5H_{11}$
13 E = $CH(OH)CHMe_2$
14 E = COPh
15 E = COC_5H_{11}
16 E = $COCHMe_2$
17 E = $C(OH)Me_2$
18 E = 2-cyclohexen-1-ol-1-yl
19 E = C_4H_9



20

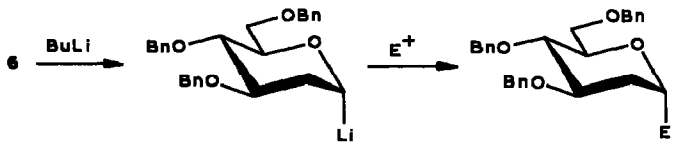
tion[8] with two equiv. of lithium naphthalenide in oxolane at −78°, followed by the addition of tributyltin chloride (70% from **1**). Hydrogenolytic removal of the benzyl groups of **3** and **6** gave triols **4** and **7**, converted into their triacetates **5** and **8**, respectively. The introduction, in equatorial position, of tin in compound **3** was readily indicated by the ^{1}H-n.m.r. data; the values of the vicinal coupling-constants of the ring protons (see Experimental section) suggested a $^4C_1$(D) chair conformation in which H-1 was axially oriented ($J_{1,2}$ 1.9 and 13.2 Hz). The stereochemical relation at C-1 in the α-D series could only be confirmed for **7** and **8**, where a $^4C_1$(D) chair-conformation was deduced from the ^{1}H-n.m.r. data with substantial differences in the $J_{1,2}$ values ($J_{1,2e}$ 1.2–4.2 Hz, and $J_{1,2a}$ 6.1–4.2 Hz). Satellites arising from coupling of H-1 with the ^{117}Sn and ^{119}Sn nuclei were only clearly resolved in the ^{1}H-n.m.r. spectra of triols **4** and **7**, and triacetates **5** and **8**. Great differences in the $J_{1,Sn}$ values, 16.3 and 16.2 Hz for **3** and **4** (β-D anomers), as compared to 27.2 and 26.9 Hz for **7** and **8** (α-D anomers), were observed.

Our attention was next turned to the use of glycosylstannanes **3** and **6** in *C*-glycosylation reactions. Treatment of the glycosylstannane **3** with butyllithium in oxolane at −78°, followed by addition of deuterium oxide, gave specifically the deuteriated derivative **10** in 74% yield. The introduction, in equatorial position, of a deuterium atom was confirmed by ^{1}H-n.m.r. spectroscopy showing the H-1 signal at δ 3.35 as a quartet ($J_{1,2e}$ 1.9 and $J_{1,2a}$ 12.4 Hz). Compound **10** most probably arose from the 2-deoxy-β-D-glucopyranosyllithium derivative **9**.

The specific formation of **10** showed that the stereochemical geometry was completely maintained throughout the sequence of reactions, both steps (tin–lithium exchange and electrophilic trapping) occurring with retention of configuration. The sequence of reactions performed with benzaldehyde, hexanal, and isobutyraldehyde afforded the expected diastereoisomeric products **11** (95%; isomeric ratio, 2:1), **12** (80%; isomeric ratio, 1:1), and **13** (80%; isomeric ratio, 3:1), respectively, in which the newly formed carbon–carbon bond was equatorial. These com-

pounds were accompanied by variable proportions of 1,5-anhydro-3,4,6-tri-*O*-benzyl-1,2-dideoxy-D-*arabino*-hexitol (**20**; 1–10%), probably resulting from the hydrolysis of the lithiated intermediate **9**. All diastereoisomeric mixtures formed were oxidized by pyridinium chlorochromate in dichloromethane[17] to give single ketones **14**, **15**, and **16**. The configuration at the anomeric center of **14**, **15**, and **16** was readily deduced from ^{1}H-n.m.r. spectra showing H-1 resonances at δ 4.32 (for **15**) to 5.19 (for **14**) as quartets with $J_{1,2}$ values 1.9–2.2 Hz ($J_{1,2e}$) and 12–12.2 Hz ($J_{1,2a}$) in a $^4C_1$(D) conformation. Glycosyllithium **9** also reacted with acetone to produce alcohol **17** and with 2-cyclohexenone in a 1,2-position to give allylic alcohol **18** as a 1:1 diastereoisomeric mixture. In the latter case, none of the corresponding 1,4-adduct could be detected. The reaction with butyl iodide gave, in low yield (39%), the *C*-butylglycoside **19**, as was the case with reactions using other alkyl iodides not described in this work. Large proportions of **20** (up to 52%) were formed, and it appears that the hydrogen transfer was preferred to alkylation, although the reason for this behavior has not yet been determined. In all reactions, exclusive formation of an equatorial carbon–carbon bond was observed, indicating the equatorial nature of the carbon–lithium bond of **9**. These results were not surprising in that strong stereoelectronic-stabilizing effects have already been demonstrated for similar stereochemical situations[18].

Similarly, treatment of tributyl-α-D-glycopyranosylstannane **6** with butyllithium in oxolane at −78°, and addition of deuterium oxide to the glycosyllithium derivative thus produced gave the deuteriated α-D anomer **22** which is identical to the product already described[8]. The actual conformation of the lithium reagent **21** is unknown, but it is possible that the lithium anomeric substituent, or the corresponding lone pair, prefers a (pseudo)equatorial orientation in order to avoid a destabilizing interaction with one of the nonbonding electron pairs of the ring oxygen atom[18] (reverse anomeric effect[19]). Coupling reactions using benzaldehyde, hexanal, and isobutyraldehyde afforded the diastereoisomeric alcohols **23** (65%; ratio 3:1), **24** (74%; ratio, 10:1), and **25** (85%; ratio 10:1), respectively, together with **20**. Pyridinium chlorochromate oxidation of **23**, **24**, and **25** occurred without isomerization to give the single ketones **26** (69%), **27** (73%), and **28** (89%),



21

22 E = D
23 E = CH(OH)Ph
24 E = $CH(OH)C_5H_{11}$
25 E = $CH(OH)CHMe_2$
26 E = COPh
27 E = COC_5H_{11}
28 E = $COCHMe_2$

respectively. Examination of the ^{1}H-n.m.r. parameters of **23**, **24**, and **25** indicated a substantial conformational deviation from the usual $^4C_1$(D) conformation (see Experimental section), which was especially noticeable for the minor isomers, as for instance for **23** where vicinal-coupling constant values of 4.6 Hz for $J_{3,4}$ and $J_{4,5}$, and 3.9 and 9.0 Hz for $J_{1,2}$ were found. This conformational distortion, probably due to steric interaction between the sugar ring and the α-hydroxy-alkyl or -aryl side-chain was no longer perceptible in the ^{1}H-n.m.r. spectra of ketones **26**, **27**, and **28**, where coupling constant values of 8.3–8.9 Hz ($J_{3,4}$ and $J_{4,5}$), 10.3–10.8 Hz ($J_{2a,3}$), 2.1–3.0 Hz ($J_{1,2e}$), and 5.8 Hz ($J_{1,2a}$) were observed, values consistent with a $^4C_1$(D) conformation.

As already established[6,8,20], such kinetically-generated lithiated compounds as **21** are configurationally stable under the conditions used (oxolane, −78°). The selectivity of the attack at the carbonyl group by the glycosyllithium reagent **9** was low (ratio 1:1–3:1), but became significant in the condensation of glycosyllithium **21** with hexanal and isobutyraldehyde (ratio 10:1*), although the like or unlike[21] nature of the stereochemical outcome is presently unknown. More examples are needed to delineate the synthetic usefulness of the facial discrimination of these asymmetric carbanions in their addition reactions to prochiral or chiral carbonyl compounds. High levels of diastereofacial selectivity would, therefore, allow the stereoselective construction of two chiral centers in a single synthetic operation.

EXPERIMENTAL

General methods. — Melting points were determined for capillary tubes with a Büchi apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter at the sodium D-line at 22±2°. ^{1}H-N.m.r. spectra were recorded with a Perkin–Elmer R-32 (90 MHz) or Bruker AM-300 (300 MHz) spectrometer for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. Mass spectra were recorded with a Ribermag R-10-10 instrument in the desorption chemical-ionization (d.c.i.) mode using ammonia as the reagent gas. All solvents and reagents were purified and dried according to standard procedures[22]. Tributylstannyllithium was prepared by the addition of butyllithium to commercial hexabutylditin in oxolane (0°, 15 min), according to Still[10]. Solution transfers were conducted under dry Ar by standard syringe techniques. T.l.c. was performed on Silica gel 60-F_{254} (Merck) with detection by quenching of fluorescence and by charring with H_2SO_4. For column chromatography, the loading was in the range 1:20–1:50 on Silica gel 60 (Merck, 63–200 μm) which was used without pretreatment. Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique.

*Erroneously reported as 3:1 for hexanal[1].

*Tributyl-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)stannane* (**3**). — 1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (**1**) was prepared essentially as described by Blackburne *et al.*[14], by benzylation (NaH, benzyl bromide) in anhydrous *N,N*-dimethylformamide, m.p. 57°, $[\alpha]_D^{22}$ −2.7° (*c* 1.89, chloroform); lit.[14] m.p. 57–57.5°, $[\alpha]_D$ −2.9° (chloroform); lit.[23] m.p. 55°, $[\alpha]_D$ −2.7° (chloroform). Dry HCl was bubbled through a stirred solution of **1** (2.39 g, 5.74 mmol) in anhydrous toluene (10 mL) at 0° for 15 min. Excess HCl was eliminated by Ar bubbling and the solution was concentrated under reduced pressure. After several co-evaporations with toluene, the colorless syrup of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl chloride (**2**) was dried under high-vacuum (1 h), and used immediately in the next step.

To a stirred solution of **2** in anhydrous oxolane (6 mL) under Ar at 0° was added, in the course of 20 min, a 0.5M solution of freshly prepared tributylstannyllithium in oxolane (17.2 mL, 8.6 mmol, 1.5 equiv.). After 1.5 h at 0°, NH_4Cl was added and the mixture was diluted with ethyl ether (100 mL) and water (30 mL). The organic phase was washed twice with sat. aqueous NH_4Cl solution, dried ($MgSO_4$), and evaporated. Column chromatography (hexane, then hexane–ethyl acetate, 6:1) of the residue provided **3** (3.46 g, 85%), colorless syrup, $[\alpha]_D^{22}$ −9.3° (*c* 1.76, chloroform); ^{1}H-n.m.r.: δ 1.84 (ddd, 1 H, $J_{2a,3}$ 10.2, $J_{2a,2e}$ 13.0, $J_{1,2a}$ 13.2 Hz, H-2*a*), 2.13 (ddd, 1 H, $J_{1,2e}$ 1.9, $J_{2e,3}$ 4.9, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 3.24 (dt, 1 H, $J_{5,6a} = J_{5,6b}$ 3.0, $J_{4,5}$ 8.9 Hz, H-5), 3.49 (t, 1 H, $J_{3,4} = J_{4,5}$ 8.9 Hz, H-4), 3.57 (ddd, 1 H, $J_{2e,3}$ 4.9, $J_{3,4}$ 8.9, $J_{2a,3}$ 10.2 Hz, H-3), 3.63 (dd, 1 H, $J_{1,2e}$ 1.9, $J_{1,2a}$ 13.2 Hz, H-1), and 3.71 (m, 2 H, H-6a,6b); m.s.: *m/z* 597 (17), 599 (28), 601 (37), (M^+ −OBn), 647 (39), 649 (77), and 651 (100) (M^+ −Bu).

Anal. Calc. for $C_{39}H_{56}O_4Sn$: C, 66.20; H, 7.98. Found: C, 66.48; H, 8.15.

Further elution of the column yielded the anomer **6** (60 mg, 1.5%), identical to the compound described later.

*Tributyl-(2-deoxy-β-*D*-arabino-hexopyranosyl)stannane* (**4**). — A solution of stannane **3** (143 mg, 0.20 mmol) in methanol (2 mL) containing 10% Pd–C (~10 mg) under H_2 was stirred for 1 h at room temperature. The mixture was filtered through Celite, and the insoluble material washed with several portions of methanol. Evaporation to dryness of the combined filtrate and washings gave a residue which was purified by column chromatography (2:3 dichloromethane–ethyl acetate) to yield **4** (77 mg, 87%), colorless syrup, $[\alpha]_D^{22}$ −8.5° (*c* 1.32, chloroform); ^{1}H-n.m.r.: δ 1.83 (dt, 1 H, $J_{2a,3}$ 10.8, $J_{1,2a} = J_{2a,2e}$ 13.2 Hz, H-2*a*), 2.03 (ddd, 1 H, $J_{1,2e}$ 2.2, $J_{2e,3}$ 5.0, $J_{2e,2a}$ 13.2 Hz, H-2*e*), 3.11 (ddd, 1 H, $J_{5,6b}$ 3.7, $J_{5,6a}$ 4.6, $J_{4,5}$ 8.9 Hz, H-5), 3.39 (t, 1 H, $J_{3,4} = J_{4,5}$ 8.9 Hz, H-4), 3.585 (ddd, 1 H, $J_{2e,3}$ 5.0, $J_{3,4}$ 8.9, $J_{2a,3}$ 10.8 Hz, H-3), 3.73 (dd, 1 H, $J_{5,6a}$ 4.6, $J_{6a,6b}$ 11.8 Hz, H-6a), 3.78 (dd, 1 H, $J_{1,2e}$ 2.2, $J_{1,2a}$ 13.2 Hz, H-1), and 3.815 (dd, 1 H, $J_{5,6b}$ 3.7, $J_{6a,6b}$ 11.8 Hz, H-6b); ^{117,119}Sn satellites for H-1: $J_{Sn,1}$ 16.3 Hz.

Anal. Calc. for $C_{18}H_{38}O_4Sn$: C, 49.45; H, 8.76. Found: C, 49.65; H, 8.92.

*Tributyl-(3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-arabino-hexopyranosyl)stannane* (**5**). — Acetylation of **4** (61 mg, 0.14 mmol) under standard conditions (acetic

anhydride, pyridine) afforded, after column chromatography (5:1 hexane–ethyl acetate), **5** (74 mg, 93%), syrup, $[\alpha]_D^{22}$ −25° (*c* 2.9, chloroform); ^{1}H-n.m.r.: δ 1.93 (dt, 1 H, $J_{2a,3}$ 10.6, $J_{1,2a} = J_{2a,2e}$ 13.2 Hz, H-2*a*), 2.03–2.04 (3 s, 9 H, 3 $COCH_3$), 2.14 (ddd, 1 H, $J_{1,2e}$ 2.1, $J_{2e,3}$ 5.0, $J_{2a,2e}$ 13.2 Hz, H-2*e*), 3.40 (ddd, 1 H, $J_{5,6a}$ 2.6, $J_{5,6b}$ 5.2, $J_{4,5}$ 9.3 Hz, H-5), 3.725 (dd, 1 H, $J_{1,2e}$ 2.1, $J_{1,2a}$ 13.2 Hz, H-1), 4.04 (dd, 1 H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.14 (dd, 1 H, $J_{5,6b}$ 5.2, $J_{6a,6b}$ 12.1 Hz, H-6b), and 4.89 (ddd, 1 H, $J_{2e,3}$ 5.0, $J_{3,4} = J_{4,5}$ 9.3 Hz, H-4); ^{117,119}Sn satellites for H-1: $J_{Sn,1}$ 16.2 Hz.

Anal. Calc. for $C_{24}H_{44}O_7Sn$: C, 51.17; H, 7.87. Found: C, 51.11; H, 8.16.

*Tributyl-(3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-arabino-hexopyranosyl)stannane* (**6**). — Chloride **2**, prepared from **1** (532 mg, 1.28 mmol) as described above, was dissolved in anhydrous oxolane (10 mL) and the solution chilled to −78° under Ar. Lithium naphthalenide (2.7 mL of a M oxolane solution[24]; 2.7 mmol, 2.1 equiv.) was added in the course of 5 min. To the dark-red solution was immediately added tributyltin chloride (0.7 mL, 2.56 mmol, 2 equiv.), and the mixture was stirred for 15 min at −78°. After addition of NH_4Cl, the mixture was diluted with ethyl ether (50 mL), and water (20 mL). The organic phase was washed with sat. aqueous NH_4Cl, dried ($MgSO_4$), and evaporated. Column chromatography (9:1 hexane–ethyl acetate) of the residue gave **6** (631 mg, 70%), colorless oil, $[\alpha]_D^{22}$ +26° (*c* 5.53, chloroform); ^{1}H-n.m.r.: δ 2.17 (m, 2 H, H-2a,2b), 3.16 (ddd, 1 H, $J_{5,6a}$ 2.1, $J_{5,6b}$ 4.1, $J_{4,5}$ 8.5 Hz, H-5), 3.50 (t, 1 H, $J_{3,4} = J_{4,5}$ 8.5 Hz, H-4), 3.55 (m, 1 H, H-3), 3.64 (dd, 1 H, $J_{5,6a}$ 2.1, $J_{6a,6b}$ 10.2 Hz, H-6a), 3.72 (dd, 1 H, $J_{5,6b}$ 4.1, $J_{6a,6b}$ 10.2 Hz, H-6b), and 4.56 (m, 1 H, H-1); m.s.: *m/z* 647 (38), 649 (77), 651 (100), (M^+ −Bu), 722 (12), 724 (22), and 726 (30) (M^+ +18).

Anal. Calc. for $C_{39}H_{56}O_4Sn$: C, 66.20; H, 7.98. Found: C, 66.16; H, 7.99.

*Tributyl-(2-deoxy-α-*D*-arabino-hexopyranosyl)stannane* (**7**) *and tributyl-(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-arabino-hexopyranosyl)stannane* (**8**). — Hydrogenolysis of **6** (50 mg, 0.07 mmol) in ethyl acetate (2 mL) under the conditions described for the preparation of **4** gave, after purification by column chromatography (20:1 dichloromethane–methanol), **7** (22 mg, 71%), colorless syrup, $[\alpha]_D^{22}$ +33° (*c* 0.36, chloroform); ^{1}H-n.m.r.: δ 2.08 (ddd, 1 H, $J_{1,2e}$ 1.2, $J_{2e,3}$ 5.4, $J_{2a,2e}$ 13.1 Hz, H-2*e*), 2.17 (ddd, 1 H, $J_{1,2a}$ 6.1, $J_{2a,3}$ 10.8, $J_{2a,2e}$ 13.1 Hz, H-2*a*), 3.03 (dt, 1 H, $J_{5,6a} = J_{5,6b}$ 4.0, $J_{4,5}$ 9.0 Hz, H-5), 3.41 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.0 Hz, H-4), 3.59 (ddd, 1 H, $J_{2e,3}$ 5.4, $J_{3,4}$ 9.0, $J_{2a,3}$ 10.8 Hz, H-3), 3.81 (m, 2 H, H-6a,6b), and 4.52 (dd, 1 H, $J_{1,2e}$ 1.2, $J_{1,2a}$ 6.1 Hz, H-1); ^{117,119}Sn satellites for H-1: $J_{Sn,1}$ 27.2 Hz.

Acetylation by standard conditions of **7** (104 mg, 0.24 mmol) afforded **8** (119 mg, 89%), colorless syrup, $[\alpha]_D^{22}$ +43° (*c* 2.69, chloroform); ^{1}H-n.m.r.: δ 2.03, 2.055, and 2.08 (3 s, 9 H, 3 CH_3CO), 2.21 (m, 2 H, H-2a,2b), 2.85 (ddd, 1 H, $J_{5,6a}$ 2.4, $J_{5,6b}$ 5.8, $J_{4,5}$ 8.9 Hz, H-5), 4.45 (dd, 1 H, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.29 (dd, 1 H, $J_{5,6b}$ 5.8, $J_{6a,6b}$ 12.1 Hz, H-6b), 4.53 (t, 1 H, $J_{1,2} = J_{1,2'}$, 4.2 Hz, H-1), and 4.91 (m, 2 H, H-3,4); ^{117,119}Sn satellites for H-1: $J_{Sn,1}$ 26.9 Hz.

Anal. Calc. for $C_{24}H_{44}O_7Sn$: C, 51.17; H, 7.87. Found: C, 51.55; H, 7.94.

General procedure for the C–C bond formation from stannanes **3** *and* **6**. — To a stirred solution of stannane **3** or **6** in anhydrous oxolane (1.5 mL/mmol) at −78°

under Ar was added butyllithium (1.6M in hexane, 1.2 equiv.). After stirring for 2 min at −78°, the electrophile (1.2 equiv.) was added neat or in oxolane solution (1 mL/mmol). The solution was then treated with NH_4Cl after being stirred for an appropriate period of time at −78° under Ar (usually 0.5 h). The mixture was diluted with ethyl ether and water, and the organic phase extracted twice with sat. aqueous NH_4Cl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by chromatography.

*(1S)-1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-(1-^{2}H)*arabino*-hexitol* (**10**). — Reaction of **3** (56.5 mg, 0.08 mmol) and D_2O (5 μL) under the conditions described above gave, after column chromatography (6:1 hexane–ethyl acetate), **10** (24.5 mg, 74%), colorless syrup, $[\alpha]_D^{22}$ +21° (*c* 2.07, chloroform); ^{1}H-n.m.r.: δ 1.70 (dt, 1 H, $J_{1,2a}$ 12.4, $J_{2a,2e} \simeq J_{2a,3} \simeq$ 13.0 Hz, H-2*a*), 2.07 (ddd, 1 H, $J_{1,2e}$ 1.9, $J_{2e,3}$ 5.0, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 3.34 (m, 1 H, H-5), 3.35 (dd, 1 H, $J_{1,2e}$ 1.9, $J_{1,2a}$ 12.4 Hz, H-2*a*), 3.49 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.0 Hz, H-4), 3.62 (ddd, $J_{2e,3}$ 5.0, $J_{3,4}$ 9.0, $J_{2a,3}$ 13.2 Hz, H-3), and 3.68 (m, 2 H, H-6a,6b).

Anal. Calc. for $C_{27}H_{29}DO_4$: C, 77.30; H, 7.45. Found: C, 77.31; H, 7.56.

*Phenyl (3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl) ketone* (**14**). — The general procedure with **3** (58 mg, 0.08 mmol) and benzaldehyde (9 μL, 0.10 mmol, 1.2 equiv.) afforded, after column chromatography (4:1 toluene–ethyl acetate), phenyl-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)methanol (**11**; 41 mg, 95%), mixture of isomers, colorless syrup; ^{1}H-n.m.r. (selected data): (major isomer) δ 1.61 (dt, 1 H, $J_{1,2a} = J_{2a,3}$ 11.5, $J_{2a,2e}$ 12.9 Hz, H-2*a*) and 1.88 (ddd, 1 H, $J_{1,2e}$ 2.1, $J_{2e,3}$ 5.1, $J_{2a,2e}$ 12.9 Hz, H-2*e*); (minor isomer) δ 1.40 (dt, 1 H, $J_{1,2a} = J_{2a,3}$ 11.5, $J_{2a,2e}$ 12.9 Hz, H-2*a*) and 1.77 (ddd, 1 H, $J_{1,2e}$ 1.9, $J_{2e,3}$ 4.3, $J_{2a,2e}$ 12.9 Hz, H-2*e*); isomeric ratio, 2:1.

A solution of **11** (35 mg, 67 μmol) in dichloromethane (1 mL) was added to a stirred solution of pyridinium chlorochromate (43 mg, 0.20 mmol, 3 equiv.) in dichloromethane (1 mL) containing molecular sieves (4A) and sodium acetate (28 mg). Stirring was continued until the oxidation was complete (t.l.c.). Ethyl ether (2 mL) was added, the suspension was then stirred for an additional 15 min and filtered through a bed of silica gel, and the insoluble material was washed several times with ethyl ether. Evaporation of the combined filtrate and washings left a residue which was purified by column chromatography (3:1 hexane–ethyl acetate) to afford **14** (25 mg, 72%), colorless syrup, $[\alpha]_D^{22}$ +7° (*c* 0.91, chloroform); ^{1}H-n.m.r.: δ 1.85 (dt, 1 H, $J_{1,2a} \simeq J_{2a,3} \simeq$ 12, $J_{2a,2e}$ 13.0 Hz, H-2*a*), 2.49 (ddd, 1 H, $J_{1,2e}$ 1.9, $J_{2e,3}$ 5.0, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 3.57 (t, 1 H, $J_{3,4} = J_{4,5}$ 8.9 Hz, H-4), 3.64 (ddd, 1 H, $J_{5,6a}$ 1.6, $J_{5,6b}$ 4.9, $J_{4,5}$ 8.9 Hz, H-5), 3.71 (dd, 1 H, $J_{5,6a}$ 4.9, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.80 (dd, 1 H, $J_{5,6b}$ 1.6, $J_{6a,6b}$ 11.0 Hz, H-6b), 3.82 (m, 1 H, H-3), and 4.58 (dd, 1 H, $J_{1,2e}$ 1.9, $J_{1,2a}$ 12.4 Hz, H-1).

Anal. Calc. for $C_{34}H_{34}O_5$: C, 78.14; H, 6.56. Found: C, 78.18; H, 6.76.

*1-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-1-hexanone* (**15**). — The general procedure with **3** (78 mg, 0.11 mmol) and hexanal (16 μL, 0.13 mmol, 1.2 equiv.) gave, after column chromatography (9:1 toluene–ethyl acetate),

1-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-1-hexanol as a mixture of isomers (**12**; 46 mg, 80%), colorless syrup; ^{1}H-n.m.r. (selected data): δ 1.59 (~q, *J* ~12 Hz, H-2*a* one isomer), 2.10 (m, 1 H, H-2*e* both isomers), 2.17 (bs, OH), 2.58 (bs, OH), 3.20 (ddd, $J_{1,2e}$ 1.7, $J_{1,CH(OH)}$ 6.6, $J_{1,2a}$ 11.0 Hz, H-1 one isomer), 3.31 (ddd, $J_{1,2e}$ 1.7, $J_{1,CH(OH)}$ 3.6, $J_{1,2a}$ 11.0 Hz, H-1 other isomer), 3.40 (m, 1 H, H-5), 3.67 (m, 1 H, H-3), and 3.72 (m, 2 H, H-6a,6b); isomeric ratio, 1:1.

Oxidation of **12** (62 mg, 0.12 mmol) by the procedure used for **11** gave, after column chromatography (9:1 toluene–ethyl acetate), **15** (59 mg, 94%), colorless syrup, $[\alpha]_D^{22}$ +31° (*c* 1.53, chloroform); ^{1}H-n.m.r.: δ 0.89 (t, 3 H, *J* 6.9 Hz, CH_3), 1.30 (m, 4 H, 2 CH_2), 1.48 (dt, 1 H, $J_{1,2a} = J_{2a,3}$ 12.1, $J_{2e,2a}$ 13.0 Hz, H-2*a*), 1.57 (m, 2 H, CH_2), 2.45 (ddd, 1 H, $J_{1,2e}$ 2.3, $J_{2e,3}$ 4.9, $J_{2e,2a}$ 13.0 Hz, H-2*e*), 2.65 (t, 2 H, *J* 7.2 Hz, CH_2CO), 3.44 (ddd, 1 H, $J_{5,6a}$ 2.2, $J_{5,6b}$ 4.0, $J_{4,5}$ 9.6 Hz, H-5), 3.50 (dd, 1 H, $J_{3,4}$ 7.9, $J_{4,5}$ 9.6 Hz, H-4), 3.69 (ddd, 1 H, $J_{2e,3}$ 4.9, $J_{3,4}$ 7.9, $J_{2a,3}$ 12.1 Hz, H-3), 3.75 (m, 2 H, H-6a,6b), and 3.79 (dd, 1 H, $J_{1,2e}$ 2.3, $J_{1,2a}$ 12.1 Hz, H-1).

Anal. Calc. for $C_{33}H_{42}O_5$: C, 76.72; H, 7.80. Found: C, 76.77; H, 7.83.

*2-Methyl-1-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-*arabino*-hexopyranosyl)-1-propanone* (**16**). — The general procedure with **3** (205 mg, 0.29 mmol) and isobutyraldehyde (32 μL, 0.35 mmol, 1.2 equiv.) gave, after column chromatography (4:1 dichloromethane–ethyl acetate), 2-methyl-1-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-1-propanol as a mixture of isomers (**13**; 113 mg, 80%), colorless syrup; ^{1}H-n.m.r. (selected data): (major isomer) δ 2.05 (ddd, $J_{1,2e}$ 2.1, $J_{2e,3}$ ~5, $J_{2a,2e}$ ~13 Hz, H-2*e*); (minor isomer) δ 2.16 (ddd, $J_{1,2e}$ ~2, $J_{2e,3}$ ~4, $J_{2a,2e}$ 12.8 Hz, H-2*e*); isomeric ratio, 3:1.

Oxidation of **13** (89 mg, 0.18 mmol) according to the procedure used for **11** gave, after column chromatography (50:1 dichloromethane–ethyl acetate), **16** (71 mg, 80%), colorless syrup, $[\alpha]_D^{22}$ +24.5° (*c* 2.53, dichloromethane); ^{1}H-n.m.r.: δ 1.10 and 1.11 (2 d, 6 H, *J* 7.0 Hz, 2 CH_3), 1.51 (~q, 1 H, $J_{2a,3}$ 11.2, $J_{1,2a}$ 12.2, $J_{2a,2e}$ 13.1 Hz, H-2*a*), 2.50 (ddd, 1 H, $J_{1,2e}$ 2.2, $J_{2e,3}$ 4.9, $J_{2a,2e}$ 13.1 Hz, H-2*e*), 3.21 (h, 1 H, *J* 7.0 Hz, C*H*Me_2), 3.45 (ddd, 1 H, $J_{5,6a}$ 2.2, $J_{5,6b}$ 3.9, $J_{4,5}$ 9.6 Hz, H-5), 3.515 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 9.6 Hz, H-4), 3.70 (ddd, 1 H, $J_{2e,3}$ 4.9, $J_{3,4}$ 8.0, $J_{2a,3}$ 11.2 Hz, H-3), 3.76 (m, 2 H, H-6a,6b), and 3.89 (dd, 1 H, $J_{1,2e}$ 2.2, $J_{1,2a}$ 12.2 Hz, H-1).

Anal. Calc. for $C_{31}H_{36}O_5$: C, 76.20; H, 7.43. Found: C, 76.35; H, 7.44.

*1-Methyl-1-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-*arabino*-hexopyranosyl)-1-ethanol* (**17**). — The general procedure with **3** (300 mg, 0.42 mmol) and acetone (48 μL, 0.63 mmol, 1.5 equiv.) gave, after column chromatography (5:1 dichloromethane–ethyl acetate), **17** (122 mg, 60%), m.p. 58–60° (pentane–chloroform), $[\alpha]_D^{22}$ +14° (*c* 1.9, chloroform); ^{1}H-n.m.r.: δ 1.21 and 1.24 (2 s, 6 H, 2 CH_3), 1.51 (~q, 1 H, $J_{2a,3}$ 11.3, $J_{1,2a}$ 11.9, $J_{2a,2e}$ 12.7 Hz, H-2*a*), 2.16 (ddd, 1 H, $J_{1,2e}$ 1.9, $J_{2e,3}$ 5.0, $J_{2a,2e}$ 12.7 Hz, H-2*e*), 3.20 (dd, 1 H, $J_{1,2e}$ 1.9, $J_{1,2a}$ 11.9 Hz, H-1), 3.45 (dt, 1 H, $J_{5,6a} = J_{5,6b}$ 3.0, $J_{4,5}$ 9.5 Hz, H-5), 3.52 (dd, 1 H, $J_{3,4}$ 8.1, $J_{4,5}$ 9.5 Hz, H-4), 3.70 (ddd, 1 H, $J_{2e,3}$ 5.0, $J_{3,4}$ 8.1, $J_{2a,3}$ 11.3 Hz, H-3), and 3.76 (m, 2 H, H-6a,6b).

Anal. Calc. for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.68; H, 7.70.

*(1RS)-(1-3,4,6-Tri-*O*-benzyl-2-deoxy-β-*D*-*arabino*-hexopyranosyl)-2-cyclo-*

hexen-1-ol (**18**). — The general procedure with **3** (405 mg, 0.57 mmol) and 2-cyclohexen-1-one (83 μL, 0.85 mmol, 1.5 equiv.) gave, after column chromatography (2:1 hexane–ethyl acetate), **18** (192 mg, 65%) as a mixture of isomers, colorless syrup; ^{1}H-n.m.r.: δ 1.55 and 1.56 (2 q, 1 H, J ~12 Hz, H-2*a*), 1.61–2.07 (m, 6 H, 3 CH_2 cyclohexenyl), 2.12 and 2.17 (2 ddd, 1 H, $J_{1,2e}$ 2.1, $J_{2e,3}$ 5.1, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 2.48 and 2.65 (2 bs, 1 H, OH), 3.26 and 3.30 (2 dd, 1 H, $J_{1,2e}$ 2.1, $J_{1,2a}$ 10.5 Hz, H-1), 3.42 (m, 1 H, H-5), 3.49 and 3.50 (2 dd, 1 H, $J_{3,4}$ 8.3, $J_{4,5}$ 9.7 Hz, H-4), 3.67 (m, 1 H, H-3), 3.73 (m, 2 H, H-6a,6b), 5.67, and 5.71 (m, 1 H, $J_{CH=CH}$ 10.2 Hz, H vinylic), and 5.92 (m, 1 H, H vinylic); isomeric ratio, 1:1.

Anal. Calc. for $C_{33}H_{38}O_5$: C, 77.01; H, 7.44. Found: C, 77.27; H, 7.74.

*1-(3,4,6-Tri-O-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)butane* (**19**). — The general procedure with **3** (331 mg, 0.47 mmol) and butyl iodide (80 μL, 0.70 mmol, 1.5 equiv.) gave, after column chromatography (15:1 hexane–ethyl acetate), **19** (86 mg, 39%) as a colorless syrup, $[\alpha]_D^{22}$ +6.7° (*c* 3.55, chloroform); ^{1}H-n.m.r.: δ 0.90 (t, 3 H, J 7.0 Hz, CH_3), 1.25–1.51, 1.62 (m, 6 H, 3 CH_2 butyl), 1.38 (dt, 1 H, $J_{1,2a} = J_{2a,3}$ 11.3, $J_{2a,2e}$ 12.9 Hz, H-2*a*), 2.14 (ddd, 1 H, $J_{1,2e}$ 1.9, $J_{2e,3}$ 5.0, $J_{2a,2e}$ 12.9 Hz, H-2*e*), 3.31 (m, 1 H, $J_{1,2e}$ 1.9, J_{1,CH_2} 5.2, 7.1, $J_{1,2a}$ 11.3 Hz, H-1), 3.37 (ddd, 1 H, $J_{5,6b}$ 2.1, $J_{5,6a}$ 4.4, $J_{4,5}$ 9.6 Hz, H-5), 3.47 (dd, 1 H, $J_{3,4}$ 8.6, $J_{4,5}$ 9.6 Hz, H-4), 3.64 (ddd, 1 H, $J_{2e,3}$ 5.0, $J_{3,4}$ 8.6, $J_{2a,3}$ 11.4 Hz, H-3), 3.68 (dd, 1 H, $J_{5,6a}$ 4.4, $J_{6a,6b}$ 10.7 Hz, H-6a), and 3.74 (dd, 1 H, $J_{5,6b}$ 2.1, $J_{6a,6b}$ 10.7 Hz, H-6b).

Anal. Calc. for $C_{31}H_{38}O_4$: C, 78.45; H, 8.07. Found: C, 78.38; H, 7.90.

*(1*R*)-1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-(1²H)*-arabino-*hexitol* (**22**). — The general procedure with **6** (69 mg, 0.1 mmol) and deuterium oxide (5 μL) gave, after column chromatography (4:1 hexane–ethyl acetate), **22** (29 mg, 70%), $[\alpha]_D^{22}$ +18° (*c* 1.58, chloroform); lit.[8] $[\alpha]_D$ +19°; ^{1}H-n.m.r.: δ 1.70 (ddd, 1 H, $J_{1,2a}$ 4.8, $J_{2a,3}$ 11.0, $J_{2a,2e}$ 13.0 Hz, H-2*a*), 2.07 (ddd, 1 H, $J_{1,2e}$ 1.7, $J_{2e,3}$ 5.0, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 3.34 (ddd, 1 H, $J_{5,6}$ 3.0, $J_{5,6b}$ 4.3, $J_{4,5}$ 9.7 Hz, H-5), 3.49 (dd, 1 H, $J_{3,4}$ 8.7, $J_{4,5}$ 9.7 Hz, H-4), 3.62 (ddd, 1 H, $J_{2e,3}$ 5.0, $J_{3,4}$ 8.7, $J_{2a,3}$ 11.0 Hz, H-3), 3.68 (m, 2 H, H-6a,6b), and 3.98 (dd, 1 H, $J_{1,2e}$ 1.7, $J_{1,2a}$ 4.8 Hz, H-1).

*Phenyl (3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-arabino-hexopyranosyl) ketone* (**26**). — The general procedure with **6** (170 mg, 0.24 mmol) and benzaldehyde (37 μL, 0.36 mmol, 1.5 equiv.) gave phenyl-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)methanol as a mixture of isomers (**23**; 81 mg, 65%), colorless syrup; ^{1}H-n.m.r. (selected data): (major isomer) δ 1.53 (ddd, 1 H, $J_{1,2}$ 5.0, $J_{2a,3}$ 8.6, $J_{2a,2b}$ 13.8 Hz, H-2a), 1.78 (dt, 1 H, $J_{1,2b} = J_{2b,3}$ 4.9, $J_{2a,2b}$ 13.8 Hz, H-2b), 3.18 (bs, 1 H, OH), 3.53 (t, 1 H, $J_{3,4} = J_{4,5}$ 7.0 Hz, H-4), 3.70 (dd, 1 H, $J_{5,6a}$ 3.6, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.79 (dd, 1 H, $J_{5,6b}$ 6.0, $J_{6a,6b}$ 10.5 Hz, H-6b), 3.79 (m, 1 H, H-3), 3.87 [dt, 1 H, $J_{1,2a} = J_{1,2b}$ 5.0, $J_{1,CH(OH)}$ 9.3 Hz, H-1], 3.96 (ddd, 1 H, $J_{5,6a}$ 3.6, $J_{5,6b}$ 6.0, $J_{4,5}$ 7.0 Hz, H-5), and 4.71 [d, 1 H, $J_{1,CH(OH)}$ 9.3 Hz, C*H*(OH)]; (minor isomer) δ 1.46 (ddd, 1 H, $J_{1,2a}$ 3.9, $J_{2a,3}$ 5.5, $J_{2a,2b}$ 13.9 Hz, H-2a), 2.17 (ddd, 1 H, $J_{2b,3}$ 3.8, $J_{1,2b}$ 9.0, $J_{2a,2b}$ 13.9 Hz, H-2b), 2.57 (bs, 1 H, OH), 3.47 (t, 1 H, $J_{3,4} = J_{4,5}$ 4.6 Hz, H-4), 3.57 (dd, 1 H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.82 (dd, 1 H, $J_{5,6b}$ 6.6, $J_{6a,6b}$ 10.5 Hz, H-6b), 3.82 (m, 1 H, H-3), 4.02 [ddd, 1 H, $J_{1,2a}$ 3.9, $J_{1,CH(OH)}$ 4.9, $J_{1,2b}$ 9.0 Hz, H-1],

4.16 (m, 1 H, H-5), and 4.93 [d, 1 H, $J_{1,CH(OH)}$ 4.9 Hz, C*H*(OH)]; isomeric ratio, 3:1.

Oxidation of **23** (45 mg, 0.08 mmol) by use of the procedure for **11** gave, after column chromatography (3:1 hexane–ethyl acetate), **26** (31 mg, 69%), colorless syrup, $[\alpha]_D^{22}$ +63° (*c* 1.5, chloroform); ^{1}H-n.m.r.: δ 1.88 (ddd, 1 H, $J_{1,2a}$ 5.8, $J_{2a,3}$ 10.8, $J_{2a,2e}$ 13.0 Hz, H-2*a*), 2.78 (ddd, 1 H, $J_{1,2e}$ 2.1, $J_{2e,3}$ 4.9 $J_{2a,2e}$ 13.0 Hz, H-2*e*), 3.36 (ddd, 1 H, $J_{5,6a}$ 2.0, $J_{5,6b}$ 4.0, $J_{4,5}$ 8.9 Hz, H-5), 3.49 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.63 (t, 1 H, $J_{3,4} = J_{4,5}$ 8.9 Hz, H-4), 3.67 (dd, 1 H, $J_{5,6b}$ 4.0, $J_{6a,6b}$ 10.5 Hz, H-6b), 3.93 (ddd, 1 H, $J_{2e,3}$ 4.9, $J_{3,4}$ 8.9, $J_{2a,3}$ 10.8 Hz, H-3), and 5.19 (dd, 1 H, $J_{1,2e}$ 2.1, $J_{1,2a}$ 5.8 Hz, H-1).

Anal. Calc. for $C_{34}H_{34}O_5$: C, 78.14; H, 6.56. Found: C, 78.47; H, 6.58.

*1-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-*D*-arabino-hexopyranosyl)-1-hexanone* (**27**). — The general procedure with **6** (133 mg, 0.19 mmol) and hexanal (34 μL, 0.28 mmol, 1.5 equiv.) gave, after column chromatography (17:3 toluene–ethyl acetate), 1-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-1-hexanol as a mixture of isomers (**24**; 72 mg, 74%), colorless syrup; ^{1}H-n.m.r. (selected data): (major isomer) δ 0.89 (t, 3 H, *J* 7.0 Hz, CH_3), 1.22–1.48 (m, 8 H, 4 CH_2), 1.74 (ddd, 1 H, $J_{1,2a}$ 3.9, $J_{2a,3}$ 7.1, $J_{2a,2b}$ 13.8 Hz, H-2a), 1.96 (ddd, 1 H, $J_{1,2b}$ 4.0, $J_{2b,3}$ 6.6, $J_{2a,2b}$ 13.8 Hz, H-2b), 3.50 (t, 1 H, $J_{3,4} = J_{4,5}$ 5.7 Hz, H-4), 3.63–3.80 (m, 5 H, H-1,3,6a,6b, C*H*OH) and 3.96 (ddd, 1 H, $J_{5,6a}$ 4.2, $J_{4,5}$ 5.7, $J_{5,6b}$ 6.1 Hz, H-5); (minor isomer) δ 1.65 (ddd, 1 H, $J_{1,2a}$ 3.2, $J_{2a,3}$ 5.7, $J_{2a,2b}$ 13.8 Hz, H-2a), and 2.19 (ddd, 1 H, *J* 3.9, 8.2 and 13.8 Hz, H-2b); isomeric ratio, 10:1.

Oxidation of **24** (31 mg, 0.06 mmol) by use of the procedure for **11** gave, after column chromatography (50:1 dichloromethane–ethyl acetate), **27** (23 mg, 73%), m.p. 67° (ethanol–water), $[\alpha]_D^{22}$ +17.5° (*c* 0.87, chloroform); ^{1}H-N.m.r.: δ 0.87 (t, 3 H, *J* 6.8 Hz, CH_3), 1.27 (m, 4 H, 2 CH_2), 1.56 (m, 2 H, CH_2), 1.75 (ddd, 1 H, $J_{1,2a}$ 5.8, $J_{2a,3}$ 10.2, $J_{2a,2e}$ 13.1 Hz, H-2*a*), 2.57 (t, 2 H, *J* 7.4 Hz, CH_2CO), 2.59 (ddd, 1 H, $J_{1,2e}$ 3.0, $J_{2e,3}$ 4.7, $J_{2a,2e}$ 13.1 Hz, H-2*e*), 3.49 (m, 2 H, H-4,5), 3.64 (ddd, 1 H, $J_{2e,3}$ 4.7, $J_{3,4}$ 8.3, $J_{2a,3}$ 10.2 Hz, H-3), 3.73 (m, 2 H, H-6a,6b), and 4.32 (dd, 1 H, $J_{1,2e}$ 3.0, $J_{1,2a}$ 5.8 Hz, H-1).

Anal. Calc. for $C_{33}H_{42}O_5$: C, 76.72; H, 7.80. Found: C, 76.92; H, 8.23.

*2-Methyl-1-(3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-arabino-hexopyranosyl)-1-propanone* (**28**). — The general procedure with **6** (155 mg, 0.22 mmol) and isobutyraldehyde (30 μL, 0.33 mmol, 1.5 equiv.) gave, after column chromatography (4:1 dichloromethane–ethyl acetate) 2-methyl-1-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-1-propanol as a mixture of isomers (**25**; 92 mg, 85%), colorless syrup; ^{1}H-n.m.r. (selected data): (major isomer) δ 0.88 (d, 3 H, *J* 6.7 Hz, CH_3), 0.98 (d, 3 H, *J* 6.7 Hz, CH_3), 1.70 (m, 1 H, $CHMe_2$), 1.71 (ddd, 1 H, $J_{1,2b}$ 4.0, $J_{2a,3}$ 6.5, $J_{2a,2b}$ 13.9 Hz, H-2a), 2.01 (ddd, 1 H, $J_{1,2b}$ 3.9, $J_{2b,3}$ 7.7, $J_{2a,2b}$ 13.9 Hz, H-2b), 2.43 (bs, 1 H, OH), 3.40 (m, 1 H, C*H*OH), 3.50 (t, 1 H, $J_{3,4} = J_{4,5}$ 5.3 Hz), 3.66 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 10.2 Hz, H-6a), 3.72–3.88 (m, 3 H, H-1,3,6b), and 3.99 (m, 1 H, H-5); (minor isomer) δ 1.71 (m, 1 H, H-2a) and 2.22 (ddd, 1 H, *J* 4.0, 8.0, and 13.8 Hz, H-2b); isomeric ratio, 10:1.

Oxidation of **25** (70 mg, 0.14 mmol) by use of the procedure for **11** gave, after

column chromatography (50:1 dichloromethane–ethyl acetate), **28** (62 mg, 89%), colorless syrup, $[\alpha]_D^{22}$ +9.5° (*c* 2.25, dichloromethane); ^{1}H-n.m.r.: δ 1.03 and 1.12 (2 d, 6 H, *J* 6.9 Hz, 2 CH_3), 1.77 (ddd, 1 H, $J_{1,2a}$ 5.9, $J_{2a,3}$ 10.3, $J_{2a,2e}$ 13.2 Hz, H-2*a*), 2.57 (ddd, 1 H, $J_{1,2e}$ 2.9, $J_{2e,3}$ 4.7, $J_{2a,2e}$ 13.2 Hz, H-2*e*), 3.12 (h, 1 H, *J* 6.9 Hz, C*H*Me$_2$), 3.46 (ddd, 1 H, $J_{5,6a}$ 2.8, $J_{5,6b}$ 3.9, $J_{4,5}$ 8.5 Hz, H-5), 3.52 (dd, 1 H, $J_{3,4}$ 7.6, $J_{4,5}$ 8.5 Hz, H-4), 3.67 (ddd, 1 H, $J_{2e,3}$ 4.7, $J_{3,4}$ 7.6, $J_{2a,3}$ 10.3 Hz, H-3), 3.73 (m, 2 H, H-6a,6b), and 4.52 (dd, 1 H, $J_{1,2e}$ 2.9, $J_{1,2a}$ 5.9 Hz, H-1).

Anal. Calc. for $C_{31}H_{36}O_5$: C, 76.20; H, 7.43. Found: C, 76.34; H, 7.57.

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